Purification and Recycling Process of Hexavalent Chromium Solutions Using a Low Cost Chemical Method

Patrick Benaben and Joseph Popakul, SMS Division. Ecole Nationale Superieure des Mines.F-42023 – Saint-Etienne Cedex 2 (France)

A new chemical method used to purify and to recycle hexavalent chromium solutions (electroplating and etching solutions) is described. This method allows extraction of the almost metallic cations (99% of iron, copper cations are removed) after precipitation and filtration. The control of the pollution/depollution efficiency can be made by conductivity measurements. The major effect of de-polluting chromic acid solution is to minimize the energy consumption in the case of electroplating and to keep the efficiency of the etching powerof chromic acid solution

An approach of process costs shows the economical interest of this method: the total cost of the purified chromic acid is less (about 20%) than the cost of chromic acid replacing when the solution is polluted.

For more informations, contact:

Dr. Patrick Benaben SMS Division Surface Treatment Laboratory Ecole nationale supérieure des mines de Saint-Etienne F - 42023 - Saint-Etienne Cedex 2 (France) FAX: (33) 4 77 42 00 00 E-mail: <u>benaben@emse.fr</u> We present in this paper a chemical method, technical results and an economical cost approach of a purification and recycling hexavalent chromium solutions process.

I - Introduction

Purification of hexavalent chromium solutions used in hard and decorative chromium plating workshops (about 250 g/l in CrO_3) or as etching solutions essentially for plastic surfaces or copper foils (CrO_3 concentration about 50 g/l), becomes more and more of a major interest.

 \Rightarrow During chromium electroplating, the concentration of impurities in chromium plating bath increases, essentially cationic impurities such as Fe, Ni, Zn, Cu, Cr (as Cr(III)) and hinders for obtaining hard chromium deposits in good way.

This is a consequence of numerous drawbacks (1) in particular:

- carrying during the different stages of pretreatment operations before chromium plating,
- anodic dissolution when using auxiliary anodes (such as iron anodes),
- slow dissolution of metallic parts by anodic dissolution (when anodes are unsufficiantly protected) or chemical etching induced on lost parts (falling down the chromium plating tanks).

→ In the case of etching solutions, the concentration of Cr^{3+} and copper ions (or ions from metal to be etched) increases as a direct consequence of the etching phenomena.

For plating processes, these impurities induce a degradation of the hard chromium conditions and some deposits caracteristics (2) :

- increasing growing of nodules and treeing in high current density,

- decreasing throwing and covering power of the bath,

- increasing number of pits in deposits
- increasing (decreasing) the resistivity (conductivity) of the bath.

It has been described in different papers (3, 4) that the conductivity of the solution decreases as the concentration of impurities is growing: for instance, we have confirmed the results (5) that the energy consumption during chromium plating increases by 25% if the concentration of metallic cations increases from 0 to 7.5 g/L. More when the concentration of cationic impurities is too important, it is difficult, due to the decrease of conductivity, to get a sufficient cathodic current density because the voltage increasing value.

For etching solutions, the increase in pollutant ions decreases notably the etching power of the solution.

So there is an important interest (on economical, technical and environmental point of view) to develop suitable method to purify hexavalent chromium solutions and there is also an important interest that the industrial exploitation cost be as low as possible.

II - Description of the process and results:

Usually, to purify and to recycle hexavalent chromium solutions, there is three general methods, the general principle of application is described by K. Newby (3):

- Ions exchange resins (IER),
- Electrochemical processes,

- Dilution of the bath.

The last one is the most common method and is applied practically when rinse water and drag out are not returned to plating bath.

Ken Newby concludes that the choice as to which method is best for a plater is usually dependent primarly upon economic considerations each type of process has its own technical and economical advantages. These processes are in industrial development, the technical and economical aspects were developped in details in several documents (1,5, 6, 7, 8).

We propose in this paper to describe a new method based on chemical separation of the pollutants by some different processes currently in used in chemical industrial processes as precipitation, filtration or concentration.

1 - Principle of the process:

In hexavalent chromium solutions, chromium is present as anionic species (chromate, dichromate, trichromate ions function of concentration). At the opposite, the almost polluting metallics species are present as cationic impurities.

In general, the solubility of metallic hydroxyde species decreases as the pH of the solution increases. At about a pH value of 9, this solubility is minimum. If pH value increases (pH value higher than 9) there is a tendancy of complexing reactions with dissolution of metallic hydroxydes.

For metallic cations as Fe(III), Ni (II), Cu (II), this solubility is less than 0.2 g/L for pH = 7.

These results let us to think that by increasing pH value of chromic acid bath between 6 or 7, it would be possible to precipitate cationic impurities (Fe, Ni, Cu, Zn, ...) and trivalent chromium as metallic hydroxydes, while hexavalent chromium ions will remain in the solution. This is the general method that we use for purification of concentrated hexavalent chromium solutions.

By adding a OH component, such as NaOH, KOH, NH_4OH , ou R-OH (where R- is an organic radical) and rising the pH value between 6 and 7, we have verified experimentally that it is possible to precipitate cationic species, hexavalent chromium remaining in the solution.

Then by filtration or centrifugation, it is possible to remove hydroxyde sludges .

Afterwards to get the solution at the efficient pH value, there is an acidification of the solution by a special chemical reactant, which is an important stage of this process and which allows in the same operation to eliminate cations introduced by the basic solution. After acidification, it is necessary to concentrate the solution (due to dilution during precipitation process).

This operation allows to realize a correct chromium plating if concentration of the different component of the solution is well adjusted (CrO_3 and/or catalyst concentration) or to realize etching of metals or plastic surfaces

2 - Main results:

We have applied this process to polluted solutions issued from industrial work shops (chrome platers and copper etching): the treated volumes varied from 3 to 15 liters

2.1 - Chromium plating bath

2.1.1 - Purification process

We show in table 1 the different results of the solution analysis of polluted and purified solutions for the three main characteristic solutions used in chromium plating with the three catalysts: sulfate ions, organics, and fluosilicic ions. These analysis has been done by volumetric titration for CrO_3 and Atomic Absortion Spectroscopy for the other elements.

Bath 🗭	Sulfate catalyst		Organic catalyst		Fluosilicate Catalyst	
Conc.g/l♥	Before	After	Before	After	Before	After
CrO ₃	245	220	235	210	255	225
Fe	10.3	0.22	14.5	0.2	8.5	0.1
Cu	2.3	0.04	0.17	0.002	1.4	0.01
Ni	0.07	0.005	0.12	0.002	0.18	0.003
Al	1.15	0.15	nd	nd	nd	nd
Zn	0.09	0.001	nd	nd	nd	nd
Sn	0.2	< 0.01	nd	nd	nd	nd
Pb	0.035	0.005	nd	nd	nd	nd

<u>Table 1</u>: Results of bath analysis before and after purification for three types of hexavalent chromium bath: sulfate catalyst, high speed bath, fluosilicate catalyst.

It is interesting to note that CrO_3 concentration decreases only for about 10% from the nominal value: this reduction corresponds to losses due to absorption of the solution in the sludges (chromic acid and catalyst).

It is also very interesting to note that the purification efficiency is better than about 95% for iron and is also very good for usual impurities of hexavalent chromium bath such as nickel, copper, and zinc. This purification efficiency is a function of the pH value but also of the initial concentration of the polluted solution as the solubility of the hydroxyde is depending on the solubilisation constant.

From rejuvenated solutions we have verified the ability to get hard chromium plating in good way.

We have realized chromium deposition from the solution 1 (sulfate catalyst) table 1, after purification. Hard chromium deposit have been made on cylindrical shape samples (steel sample type XC 38, diameter 10 mm., lengh 40 mm) with a cathodic current density of 40 A/dm² and a bath temperature of 50° C.

Characteristics of deposits and results obtained are summarized in table 2. The thickness values are determined by measuring the mass of the deposit.

Bath	Duration of deposition (mn)	Deposit thickness (µm)	
	60	30	
Sulfate catalyst	120	50	
(before purification)	240	125	
	60	30	
	120	55	
Sulfate catalyst	240	125	
(after purification)	480	225	
	900	475	
	1440	660	

Table 2: Thickness of deposit function of deposition time for polluted and purified sulfate catalyst baths.

We have verified the good functionning of the purified solution by using the solution in an intensive way and adjusting the CrO_3 concentration by additions of purified solution until a turnover. The deposit conditions, efficiency, rate of deposition and the physical properties of the deposits have been constant along this study.

We have made deposits from High Speed Bath (organic catalysts) with purified and non purified solutions. We have checked the quality of the deposits after purification by cross section examination after polishing. Cross-section layers of hard chromum get by a depolluted solution show the microcracking of the deposit and also the microhardness.

The chromium deposits obtained from the two bath (purified and non purified) seems to be about the same, microcracking seems to be equivalent, the rate of deposition is equal in the two cases and the microhardness does not vary. This shows that impurities in chromium plating bath seems to have a minor influence in the **usual cathodic current density zone**.

We have evidenced that purification of chromic acid solutions seems to have a minor influence on chromium deposit structure but has a major influence on throwing and covering power of the bath in chromium plating: these characteristics decrease when concentration in pollutants species increases and this variation explain the degradation (nodules, treeing, pits) of the deposit.

2.1.2 – Control

For the routine pollution control of the solution, we used conductivity measurement.

It has been described in previous papers (3, 4) that the conductivity measurement of a bath is an excellent method to check and control the purity of the chromium bath. For instance, we have described (4) that by using a simple apparatus to measure the conductivity, it allows to determine the concentration of cationic impurities in the chromium plating bath: there is an approximatively linear relation between the sum of metallic cations concentration ((Cr(III)) + (Fe) + (Ni) + ...) in the chromium bath and the decrease of the conductivity. Generally, when the ionic species concentration increase in an aqueous solution, there is an increase of conductivity value (if the concentration of the constituant are not near the solubility maximum). In the case of chromic acid solution the contrary appears: the conductivity of the solution decreases when cationic metallic concentration increase.

We have shown that this contradiction is due to the fact that hexavalent chromium ions are engaged in complexes with cationics impurities (Fe, Cu, Ni...) (which are, by nature, not dissociated) and so there is an apparent decrease of hexavalent chromium concentration ions which explain the decreasing value of the conductivity.

To verify this assertion we have controlled that the conductivity of an hexavalent chromium solution \mathbf{A} with cationic impurities, has the same value as a synthetic hexavalent chromium solution prepared with a concentration in chromium ions which is defined as equal to \mathbf{A} reduced by the concentration of hexavalent chromium assumed engaged in complexes with the total cationics impurities.

For instance, the conductivity decreases from 720 mS.cm⁻¹ (50°C) for a non polluted chromium plating bath (250g/l CrO₃, 2,5g/l SO₄²⁻) to about 580 mS.cm⁻¹ (50°C) for the same solution with 7.5 g/l of total impurities, and about 440 mS.cm⁻¹ (50°C) for the same solution with 16 g/l of total impurities (Fe : 9 g/l, Cu: 2 g/l, Cr(III): 5 g/l...). This decreasing conductivity of 25% (720 to 580) value explains the increase of cathodic potential to get the same cathodic current density and so the increase of energy consumption: about 25% for 7 g/l of total impurities (see introduction).

This conductivity measurement can be used in Work Shops to check the total concentration of cationic metallic impurities in the chromium plating bath after standardisation.

It appears also that purification of chromic acid solution allows:

- to use less electric power: for the same cathodic current density, the voltage value is inferior in the case of purer solution,
- to use less energy for decreasing the temperature value: the lower electric power prevent the increasing Joules effect,
- to increase throwing and covering power.

2.2 - Etching solutions:

In the case of etching solutions, we have applied the purification process to polluted CrO_3 solutions. A polluted CrO_3 solution (5 l) provided by a workshop which etches copper foils, has been purified using the process describes previously.

Results of solution analysis before and after purification are presented in the following table 3:

	Polluted solution (g.l ⁻¹)	Purified solution (g.l ⁻¹)
CrO ₃	54	42
Cr ³⁺	4,8	< 1
SO ₄ ²⁻	42	30
Cu ²⁺	0.25	0.002
Ni ²⁺	0.003	0.001

Table 3: Results of bath analysis before and after purification for a solution used in etching copper process.

For the two solutions (polluted and purified) the pH value is the same: about 0,4. For highly acidic solution the pH measurement is difficult because the standardisation of the apparatus.

III - Economical aspects of the different processes:

We present in the following discussion a (very) rough estimation of the different costs.

This economical estimation is done following the two cases:

- 1 bath is sent to be destroyed,
- 2 purification and recycling of the bath,

for hexavalent chromium plating solutions.

1 – Generalities:

In this estimation the carrying cost of the bath is not included (about the same in the two cases: to the destruction place and to the purification place).

This estimation is done following the French hexavalent chromium market and more particularly the chromium electroplating: it would be easy to applied this estimation in Europe, U.S.A., Japan....

Currently, about 800 Tons by Year (T/Y) of chromic acid are consummed in France for chromium plating. Following informations from Chromium Platers, about 400T/Y are sent out workshops to be destroyed.

Calculation for estimation of purification costs is done by supposing that only half rejected hexavalent chromium is to be rejuvenated or destroyed: in France about 200 T/Y (from 400T/Y) are to be purified and recycled

2 - Estimation of actually destruction costs:

Using the same estimation for volume to be destroyed, this is equivalent to about 800 m^3 of solution (250 g/l).

Currently the cost for destruction is about 300 / m^3 , so:

the total cost of destruction is: 800 x 300 $\text{/m}^3 = 240\ 000\$

For 200 000 kg (200 T) of CrO_3 , it is possible to estimate the destruction cost for one kg:

$240\ 000\$ / $200\$ T = $1.2\$ /Kg

This estimation allows to calculate the total cost for replacement of 1 kg of CrO_3 in a plating workshop when the bath is too polluted:

the total cost for 1 kg is the sum of destruction cost and cost of commercial CrO₃.

Actually, the cost for commercial CrO_3 is about: **2.5** Kg, (to replace used bath of CrO_3 in a chrome platers workshop).

The total cost will be 1.2 + 2.5 = 3.7 \$/Kg CrO₃

3 - Estimation of purification costs

To compare, we have evaluated the cost (approximatively) to purify and recycle a volume (or a mass) equivalent with chemical purification process.

It is possible to estimate the costs to purify 1000 liters (250 Kg of chromic acid).

The different costs are:

- 250 \$ (Chemical reagents)

- 320 \$ (Human Labour)

that is to say: 570 \$ /250 Kg = 2.28 \$/Kg

The cost of the installation is about 400 000 with a duration of about 3 Years. If it is possible to treat 200 T/Y, the surcost is about **0.66 /Kg**

Total cost is : 2.28 + 0.66 = 2.94 \$/Kg.

So, we have to compare 2.94 \$/kg to 3.7 \$/Kg: the difference is favourable to the recycling process (about 25% save). This result is increased by the environmental aspect.

This rough draft estimation give an idea of the interest of this process.

Note: In this estimation, the destruction costs of sludges which this process generates are not included in the calculation. We suppose that the valorisation of metals which are included in sludges (Fe, Ni, Cr...) (for example by heat treatment and reduction under hydrogen gaz) could balance the total cost of sludges destruction.

IV - Conclusions:

The conclusion that we can do with this chemical purification and recycling process are following:

- purification and recycle of hexavalent chromium solution are useful for plating and etching solutions, in the two cases the technical benefit is important for the quality of the process,

- the purification cost using this process is interesting compare to the renewing of a polluted solution (about 25% save, compare 3.7 \$/Kg to 2.95 \$/Kg),

- usually in France and Europe, the true destruction cost is more important because in the different cost used in our estimation, until now there is Government grants for encouraging environmental aspects: these grants will be decreased (or disappeared) in few times,

- the chemical products cost could be less important by using large quantities,

- the treatment and valorisation of sludges (for instance by heat treatment under hydrogen athmosphere) is not included in this estimation (valorisation of metallic hydroxydes).

This process seems to be interesting in the way that it does not necessitate high technical process and apparatus as electrodialysis or IER, and it allows recycling of one of the most polluting agent (Cf. the different regulations worldwide).

Bibliographie:

1 - N.V. Mandich, C.C. Li & J.R. Selman : Practical & theoretical aspects of regeneration of chromic acid plating solutions via electrolytic purification (porous pot method) - *Plating and Surface Finishing* - Vol. 84 - N°12 - Décembre 1997 - P.82-90.

2 - F. Mortier, A. Pasquiou and G. Garcia - CETIM Informations N°51, P. 27.

3 - K.R. Newby – Impurities in Functional Chromium Plating Baths and What To Do About Them.- *Hard and Decorative Chromium Plating: New Trends and New Applications* – *Proceedings* 2^{nd} *International Colloquium* – p.95, 109 – April 22 – 24 – 1998 – Ecole des Mines – 42023 – Saint-Etienne - France

4 - **P. Benaben, J. Popakul** - Chromium plating bath pollution control: the apport of conductivity measurement - *Galvano-Organo* N°686 Juin/Juillet 1998 - P.471-475.

5 – P. Pajunen – Hard Chrome Bath Purification and Recovery using Ion Exchange.

Hard Chromium Plating: Techniques, Markets and alternative Process - Conference Acts – p. 178, 188. May 10 – 12, 1995 – Ecole des Mines – 42023 - Saint-Etienne- France

6 - Hard Chromium Plating: Techniques, Markets and alternative Process – Conference Acts - p.135, 188 - May 10 - 12, 1995 - Ecole des Mines – 42023 - Saint-Etienne - France

7 - Hard and Decorative Chromium Plating: New Trends and New Applications - Proceedings 2nd International Colloquium - p.131, 172 - April 22 - 24 - 1998 - Ecole des Mines – 42023 - Saint-Etienne - France

8 - P. Benaben, J. Popakul and J.P. Emmanuel - French Patent N° 2669323