New Techniques For Minimization Of Waste And Contaminated Water

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Waste process water has an important cost which should be minimized in a direct way to have a good quality water for chemical and electrolytic process. Water contaminants are: sales, carbonates, nitrates, nitrites, etc, jeopardise surface treatments.

Flow membranes units of inverted osmosis are used. The ionic interchange units, ionic carbon interchange units and filtering with diatomaceous earths, etc is considered obsoletes.

In the surface treatment process it is important both electrolytic and chemical, the water consumption should be reduce as much as possible. Baths contamination should be avoid by minimization of dragging when treating parts in barrel or tank.

The use of chemical or manufactured products is basic in the resulting sludge. They minimize contamination and cations and anions migration by chemical reaction. Also, physical-chemical and biological purifying plants and recovery flow membranes and ultra-filtration units and evaporators are appropriated.

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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, cost-effective 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 ºF), 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 nanoestructured 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 nanoparticulated 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.

Chrome from Aerospace aluminium for Stainless Plows

Most Aerospace 5xxx, 6xxx and 7xxx aluminium alloys include chromium. Aluminium deoxidation is accomplished by strong nitric-and this “withces breew” accumulates Cr^{+6} . Attempts to isolate and/or characterize the reduced, precipatated hydroxide ($Cr(OH)_3$) or derived magnesium chromite ($MgCr_2O_4$) showed negative by XRD and EDS. The purpose was to get to recycle cromium metal via commercial electrowinning of chrome III alum, $K[Cr(SO_4)_2]$ and possible investigaste chrome plating from $Mg[Cr(SO_4)_2]_2$. Nontheless, treating spent “bitches brew” with only HSO_3 & $Mg(OH)_2$ gave impressive results as seen by ICP AA analysis.

Metal Charged Effluents Treatment by Electrolysis

The electro-oxidation and electro-reduction phenomena are ruled by electrolysis laws, which we are going to remind now.

Principles of Electrolysis

The dissolution of an electrolyte in a solvent induces formation of species positively charged (cations) and negatively charged (anions). The fact of applying a difference of potential between two electrodes immersed in an electrolyte solution creates an electric field, thus causing ions migration. There are three characteristic ways of transporting matter to the electrolyte: migration, convention and diffusion.

The Migration

It refers to the movement of the charges. Cations move in the field direction towards the cathode and the anions in the opposite direction.

The Convention

Under the effect of different factors like temperature, agitation, different density, the transportation of matter can be modified. Therefore, the convention's reaction is conditioned by the mentioned variables.

The Diffusion

This is a phenomenon due to the existence of a concentration gradient around the electrode. The gradient is generated by the electrochemical reaction developing in the interface of the electrode/solution. This variation in the concentration provokes the spices moving from the mores concentrated areas to less concentrated ones. Unlike the other two ways of transporting matter, the diffusion phenomenon takes only place in the area corresponding to the interface of the electrode/solution.

These are the basic principles of electrolysis where oxidation reaction, oxidation-reduction, and stronger reducers occur, according to the potential scale values of metal electro-negativity, that is, Nernst's law.

Application and Implementation of An Electrodeposition Unit for Purifying Heavy Metal Effluents

Electrodeposition is a technique particularly well adapted to effluent treatment charged with heavy metals (Cd, Cr, Pb, Zn, Ni, Cu, Hg) or precious metals (Au, Ag, Pd). The metal deposit in the cathode can be retrieve, purified and recycled en in process.

The system is suitable for different application, like recovery of metals in static rinsing. If a cellule is fitted in the "dead" rinsing circuit, it will increase considerable the circuit's life and it will avoid environment pollution or contamination. It also achieves a reduction of environment cost and energetic consume.

However, the non-electroactive components will be preserved. Consequently, it will not be possible to recycle the rinse indefinitely. Therefore, it should be purified.

This type of electrodeposition process, can be used for holding and recuperating metals in the three types of zinc baths: cyanide, acid, and exempt. It can also be applied for rinsing nickel, nickel wood, watts, chemical nickel, etc.

Other Factors to Avoid Contamination

There are enumerated below, other important parameters which are beginning to be taken into consideration and that are getting an environment grant for them by the EU:

- Decyanidation
- Chemical o mechanical destruction of cyanide
- Dichromate
- Specific traitment for water: to decarbonate
- Coagulation
- Neutralization
- Microfiltering for electrolytic regeneration
- Flocculation and decantation
- Final filtering with sand
- Ionic plasma

The processes are intended to reach environmental self-controlled parameters of the following values:

pH	5.5 to 8.8
MES	⟨6 mL
Cr^{+6}	⟨0.01 mL
CN^{-}	⟨0.001 mL
Ni	⟨1 mL
Fe	⟨0.2 mL
Al	⟨0.2 mL
Cu	⟨0.05 mL
Zn	⟨0.5 mL
Ob	⟨0.2 mL
Sn	⟨1 mL
Cd	⟨0.5 mL
Cr^{3+}	⟨0.05 mL
P	⟨5 mL

F ⟨5 mL

Reciprocating Flow Ion Exchange – System Operation

As outlined in Figure 1, chrome bath solution is treated in a bath wise manner. A volume of contaminated solution required for purification is transferred to a feed tank. The solution is allowed to cool by radiant means (90°C) prior to being purified by the reciprocating flow ion exchange system.

The solution is subsequently processed through dyak 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 hard chrome bath.

After a predetermined amount of feed solution hast 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 correct strength an pumped through the bed. Excess sulphuric acid is washed out of the bed with water. This step generates a diluted waste stream containing 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 regenerating sequence, the unit begins to process more feed solution. This cycle repeats itself continuously and automatically.

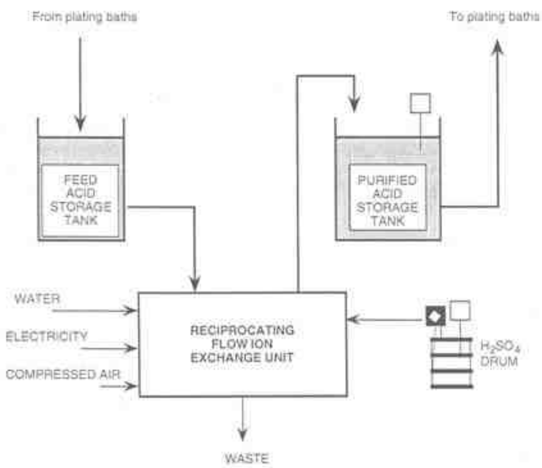

Figure 1 - Typical Process Schematic

Economic consideration

An economic comparison of three methods of processing 1000 gallons of contaminated chromic acid plating solution is outlined in Table 1. 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 fallowing into disfavour since many of the recycling centres are no longer accepting liquid chrome waste due to the transport liabilities involved. The chemical cost for treatment and batch 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, chrome bath operating costs would be lower as savings dur to lower electrical requirements, higher productivity, and lower reject rates become significant.

Table 1 – Purificacion Economics

Item	On-Site Treatment	Recoflo Ion Exchange	Off-Site Disposal
Bath replacement	3,500	-	
Chemicals	1,735	539	3,500
Solids disposal	1,341	139	-
Liquid disposal	-	-	-
Total Costs	$ 6,576	$ 678	$ 11,500

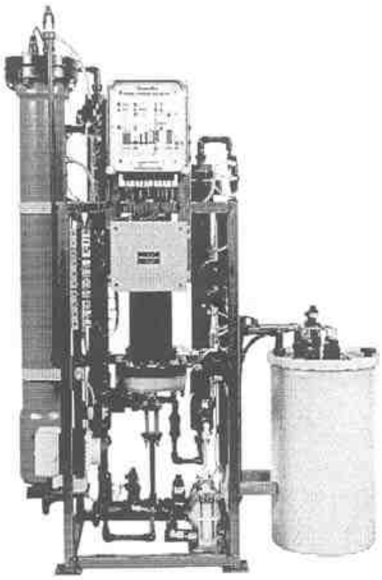

Figure 2 – Typical reciprocating Flow Ion Exchange Unit
Basis: 1000 gallon bath volumen 32 opg chrome; 2opg metals

Table 2-Evolution Of Environment Regulations In The European Union

mg/l	1999	2003	Study for existing plants	Study for new plants
Aluminium	---	1.0	1.0	1.0 (Al+Fe)
Silver	---	---	0	0
Cadmium	3.0	0.1	0	0
Hexavelant Chrome	0.1	0.1	0	0
Total Chrome	3.0	1.0	0.5	0.5
Copper	2.0	2.0	1.0	1.0
Tin	2.0	0.5	0	0
Iron	3.0	3.0	3.0	2.0 (Al+Fe)
Nickel	2.0	2.0	1.0	0.5
Lead	1.0	0.5	0	0
Zinc	2.0	1.0	0.5	0.2
Cyanide	0.1 or 1.0	0.1	0	0
Fluoride	15.0	10.0	10.0	10.0
Phosphorus	15	10.0	10.0	10.0
DCO	250	150	100	100
MES	30	30	30	30
pH	5 to 9	6.5 to 9	6.5 to 9	6.5 to 9

Zinc

It has been suggested reverse osmosis for effluent treatment (both Zn-chloride and Zn-cyanide).In order to protect the membranes it is advisable to maintain feeding pH between 5 and 11 units in order to protect membranes. However, it must be emphasised that reverse osmosis on its own does not achieve completed recovery in a closed circuit..

In 1978 a reverse osmosis plant was set up In California, USA, to treat effluents from zinc-phosphate processes. The company's compromise to drastically reduce its residual effluent forced it to think how to reduce 90 % its wastewater and how to re-use effluents. For a pre-treatment prior to implementing the reverse osmosis process, it proved necessary the effluent homogenisation , multilayer dispersants addition and anti-scaling chemicals to protect membranes adequately.

The following table provides average feeding quality and reverse osmosis production data of the plant:

Table 3 - Average Output On Zinc Recover Process

Parameter	Feed in Concentration	Permeate Concentration
pH	**5.1**	**4.9**
Zinc (ppm)	**7.3**	**2.2**
Iron (ppm)	**0.5**	**< 0.2**
Phosphate (ppm F)	**414**	**109**
TDS (ppm)	**750**	**238**

Reverse osmosis was also tested for various industrial effluent treatments with important zinc contain. Results are shown in the table below:

Industrial Sector	Feed in Concentration (Zinc ppm)	Permeate Concentration (Zinc ppm)	Retention %
Zinc plating rinse	1700	30	98
Central condensers	300	53	82
Power station	780	3	99
Textile plants	720	140	98
	460	250	46
	520	360	31
	7200	360	95
	1400	30	96
	4100	180	96
	1200	22	98
	24000	430	98
	9700	37	> 99
CoolingTowers Purging	10000	300	97

Table 4- Average Output On Zinc Processes Separat

Summary

1. Maintenance of hexavalent chrome plating solution no longer requires wasting the solution to control contaminant build-up.
2. Continuous bath purification enhances productivity by maintaining contaminant concentrations within acceptable range and provide 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 cost at new and existing facilities can be reduced significantly because most of the hexavalent chromium is recovered and only the contaminant cations are sent to treatment. Purchasing recovery/purification equipment can reduce treatment equipment cost for the new facility.

Conclusions

After careful considering to different hard chromium purification option, it is apparent that reciprocating flow ion exchange process is the best solution for continuously purifying chromic acid solution.

With low operating costs and small floor space requirement, it has become readily accepted in the industry as an economical solution to remove metals from hard chrome plating baths.

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