Chromium Recovery and Minimization in Industrial Surface Treatment Processes

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A proposed OSHA standard drastically reduces the permissible exposure limit (PEL) on hexavalent chromium and its compounds from 52 to 1 µg/m3 on an 8-hr time weighted average. In this paper, chromium recovery and minimization are reviewed for a variety of industrial surface treatment processes. These include zinc passivation and aluminum sealing, as well as decorative and hard chromium plating.

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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.

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
- Dechromate
- 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

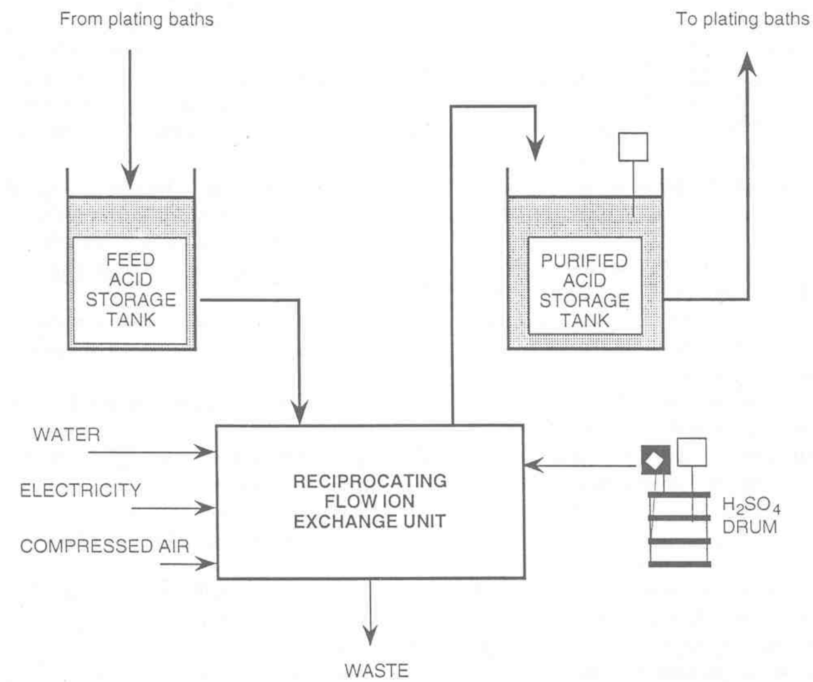
Reciprocating Flow Ion Exchange – System Operation

As outlined in Figure 1, chrome bath solution is treaten in a bathc 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 trhough dyak cartridge filters and through the ion exchange bed os 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.

Aftet a predetermined amount of feed solution hast been processed, the unit will automatically effect a regeneration of the resin using sulfuric acid and water. 93% w/w sulfuric acid is supplied, automatically diluted to the correct strength an pumped through the bed. Excess sulfuric acid is washed out ot the bed with water. This step generates a diluted waste stream which constains the metal acontaminants, some small traces of chromic acid, and sulfuric acid. Ythe waste stream is to be treated prior to discharge. Upong completion of the regeneration 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.

Liquida haulage is the most expensive option and is increasingly faloing intyo disfavor since many of the recycling centers are no longer accepting liquid chrome waste due to the transp.ort 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 loewer electrical requirements, higher productivity, and lower reject rates become significant.

Table 1 – Purificacion Economics
Basis: 1000 gallon bath volumen 32 opg chrome; 2opg metals

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

Figure 2 – Typical reciprocating Flow Ion Exchange Unit

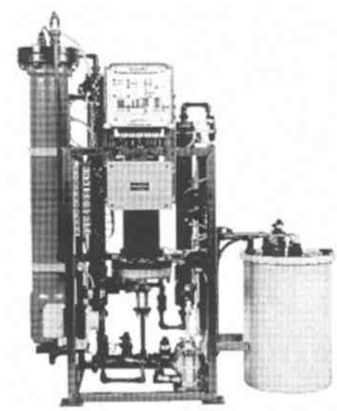


Table 2-

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

NEW TECHNOLOGIES TO MINIMIZE ENVIRONMENTAL IMPACT ECONOMIC COST

Processing With Silanes

Fewer stages are required compared with conventila treatments. In addition, the silane treatment stage may be at room temperatureand without need for subsequent rinses.

Advantages Of New Silane Treatments

These advantages are clearly indicated in Table 6. Muchs work has been done, and is continuing, to develop these treatments into robust industrial processes. This means that treatment solutions must be optimised for stability, addifives thar reduce the rate of condensation must be considered and sensitivity to contaminants and drag-in established. In addition, research is continuing to develop new silanes and applications.

Silanes

Silanes are not new materials. They have been used in many industrial applications in corrosion prevention and metal pre-treatment are provided some exciting results, which wil have a profound effecto on the metal treatment industry.

Silanes Effective On Metals

Some examples of silanes have been used successfully on a variety of metals. Each is characterised by having a triethoxy or trimethoxy grouping at one end of the molecule and an organic grouping of various types at the other. In simple terms, the alkoxy groups are hydrolysed when added to water, forming silanols. The silanol reacts with oxides on the surface of the metal to form strong covalent bonds that will not wash off.

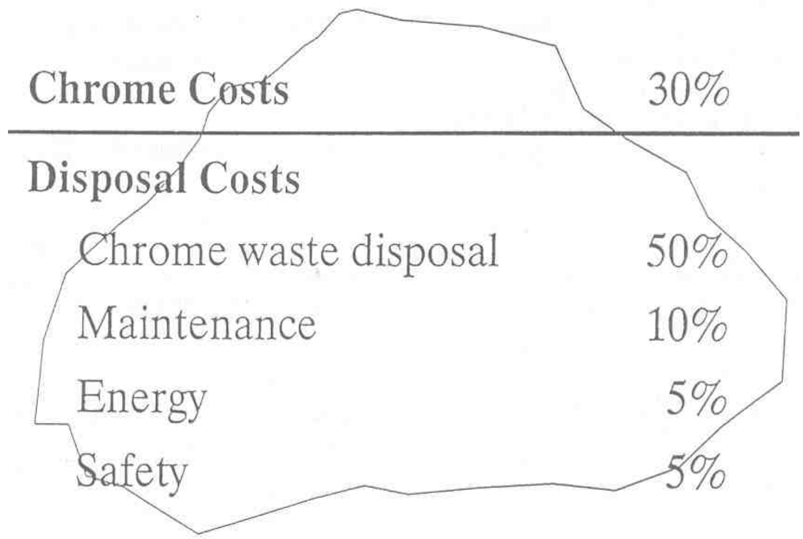
The organofunctional end of the molecule is able to interact with a suitable paint or other polymeric material to provide a strongly adherent link with the metal surface. The BTSE (1,2-bis-[triethoxy silyl]ethane) is a different type of molecule with three ethoxy group at each end. This creates a strongly acidic character for the molecule and facilitates strong covalen bonding with a wider variety of metals with weakly basic proporties. If BTSE (a non-functional silate) is used first, followed by an organo-functional silane (such as vinyl silane) then a strongly cross-linked network is formed with superior adhesion and enhanced metal protection. Thi is the basis o Brent's proprietary technology.

Patents

Brent's portfolio of patents is wide-ranging, with 16 filing since 1990, and further work is on-going.

THE ICEBERG PRINCIPLE

Figure 3 - Typical Chromating cost breackdown at a coil-coating mill



EFFLUENT TREATMENT

Comparison of Silane and Chromate

Figure 4 – Benefit of non-chrome process for 1,000 litres working solution

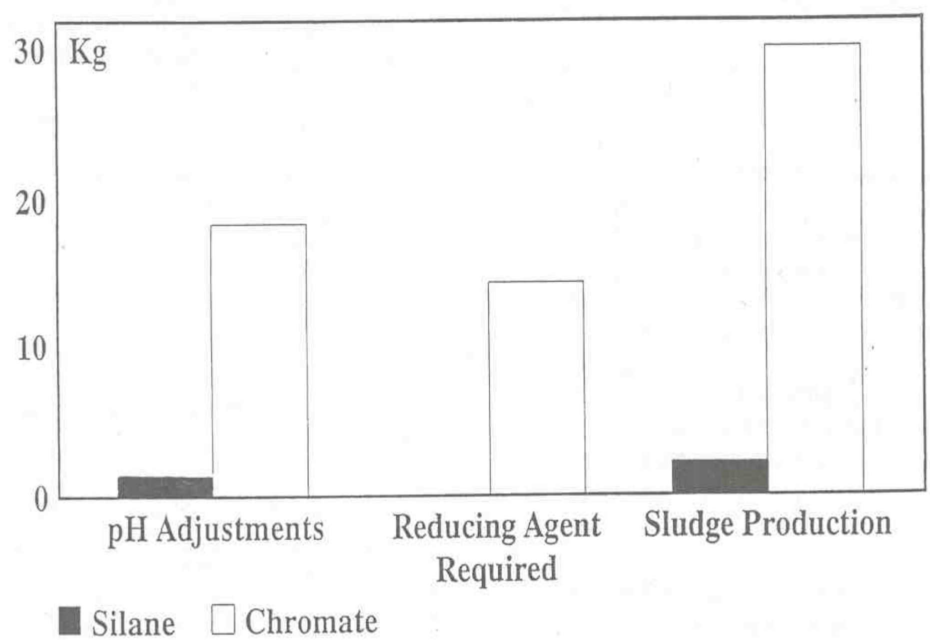


Figure 5 - Simplistic mechanism of cros-linking between metal and polymer

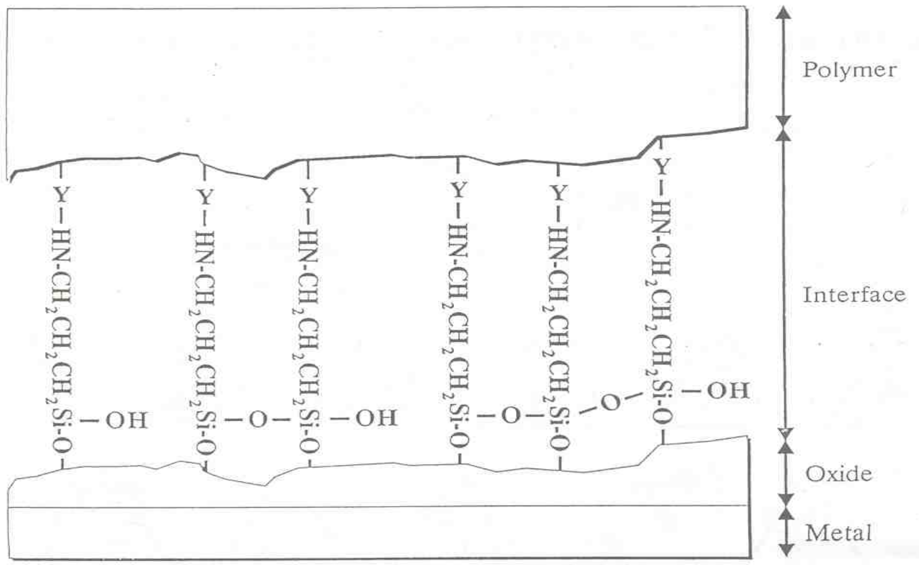


Figure 6 – Formation of interpenetrating network and cross -linking

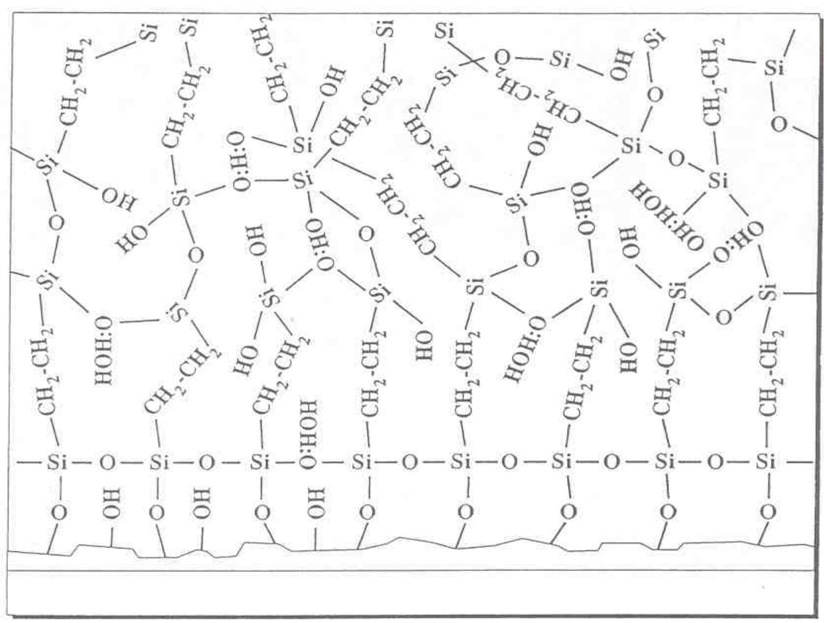


Table 3 – Silane Chemistry

	SILANE CHEMISTRY
BTSE	$(C_2H_5O)_3$-Si-CH_2CH_2-Si-$(OC_2H_5)_3$
VS	H_2C=CH-Si-($OC_2H_5)_3$
γ-UPS	H_2N-CO-NH-CH_2-CH_2-CH_2-Si-$(OC_2H_5)_3$
γ-APS	H_2N-CH_2-CH_2-CH_2-Si-$(OC_2H_5)_3$
A-1170	$(C_2H_5O)_3$-Si-CH_2CH_2-CH_2-NH-CH_2CH_2-CH_2-Si-$(OC_2H_5)_3$
A-1289	$(C_2H_5O)_3$-Si-CH_2CH_2-CH_2-S_4-CH_2CH_2-CH_2-Si-$(OC_2H_5)_3$
SAAPS	H_2C=CH-C_4H_4-CH_2-NH-CH_2-CH_2-NH-$(CH_2)_3$-Si-$(OCH_3)_3$.HCI

Table 4 - Successful Application of Silane Treatments on Painted Systems

WHERE DO SILANE TREATMENTS WORK
Painted Systems:
• Painted cold-rolled steeel
• Galvalume coil paint lines
• Painted hot-dip galvanized steel
• Cast aluminium wheels
• Coated aluminium beverage cans

Table 5 - Successful Application of Silane Treatments on Unpainted Systems

WHERE DO SILANE TREATMENTS WORK ?
Unpainted Systems:
• White rust inhibition of hot-dip galvanized steel
• Al 2024 aircraft alloys
• Weathering of TiZn roofing sheet

Table 6 - Advantages Of New Silane Treatments

ADVANTAGES OF NEW SILANE TREATMENTS
• Optimised for the metal and application
• Environmentally compliant
• Corrosion performance superior to chromate and phosphate
• Corrosion resistance even without paint
• Fewer steps than phosphating

SUMMARY

It is intended holding contaminants in surface traitment for minimizing toxic by-products and to avoid damage to the environment. Also to save electrical energy. Therefore, we should always minimize and optimize the parameters of discharge to match them with the values allowed by regulations.

It should be bear in mind that in the surface treatment industry (in the EU at least) a physical-chemical purifying system with press-filter is installed in 90% of factories approximately. The remainder 10% fits out the indicated new technology. It is advisable, necessary and vital to protect the environment and before implementing a purifying process to analyze individually each installation and equipped it with new techniques, bearing in mind the following parameters:

- Number of rinsing.
- Rinsing rationalization.
- Water recovery from rinsing.
- Cascade effect.
- Working temperature.
- Water quality before and after the electrolytic or chemical process.
- Kind of cation and anions the line is working with.

To avoid damage to the environment, the different purifying processes should be adjusted to the particular chemical process used. That is, the purifying process is different for an anodizing line that for a nickel electroplating, and a chrome electroplating one is different from zinc electroplating.

CONCLUSION

I. Implementation of new technology, together with certification of environmental quality in order to minimize environment impact.

II. Environment auditing and internal process control in the company.

III. Implementation of new technology for energetic and chemical saving in physical-chemical purifying plants.

IV. Mud recovery of by-products from surface treatment muds for making bricks, adobes or construction elements.

V. Reusing environment energy from the evaporator system for general heating.

VI. Each surface treatment process should be a particular study for minimizing manufacturing cost and environment damage.

VII. After careful consideration to different hard chrome 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 cost, and small floor space requeriments, it has become readly accepted within the industry as an economical sooutin to remove metals from hard chrome plating baths.

VIII. Clearly, the silane processes are the most promising to replace chromates in many metal finishing industries and, in general, the advent of organofuctional and non-organofuctional silanes for corrosion control of metals may be considered the most significant development in corrosion engineering of metal surfaces in recent years.

References

1. Bureau Veritas Quality International. Ivon Briand, Centre d'Angers.
2. EDF, Departamento de Aplicaciones de Electricidad en la Industria.
3. Alain Gauthier, Departamento de Industrias del Parque de Saint Christophe.
4. Raphael Hiritz, EDF Dirección de Investigación y Desarrollo.
5. 'Legislation for the European Community on Waste Characteristics, Lexiviation Test forElectroplating Muds', SUR/FIN '97, Detroit, Dr. Xavier A. Ventura.
6. 'Elimination of Mud, Toxic Waste & Inert Materials Produced by Surface Treatment By Using Ionic Plasma', SUR/FIN '98, Minneapolis, Dr. Xavier A. Ventura.
7. R. Guffie, "Hard Chrome plating", 38,1986.
8. C. Brown, C fletcher, "The Recoflo Ion Excchange Process", Ion Exchange for Industry, 1988.
9. G. Cushnie,, W. Anderson, "Removal of metal cations from chromium plating solutions", 1990.
10. Dejak, "Chromic Acid Purification By Ion Exchange", 1988.
11. C. Fletcher, V. Pac "New Performance Standards For Demineralization Set By Recoflo Tecnology", 1995.
12. P. Pajunen, "Electroplating.Making Environment Friendly", Julio 1998.

13. W.J. van Ooij, Proc. 2nd Information Exchange On Chromium Alternatives, NDCEE, November 7-10, 1995. Seven Seprings, PA., "Corrosion Control Of Metals By Silanes".
14. W.J. van Ooij, Proc. 3rd Information Exchange On Chromium Alternatives, NDCEE, November 4-6, 1966, Seven Seprings, PA., "Corrosion Control Of Metals By Silanes".

