"Chromium Recovery and Minimization in Industrial Surface Treatment Processes"

Dr. Xavier Albert Ventura, Laboratory of Electrochemical Research & Development, Integral Centre, Barcelona, Spain

In surface treatment processes we face a great problem when chromium is involved as it happens in zinc passivating, aluminium sealing, decorative chromium and hard chromium, and the emission of chromo oxide to the atmosphere.

The European Union will completely ban the use of chromium hexavalent by the year 2007.

This work shows how to purify a chromium bath through electrolytic recovery, anode-cathode and separating cell or membrane cell, using for this tanks and a transfer pump, rectifier, membrane cell and interchanging anodes. We also recuperate by electro-dialysis, washing and recovering it and using an evaporator to minimize environmental impact.

In chromium emission to the atmosphere zero emission is achieve using EED (Emission Eliminating Device) that reduces energy's costs about 70-80 %.

Also we try to minimize chromium converting it into solid, liquid or gaseous state.

For more information, contact:

Dr. Xavier Albert Ventura Carabela La Niña, 22, 2°, 1ª 08017 Barcelona, Spain Phone: (34) 933 37 03 22 / Mobile (34) 639 72 10 65 Fax: (34) 933 38 92 31 e-mail: javieralbort@menta.net

©2004 AESF

Introduction

Attention to improved quality and excellence must be the priority of hard plating. The purification of hard chromium plating solution is an important contributor to these goals. Chromium bath purification enhances the performance of the bath by eliminating inconsistencies that can arise as a result of the contamination of dissolved metallic cations. In the European Community and especially in the Scandinavian countries metal behaviour, such as nickel, zinc, copper, lead and particularly chromium, is minimized and regulated. This is what this paper is about and a continuance of the work already initiated in 2003.

When cations build up in the bath, different problems associated with the conductive nature of the bath become apparent. Voltages are gradually turned up, plating times get longer, and the quality of parts decreases. Eventually the problems become so severe that the bath must be dumped and replaced by a fresh, clean solution. An innovation in ion exchange technology is available to effect chromium bath purification.

Known as the reciprocating flow ion exchange technique, it has been developed and implemented to improve product quality, eliminate bath dump, and aid in the reduction of power costs by maintaining a clean, conductive bath solution at all times. Other important fact is the technologies and new technologies, as an alternative to chromium, are marking its trajectory on the army and the automation field. Because of this, working with chromium III coating or other alternatives such as cobalt coatings is usual nowadays.

Purification of hard chromium plating solutions using this technique has been utilized for years to achieve these better bath performance characteristics. But it is concierge and produces contaminant emissions and, therefore, its environment impact has to be minimized both as gas and for its metal impurities. These metal impurities are mixed with nickel, iron, copper and so on. They have to be purified and recycled.

Therefore, chromium substitution and optimization is determined with different alternatives. The aeronautical, automation and general industry are the determinant leading trades, in respect to both production and research, together with legislation, for protecting the environment from contaminants. As an example, the Defence Ministry CHAT changed the use of electrolytic by projection of thermal spray coating.

The U.S. Hard Chromium Alternatives Team (HCAT) is currently executing projects to quality HVOF thermal sprays coatings (principally WV/Co) as a technologically superior, costeffective alternative to electrolytic hard (EHC) plating, which is extensively used in manufacturing and repair of military aircraft components. Two projects on landing gear and propeller hubs have been completed and the technology is being inserted into repair depots. Projects are in progress on hydraulic actuators and gas turbine engine components. Results of rod/seal testing on deformer and materials and component rig testing on the latter will be presented. Standards and specifications for deposition, grinding, and stripping of the thermal spray coatings have been developed and issued by SAE. In general, thermal spray coatings have demonstrated superior fatigue, corrosion and wear properties to the EHC coatings. Other alternative is the nanocrystalline electrodeposition coating plating. Both the Defence Ministries and Universities are working simultaneously on that field.

Wear resistance and hydrogen embrittlement are issues of great concern for steel plating operations. Steels that are susceptible to hydrogen embrittlement should be heat-treated to remove hydrogen. The temperature used is on the order of 205 °C (400 °F), and exact

temperature may be alloy dependent. Why not use this temperature to make thee coating harder and more wear resistance? In this paper, friction, wear and hydrogen embrittlement tests were conducted before and after heat-treatment, and where compared to coatings. The microstructures of nanocrystalline coating, before and after heating-treatment, where analysed by SEM, TEM and X-ray. The mechanism of the excellent wear resistance of the nanostructure material is described.

Evaluation Of Nanocomposite Coatings As Environmentally Acceptable Alternative To Hard Plating

The US Air Force Research Laboratory has been working with Current Technologies Cooperation (CTC) to evaluate alternatives to electroplated hard (EHC) for a variety of applications. One effort focused on performing screening tests on numerous nanostructured coatings or amorphous coatings containing nanoparticles or micro-particles. Electrodeposited nanocrystalline cobalt, with and without tungsten carbide particles, electroless nickel (mid-phosphorous, ENP) coatings with various sizes of diamond particles (150, 1,000, 2,000 and 150 nm + 1,000 nm), and electroless nickel-.cobalt phosphorous (Eni-CoP), cobalt phosphorous (Eco-P), and cobalt boron (Eco-B) –all with and without co-deposited diamond particles, were tested and compared to EHC, polycrystalline cobalt, and electroless nickel coatings without occluded particles. The intent was to elucidate the improvements in performance that can be obtained with decreasing grain or particles size. Preliminary results, which were reported in the earlier paper, suggested that all of the ENP, Eni-CoP, and Eco-P process with occluded diamond particles have the potential to impart the required tribological properties, while reducing the environmental impact to plating process. To conclude this phase of work, additional studies where performed to obtain thicker (e.g., 5-10 mils or thicker) ENP coatings with 150 nm diamond particles occluded and 2-mil thick Eco-B and electrodeposited nanostructure nickel-cobalt coatings, both with 150 nm diamond particles occluded. This paper discusses the adhesion, thickness analysis, hardness, and abrasive wear resistance results that were obtained during screening test, and plans for follow-on work in nanostructured coatings and nanoparticulate occlusion plating.

Hexavalent plating has been used for many years to provide hard, durable coatings with excellent wear and corrosion resistance properties. However, hexavalent baths have come under increasing scrutiny because of the toxic nature of the bath, effects on the environment, and workers' health. This project is investigating the various parameters affecting plating from a trivalent bath. This is an update on our accomplishments to date involving the plating of pump rotors in regard to the hydrodynamics and electrical field effects on the varying geometry of the pump rotor. Continuing work on the bath chemistry, diffusion layer, hydrodynamics, and electrically mediated process parameters will be discussed. The project is being founded by CTMA and a commercial partner.

Some companies are developing a new way to protect metals from corrosion using only silicates-common sand-like minerals found in the earth's crust. No . No phosphate. Just better performance without environmental or regulatory worries. A pilot line was installed to validate chromate replacement over zinc plating. This paper details the capabilities of the pilot line and documents the better adhesion, better heat tolerance, better flexibility, and better stress performance of the environmentally friendly proprietary coating.

Key Words

- Higher production compared with traditional plan at the same operational conditions
- Lower energy and water consume
- Reduction of maintenance costs
- Lower ambient emissions
- To minimise the space required for the plant installation

After reviewed the alternative, new chromium technologies of electrodeposited nanocrystalline coating plating, which are not yet defined in all trades, except passivating for acid zinc baths Zn/Fe, Zn/Ni, Zn/Co, etc and automation or aeronautical business,

After reviewed the nanocomposite coatings new technology as an alternative to chromium, we see that there are not yet well defined in surface treatment areas -mechanical, automotive and aeronautic- with the exception of pasivation treatments for acid zinc baths, Zn/Fe, Zn/Ni, Zn/Co, etc.

Purification and Recovery Techniques

The biggest advantage of eliminating bath dumps or periodic bailouts in a high production facility is the ability to maintain consistent production quality and plating rates. Several techniques are utilized to control contaminant build-up to enable continuous operation of hexavalent plating solutions. The most efficient technology is dictated by the plating solution type (decorative or hard) and the relative production loading.

"Porous Pot" Purification

One early method of controlling contaminant build-up employed the use of a "porous pot" and an electrode system where the where the cathode is located inside the porous pot.





The concept is simple. It relies on the principle that contaminant metal cations are reduced at the cathode surface while most of the trivalent is re-oxidized to the hexavalent state at the anode surface. Periodically, the catholyte solution is adjusted to an alkaline pH where the reduced metals that have not precipitated on the surface of the cathode are precipitated as hydroxides and then filtered from the solution. The filtrate is then added back to the plating solution. The volume of athlete is relatively small. The excess acidity in the plating bath easily compensates for the alkalinity of the catholyte. This method has been improved by utilizing synthetic membrane compartments instead of the old porous pots, but it remains a messy and inefficient process. Contaminants can be removed from the plating bath, but the method does not address chromium recovery from the rinse waters.

Evaporation Recovery

The earlier attempts at recovery employed a simper evaporator on a drag-out rinse station. This approach accomplishes contaminant control with limited chromium recovery by achieving a balance between contaminant loadings in the bath with drag-out losses from the drag-out rinse. Unfortunately, it only works at very high, production facilities where drag-out volumes are high enough to remove contaminants. The drag-out rinse solution is directed to an evaporator where volume reduction is accomplished to allow return of the concentrate back into the plating tank Although is recovered to a limited extent, periodic bailouts (albeit at less frequent intervals) may still be required to control contamination.





Evaporation Recovery and Ion Exchange Removal of Contaminants

A hybrid system utilizing evaporation and ion exchange on a drag-out rinse station can recover a much higher percentage pf chromium and eliminate all dumps and bailouts. Cation exchange resins can effectively remove all of the previously mentioned cation contaminants from the drag-out rinse solution.

The DO rinse is recirculated through a cation exchanger to continuously remove the contaminant cations. An evaporator is utilized after the ion exchange to return a contaminant-free concentrated chromium solution back to the plating tank. This approach achieves complete control of contaminant build-up and is limited only b y the amount of evaporation from the plating tank, which determines how much liquid can be returned to the plating solution. The IX resin must be regenerated periodically with dilute mineral acid to remove the contaminant cations. The quantity of waste produced is small compared to treating a bath dump. In addition, no hexavalent is produced, thereby, eliminating the need for reducing chemicals. This waste is treated like any other non-hexavalent acid waste concentrate and may be sent directly to a rinse water treatment system, provided sufficient equalization is available.

Ion exchange purification offers the advantage of consistent performance because it is a concentration driven process. Contaminant metals can be maintained at approximately one g/l or less eliminating all problems associated with the quality of the plate. Purification to this low level of contamination is not always required.





Rinse water Recovery

Chromium recovery approaching 100 percent can be accomplished utilizing the evaporation/IX technique, as described above, in combination with complete ion exchange of the subsequent flowing rinse waters. Complete ion exchange utilizing separate cation/anion exchange resin beds can recycle all flowing rinses to produce high purity DI water.





The cation regeneration is directed to a waste treatment system (as mentioned above).

The anion resin is regenerated with sodium hydroxide and will contain sodium. Anion regeneration essentially contains sodium dichromate and sodium salts of the other bath constituents. Control of excessive sulphate and chlorides (when necessary) are handled as normal maintenance of the plating solution. As a result, the anion regenerations can be directed back to the plating solution by first passing the anion regenerator solution through a second cation exchanger with the resin in the hydrogen form. The sodium is exchanged for hydrogen, which converts the sodium dichromate to chromic acid. This conversion is very inefficient and can result in some sodium being returned to the plating bath. Testing has shown sodium does not adversely affect the performance of the plating solution even at concentrations as high as 50 g/l.

Ultimately, the sodium concentration may become a concern because there are no losses from this closed loop approach. This could be addressed by periodic bail out of the plating solution. This approach is essentially no different from the original solution to the contaminant problem except that the need to bail out that bath is significantly reduced. Systems of this design have been on operation for years without problems. Under these circumstances, a small volume periodic bail out may be an acceptable trade-off for the higher quality rinsing and reduced water consumption. The quantity of recovered from the anion resin is actually a small percentage compared to the amount recovered by evaporation system. The alternative would be to eliminate recovery of the content from the onion regenerations by directing them to waste treatment. This would make sense if there were other bearing wastes in the facility such as chromium solutions requiring treatment.

Hard Chromium Plating Applications

Hard chromium plating operations often require another approach for controlling contamination build-up. Long plating cycles and high evaporative losses allow rinsing over the plating tank, and supplemental rinsing is minimal or not required. As a result, drag-out losses cannot be relied on to remove cation contamination from the plating solution. For this application, ion exchange can be applied directly on the plating solution. Specialty high purity resins, with a high percentage of cross linking, can perform for a limited time on concentrated chromium solutions, but will suffer a high attrition rate and more frequent replacements will be necessary. When evaporation losses are high, dilution of the plating solution prior to sending it to the ion exchanger helps extend the life of the resin.





Other Bath purification Methods

Electro-dialysis (ED) is another technique used to keep cation contamination at low levels. ED utilizes a cation selective membrane to allow cationic impurities to move under the influence of an electric potential and concentration gradient through the membrane. After migrating trough the membrane, cations can be plated out on a cathode, but usually removed by conventional precipitation techniques. This process is similar to the porous pot method and can be operated directly on the plating solution. Membranes are chemically resistant to oxidative attack. However, there are not 100 percent efficient and allow some migration of both cations and anions across the membrane. Operational cost for these systems are not readily available, but the literature indicates costs are higher than other approaches. Flux rates for contaminants heavy metal cations are low requiring a large membrane surface area and higher equipment costs.



Table 1

Table 2





Figure 6 - "Alternative Bath Purification Method

Figure 7











Economic Considerations

The relative costs associated with the purchase and operations of all technologies discusses above. The advantages and disadvantages of each approach must be kept in perspective. For example, recovery techniques will improve plating efficiency and reduce rejects.

The cost associated with treatment and/or recovery of hypothetical 4,000 litres chromium plating solutions. Several approaches have been compared. The electricity costs shown includes only those components associated with the recovery process and does not account for the additional cost savings associated with operating a plating bath with low contamination levels. It has been demonstrated that a bath contaminated with \sim 7.5 g/l of metal impurities requires an additional 1.5 v to maintain a 1,000 amp current.

The first column assumes in-house treatment of an entire bath dump on a yearly basis. All chemical requirements are theoretical and represent a best-case scenario. This calculations produced a treatment cost of ~ $1.52 \in$ /litre of spent bath. One of our clients has reported a documented cost of ~ $2.10 \in$ /litre

The off-site treatment cost of ~ 1.60/litre does not include transportation costs. The evaporation only technique may provide a limited recovery of plating solution. However, bath purification still relies on high drag-out rates to keep contamination low and waste treatment/disposal costs will remain high. A combined IX evaporation approach achieves both bath purification and a high degree of recovery for approximately $1.14 \notin$ /litre/year. Compared to the conventional treatment options listed above. This approach would safe ~ 1,300 \notin to 2,000 \notin per year using conservative estimates. In addition, the economic benefits of operating a consistent plating solution have not been included in this comparison.

If IX water recycling is included on the flowing rinse waters, the additional operating cost is estimated at ~ $65.00 \notin$ /day assuming 90 percent water recovery of a 2.39 lpm flow. This estimated does not include the saving associated with water a sewer charges. At a combined water/sewer rate of $4.00\notin/4,000$ gallons, a savings of ~ $52,00\notin$ /day would be realized and would reduce the actual cost of recycling water to ~ \$16.00/day. This offers a great advantage. Deionised rinse water will provide superior rinsing for an additional cost of approximately \$0.0014/gallon.

Recovery Technique	Capital Equipment	Labour	Recovery Efficiency	Utilities	Chemical	Miscellaneous
Porous Cup	Low	Low	Low	Low	Low	Bath Purification / Recovery
Evaporation	Low	Low	Moderate	High	N/A	Bath Recovery Only
IX Evaporation	Moderate	Moderate	High	High	Low	Bath Purification / Recovery
IX Evaporation with Rinse Water recycle	High	Moderate	High	High	Moderate	Bath Purification / Recovery & Rinse Water Recovery
Electro- dialysis	Moderate	Moderate High	Moderate	Moderate	Low	Bath Purification / Recovery
Conventional Treatment	Moderate	High	N/A	Low	High	No Recovery & High Disposal Cost

Table 3 - Chromium Plating Solution Recovery - Relative Cost comparison

Reciprocating Flow Ion Exchange –System Operation

As outlined in Figure 2, chromium bath solution is treated in a batch wise manner. A volume of contaminated solution required for purification in transferred to a feed tank. The solution is allowed to cool by radiant means (32°C) prior to being purified by the reciprocating flow ion exchange system.

The solution is subsequently processed through dual cartridge filters and through the ion exchange bed of the system. As the chromic acid solution at 60 % of its normal bath strength passes through the ion exchange bed, the metal contaminants are stripped out of the solution (up to 80 % in a single pass). The purified chromic acid flows to the product storage tank. The excess

volume that results from dilution is easily matched by the natural evaporation loss from the heart chromium bath.

After a predetermined amount of feeding solution has been processed, the unit will automatically effect a regeneration of the resin using sulphuric acid and water. 93 % w/w sulphuric acid is supplied, automatically diluted to the current strength and pumped through the bed. Excess sulphuric acid is washed out of the bed with water. This step generates a diluted waste stream, which contains the metal contaminants, some small traces of chromic acid, and sulphuric acid. The waste stream is to be treated prior to discharge. Upon completion of the regeneration sequence, the unit begins to process more feeding solution. This cycle repeats itself continuously and automatically

Economic Consideration

An economic comparison of three processing methods for thousand gallons of contaminated chromic acid plating solution is outlined Table 3. The three methods consider hauling the liquid waste, full in-house waste treatment of the bath solution, or the use of reciprocating flow ion exchange.

Liquid haulage is the most expensive option and is increasingly falling into disfavour since many of the recycling centres are no longer accepting liquid chromium waste due to the transport liabilities involved. The chemical cost for the treatment and bath replacement combine to make on-site treatment an expensive alternative. The sludge generated when the reciprocating flow ion exchange is employed is only a fraction of the volume that would otherwise be produced.

In addition, chromic bath operating costs would be lower as saving due to lower electrical requirements, higher productivity and lower reject rates become significant.

Basis: 4,600 L Bath Volume - 32 gr; 2 gr Metals

ITEM	ON-SITE TREATMENT	RECOFLO ION EXCHANGE	OFF-SITE DISPOSAL
Bath replacement	2,800€		2,800€
Chemicals	1,388€	432€	
Solid disposal	1,073€	112€	
Liquid Disposal			6,400 €
Total Cost	5,261€	544 €	9,200 €

Table 4 – Purification Economics

Summary

1. Maintenance of hexavalent plating solution no longer requires wasting the solution to control contaminant build-up.

- 2. Continuous bath purification enhances productivity by maintaining contaminant concentrations within and acceptable range and provides more predictable performance from the plating solution.
- 3. Careful evaluation of the production operation is essential to document actual loadings, which determine the most efficient recovery and contaminant control method.
- 4. Total treatment costs at new and existing facilities can be reduced significantly because most of the hexavalent is recovered and only the contaminant cations are sent to treatment. Purchasing recovery/purification equipment can reduce treatment equipment cost for new facilities.

Conclusions

After careful consideration to different hard chromium purification options, it is apparent that the reciprocating flow ion exchange process is the best solution to continuously purify chromic acid solution. With low operating costs, and small floor space requirements, it has become readily accepted within the industry as an economical solution to remove metals from hard chromium plating bath.

References

- 1. R. Guffie, "Hard Chromium Plating", 38, 1986.
- 2. C. Brown, C. Fletcher, "The Recoflo Ion Exchange Process", Ion Exchange for Industry, 1988.
- 3. G. Cushnie, W. Anderson, "Removal of Metal Cations from Plating Solution", 1990.
- 4. M. Dejak, "Chromic Acid Purification by Ion Exchange", 1988.
- 5. C. Fletcher, V. Pace, "New Performance Standards for Demineralization Set by Recoflo Technology", 1995.
- 6. P. Pajunen, "Electroplating-Making Environment Friendly", July 1998.

Acknowledgement

We would like to thank Tecnocrom Industrial, SA, Cabrera de Mar, Barcelona, Spain and particularly to Mr. Rafael Fontanals, General Manager, for it collaboration to this work and research. Also, to Ingenieria, Contrataciones y Servicios, SL (INCOSE), Barcelona, Spain, for his help and collaboration.