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CYANIDE REDUCTION IN BRIGHT STRIPPING USING AN ELECTROLYTIC PROCESS

THE ROBBINS COMPANY

Technical Report No. 18

1994

University of Massachusetts Lowell

Cyanide Reduction in Bright Stripping Using an Electrolytic Process

The Robbins Company

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The Toxics Use Reduction Institute Matching Grants Program

December 1994

The Toxics Use Reduction Institute
University of Massachusetts Lowell

The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

Toxics Use Reduction Institute Matching Grants Program

The Institute annually provides direct funding to Massachusetts industries on a matching basis for toxics use reduction (TUR) feasibility and technology studies. The matching Grants Program was initiated in FY 93 to facilitate the development and use of innovative techniques that reduce the use of toxic chemicals or the generation of toxic byproducts in Massachusetts businesses. Grants are awarded on a competitive basis for companies to conduct TUR studies at their facilities. Recipients prepare project reports which assist in transferring toxics use reduction technologies and methods to other companies.

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ACKNOWLEDGEMENTS

My thanks and appreciation for their assistance on this project are extended to Ernie Hustler and John Camara of The Robbins Company as well as the staff of the Massachusetts Toxic Use Reduction Institute, the sponsor of this Matching Grants Project.

EXECUTIVE SUMMARY

The Robbins Company, located in Attleboro, Massachusetts is a manufacturer of recognition awards. The manufacturing process involves metal plating and finishing operations for producing emblematic jewelry. One process in the metal finishing operation, bright stripping; better known in the industry as "bombing"; removes the surface oxidation and fire-scale from metal substrates. Typically, this is accomplished by immersing the substrates in a mixture of two hazardous chemicals, hydrogen peroxide and sodium cyanide, which generates a powerful, and dangerous, chemical reaction.

This project investigates electrolytic bright stripping as an alternative technology to chemical stripping. It was found that using different electrolyte solutions for specific substrate compositions gave great results on gold alloys, copper, brass, and silver . We experimented mostly with a gold alloy electrolyte which after some modifications also gave us acceptable results with brass substrates as well. We are now successfully electrolytically stripping approximately 85% of the substrates that were once exclusively stripped by the use of chemicals. Worker safety has also improved due to the use of a less toxic and more controllable technology.

The results of implementing this technology at The Robbins Company has proved it to be effective, economically feasible, and capable of reducing the use of hydrogen peroxide and sodium cyanide.

PROJECT SCOPE

The goal of this project was to reduce the use of two hazardous chemicals: hydrogen peroxide, a strong corrosive oxidizer; and sodium cyanide, which is highly toxic, by implementing an alternative technology to eliminate, or at least significantly reduce, the use of these chemicals in the stripping operation. We endeavored to discover if the Electrolytic Bright Strip (EBS) would accomplish this while being technically effective and economically feasible.

In ascertaining the effectiveness of this technology from a production viewpoint, we decided not to compare the results of substrates going through the EBS directly with those that underwent chemical "bombing", but to judge them on how effective it was in getting the substrates as clean as they needed to be. The reason for setting this criteria was that although chemical stripping leaves a more reflective surface than electro-stripping and although a shiny surface might be required in some applications, a high percentage do not, since subsequent finish processes, such as sandblasting or coloring, negate the need for an enhanced surface. In applications where a shiny surface is critical, its effectiveness was judged on the quality of the surface from a customers' expectation perspective.

The substrates tested were the typical units manufactured on a daily basis. Various sizes, designs, and materials of substrates were picked out of the production cycle in order to evaluate how the EBS would perform and get an idea of the limitations of the technology. Supply voltage, current densities (C.D.), and duration were varied to find what provided the best results. Regular processes prior to the stripping operation were maintained regardless of whether the substrates would be chemically or electrolytically stripped.

Economic feasibility was also investigated to determine if the technology had any competitive advantage or cost savings potential. Some of the quantitative costs such as initial investment for start-up, operational costs, labor costs, chemical costs, and refinement costs were calculated and compared to the chemical stripping costs. Other qualitative costs, such as worker health and safety, environmental effects and liabilities were considered but no attempt to quantify those costs was made.

Reduction in usage in the two aforementioned hazardous chemicals was estimated by comparing the chemical usage since the project was implemented (1/94 - 6/94) to the chemical usage over the same period in 1993, . The project also initiated other TUR efforts by forcing us to investigate the root causes that require the stripping process to begin with, and what we could do to eliminate those causes.

TECHNOLOGICAL ASSESSMENT

Electrolytic bright stripping, or electro-stripping, is not a new technology, but it is being assessed in this project as an alternative to the chemical stripping process which uses hydrogen peroxide and sodium cyanide to remove fire-scale and oxidation from metal substrates.

The mixing of cyanide, a strong reducing agent, and hydrogen peroxide, a strong oxidizer, creates a violently exothermic reaction that has given it the nickname "bombing". According to Cleinman, this reaction liberates tiny gas bubbles along the metal surface with such energy that the surface is stripped of a layer of metal and with it any scale or oxidation. Electro-stripping uses electricity to produce the same type of reaction as the chemical process. The oxidation that occurs electro-chemically at the anode where the substrates are attached liberates the gas bubbles which act as the scrubbing mechanism similar to the chemical process.

In essence, electro-stripping is the opposite of electro-plating. Instead of the substrate being the cathode and attracting the positively charged metal cations in the plating bath, it becomes the anode and dissolutes the metal into ions which then go into the solution. Because this reaction does not happen spontaneously, a direct current (D.C.) rectifier power supply is required to drive the reaction. Metal dissolution of the substrate will occur at a rate which is controllable by adjusting the current density and voltage settings on the rectifier. The power required varies with the size of the solution tank and production rates, with larger tanks requiring more power. Fifty amps is adequate for most small operations, but tanks of 15 gallons or more could require 100 amps or more. Because of gas formation at both the anode (oxygen) and cathode (hydrogen and traces of hydrogen cyanide) local exhaust is a must to preclude the creation of a toxic or explosive atmosphere. Figure 1 below shows the electrolytic cell.

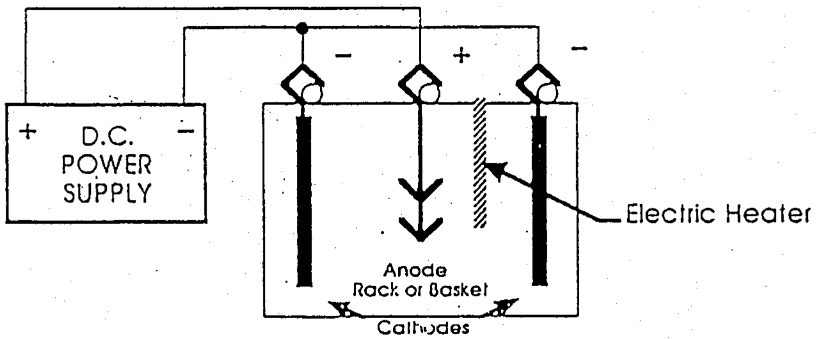

FIGURE 1 ELECTROLYTIC BRIGHT STRIP

The composition of the electrolyte solution is a critical factor in obtaining good results from the EBS. The solution forms a thin surface film on the submersed substrate that prevents surface etching and allows for an even passage of the metal ions across the metal/film interface, giving the surface a brighter finish. Different solutions work best with certain substrate material compositions, however we found that modifications can be made to the solution that will allow it to work with a broader range of metal compositions - but with less than optimum results. The solution usually needs to be heated, although overheating can interfere with the surface film mechanism by lowering of the solution viscosity. Mild agitation of the anode while immersed in the solution is recommended and air sparging of the solution has been suggested by Cleinman.

Electrolyte solutions are available, both in proprietory pre-mixed forms or as "home-brews". Our solution was found in an old electroplaters' handbook by Linick . This formula is recorded in Table 1 below. Other formulas recommended for gold, copper, brass, and silver can be found in Table 2, Table 3, Table 4, and Table 5 respectively.

This technology has its advantages and disadvantages. It is very controllable, relatively safe, easy to use, and is great for stripping small batches or single items. On the other hand, it has a relatively small through-put capacity, and the solution is substrate selective and sensitive as far as what kind of substrates it performs well on. Serious consideration needs to be given to its pro's and con's and, as with any technology, pilot testing should be performed on your product before any substantial investment is made.

TABLE 1: Formula for Gold Alloy Bright Strip (Linick)

disodium phosphate	3 ounces
potassium ferrocyanide	6 ounces
potassium cyanide	5 ounces
85% phosphoric acid	3 ounces
potassium hydroxide	3 ounces
water	1 gallon

Cell voltage : 12 -18
Current density: 80 - 130 A/dm^2
Cathode: Stainless Steel
Temp: 140 ^{o}F
Duration: .5 - 2 min

TABLE 2: Formulas for Gold Bright Strip (Tegart)

Composition	Cathode	Volts*	C.D. (A/dm^2)	Duration	Temp(ºC)
potassium cyanide, 67.5g potassium sodium tartrate, 15g potassium ferrocyanide, 15g phosphoric acid (solid), 22.5 g ammonium hydroxide, 2.5 mL water, 1000mL	Stainless Steel, or Carbon, or Platinum	9 - 10	150	1-2 min	60+
potassium cyanide, 75g potassium sodium tartrate, 16g potassium ferrocyanide, 19g phosphoric acid (solid), 16 g ammonium hydroxide, 3.5 mL copper cyanide, 4g water, 1000mL	Stainless Steel, or Carbon	12 +	150	1-2 min	60

Note: The above solutions are toxic and must be used with good local ventilation.
*Approximate voltage drop across cell

TABLE 3: Formula for Copper Bright Strip (Tegart)

Composition	Cathode	Volts*	C.D. (A/dm^2)	Duration	Temp(ºC)
orthophosphoric acid (sp. gr. 1.04)	Copper	30	30 - 60	1 min	20

Note: Produces " polish attack" finish. Electrolyte may require cooling if used frequently.
*Voltage applied to circuit

TABLE 4: Formulas for Brass Bright Strip (Tegart)

Composition	Cathode	Volts*	C.D. (A/dm^2)	Duration	Temp(°C)
orthophosphoric acid, 950mL sulfuric acid, 50 mL	Copper†	5 - 10	22 - 65	10 min	65

Note: Cathode area should be at least 20 times the anode area.
*Voltage applied to circuit
†Copper sheet or tubing preferably coated with a tin-lead alloy, lead, or speculum.

orthophosphoric acid, 100-300 mL water, 700-900 mL sodium chromate, 420 g/L sulphuric acid, 80-85 g/L chromium troxide, 180 g/L hydrofluoric acid, 3-6 g/L propionic acid, 80-150 g/L	Copper	14	15 - 38	5 - 10 min	30

TABLE 5: Formula for Silver Bright Strip (Tegart)

Composition	Cathode	Volts*	C.D. (A/dm^2)	Duration	Temp(°C)
silver cyanide, 35g potassium cyanide, 37g potassium carbonate, 38g water, 1000 mL	Silver	2.5 - 3	approx. 1	10 min	20

Note: Slow stirring of anode should be used
*Approx. voltage across cell

IMPLEMENTATION RESULTS

The electrolytic bright strip performed well on a number of different substrates. The solution we used mostly was Linick's formula shown in Table 1. Although this solution is designed for gold alloys, on which it performed excellently, it did a satisfactory job on many of the brass substrates as well. Sterling silver presented some problems with this solution; better results can be attained by using the silver bright strip solution found in Table 5.

The limitations of this technology showed up with certain substrates, especially those with intricate designs that required a uniformly bright surface. Some other substrates were difficult to strip by virtue of their size or density. Variations in voltage, current densities, and duration were experimented with to find optimum settings that would give the best results for most substrates. Approximately 85% of the substrates that require stripping are now done electrolytically instead of chemically. We are still investigating ways to eliminate the need for stripping altogether - or at least be able to electrolytically strip - the other 15% of the product line.

For most of our applications at The Robbins Company, electrolytic bright stripping was found to be a viable alternative to chemical bombing. It has the potential, as we learn more and more by research and experience, to effectively replace the chemical stripping process.

ECONOMIC ASSESSMENT

The start-up of an electrolytic stripper can incur a moderate initial capital investment. We needed to purchase a quality D.C. power supply, a 25 gallon strip tank for the electrolyte solution, a rinse tank, and an exhaust hood. These items, plus the solution, added up to almost $6000.

One of the advantages to the EBS is its minimal operating costs. The labor and operational cost savings over chemical stripping are estimated at $5000 annually . So far we have experienced a 30% reduction in chemical costs over the same period in 1993, saving $300 annually. Those savings are slightly offset by the need to replenish the bath occasionally (1 - 2 months) from dragout losses, and periodic dumping (6-12 months).Refining the bath for its gold and silver content could bring in around $1000 annually. Payback on the investment has been calculated to be approximately one year.

TOXIC USE REDUCTION ASSESSMENT

The assessment of the electrolytic bright strip for reducing toxic chemical use is promising. We have experienced a 17% reduction in the use of hydrogen peroxide and a 26% reduction in sodium cyanide per production unit over the first five months of last year. We expect greater reduction in the next six months as we continue to use it on a larger percentage of the production line as the developmental phase of the implementation stage ends and employees become more acclimated with it and use it more consistently.

The larger implications of using this technology are the reduction of worker health and safety risks that were an inherent part of chemical stripping and the reduction in the generation of a toxic wastestream to enter into the facility's closed-loop rinsewater recycling and recirculation system. We employ a double still rinse after the electrolyte tank to minimize any drag-out and to maximize the life of the bath by using the dragout for feedwater to make up for evaporative losses in the heated solution.

Although som electrolytes contains cyanide, worker health risks are lessened because the process is better controlled, avoiding the splash potential created by chemical bombing. Since chemicals only need to be added two or three times a year, there is also a reduction in the risk of employee exposure associated with the transfer of hazardous chemicals. Also, the cyanide in the solution is highly complexed and therefore less toxic and employee exposure to it is much more limited compared to the chemical reaction. Of course, appropriate personal protective equipment should still be worn during the process and adequate local ventilation should be supplied for the solution tank since it is posssible to generate hydrogen cyanide at the cathode.

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