1. Best technologies applied to Non-Ionic Degreases

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7. Best technologies applied to Trivalent Chromium-Based Passivations
Best technologies applied to Non-Ionic Degreases

march, 2008

Key words: aqueous degrease, non-ionic surfactants, fog point, cross-flow filtration, vacuum evaporation, electrocoagulation
The BREF on “Surface Treatment of Metals and Plastic Materials” does not establish any differences in the behavior of anionic and non-ionic aqueous degreases. As a consequence, the BATs\textsuperscript{1} proposed for separating emulsified oils, and particularly, cross-flow filtration techniques, are not efficient when applied to non-ionic degreases. The Zero Plus Project proposes an interesting alternative – and candidate to BAT – for these cases, consisting in the association of vacuum evaporation and electrocoagulation. Vacuum evaporation is used for the batch treatment of spent degrease bath volumes generated in time, whereas electrocoagulation is used for the continuous treatment of the drag-outs from the degrease bath that reach the aspersion rinse stage. As a result of this work, a significant reduction in effluent volumes produced and an almost total recovery of rinse waters have been achieved, with an insignificant volume of sludge and a very reduced volume of energetically valuable concentrated effluents as a tradeoff. The Zero Plus Project, through the results achieved, promotes the revision of BREF contents both regarding the difference in behavior of aqueous degreases, as well as considering the alternative herein proposed as a strong candidate for BAT.

\textsuperscript{1} BAT: Best Available Techniques
Introduction

One of the main contributions of the European Project ZERPLUS (LIFE ENV / E / 256) is the revision of the BATs included in the BREF “Surface Treatment of Metals and Plastics” in applications where the behavior of these techniques is not adequate or satisfactory.

The tasks carried out with non-ionic degreases for steel surfaces, and their corresponding rinses, are indicative of the relevance of the approach of the Project, given the significance of the results obtained.

Since the BREF does not make any distinctions in the behavior of degreases based on their detergent properties, the ZERPLUS Project decides, at a first stage, to use the same BATs proposed by the BREF for aqueous degreases, that is, a combination of the following technologies:

- Belt oil skimming: as pre-treatment for the continuous removal of non-emulsified and disperse oil, to reduce drag-outs to rinses
- Micro/Ultrafiltration: as regeneration treatment for degreases by separating of the emulsified oil and also reducing its drag-out

Additionally, and even though the BREF does not consider issues relating to rinses, given their amount and volumes consumed at the facility under study, the ZERPLUS Project complements the option by applying continuous electrocoagulation in an attempt to reduce rinse COD to discharge levels with a possible re-utilization of water.

Results obtained with cross-flow filtration

Cross-flow filtration, be it microfiltration or ultrafiltration, yields very poor results:

- Non-ionic surfactants recovery rate between 5-20%

Even though deoiling removes 97% of supernatant oils, the drag-out of emulsified oils and degreasing components to the rinse stage is still high.

The issue that arises is, how is it possible that recovery levels are so low when the same technology achieves recovery rates of 80-90% surfactants for anionic degreases?²

This is due to the properties of non-ionic degreases and their micellar aggregation capacity, which increases with temperature and under the operating conditions.

² AIMME previous experiences: “Zero Discharge” Project (LIFE 93 /E/A121/E 1523). 
“Urbanbat” Project (LIFE 03 ENV/E/160).
There is a temperature point at which aggregation reaches its maximum value (fog point), and which substantially modifies the characteristics of the degrease:

- Surfactant reversible insolubility
- Minimal foaming power
- Maximum detergent power

Despite being highly valued due to their improved degrease cleaning capacity, the new characteristics have other effects that play against their recycling through cross-flow filtration caused by:

- An increase in the size of the polyoxyethylene chains formed
- The integration of hydrocarbons into these chains, which causes their aggregation number to increase
- A reduction in membrane permeation capacity regardless of membrane porosity

One of the major consequences of this article is that the BREF will have to revise its contents and establish the differences between the behaviors of anionic and non-ionic degreasers.

**New approach**

The system formed by a non-ionic degrease bath and its associated rinse stage requires a new approach to overcome these difficulties. This approach can be summarized as follows:

- Waiting until the degrease bath is spent
- Keeping its high production of drag-outs to the rinse stage throughout its life (equivalent to continuous purging)
- Treating the spent degrease bath in situ with the vacuum evaporation (VE) technique
- Treating the rinse continuously with electrocoagulation, as initially posed

This proposal refers to technologies that the BREF defines as zero discharge technologies (such as VE) and, even though it states that they are not BATs, generally because of their cost, it does mention that in isolated cases they may be used due to particular reasons (Cf. BREF sections 4.16.12 and 5.1.8.4.)
Results obtained with vacuum evaporation

After applying VE to two loads/year of spent non-ionic degreases, the results obtained are as follows:

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated spent degrease volume</td>
<td>3 m³/year</td>
</tr>
<tr>
<td>Separated oil volume (deoiling)</td>
<td>36 l/year</td>
</tr>
<tr>
<td>Recovered water volume (distillation)</td>
<td>2.81 m³/year</td>
</tr>
<tr>
<td>Rejects volume (concentrate)</td>
<td>154 l/year</td>
</tr>
<tr>
<td>Volume concentration factor (VCF)</td>
<td>20</td>
</tr>
<tr>
<td>Power consumption</td>
<td>1,300 kWh/year</td>
</tr>
</tbody>
</table>

The consequences of these results can be summarized as:

- Recovery of 94% of the volume as high-quality water to prepare new degrease baths.
- Equivalent reduction of waste volumes to manage.
- Possibility of increasing the value of the remaining 6% waste as fuel due to its high organic load and absence of chlorinated organic matter (COD: 600 g/l and oils: 25 g/l.).
- The volume concentration factor can be doubled (to VCF = 40) without affecting distillation quality, but at the cost of also doubling treatment time and energy consumption.

Results obtained with electrocoagulation

The continuous application of electrocoagulation to the aspersion rinse stage has allowed obtaining the following results:

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated rinse water volume</td>
<td>740 m³/year</td>
</tr>
<tr>
<td>Recovered water volume</td>
<td>724 m³/year</td>
</tr>
<tr>
<td>Dry sludge volume to manage</td>
<td>0.5 m³/year</td>
</tr>
<tr>
<td>Flocculant volume to add.</td>
<td>1.5 m³/year</td>
</tr>
<tr>
<td>Energy consumption for electrocoagulation</td>
<td>40 kWh/year</td>
</tr>
<tr>
<td>Energy consumption for pumping</td>
<td>5,300 kWh/year</td>
</tr>
</tbody>
</table>
The consequences of these results can be summarized as:

- Recovery of almost all of the water (98%) with an acceptable quality for recycling as new rinse water;
- Equivalent reduction of the discharge volume sent to physicochemical treatment;
- Exchange of 740 m³/year of semi-concentrated effluent by 0.5 m³/year of oily sludge + 15.5 m³/year of sludge dehydration water.

Candidacy as BAT

Quality indicators for the recovered water show very interesting behavior rates for electrocoagulation, which makes the combination of vacuum evaporation and electrocoagulation a strong candidate as BAT for the system formed by a non-ionic degrease stage and its associated rinse stage.

These indicators can be summarized as:

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>500-800 mg/l</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>&lt; 10 mg/l</td>
</tr>
<tr>
<td>Oils</td>
<td>&lt; 10 mg/l</td>
</tr>
</tbody>
</table>

The assessment of the economic feasibility of vacuum evaporation as BAT candidate for non-ionic degreases indicates that:

- VE is only feasible when combined with other applications at the facility, since the investment is used for two annual treatments of the corresponding spent degrease bath loads.
- In the case at hand, VE is feasible because it is shared by this application (spot) and that of cyanide copper rinses (continuous).
- The global study of costs yields a return of investment period of 4.5 years for the particular situation of the company under study, considering an annual inflation rate of 3.5%.

As regards electrocoagulation, the assessment of its economic feasibility as BAT candidate for the rinse stage that receives deoiling drag-outs indicates that:

- The electrocoagulation process is run continuously and its cost is chargeable to this application entirely.
- The global study of costs yields a return of investment period of 10 years for the particular situation of the company under study, also considering an annual inflation rate of 3.5%.

Consequences

The combination of vacuum evaporation and electrocoagulation is a strong candidate as BAT to solve the problem of non-ionic degreases and their associated rinse stages.

The ZERO PLUS Project promotes the revision of the contents of the BREF “Surface Treatment of Metals and Plastic Materials (MST)” relating to aqueous degreases, and also proposes considering the alternative herein presented as a BAT candidate.
Best technologies applied to Sulfuric Etching

September, 2008

Key words: Sulfuric etching, ion retardation, aeration, acid adsorption, metal exclusion, rejects
The techniques described as BATs\textsuperscript{1} in the BREF “Surface Treatment of Metals and Plastics” for the recovery of sulfuric acid-based etching baths, and particularly diffusion dialysis with anion membranes, are non-viable for most electrocoating companies because of their price and associated exploitation costs.

Even though the ion retardation technique is mentioned in the BREF as a possible BAT candidate for sulfuric etching (cf. Section 4.11.14.2), it is only analyzed in the context of sulfuric anodizing baths for aluminum, which is not evidently relevant to the case at hand.

This article shows the results obtained in the European Project ZERO PLUS (LIFE 05 ENV / E / 256), where the ion retardation and aeration technologies have been combined for recycling sulfuric etching baths and their associated rinses.

Ion retardation allows recovering most of the sulfuric acid and keeping a low and stable concentration of iron due to the synergy of two mechanisms:

- Acid adsorption
- Exclusion of ferrous ions.

It should be noted that this technology does not reduce effluent volume, but it decreases its polluting load instead. Thus, it generates a rejects fraction consisting of a solution diluted in acid and rich in iron.

This fraction, or unavoidable waste, mixed with etching rinse waters, is treated in situ with aeration. Very interesting results have been obtained, since it is possible to re-use this water as fresh rinse water, given the dramatic reduction in COD, iron contents, and conductivity.

These results support considering the association of ion retardation and aeration as a BAT, as well as reviewing BREF contents in this regard.

\textsuperscript{1} BAT: Best Available Techniques
Introduction

The surface preparation process of electrocoating companies places etching as an intermediate stage, between chemical degreasing and electrolytic degreasing.

A chemical degreasing process allows ensuring residual organic contamination levels of 10-8 g/cm² which, despite being suitable for other surface treatment processes (painting, aluminum anodizing, or hot electrocoating), are still inadequate to achieve quality metal coatings by electrolytic means.

In order to reach lower residual organic contamination levels, the detergent action of the degreasing stage and surface polarization (electrolytic degreasing) should be combined, since the latter is capable of modifying the equilibrium state of the metal substrate interface towards other, more active states.

Before the electrolytic degreasing itself, a pre-activation stage is needed to remove the various chemical layers (oxides and calamines) and favor the creation of adherent and continuous coats. This is achieved through etching, by means of an acid solution and through two distinct mechanisms:

- An acid-base reaction (activation), where hydrated metal oxides are dissolved.
- A redox reaction (decalamination), to remove non-stoichiometric oxides that behave as cathodes with the base metal or anode.

Hydrochloric etching processes present a prevalence of the acid-base mechanism, whereas in sulfuric etching processes there is a prevalence of the redox mechanism combined with the mechanical action caused by hydrogen release.

A sulfuric etching of steel has between 5-15 mass percent of acid (90-260 g/l), and is used at temperatures above 50°C.

Unlike hydrochloric acid, the concentration of ferrous salts has a strong redhibitory effect that negatively impacts sulfuric acid etching speed. When the contents of ferrous sulfate reach 75 g/l (expressed as metal iron), a sulfuric etching bath can be considered to be spent, since its dissolution speed decreases by 40%, treatment time increasing in a similar proportion.

Reducing ferrous sulfate contents carries the risk of causing saline precipitations on the material, their removal by rinsing being difficult.

For this reason, the etching solution is completely substituted by a new one, generating a waste that has to be physicochemically treated at the WWTP².

² WWTP: Waste Waters Treatment Plant
Focusing the problem

There are five sulfuric etching baths connected to a buffer tank at the facilities. Operating conditions can be considered to be atypical:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching volume</td>
<td>18 m³</td>
</tr>
<tr>
<td>Concentration of sulfuric acid</td>
<td>125 – 135 g/l (7 – 7.5 mass %)</td>
</tr>
<tr>
<td>Limit Fe concentration</td>
<td>20 g/l</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>Room temperature (25 – 30 °C)</td>
</tr>
<tr>
<td>Substitution frequency</td>
<td>Annual (by means of partial discharges)</td>
</tr>
</tbody>
</table>

The peculiarity of these conditions is due to temperature, unusual for a sulfuric etching process, which forces an increase in the substitution frequency due to the significant decrease of the solubility of ferrous salts under such conditions.

Therefore, and as way of precaution, the facility keeps a limit concentration of 20 g/l of ferrous sulfate (expressed as metal iron).

The final objective is obtaining a smooth etching with as little hydrogen release as possible to reduce the risk of induced embrittlement. Therefore, the etching process adds significant concentrations of non-ionic surfactants that act as inhibitors.

This situation carries an added difficulty, since iron initial concentration levels will be close to those that would be released by retarding resins in the treatment of “normal etchings” after regeneration with water.

Resin selection and results obtained with ion retardation

A series of pre-industrial tests were carried out with four different retarding resins that allowed selecting a strong base, gel-like resin, as the most suited for this case.

Initial conditions and industrial test results are summarized as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration of sulfuric acid</td>
<td>125 g/l</td>
</tr>
<tr>
<td>Final concentration of sulfuric acid</td>
<td>106 g/l</td>
</tr>
<tr>
<td>Acid recovery index</td>
<td>85 %</td>
</tr>
</tbody>
</table>
Iron initial concentration \(12.6 \text{ g/l}\)
Iron final concentration \(7.7 \text{ g/l}\)
Iron removal index \(40\%\)

Once the retarding resin has been regenerated with water, an acid recovery index above 80% is achieved, and the difference needs to be replenished. Iron is stable at levels below 8 g/l.

There is no reduction of the waste volume, but of its contaminant load, since resin regeneration is carried out with equal volumes of water and treated bath.

The consequences can be summarized as:

- Constant operating conditions and etching speed
- Reduced production of etching sludge
- Possibility of keeping etching concentration at its lowest range: 5 mass % of acid (90 g/l), maintaining its cleaning efficiency and constant operating conditions
- Equivalent reduction in acid consumption: 40% (from 23.4 m³/year to 14.5 m³/year)
Aeration treatment application

The reject fraction from ion retardation (18 m³/year), mixed with cascade rinse waters from etching stages (10,000 m³/year), is treated by aeration under the following conditions:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial</th>
<th>Final</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of anion flocculant</td>
<td>2 ml/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Addition of 50% caustic soda</td>
<td></td>
<td>6 l/m³</td>
<td></td>
</tr>
<tr>
<td>pH = 7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aeration time</td>
<td>30 minutes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flocculation time</td>
<td>3 minutes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sedimentation time</td>
<td>60 minutes</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Initial conditions and industrial test results are summarized as follows:

- **COD (mg/l)**: Initial 510, Final 132, Reduction 75%
- **Fe (mg/l)**: Initial 730, Final <0.5, Reduction >99%
- **Conductivity (mS/cm)**: Initial 27.8, Final 14.1, Reduction 49%

The characteristics of this water allow reusing it for as long as sulfate accumulation (or the equivalent increase in conductivity) allows it. Two limit options are set based on the required rinse quality: daily purge or weekly purge.

Under these conditions, the consequences can be summarized as:

- **Current water consumption**: 10,000 m³/year
- **Current water consumption with daily purge**: 2,250 m³/year (77% de ahorro)
- **Current water consumption with weekly purge**: 445 m³/year (95% de ahorro)
- After applying ion retardation + aeration, the global management of wastes is reduced to:
  - 56 m³/year of dry sludge
  - 1,700 m³/year of dehydration waters
- **Global energy consumption** (including filtration and pumping): 35,200 kWh/year
Candidacy as BAT

The previous rates make the association of ion retardation and aeration a strong candidate as BAT for the system formed by a sulfuric etching process and its associated rinse stage.

The global study of costs, applied in particular to the company affected by the project and considering an annual inflation rate of 3.5%, yields a return of investment period between 7 and 10 years, depending on the type of purging operation used.

The ZERO PLUS Project promotes the revision of the contents of the BREF “Surface Treatment of Metals and Plastic Materials” relating to etching processes, suggesting the following recommendations for its different sections:

- **Section 2.3.6., “Etching”**: To consider the advantages of using etching baths with low concentrations of sulfuric acid (5 mass % at 60°C) regarding the reduction of drag-outs and the reduced generation of sludge.
- **Section 2.7., “Frequent Treatment Techniques”**: To include aeration as an appropriate technique for removing ferrous ions and thus reducing COD.
- **Section 2.7.3., “Crystallization”**: To emphasize that the technique is only feasible for large facilities, such as continuous etching of steel flat products, but not for conventional electrocoating installations.
- **Section 4.11.14.2., “Diffusion dialysis”**: To establish the unsuitability of diffusion dialysis and electro-electrodialysis due to the excessive cost per liter of the recovered acid, specially with low added value acids.
- **Section 4.11.3., “Retardation”**: To develop the application for steel etching in sulfuric medium, emphasizing that its behavior bears little relation with aluminum anodizing baths. To provide further details for etching baths other than sulfuric etching.
- **Section 4.11.14., “Etching solutions”**: To include a new sub-section that establishes the candidacy as BAT for the combination of ion retardation and aeration for the treatment of etching baths and their associated rinse stages.
Best technologies applied to Cyanide Copper Rinses (Barrel Line)

April, 2009

Key words: Cyanide copper, vacuum evaporation, anodic oxidation, heterogeneous catalysis, cathodic electrodeposition
The treatments of cyanide baths and their rinses in a closed loop by means of techniques such as vacuum evaporation are considered as BATs\(^1\) in the BREF document “Surface Treatment of Metals and Plastics”. However, the catalytic anodic oxidation treatments of cyanide solutions are only considered as BAT candidate, but their characteristics are not specifically described.

The ZERO PLUS Project (LIFE 05 ENV / E / 256) proposes the combined use of vacuum evaporation, catalytic anodic oxidation and electrodeposition as an interesting solution for the full recovery of the drag-outs from the bath to the first recovery rinse and in situ removal (instead of at the WWTP) of cyanide, COD and heavy metals dragged out to a second recovery rinse.

This article shows how vacuum evaporation allows the full recovery of bath components, the full reuse of extraordinarily high-quality water, and the elimination of current purging requirements of the recovery rinse.

The combination of catalytic anodic oxidation and electrodeposition ensures the presence of very low levels of cyanide, COD, and parasite metals in the second recovery rinse, as well as the optimum quality of its waters.

These results support considering the combination of the three technologies as BAT, as well as reviewing the contents of the BREF document for their use either independently or in combination.

\(^1\) BAT: Best Available Techniques
Introduction

There are three different options in cyanide copper baths:

- Strike-plate baths for low-thickness deposition
- General purpose baths for medium-thickness
- High-efficiency baths for high-thickness and high-speed deposition

The first two types of baths contain Rochelle salts and are characterized by their good throwing power and lower sensibility to carbonates and parasite metals. They are mainly used to deposit copper on zamack and aluminum items.

High cathodic efficiency (almost 100 %) baths do not use Rochelle salts, they have a lower distribution power, and they are more sensitive to contamination. They are generally applied on steel surfaces to improve the adherence of subsequent coatings.

High-efficiency baths can be considered as modified conventional baths, where the concentration of the basic components has been doubled (metal copper: 60 g/l and free potassium cyanide: 25 – 30 g/l). Their operating conditions (air agitation, temperature: 70ºC, and current density up to 11 A/dm²) are above the stability limit of cyanide salts. The decrease in some of its properties, such as distribution power, is not relevant, since the main purpose is increasing its performance and deposition speed.

As a consequence of their greater saline contents, these baths have a greater viscosity, so strong anion wetting agents at high concentrations are added (surface tension range: 20-25 dyn/cm) in order to improve substrate and dry substrate wettability. Despite this, there is significant drag-out, and substantial amounts of cyanide, metals and COD reach rinsing waters.

Previous experiences¹, for which conventional baths were used, did not consider product recycling, but reusing rinse waters after removing in situ dragged out cyanide, COD and metals. To this end, the catalytic anodic oxidation technique was used in combination with electrodeposition.

However, since the copper baths that are relevant for the ZERO PLUS Project are high-efficiency baths, and their drag-outs are therefore more concentrated, a proposal for the joint recovery of components and water has indeed been made.

The option selected as base BAT is that of a closed-loop recycling system by means of vacuum evaporation, as described in the BREF² (Sections 4.7.11.3 y 5.1.6.3). This option is now modified to add anodic oxidation and electrodeposition as supplementary BATs.

¹ European Project ENVIREDox (IPS-2000-035)
² Reference Document on BATs for the Surface Treatment of Metals and Plastics (August, 2006)
Focusing on the problem

The current installation of the nickel-chromium jig (rack) line has a cyanide copper position whose rinsing function is divided in a recovery rinse and a running rinse, with the following characteristics:

<table>
<thead>
<tr>
<th></th>
<th>Recovery rinse</th>
<th>Running rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (g/l)</td>
<td>1.4</td>
<td>0.002</td>
</tr>
<tr>
<td>COD (g/l)</td>
<td>2.5</td>
<td>-----</td>
</tr>
<tr>
<td>Cyanide (g/l)</td>
<td>2.5</td>
<td>0.003</td>
</tr>
<tr>
<td>Volume (l)</td>
<td>850</td>
<td>850</td>
</tr>
<tr>
<td>Drag-out (l/hour)</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Feeding flow (l/hour)</td>
<td>-----</td>
<td>200</td>
</tr>
<tr>
<td>Return to bath (l/day)</td>
<td>100</td>
<td>100 *</td>
</tr>
<tr>
<td>Purge (m³/year)</td>
<td>3.4</td>
<td>10.2</td>
</tr>
</tbody>
</table>

* The volume returned is directed to recovery rinse

After the running rinse is turned into a second recovery rinse, keeping the daily returned volume to rinse 1, concentrations are stabilized at [Cu] = 0.5 g/l and [cyanide] = 0.8 g/l.

Under these conditions, the addition of vacuum evaporation in a closed loop between the copper bath and recovery rinse 1 is proposed. The concentrate should make up for bath volume lost through evaporation (6 l/h), with a copper content of around 50% of its nominal value, that is, 30 g/l. The distillate is returned to the rinse as quality water.

Similarly, recovery rinse 2 re-circulation through an electrolytic cell with catalytic anodes is proposed for the anodic oxidation of cyanide and COD, as well as for recovering metal copper. Thus, the final quality of the treated water should reduce rinse purging frequency.

The anticipated difficulties are: co-distillation of cyanides and foam drag-out in vacuum evaporation, as well as low faradic yields due to dilution in electrolysis.
Results obtained with vacuum evaporation

By applying a volume concentration factor VCF = 20, two well-differentiated fractions are obtained as follows:

<table>
<thead>
<tr>
<th></th>
<th>Concentrate</th>
<th>Distillate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>(g/l) 32</td>
<td>Negligible</td>
</tr>
<tr>
<td>Cyanide</td>
<td>(g/l) 39</td>
<td>0.03</td>
</tr>
<tr>
<td>Carbonate</td>
<td>(g/l) 25</td>
<td>0.02</td>
</tr>
<tr>
<td>COD</td>
<td>(g/l) 42</td>
<td>0.09</td>
</tr>
<tr>
<td>Iron</td>
<td>(g/l) 1.4</td>
<td>Negligible</td>
</tr>
<tr>
<td>Zinc</td>
<td>(g/l) 0.2</td>
<td>Negligible</td>
</tr>
</tbody>
</table>

However, to achieve such remarkable results, a 2,400-l/day vacuum evaporator is required, which generates a power consumption of 210,000 kWh/year.

The proposed solution turns out to be industrially unfeasible, both due to its high investment and exploitation costs, as well as because of the excessive return-of-investment resulting periods.

In these circumstances, the application of electrolysis (anodic oxidation + electrodeposition) in rinse 2 is no longer justified.

It is therefore concluded that, even though rinse 1 has a certain concentration level, it is insufficient for the industrial feasibility of vacuum evaporation.

It is of the utmost importance that the BREF depicts the situation herein described in order to prevent mistakes that would have serious consequences.
Reconsidering the problem

However, the installation under study has a nickel barrel line with an alkaline copper bath with similar characteristics and whose recovery rinse may reach a concentration level 13 times higher.

The environmental conditions of the rinsing function differ from those of the rack line. After converting rinse 2 into a still rinse, these are:

<table>
<thead>
<tr>
<th></th>
<th>Recovery rinse 1</th>
<th>Recovery rinse 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (l)</td>
<td>1.300</td>
<td>1.300</td>
</tr>
<tr>
<td>Drag-out (l/hour)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Return to bath (l/day)</td>
<td>120</td>
<td>120 *</td>
</tr>
<tr>
<td>Purging (m³/year)</td>
<td>5.2</td>
<td>2.6</td>
</tr>
</tbody>
</table>

* The volume returned is directed to recovery rinse 1

Industrial tests are reviewed and modified so that, with VCF = 2, the evaporator keeps a constant cyanide concentration of 15 g/l in rinse 1 and compensates the loss of bath volume through evaporation (7.3 l/h) by using a concentrate that contains Cu: 22 g/l and total cyanide: 40 g/l. The distillate returned to the rinse contains 0.1 g cyanide/l.

The characteristics of the evaporator are: capacity of 400 l/day and power consumption of 27,500 kWh/year.

Under these conditions, a re-adjustment of the concentrate to 50% of the nominal value of the bath is optional. Additionally, drag-out to rinse 2 is stabilized at 30 g cyanide/hour, and the faradic yield of anodic oxidation + electrodeposition is well above that of the previous case.

In such conditions, rinse 2 keeps a negligible concentration of Cu, cyanide: 30 mg/l, and COD < 100 mg/l. All water is reused and bimonthly purging is no longer required.

An electrolysis cell with a capacity of 217 liters containing 25 cross-linked cathodes and 26 Ir-based MMO⁴ catalytic anodes is required. Its power consumption is 6,200 kWh/year.

⁴ MMO: Mixed Metallic Oxides
The consequences can be summarized as:

- **Reduction of concentrated waste volume to manage:**
  - 5 m³/year (100 %)
- **Water recovery:** 622 m³/year (99.5 %)
- **Product recovery:** 800 kg/year of cyanide salts and potash
- **Drag-out reduction:** Cu from 38 to 0 g/hour and cyanide from 60 to 0.06 g/hour
- **Reduction of treatment sludge:** from 1,200 to 0.5 kg/year
- **Re-introduction of metals and parasite salts to the bath:** Negligible
Candidacy as BAT

This industrial development proves that the greater dilution of rinses in jig-line installations makes it impossible to propose this application as BAT.

The global analysis of costs, considering an annual inflation rate of 3.5 %, yields variable return-of-investment periods depending on the cost of water and the efficiency in the use of energy by the evaporator. With a power consumption of 0.2 kWh/liter, the following situations are distinguished:

• Water costs around 0.5 €/m³: Return of investment in 11 years (applicable in Spain).
• Water costs around 3 €/m³: Return of investment in 8 years (applicable in France).

The ZERO PLUS Project proposes reviewing the contents of the BREF “Surface Treatment of Metals and Plastic Materials” in relation to vacuum evaporation, closed-loop recycling systems, anodic oxidation, and their application to problems related to the presence of COD and metal compounds. The following recommendations are presented:

• Section 4.7.11.3., “Evaporators”: Review contents relating to vacuum evaporation and its dependence on the concentration of the solution.
• Section 4.7.11.3., “Evaporators”: Clarify the significance of vacuum evaporation, not only as a concentration technique but also as a drag-out reduction technique based on its power consumption.
• Section 4.12.1., “Electrolysis”: Clarify the significance of anodic oxidation as a processing technique (not EOP5) for the catalytic removal of COD, free cyanide and cyanide compounds without adding reagents or generating collateral sub-products (AOX6).
• Section 4.16.4., “Cyanide oxidation”: Develop the significance of catalytic anodic oxidation for the clean removal of simple and complex cyanides in relation to the previously described case.
• Section 4.16.8., “Complexing agents”: Include catalytic anodic oxidation as a processing technique to destabilize and destroy certain metal compounds, such as cyanide compounds, amine compounds, etc.
• Section 5.1.6.3., “Closed-loop recovery”: Consider cyanide copper among the processes whose rinses can be treated in a closed loop.
• Chapter 4, “Techniques to consider as BATs”: Value the combination of vacuum evaporation and catalytic anodic oxidation as a strong candidate for BAT (for example, in Section 4.16.11., “Combining techniques”).

5 End Of Pipe treatment technique
6 Absorbable halogenated organic compounds
Best technologies applied to Bright Nickel Rinses (Barrel Line)

May, 2009

Key words: Bright nickel, vacuum evaporation, concentration, drag-out, crystallization, encrustations, volume concentration factor
The treatments of galvanic baths with simple salts (as opposed to complex salts) and their rinses, as in the case of bright nickel, in a closed loop by means of techniques such as vacuum evaporation are considered as BATs in the BREF document “Surface Treatment of Metals and Plastics”.

The ZERO PLUS Project (LIFE 05 ENV / E / 256) proposes the use of recycling to achieve substantial volume concentration factors for the application of vacuum evaporation to the still recovery rinse of a nickel bath, with or without monitoring the pH of the solution.

The lack of experiences in this type of adaptations, as well as the need to modify the initial proposals due to their technical unfeasibility, make this section of the demonstration project of particular interest.

In fact, considering the impossibility of implementing a first block of pre-industrial results for a jig (rack) line, the ZERO PLUS Project performed new eco-approximations for vacuum evaporation as a drag-out reduction technique, rather than a concentration technique, applied to a nickel barrel line.

Regardless of the unfavorable result of the final economic feasibility study, and its negative contribution to the candidacy of the application herein described as BAT, this article provides interesting information that the BREF should consider during its new reviewing period.

1 BAT: Best Available Techniques
Introduction

Bright nickel baths are a paradigmatic example of a galvanic process formed by simple salts and soluble anodes to compensate the cathodic discharge of the metal.

These baths are characterized for their significant saline and organic matter contents contributed by their additives – primary brighteners (carriers), auxiliary brighteners (levelers), and secondary brighteners, as well as wetting agents.

The typical structure of a nickel station is formed by the bath itself and the associated rinsing function, which is usually divided in two stages: recovery and running rinse.

The nickel bath operates at a temperature of approximately 60°C, which results in a significant loss of solution through evaporation. The purpose of the recovery rinse is to compensate this loss by returning an equivalent volume to the original bath.

However, the dimensions of the rinse assume a liquid volume that is larger than the volume lost through evaporation and therefore, since the entire capacity is not used for the intended end, there is always a remnant that is not re-used.

In the absence of agitation, the efficiency of the rinse is reduced to a more or less complex diffusion problem due to the presence of the organic additives and, mainly, the surfactants (surface tension range: 30 – 35 dyn/cm). Additionally, the dilution effect that takes place is accompanied by side effects such as:

- Turbidity
- Destabilization of colloidal additives

For this reason, the solution must be periodically purged and fully renewed with fresh water, while the waste solution is sent to the WWTP for physical-chemical treatment.

The application of vacuum evaporation in a closed loop between the nickel bath and its recovery is aimed at using all of the rinsing volume and its components, which eliminates the need for periodical purging.

Consequently, the option selected as BAT is the one described in Sections 4.7.11.3 and 5.1.6.3 of the BREF².

² Reference Document on BATs for the Surface Treatment of Metals and Plastics (August, 2006)
Focusing on the problem

The current nickel-chromium rack installation has a three-station bright nickel bath and a rinsing function consisting of a recovery rinse and an aspersion running rinse. The characteristics of the recovery rinse are:

<table>
<thead>
<tr>
<th></th>
<th>Recovery rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (g/l)</td>
<td>1.0</td>
</tr>
<tr>
<td>Boron (g/l)</td>
<td>0.08</td>
</tr>
<tr>
<td>Volume (l)</td>
<td>850</td>
</tr>
<tr>
<td>Drag-out (l/hour)</td>
<td>0.17</td>
</tr>
<tr>
<td>Return to bath (l/day)</td>
<td>80</td>
</tr>
<tr>
<td>Purge (m³/year)</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Currently, the company returns only 80 liters per day to the bath to compensate the loss through evaporation, which means that more than 90% of the contents of the recovery rinse are wasted.

A closed-loop, vacuum evaporation process is implemented between the bath and its recovery rinse. The concentrate should make up for bath volume lost through evaporation (5 l/hour), with a nickel content of around 50% of its nominal value, that is, 40 – 45 g/l.

Results obtained for the jig-line installation

Pre-industrial tests reveal the need to achieve a volume concentration factor VCF = 50 for the concentrate to reach a content of 45 g nickel/l.

From an industrial standpoint, this means that a flow of 0,1 l/hour of concentrate should be returned to the bath, and that 4,9 l/hour should be sent back from the rinse itself to make up for the 5 l/hour that are lost through evaporation of the bath.

Additionally, it is observed that, starting from VCF = 20, the solution exceeds pH = 6,5, precipitating nickel and boron. Therefore, and regardless of its value, metal concentrations remain invariable once this value of VCF is reached – Ni: 8 g/l and B: 0,7 g/l.
This problem is solved by adjusting the pH of the rinse at 4.5 by means of a continuous dosing of sulfuric acid to the recovery rinse.

However, the real problem is the low flow of the concentrate, since, regardless of costs, it is not possible to have an industrial evaporator to set these conditions. **Thus, the industrialization of the nickel jig line is not feasible.**

### Technical unfeasibility

There is a series of obstacles to reproducing the desired objective at an industrial level. These hindrances are related to the footprint of a vacuum evaporator, and can be summarized as follows:

1. Making up for bath volume lost through evaporation (linked to concentrate flow)
2. Limit concentration of the recovery rinse (linked to the dilution level of the drag-out)
3. Concentrate saline contents (linked to rinse concentration and, therefore, to drag-out concentration as well)

Based on these criteria, the evaporator should have the following characteristics:

- Feeding flow: 10 l/hour, concentrate flow: 5 l/hour, and condensate flow: 5 l/hour; equivalent to VCF = 2
- For a Ni concentration of 75 g/l in the bath and a drag-out of around 0.2 l/hour, the recovery rinse would be stabilized at a concentration of 1.5 g/l of Ni.
- Ni return to the bath would be 3 g/l.

These results, corresponding to the rack line installation under study, are by no means near the desired objective due to the dilution level of the rinse and the low drag-out flow.
Reconsidering the problem

However, the installation under study has a nickel barrel line with two nickel baths with similar characteristics and whose recovery rinse may reach a concentration level 11 times higher than that of the rack line.

The boundary conditions of this barrel-line rinsing stage differ from those of the rack line and, in addition to this; the running rinse can be optionally converted into a second recovery rinse, in accordance to:

<table>
<thead>
<tr>
<th>Recovery rinse 1</th>
<th>Recovery rinse 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (l)</td>
<td>1.300</td>
</tr>
<tr>
<td>Drag-out (l/hour)</td>
<td>2</td>
</tr>
<tr>
<td>Return to bath (l/day)</td>
<td>235</td>
</tr>
<tr>
<td>Purging (m³/year)</td>
<td>5.2</td>
</tr>
</tbody>
</table>

* The volume returned is directed to recovery rinse 1

Unlike the rack line, no VCF value is set beforehand, but a 50-percent reduction of drag-out from rinse 1 (from 20 to 10 g nickel/hour).

By means of an evaporator with a capacity of 700 l/day and VCF = 2, the concentration of the rinse is stabilized at 5 g Ni/l. With a feeding flow of 30 l/h, the following is obtained:

- A concentrate flow of 14.6 l/h with 10 g Ni/l that is returned to the bath and makes up for volume loss through evaporation
- A diluted flow of 15.4 l/h with 0.4 g Ni/l that is recycled to the rinse as high-quality water

As bath concentrations are [Ni] = 75 g/l and [B] = 8 g/l, the return of a solution with [Ni] = 10 g/l, even if far from the desired objective of 50%, is much more realistic.

The level of re-introduced parasite metals (Fe: 7 mg/l and Zn: 7 mg/l) is admissible because the system keeps a certain self-detoxification capacity associated to the drag-out.

Rinse 1 is kept at pH = 4.5 as a preventive measure to avoid the precipitation of nickel and boron inside of evaporator.

The evaporator consumes 55,000 kWh/year.
The consequences can be summarized as:

- Reduction of concentrated waste volume to manage: 5 m³/year (100%)
- Equivalent water recovery: 5 m³/year
- Product recovery: 320 kg/year of nickel salts and 50 kg/year of boric acid
- Reduction of Ni drag-out from 20 g/hour to 10 g/hour
- Characteristics of the water recovered as distillate, Ni: 0.4 mg/l
- Reduction of treatment sludge: from 1,400 kg/year to 360 kg/year (74%)
- Re-introduction of parasite metals to the bath: Negligible

**Conclusions and additional consequences**

If a 70-percent reduction of drag-out, equivalent to VCF = 3, from rinse 1 is achieved, the results are:

- Rinse concentration is stabilized at Ni ≈ 3.3 g/l
- Drag-out decreases from 20 g/hour to 6.6 g/hour
- The system’s self-detoxification capacity decreases because the contents of parasite metals of the concentrate, mainly Fe and Zn, exceed the threshold of 10 mg/l.

As a consequence, there is a marked increase in investments and operational costs due to:

- The need to increase the capacity of the evaporator to 1,400 l/day which means an 30% increase of the equipment investment.
- One-hundred percent increase in power consumption (110,000 kWh/year)
- The need to incorporate a selective hydrolysis stage for conditioning the concentrate by reducing its Fe and Zn contents before returning it to the bath,
- which means an additional 25-percent increase of equipment investment (power consumption is barely modified)

Therefore, the feasibility of the system is substantially penalized for VCF values above 2.
Candidacy as BAT

The application has a higher cost for the company than the current situation (treatment at the WWTP). Consequently, there is no return of investment period and it is impracticable.

Unlike the case of cyanide copper, one of the main causes for unfeasibility is the low level of water recovery achieved, since, even if the second running rinse is turned into a still rinse, a final running rinsing stage would still be required.

It is concluded that, even though the solution is flawless from a technical standpoint, it is economically unfeasible both for rack-line and barrel-line installations, which makes it impossible to propose as a BAT.

However, some of the technical conclusions drawn are of interest for the BREF in relation to the application of vacuum evaporation to closed-loop treatment systems. Thus, the following recommendations are presented:

- Section 4.7.11.3., “Evaporators”: Review contents relating to vacuum evaporation and its dependence on the concentration of the solution.
- Section 4.7.11.3., “Evaporators”: Clarify the significance of vacuum evaporation, not only as a concentration technique but also as a drag-out reduction technique based on its power consumption.
- Section 5.1.6.3, “Closed-loop recovery”: Consider the difficulties of vacuum evaporation as a recovery technique in nickel barrel line installations.
- Section 5.1.6.3., “Closed-loop recovery”: Establish the possible use of vacuum evaporation as a closed-loop technique for the reduction of drag-outs from recovery rinses, rather than for concentration and return of components to the bath.
- Section 5.1.6.3., “Closed-loop recovery”: Establish the advisability of continuous pH adjustment in recovery rinses where its modification in the concentrate produced by the evaporator may cause saline precipitation or crystallization.
Best technologies applied to Decorative Chromium Rinses

Key words: Decorative chromium, alternate flow ion exchange, parasite metals, multivalent cations

may, 2009
Within maintenance operations in plating baths, the BREF document “Surface Treatment of Metals and Plastics” considers those operations used for the removal of parasite metals as BAT¹ candidates, since the presence of parasite metals can cause operation problems as well as result in the bath being spent.

This is what happens with decorative chromium conventional baths and their rinsing stages, where high concentrations of iron, aluminum, zinc, copper, nickel and chromium (III) can accumulate.

The ZERO PLUS Project (LIFE 05 ENV / E / 256) assesses the application of alternate flow ion exchange for the selective decontamination of the rinsing stage and the concentration of the chromic acid it contains. The objective pursued is returning to the bath or other positions of interest all of the chromium (VI) – free of impurities – that was dragged out from the bath.

The conclusions drawn are similar to those of the BREF because, even though the application of the technique yields excellent results, it is not suitable for small baths and installations, where the return of investment is appreciably unfavorable.

¹ BAT: Best Available Techniques
Introduction

Decorative chromium baths based on hexavalent chromium are one of the most atypical families of the electroplating industry because their deposition mechanism is initiated by an anion (chromate) instead of the corresponding metal cation.

This fact, together with the multiple stages involved in the transformation of hexavalent chromium into metal chromium (through trivalent and bivalent chromium), leads to very low current cathodic yields, of the order of 15%.

To improve this yield, as well as deposition and penetration rates, chromium baths add a dual, low-concentration catalyzing system that allows reaching efficiency figures above 25%.

Based on the catalyzing system used, the following are distinguished:

- Conventional or self-regulating baths.
- Cutting age or high-efficiency baths.

Both types of baths use the sulfate anion as main catalyst with a concentration equal to 1% of that of chromic acid (expressed as CrO₃). The secondary catalyst is the differentiator:

- Conventional baths contain hexafluorosilicates, generally magnesium hexafluorosilicate, with a concentration of 0.5-0.6 g/l expressed as fluoride ion.
- Cutting age baths use alkene sulfonic acids (for example, methane disulfonic acid) at proportions between 1-3 percent weights.

One of the differences of conventional baths is that they are very aggressive to the substrate due to the presence of small amounts of hydrofluoric acid as a consequence of the acidic medium.

This carries the progressive accumulation of parasite metals, both trivalent (Fe and Al) and bivalent (Ni, Cu and Zn), as well as the Cr (III) present as a sub-product of the transformation of Cr (VI) into metal chromium.

ven though the tolerance to these contaminations is high (admissible limits are Fe: 15 g/l, Cr (III): 10 g/l, Cu: 0.2 g/l), they favor the proliferation of non-active chromium species and the need to increase the contents of total chromic acid to ensure a concentration of free chromic acid of at least 250 g/l (expressed as CrO₃).

The increase of total chromic acid concentration up to values of 400 and 500 g/l is in detriment of the operating conditions of the bath:
• It results in an increased conductivity and a reduced cathodic yield, which in turn forces the use of higher current densities at a given voltage.

• Bath density and viscosity are considerably increased, contributing to excessive drag-out as a consequence of the greater thickness of clinging liquid film deposited on the pieces.

This situation is a loop where the losses through drag-out may imply more than 90% of the consumption of bath components. In other words, less than 10% of the bath ingredients are used for chromium plating.

To attenuate this effect, bath contents of anion wetting agents is increased (polyfluorinated octyl sulfonates or PFOS) in order to obtain surface tension values below 35 dyn/cm and thus facilitate greater dripping levels. However, even though chromium baths are one of the exceptions included in 2006/112/CE Directive or PFOS, this methodology is completely objectionable.

These high drag-out levels have a significant self-detoxification effect that reduces the contents of parasite metals in the bath. However, they have a negative consequence – a progressive increase of concentration in the recovery rinse. This increase is due to the low liquid volume that is returned to the bath on a daily basis, and which is a result of its low evaporation rate.

The advantages of applying the alternate flow ion exchange technique to the rinsing stage of this chromium plating line are clear:

• Continuous removal of dragged out parasite metals.

• Full recovery of chromic acid, which is returned to the bath as a concentrated solution containing the remaining intrinsic anion forms: sulfates, fluorides, hexafluorosilicates, and polyfluorinated octyl sulfonates.

• Progressive restoration of the ideal operating conditions of the chromium bath: reduction of total contents of chromic acid keeping a stable concentration of active chromic acid at 250 g/l (expressed as chromium CrO₃).

Consequently, the option selected as BAT is the one described in Section 4.11.7 of the BREF. Other options, such as the membrane electrolysis or electro-electrodialysis techniques described in Section 4.11.11, are ruled out right from the start due to the poor results obtained in previous experiments.

In fact, given the strongly oxidizing characteristics of the medium, it is not possible to recover chromic acid concentrations above 17 g/l of CrO₃, even when using cation membranes that are highly resistant to oxidizing media (such as NAFION, 400 series). Despite being strongly acidic and reinforced with sulfonic polymers, these membranes undergo a progressive deterioration if they are continuously used in this concentration range.

1 Reference Document on BATs for the Surface Treatment of Metals and Plastics (August, 2006)
2 European Project "Vertido Cero" (LIFE 93 /E/A121/E 1523)
On the other hand, exchange resins like the ones used are more stable at higher concentrations of chromic acid (40-50 g/l), provided that the temperature does not exceed 35 °C throughout the cycle (to minimize the oxidizing effects of chromic solutions).

Closed-loop options through vacuum evaporation, described in Sections 4.7.11.6 and 5.1.6.3 of the BREF document, are also ruled out because, this being a fluoride-catalyzed conventional bath, the aggressive nature of the medium will inevitably affect the stainless steel components of the evaporator.

Focusing on the problem

The installation of the nickel-chromium rack line has a chromium plating position whose rinsing function is divided into a recovery stage and an aspersion rinsing stage. At the time this activity was carried out, the characteristics of this position were those of a used bath with a high content of chromic acid, as shown in the second table below.

Under these conditions, feeding the anion resin from the recovery rinsing stage is considered to be detrimental because an initial concentration of 14 g/l of Cr (VI) will result in very short cycles due to its fast saturation.

Therefore, exchange columns are fed from the aspersion running rinsing stage, whose Cr (VI) content is of about 100 mg/l. In addition to the removal of parasite metals and the recovery of chromic acid, a complete reuse of this water as demineralized water is sought.

<table>
<thead>
<tr>
<th>Volume (l)</th>
<th>Recovery rinse</th>
<th>Running rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drag-out (l/hour)</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Feeding flow (l/hour)</td>
<td>-----</td>
<td>100</td>
</tr>
<tr>
<td>Return to bath (l/day)</td>
<td>16</td>
<td>16 *</td>
</tr>
<tr>
<td>Purge (m³/year)</td>
<td>1.7</td>
<td>-----</td>
</tr>
</tbody>
</table>

*The volume returned is directed to the recovery rinse

<table>
<thead>
<tr>
<th>Chromium bath (g/l)</th>
<th>Recovery rinse (mg/l)</th>
<th>Running rinse (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium (VI) total</td>
<td>192</td>
<td>14,100</td>
</tr>
<tr>
<td>Chromic acid equivalent</td>
<td>370</td>
<td>27,100</td>
</tr>
<tr>
<td>Chromium (III)</td>
<td>0.92</td>
<td>68.0</td>
</tr>
<tr>
<td>Sulfates</td>
<td>1.20</td>
<td>88.0</td>
</tr>
<tr>
<td>Fluorides</td>
<td>0.54</td>
<td>40.0</td>
</tr>
<tr>
<td>Iron</td>
<td>0.10</td>
<td>7.1</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.40</td>
<td>28.0</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.06</td>
<td>4.4</td>
</tr>
<tr>
<td>Copper</td>
<td>0.26</td>
<td>19.0</td>
</tr>
</tbody>
</table>

*Expressed as chromium CrO₃
The treatment involves a sequential passage through two exchange columns each containing a resin:

- Strong cation resin with a theoretical exchange capacity of 1.8 eq/l
- Weak anion resin with a theoretical exchange capacity of 1.3 eq/l

The cycle ends when the anion resin is spent, which occurs when the concentration of Cr (VI) leaving the system is higher than 5 mg/l.

The cations held by the cation resin are eluted with sulfuric acid and sent to the WWTP.

The anions held by the anion resin are eluted with sodium hydroxide so that all chromate ions are moved as sodium chromate. The other anion species remain intact in solution.

The sodium chromate solution is then sent in the opposite direction and goes through a cation column where the salt is transformed into chromic acid, which is stored. The sodium-saturated cation resin is regenerated with sulfuric acid, thus returning to its initial state.

After rinsing both columns with demineralized water, the system is ready to begin a new cycle.

The greatest difficulty that is anticipated is maintaining the demineralization of the aspersion rinsing stage in order to be able to reuse all running water. This difficulty is related to the correlation between water quality and the maximum admissible concentration for chromic acid recovery.

**Results obtained with alternate flow ion exchange**

The following table shows the characteristics of the solution that is returned to the recovery rinsing stage:

<table>
<thead>
<tr>
<th>Recovered components (g/l)</th>
<th>Presence of pollutants (μg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium (VI) total</td>
<td>13</td>
</tr>
<tr>
<td>Chromic acid* equivalent</td>
<td>25</td>
</tr>
<tr>
<td>Sulfates</td>
<td>0.40</td>
</tr>
<tr>
<td>Fluorides</td>
<td>0.20</td>
</tr>
<tr>
<td>Chromium (III)</td>
<td>200</td>
</tr>
<tr>
<td>Iron + Nickel + Zinc + Copper</td>
<td>less than 0.5</td>
</tr>
</tbody>
</table>

*Expressed as chromium CrO₃
The saturation of the anion resin is controlled through chromic acid leakage. Thus, resin saturations above 25 g/l of chromic acid are avoided since, at that point, outgoing demineralized water already contains 5 mg/l of Cr (VI) meaning that:

- There is an increasing loss of chromic acid when resin saturation increases.
- There is a loss of quality of demineralized water, which prevents reusing it for the aspersion rinsing stage.
- The production of chromic acid is lower than expected given the competition with the remaining anion species (fluorides, chlorides, sulfates, sulfonates, etc.) in the anion resin.

The consequences can be summarized as:

- Return of 9 l/day of chromic solution to the recovery rinsing stage.
- Recovery of 50 kg/year of parasite metal-free CrO₃.
- Reduction of the annual consumption of CrO₃ by 52%.
- Full reuse of 418 m³ of running rinsing stage water.
- Elimination of the six-monthly purging of the recovery rinsing stage (1.7 m³/year).
- Elimination of the annual flow of chromic acid sent to the WWTP: 100 kg/year.
- Reduction of treatment sludge by 95%: from 400 to 20 kg/year.
- No re-introduction of parasite metals in the recovery or the bath.
- Progressive reduction of non-active chromium species in the bath.
- Progressive reduction of drag-outs and consumption of PFOS in the bath. Stabilization of bath surface tension at 40 dyn/cm.
- Restoration and progressive stabilization of bath operating conditions to its nominal values: 250 g/l of CrO₃.
Candidacy as BAT

Despite the lengthy list of advantages described for the alternate flow ion exchange technique, its use is closely conditioned by its cost, and the return of investment depends on the size of the installation where this technique is to be applied.

The global analysis of costs for an installation similar in dimensions to that of the company included in the Project, considering an annual inflation rate of 3.5%, varies depending on the price of water. Thus:

- For a water cost of around 0.5 €/m³: Return of investment in 65 years (applicable in Spain).
- For a water cost of around 3 €/m³: Return of investment in 25 years (applicable in France).

The ZERO PLUS Project fully confirms the indications included in Section 4.11.7 of the BREF document in relation to considering this technique as BAT candidate, including their unfavorable considerations regarding return of investment for small installations. However, there are a few recommendations in relation to:

- Section 2.5.3.1., “Bright chromium plating with hexavalent chromium”: Considering the existence of cutting age or fluoride-free baths, that are mildly aggressive to metal substrates.
- Section 4.7.11.6., “Electrolytic chromium plating - closed loop electroplating”: Distinguishing between cases where there is corrosion risk for an evaporator (classic baths with fluoride content) from those where there is no such risk (cutting age or fluoride-free baths).
- Section 4.11.11., “Membrane electrolysis”: Establishing admissible threshold concentration restrictions for chromic acid to ensure the integrity of perfluorinated membranes and, in particular, cation membranes.
- Section 5.1.6.3., “Closed-loop recovery”: Same recommendations as those mentioned for sections 4.7.11.6 and 4.11.11.
- Section 5.2.5.7.2., “Hexavalent chromium baths”: Same recommendations as those in Section 5.1.6.3.
Best Technologies applied to Alkaline Zinc-Nickel Rinses (Barrel Line)

May, 2009

Key words: alkaline zinc-nickel, anodic oxidation, advanced oxidation, heterogeneous catalysis, cathodic electrodeposition, hard COD.
The availability of techniques that simultaneously allow reducing COD and destabilizing metal complexes is very restricted.

In this regard, advanced oxidation processes (AOP\(^1\)) based on photoelectrochemical processes (PEC\(^2\)), as in the case of titanium dioxide-mediated photocatalysis or photolysis in the presence of hydrogen peroxide or ozone, are being successfully used in various applications (Cf. BREF\(^3\) Section 4.16.8).

If, in addition to reducing COD and destabilizing metal complexes, heavy metals need to be removed, with recycling options, satisfactory results can be obtained only by associating electrocatalytic techniques and electrodeposition (electrowinning) (Cf. ZERO PLUS Project: cyanide copper rinses). (Cf. BREF Section 4.16.4).

The drag-out from the alkaline zinc-nickel baths to their rinses has become a typical problem, due to its difficult treatment, where the three issues mentioned are combined: COD, metal complexes, and heavy metals.

The ZERO PLUS Project (LIFE 05 ENV / E / 256) assesses the application of the catalytic anodic oxidation technique for the in situ treatment of COD and the destabilization of aminated complexes and nickel cyanide sub-complexes, associated with cathodic electrodeposition, for the recovery of zinc and nickel.

The results obtained support considering this combination as BAT\(^4\), as well as reviewing BREF contents, since in this document anodic oxidation is treated without considering its catalytic nature or its advantages as an AOP technique that does not require the consumption of reagents.

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1 AOP: Advanced Oxidation Processes
2 PEC: Photo-electrochemical Systems
3 Reference Document on BATs for the Surface Treatment of Metals and Plastics (August, 2006)
4 BAT: Best Available Technique


Introduction

Alkaline zinc-nickel baths are non-cyanide processes that provide alloy coatings with a high content of nickel (in this case, between 12–15%) that are highly valued due to their columnar structure. This quality allows combining anticorrosion characteristics with a remarkable resistance to mechanical deformations.

The composition of an alkaline zinc-nickel bath is similar to that of cyanide-free zinc baths, but the former incorporate a nickel cation complex to the zincate solution.

Nickel complexes are polyaminated and nitrilated in nature which, combined with the use of polypeoxyamines such as brighteners, is the main cause of the high COD value of the bath.

The anodes used are insoluble, and nickel anodes are preferred to steel anodes coated with a nickel-phosphorous alloy. They operate at current densities above 4 A/dm². Under these conditions, the oxidation of polyanines to nitriles is favored, obtaining nickel nitrile compounds which, given the alkalinity of the medium (pH ≈ 14), are hydrolyzed and transformed into nickel tetracyano complexes.

The presence of nickel cyanide sub-complexes, which form at a rate of 10 mg/ampere-hour, represents an additional complication for the treatment of waste waters, since, due to their stability, these compounds are very resistant to wet oxidation treatments with hypochlorite.

In order to isolate nickel cyanide complexes, a preventive system based on the membrane electrolysis technique has been developed. It consists of introducing the anodes in a basket lined with a perfluorinated cation membrane (NAFION 400 series) that prevents the transfer of anion species to the bath.

In fact, this is an adaptation of the electro-electrodialysis technique – there are two compartments separated by a cation membrane, and each and every anode position in the bath is transformed into electrolysis cells with membranes. The objects to be coated function as cathodes.

The only advantages of the system are that cyanide species cannot reach the bath and there is a reduced formation of carbonates. However, there is still COD and heavy metal drag-outs to the rinses, which, combined with the cost and maintenance requirements of this method, has a negative impact on its benefits.

The solution proposed by ZERO PLUS is simpler and more pragmatic: instead of preventing the generation of cyano complexes, treat them in drag-outs, together with COD and heavy metals, by means of the combination of catalytic anodic oxidation and electrodeposition, until the threshold for urban water discharge is reached. In other words, the main objective would be the transformation of “hard COD”, or COD that is resistant to the biological treatment, to intrinsically biodegradable COD.

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Focusing on the problem

The rinsing stage of the installation has three running rinses, the first one with a volume of 600 liters, and the remaining two with a volume of 800 liters. All of them are fully purged on a weekly basis.

The lack of a recovery rinse at the first stage may seem odd. This is because a non-passive surface that is compatible with the subsequent chromating passivation process is required. To this end, the rinsing solution has to be kept at a pH ≤ 10.

Considering that the zinc-nickel bath operates at pH ≈ 14 and that there is a drag-out to the rinsing station of 1.3 l/h, the current configuration is adequate despite the significant water consumption involved.

The COD for the bath is around 125 g/l, whereas total cyanide concentration in the bath becomes stable at 300 mg/l for the drag-out value mentioned above.

In order to incorporate an electrolytic cell that combines catalytic anodic oxidation and electrodeposition, the following changes are implemented:

• Transformation of the first running rinse into a static rinsing stage.
• Connection of the electrolysis cell to an auxiliary tank with a total capacity equal to that of the first rinsing station (600 liters).
• Implementation of a closed loop between both tanks and the electrolysis cell.
• Optionally, transformation of the second, running rinse into a still rinsing stage.

With these changes, the installation would have the following characteristics:

<table>
<thead>
<tr>
<th></th>
<th>Bath zinc-nickel</th>
<th>Rinse 1 (still)</th>
<th>Rinse 2 (running)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>13.5</td>
<td>12.3</td>
<td>≤ 10</td>
</tr>
<tr>
<td>Volume (l)</td>
<td>1.900</td>
<td>1.200*</td>
<td>800</td>
</tr>
<tr>
<td>Drag-out (l/hour)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Feeding flow (l/hour)</td>
<td></td>
<td></td>
<td>400</td>
</tr>
<tr>
<td>Weekly purge (m³/year)</td>
<td></td>
<td>62</td>
<td>42</td>
</tr>
</tbody>
</table>

* Two connected tanks (600 + 300 liters) and an electrolysis cell (300 liters)
Initial concentrations, both for the bath and the first rinsing stage, are:

<table>
<thead>
<tr>
<th></th>
<th>Bath zinc-nickel</th>
<th>Rinse 1 (still)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>13.5</td>
<td>12.3</td>
</tr>
<tr>
<td>COD (g/l)</td>
<td>123.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Total nitrogen (g/l)</td>
<td>22.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Nitrogen (ammonium) (g/l)</td>
<td>0.4</td>
<td>0.005</td>
</tr>
<tr>
<td>Nitrogen (nitrates) (g/l)</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Carbonates (g/l)</td>
<td>58.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Total cyanide (g/l)</td>
<td>0.3</td>
<td>0.004</td>
</tr>
<tr>
<td>Zinc (g/l)</td>
<td>10.3</td>
<td>0.33</td>
</tr>
<tr>
<td>Nickel (g/l)</td>
<td>1.6</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The largest electrolytic cell available for treatment has a capacity of 360 liters and contains 50 cross-linked cathodes + 51 tin-based MMO⁶ catalytic anodes. For greater requirements, several cells can be serially connected.

The anticipated difficulties can be summarized as: stability of nickel amine and cyanide complexes and pH evolution in rinsing stages. At pH values > 10, the zinc-nickel surface becomes passivated and has a low receptivity for additional chromating conversion coatings.

Results obtained with catalytic anodic oxidation and electrodeposition

The first proposal of the ZERO PLUS Project is achieving a complete mineralization of COD, that is, reaching a level no less than 75% lower than the original concentration. The results obtained are:

<table>
<thead>
<tr>
<th></th>
<th>Rinse 1 (still)</th>
<th>Rinse 2 (running)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD to treat (kg/day)</td>
<td>25.6</td>
<td>------</td>
</tr>
<tr>
<td>COD destroyed (kg/day)</td>
<td>20.7</td>
<td>------</td>
</tr>
<tr>
<td>COD reduction (%)</td>
<td>81</td>
<td>------</td>
</tr>
<tr>
<td>Stationary COD (mg/l)</td>
<td>1.000</td>
<td>3</td>
</tr>
<tr>
<td>Stationary zinc (mg/l)</td>
<td>15</td>
<td>0.05</td>
</tr>
</tbody>
</table>

This option produces:

- A discontinuous discharge, with a purge volume of 1200 l/week, with COD contents of approximately 1 g/l and Zn + Ni + total cyanide contents < 1 mg/l.
- A continuous discharge of 400 l/hour, intrinsically biodegradable.
- A discontinuous discharge, with a purge volume of 800 l/week, also intrinsically biodegradable.

⁶ MMO: Óxidos Metálicos Mezclados
Under these conditions, running rinse 2 can be transformed into a still rinsing stage, purged daily, allowing global water savings of approximately 2600 m³/year (98% reduction of current consumption).

However, this proposal assumes the use of two serially connected electrolysis cells equipped with a total of 100 cathodes and 102 catalytic anodes, which would involve a substantial investment and a power consumption of 53,000 kWh/year.

For this reason, a new proposal is presented, less ambitious and more realistic, consisting of the partial mineralization of COD until reaching a 50-percent reduction. This allows using only one electrolysis cell, thus reducing the required investment and exploitation costs by half.

The results achieved with this second proposal are:

<table>
<thead>
<tr>
<th></th>
<th>Rinse 1 (still)</th>
<th>Rinse 2 (running)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD to treat (kg/day)</td>
<td>25.6</td>
<td>------</td>
</tr>
<tr>
<td>COD destroyed (kg/day)</td>
<td>12.8</td>
<td>------</td>
</tr>
<tr>
<td>COD reduction (%)</td>
<td>50</td>
<td>------</td>
</tr>
<tr>
<td>Stationary COD (mg/l)</td>
<td>4.100</td>
<td>12</td>
</tr>
<tr>
<td>Stationary zinc (mg/l)</td>
<td>64</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Under these conditions, the discontinuous discharge through purging (1200 l/week) contains a COD of approximately 5.3 g/l, the total contents of Zn + Ni + total cyanide being still < 1 mg/l.

Both discharges from the second running rinse, one of them continuous (400 l/hour) and the other one discontinuous (through purging, 800 l/week), are still intrinsically biodegradable. The same as in the previous case, this rinse can still be turned into a still rinsing stage that would have to be purged on a daily basis and would allow identical water savings.

The pH of the first rinsing stage decreases as oxidation advances until stabilization at a value near 9. This is due to the release of acidity in the two transformation stages of the nickel amine complexes – first, the transformation into a nitrile complexes and the subsequent hydrolysis of this compound to alcohol and a nickel cyanide complexes.

During the hydrolysis of nitrile complexes, the contents of nickel cyanide sub-complexes is quadrupled, but at the end of the oxidation process, total cyanide levels are below discharge thresholds (0.5 mg/l).

Organic nitrogen is reduced by more than 50% (from 0.75 to 0.33 g/l). The content of ammonium increases (from 5 to 140 mg/l), as well as that of nitrates (from 2 to 40 mg/l). These transformations favor the treatment of the discharge at the WWTP.
Power consumption for the electrolysis process, operating 6 days/week and 24 hours/day, is 27,400 kWh/year.

The consequences can be summarized as:

- Reduction of the waste volume to manage from 2,640 to 60 m³/year (98%).
- Reduction of water consumption at a similar rate (2,580 m³/year).
- Reduction of discharged COD, from 670 to 334 kg/year (50%).
- This reduction could reach 85%, but treatment costs would be doubled.
- Reduction of organic nitrogen by 55% with partial transformation into ammonium.
- Reduction of zinc, nickel and cyanide drag-outs by 100%.
  - Zinc: from 13.4 g/hour to 0.001 g/hour.
  - Nickel: from 2.2 g/hour to zero.
  - Cyanide: from 0.35 g/hour to zero.
- Maintenance of rinsing stage characteristics: pH < 10.
- Recovery of a Zn-Ni alloy (55 kg/year of zinc and 9 kg/year of nickel that can be managed as common waste.
- Reduction of treatment sludges, from 35.5 to 0.8 t/year (98%).

Candidacy as BAT

The global analysis of costs for an installation similar in dimensions to that of the company included in the Project, considering an annual inflation rate of 3.5 %, varies depending on the price of water. Thus:

- For a water cost of around 0.5 €/m³: Return of investment in 10.5 years (applicable in Spain).
- For a water cost of around 3 €/m³: Return of investment in 4.5 years (applicable in France).
The ZERO PLUS Project proposes reviewing the contents of the BREF document “Surface Treatment of Metals and Plastic Materials” in relation to the combination of catalytic anodic oxidation and cathodic electrodeposition for their application to issues related to the presence of COD, metal compounds and heavy metals. The following recommendations are presented:

- Section 2.5.4.4., “Zinc alloy plating”: Reviewing contents relating to alkaline zinc-nickel baths and their reference to cyanide-free alkaline effluents.
- Section 2.5.4.4., “Zinc alloy plating”: Reviewing chlorination treatment recommendations, both due to their inefficiency with nickel cyanide complexes as well as for the generation of chloramines in the treatment of nickel amine and nitrile complexes. Treatments that can cause collateral contamination are not advisable.
- Section 4.11., “Process solution maintenance”: Including a new section, after 4.11.9. and 4.11.10, to consider the advantages of combining metal electrodeposition and catalytic anodic oxidation to solve the simultaneous presence of high COD levels, metal complexes and heavy metals.
- Section 4.12.1., “Electrolysis: Recovery of metals”: Similar recommendations as for the previous section, emphasizing the suitability of catalytic anodic oxidation for destabilizing metal complexes and the subsequent metal recovery by means of cathodic electrodeposition.
- Section 4.12.1., “Electrolysis: Recovery of metals”: Expanding the recommendations for anode materials with catalytic properties. Distinguishing between active metal oxide and inert metal oxide catalytic coatings. Highlighting the importance of doping the latter in order to improve their oxygen overtension. Including coatings of common metal oxides, such as antimony-doped tin oxide. Also including new non-metal catalytic materials, such as boron-doped diamond.
- Section 4.16.4., “Cyanide oxidation”: Establishing the importance of the catalytic anodic oxidation technique for the destruction of highly stable cyanide complexes that are resistant to wet oxidation with hypochlorite. Documenting the significance of the technique for destabilizing and destroying the nickel cyanide complexes that result from the oxidation of nickel amine and nitrile complexes in alkaline zinc-nickel baths.
- Section 4.16.8., “Complexing agents”: Similar recommendations as for the previous section, emphasizing cation metal complexes in the alkaline zinc-nickel bath. Highlighting the substantial reduction of COD, by-product of amine and nitrile complexes, that is achieved with the use of catalytic anodic oxidation. Pointing out its high destabilization capacity for this type of complexes.
Best technologies applied to Trivalent Chromium-Based Passivations

may, 2009

Key words: Chromic passivation, conversion treatments, trivalent chromium, parasite metals, selective ion exchange, cation resin, separation factor
The BREF\(^1\) document “Surface Treatment of Metals and Plastics” considers in its chapter on consolidated BATs\(^2\) (Cf. Section 5.2.5.7. “Hexavalent chromium”) the substitution of hexavalent chromium-based passivations by those based on trivalent chromium. However, the BREF document is not fully decisive in this regard due to the anticorrosion characteristics of the layers obtained.

The ZERO PLUS Project (LIFE 05 ENV / E / 256) presents a proposal that goes beyond the simple substitution of processes, since chromium (III)-based solutions also get spent due to the progressive accumulation of parasite metals such as zinc, nickel or iron.

This proposal consists in applying a technique that allows the continuous regeneration of chromium (III) baths beforehand, such as the separation of these metals through cation exchange.

This paper presents the tests carried out with the selective cation exchange technique using extractant-coated resins to achieve cation selectivity. The objective was separating trivalent cations from bivalent cations through retention of the latter.

This technique, applied to colorless chromating baths, is still far from being a BAT candidate due to the poor results obtained. However, this experience is unquestionably valuable considering the other alternatives available or the progress in the development of new resins with improved selectivity and, consequently, separation capacity.

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\(^1\) Reference Document on BATs for the Surface Treatment of Metals and Plastics (August, 2006)
\(^2\) BAT: Best Available Technique
Introduction

The initial plan of the Project considered a hexavalent chromium-based yellow passivation bath and assessing diaphragm electrolysis as BAT candidate for bath regeneration. However, due to the operating conditions specifications imposed by the automobile industry, the company modified its passivation baths and began using trivalent chromium during the development of the project.

In this case, a colorless chromating bath aimed at providing a medium-grade protection to surfaces coated with a zinc-nickel alloy has been used.

Unlike chromate-based coatings, which have a remarkable self-healing capacity due to the presence of hydrated polymeric gels, trivalent chromium passivations lack this property due to the nature of the film – it is an anhydrous combination of chromium (III) oxides and hydroxides with zinc oxides.

To compensate for this disadvantage, current chromium (III) formulations contain cobalt salts to enhance their anticorrosion capacity, and silica to act as corrosion inhibitor.

In the case of colorless or bluish passivations, very thin and fissure-free, the bath adds substantial concentrations of ammonium bifluoride to ensure, through the presence of fluorides, a strong complexation of chromium (III).

On the other hand, the absence of oxidizing agents, such as chromates, forces the addition of nitric acid to make the solution aggressive enough towards the zinc surface. The operating conditions of the bath are: pH ≈ 3.5 and room temperature.

This aggressive nature, reinforced by the presence of fluorides, causes the progressive accumulation of parasite metals (Zn, Ni and Fe), all of them bivalent cations.

The presence of these ions, and in particular the Fe (II) that is generated by the attack of the substrate in unprotected areas, has a strong inhibitory effect that cannot be corrected by reinforcement additions and pH adjustment. For this reason, the bath will eventually get spent.

The option selected as BAT candidate is that of a closed-loop recycling system by using a chelating resin with strong affinity towards bivalent ions in general and zinc in particular. The circuit is established in the bath itself rather than its rinsing stage, since the dilution level of the latter does not allow a good separation between Zn (II) and Cr (III).

Isolated experiences have been carried out with acceptable results for yellow passivations. However, these practices have not been applied to colorless passivations since, in addition to their relatively low cost, the presence of fluorides can create a reaction that is too aggressive towards the extractant coating of the resin.
Focusing on the problem

The installation has a passivation bath and rinsing stages with a first running rinse and a second rinse with recirculating demineralization water. All positions are purged at different periods as shown on the table:

<table>
<thead>
<tr>
<th></th>
<th>Chromium (III) passivation bath</th>
<th>Rinse 1 (running)</th>
<th>Rinse 2 (deionized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.0 – 3.5</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Volume (l)</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Drag-out (l/hour)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Feeding flow (l/hour)</td>
<td>------</td>
<td>350</td>
<td>------</td>
</tr>
<tr>
<td>Purging (period)</td>
<td>Quarterly</td>
<td>Weekly</td>
<td>Bimonthly</td>
</tr>
</tbody>
</table>

The selective ion exchange technique is added to the bath by means of a closed-loop circuit in an attempt to avoid quarterly purging through the continuous removal of Ni, Fe and mainly Zn.

The main objective of the application is achieving constant operating conditions, during the chromic conversion treatment, by stabilizing parasite metals contents.

This generates modest water and product savings, corresponding to bath purging, of approximately 2.4 m³/year of water and 11 kg/year of chromium (III).

Any proposal to transform the running rinsing stage into a still rinsing stage, to allow an optional recycling of materials, is not feasible because the bath operates at room temperature and there is no loss of level through evaporation. Additionally, drag-outs are compensated by drag-ins, which results in a progressive dilution and loss of components that have to be regularly replenished.

Another disadvantage is the inconvenience of using the rinsing stage in an ECO mode, since this would involve starting the transformation of the surface under very unfavorable conditions (concentration of components at 50% of the nominal value).

The following table shows the state in which the bath has not exceed its half lifespan, due to zinc admissible limit concentration is of around 10 g/l:

<table>
<thead>
<tr>
<th></th>
<th>Chromium (III) passivation bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.40</td>
</tr>
<tr>
<td>Chromium (III) (mg/l)</td>
<td>5.400</td>
</tr>
<tr>
<td>Nitrates (mg/l)</td>
<td>3.400</td>
</tr>
<tr>
<td>Fluorides (mg/l)</td>
<td>1.200</td>
</tr>
<tr>
<td>Chlorides (mg/l)</td>
<td>7.700</td>
</tr>
<tr>
<td>Silica (mg/l)</td>
<td>20</td>
</tr>
<tr>
<td>Cobalt (mg/l)</td>
<td>1.3</td>
</tr>
<tr>
<td>Zinc (mg/l)</td>
<td>3.000</td>
</tr>
<tr>
<td>Nickel (mg/l)</td>
<td>61</td>
</tr>
<tr>
<td>Iron (mg/l)</td>
<td>62</td>
</tr>
</tbody>
</table>
Results obtained with selective ion exchange

The exchange capacity of the resin used is weak: 0.32 - 0.55 eq/l. Also, its suitability for retaining zinc is partial and non-selective.

The Cr/Zn separation factor decreases as the volume of treated bath increases, as shown in the following table with initial concentrations defined by: \( \text{Cr}^{3+} = 4.45 \, \text{g/l} \) and \( \text{Zn}^{2+} = 2.82 \, \text{g/l} \).

<table>
<thead>
<tr>
<th>Treated volume (BV)</th>
<th>( \text{Cr}^{3+} ) (g/l)</th>
<th>( \text{Zn}^{2+} ) (g/l)</th>
<th>Separation ratio (Cr III / Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.77</td>
<td>0.31</td>
<td>8.9</td>
</tr>
<tr>
<td>3</td>
<td>3.21</td>
<td>0.56</td>
<td>5.8</td>
</tr>
<tr>
<td>4</td>
<td>3.47</td>
<td>0.83</td>
<td>4.2</td>
</tr>
</tbody>
</table>

The maximum separation factor is obtained with a production volume of 1.6 BV and a circulation flow of 10 BV. Considering the results shown on the table, it is advisable to use production volumes of 2 BV at most, since, after this limit, there is a progressive increase of zinc leakage with chromium.

Thus, only low bath volumes can be processed, and resins cannot be saturated if the quality of the recovered solution is to be acceptable.

As a consequence, regular purging will still be required and the objective of maintaining stable operating conditions is unattainable. Therefore, it is concluded that:

The solution is technically unfeasible

Consequently, any investment in this solution is completely useless, at least with the current state of the technology. This is due to the fact that, when in contact with certain components of the passivating solution (such as fluorides), the stability of the extractant product covering the resins is weakened.
Candidacy as BAT

Based on these results, cost studies are futile, as well as the presentation of grounds for considering the technique as BAT candidate. However, there are some recommendations for the BREF document, both specific regarding the results obtained as well as general in relation to its current contents.

The following specific recommendations are made:

- Section 4.9.10 2., “Trivalent chromium conversion processes”: Depict the poor behavior of selective cation exchange decontamination techniques if stable operating conditions are to be maintained in colorless passivation baths.

- Section 4.11.7., “Ion exchange purification of metallic contamination”: Explain the statements included in the examples about chromic passivations depending on the type of passivation and, particularly, those for colorless or white-bluish treatments. Gather the poor results obtained with the technique, at least with the type of resins currently available.

The following general recommendations are made:

- Section 2.5.17.6., “Chromium conversion coatings with trivalent chromium on electroplated zinc”: Lower the level of functional advantages that extol chromium (III)-based passivations as compared to chromium (VI)-based ones, since, under equal application conditions by incorporating sealants and topcoats, such advantages are not so marked due to durability and price issues.

- Section 4.9.10, “Chromium conversion coatings”: Explain the statements about the development of alternatives to chromium (VI) passivations mandated by European Directives ELV and RoHS to avoid being part of a game promoted by interested parties. These Directives admit a threshold value for chromium (VI) contents of 0.1 mass-percent for homogeneous material.

- This threshold value is never reached with colorless passivation coatings and hardly reached with yellow-iridescent, white, and some black passivation coatings, taking into account the thicknesses that are usually specified for zinc in most of these applications.

- Section 5.2.5.7.3., “Chromium conversion coatings”: Same recommendations as those in Section 4.9.10.

- Section 6.3., “Substitution of chromium (VI) by chromium (III) conversion layers”: Same recommendations as those in Section 4.9.10.
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