## Purification & Recycling Process For Hexavalent Chromium Solutions Using a Low-cost Chemical Method

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A new chemical method used to purify and to recycle hexavalent chromium solutions (electroplating and etching solutions) is described. This method allows extraction of almost all of the metallic cations (99 percent of iron and copper cations are removed) after precipitation and filtration. Control of the pollution/depollution efficiency can be made by conductivity measurements. The major effect of de-polluting chromic acid solution is to minimize energy consumption in the case of electroplating and to preserve the efficiency of the etching power of the chromic acid solution. A process costs approach shows the economic interest of this method. The total cost of the purified chromic acid is less (about 20 percent) than the cost of chromic acid replacement when the solution is polluted.

Purification of hexavalent chromium solutions used in hard and decorative chromium plating shops (about  $250 \text{ g/L CrO}_3$ ) or as etching solutions, essentially for plastic surfaces or copper foils (CrO<sub>3</sub> concentration about 50 g/L), is becoming more and more a major interest.

During chromium electroplating, the concentration of impurities in the bath increases, essentially cationic impurities, such as Fe, Ni, Zn, Cu, Cr (as Cr(III)), which tend to degrade good hard chromium deposits. This is a consequence of numerous drawbacks,<sup>1</sup> 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 insufficiently protected) or chemical etching induced on lost parts (falling down the chromium plating tanks).

In the case of etching solutions, the concentration of Cr<sup>+3</sup> and copper ions (or ions from the metal to be etched) increases as a direct consequence of the etching phenomena. For plating processes, these impurities induce degradation of the hard chromium conditions and some undesirable deposit characteristics:<sup>2</sup>

- 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.

We have described in a recent paper<sup>3</sup> that the conductivity of the solution decreases as the concentration of impurities

grows; for instance, we have confirmed the results<sup>4</sup> that the energy consumption during chromium plating increases by 25 percent if the concentration of metallic cations increases from 0 to 7.5 g/L. Moreover, when the concentration of cationic impurities is too great, it is difficult, because of the decrease in conductivity, to get a sufficient cathodic current density even with increased voltage. For etching solutions, the increase in pollutant ions decreases notably the etching power of the solution.

Thus, it is important (from the economic, technical and environmental points of view) to develop a suitable method to purify hexavalent chromium solutions and that the industrial exploitation cost be as low as possible.

#### Process Description & Results

Usually, to purify and recycle hexavalent chromium solutions, there are two major types of processes:

- Ion exchange resins (IER)
- Electrochemical processes

These processes are in industrial use; each type has its own technical and economic advantages. The technical and economic aspects were developed in detail in several publications.<sup>1, 4-7</sup> A new method is proposed, based on chemical separation of the pollutants by such different processes, currently in use in the chemical industry, as precipitation, filtration or concentration.

#### **Process Principles**

In hexavalent chromium solutions, chromium is present as anionic species (chromate, dichromate, trichromate ions). On the other hand, almost all polluting metallic species are present as cationic impurities.

In general, the solubility of metallic hydroxide species decreases as the pH of the solution increases. At about pH 9, this solubility is minimum. If pH increases (higher than 9), there is a tendency for complexing reactions, with dissolution of metallic hydroxides. For metallic cations such as Fe(III), Ni(II), Cu(II), this solubility is less than 0.2 g/L for pH 7. These results led us to think that by increasing the pH of a chromic acid bath to 6 or 7, it should be possible to precipitate cationic impurities (Fe, Ni, Cu, Zn, ...) and trivalent chromium as metallic hydroxides, 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 an OH<sup>-</sup> component, such as NaOH, KOH, NH<sub>4</sub>OH, or R-OH (where R- is an organic radical) and raising the pH 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 cen-

#### Table 1 Results of Bath Analysis Before & After Purification\*

Bath	Bath Sulfate catalyst		Organic catalyst		Fluosilicate catalys	
Conc. g/L	Before	After	Before	After	Before	After
CrO <sub>3</sub>	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



\* For three types of hexavalent chromium bath: sulfate catalyst, high-speed bath, fluosilicate catalyst.

Optical microscope photo of chromium cross section after polishing. Deposit obtained after purification of a high-speed bath. 500X.

trifugation, it is possible to remove the hydroxide sludges. Afterward, to get the solution to the efficient pH value, there is acidification of the solution by a special chemical reactant, which is an important stage of this process and which allows, in the same operation, elimination of cations introduced by the basic solution. After acidification, it is necessary to concentrate the solution (because of dilution during the precipitation process). This operation allows correct chromium plating if concentration of the different components of the solution are well adjusted (CrO<sub>3</sub> and/or catalyst concentration), or satisfactory etching of metals or plastic surfaces.

#### **Principal Results**

We have applied this process to polluted solutions from industrial shops (chromium plating and copper etching); the treated volumes varied from 3 to 15 liters.

### Chromium Plating Bath—

#### Purification Process

In Table 1, the different results of the solution analysis of polluted and purified solutions are listed for the three main characteristic solutions used in chromium plating with the three catalysts: sulfate ions, organics, and fluosilicic ions. This analysis was done by volumetric titration for  $\text{CrO}_3$  and by atomic absorption spectroscopy (AAS) for the other elements.

It is interesting to note that  $CrO_3$  concentration decreases only about 10 percent from the nominal value; this reduction corresponds to losses resulting from 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 percent for iron and is also very good for the usual impurities of hexavalent chromium baths, such as nickel, copper, and zinc. This efficiency is a function of the pH, but also of the initial concentration of the polluted solution, because the solubility of the hydroxide depends on the solubility constant.

From rejuvenated solutions, we have verified the ability to get good hard chromium plating. We have obtained chromium deposition from Solution 1 (sulfate catalyst), Table 1, after purification. Hard chromium deposits have been made on cylindrically shaped samples (steel sample type XC 38, diameter 10 mm., length 40 mm) with a cathodic current density of 40 A/dm<sup>2</sup> and a bath temperature of 50 °C. Characteristics of deposits and results obtained are summa-

rized in Table 2. The thickness was determined by measuring the mass of the deposit.

Proper functioning of the purified solution was verified by using the solution intensively and adjusting the  $CrO_3$  concentration by additions of purified solution until a turnover. The deposit conditions, efficiency, rate of deposition and physical properties of the deposits were kept constant during this study.

Deposits were made from a high-speed bath (organic catalysts) with purified and unpurified solutions. The quality of the deposits was checked after purification by cross section examination after polishing. Cross section layers of hard chromium deposited by a depolluted solution show microcracking of the deposit, also the microhardness. The chromium deposits obtained from the two baths (purified and unpurified) seem 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 seem to have a minor influence in the *usual cathodic current density zone*.

It has been reported<sup>5, 6</sup> that purification of chromic acid solutions seems to have a minor influence on chromium deposit structure, but has a major influence on the throwing and covering power of the bath. These characteristics decrease when the concentration of pollutant species increases; this variation explains the degradation (nodules, treeing, pits) of the deposit.

#### Control

For routine pollution control of the solution, we used conductivity measurements. In a previous paper, it was reported in a previous paper<sup>3</sup> that the conductivity measurement of a bath is an excellent method to check and control the purity of a chromium bath. For instance, we have described a simple apparatus to measure the conductivity, allowing determination of the concentration of cationic impurities in the bath. There is an approximately linear relation between the sum of the metallic cations concentration [Cr(III)] + [Fe] + [Ni] + ...)in the chromium bath and the decrease of the conductivity. Generally, when the ionic species concentration increases in an aqueous solution, there is an increase of conductivity (if the concentration of the constituents is not near the solubility maximum). In the case of chromic acid solution, the contrary appears-the conductivity of the solution decreases when the cationic metallic concentration increases. We have shown<sup>3</sup>



*Optical microscope photo of chromium deposit obtained after purification of a high-speed bath. 1000X.* 



Optical microscope photo of cross section of chromium deposit after solution purification. Vickers indentation shown on deposit and on the substrate (Steel XC 38).

that this contradiction is results from the fact that hexavalent chromium ions are engaged in complexes with cationics impurities (Fe, Cu, Ni ...) which are, by nature, not dissociated; so there is an apparent decrease of hexavalent chromium concentration ions which explains the decrease in conductivity.

To verify this assertion, we have determined that the conductivity of a hexavalent chromium solution A with cationic impurities, has the same value as a synthetic hexavalent chromium solution prepared with a concentration of chromium ions equal to A reduced by the concentration of hexavalent chromium engaged in complexes with the total cationics impurities. For instance, the conductivity (50 °C) decreases from 720 mS/cm for an unpolluted chromium plating bath (250 g/L  $CrO_3$ , 2.5 g/L  $SO_4^{-2}$ ) to about 580 mS/ cm for the same solution with 7.5 g/L of total impurities, and about 440 mS/cm 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 percent (720 to 580) explains the increase of cathodic potential to get the same cathodic current density, so the increase in energy consumption is about 25 percent for 7 g/L of total impurities. This conductivity measurement can be used in plating shops to check the total

# Table 2Thickness of Deposit as Function of Deposition Time<br/>For Polluted & Purified Sulfate Catalyst Baths

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

Table 3
Results of Bath Analysis Before & After Purification
For a Solution Used in Copper Etching Process

	Polluted solution, g/L	Purified solution, g/L
CrO <sub>3</sub>	54	42
$Cr^{+3}$	4.8	< 1
SO <sub>4</sub> -2	42	30
$Cu^{+2}$	0.25	0.002
Ni <sup>+2</sup>	0.003	0.001

concentration of cationic metallic impurities in the chromium plating bath after standardization. It appears also that purification of chromic acid solution allows:

- Use of less electric power: for the same cathodic current density, the voltage can be lower in the case of a purer solution
- Use of less energy, resulting in lower temperature

#### **Etching Solutions**

In the case of etching solutions, the purification process has been applied to polluted  $\text{CrO}_3$  solutions. A polluted  $\text{CrO}_3$ solution (5 L), provided by a shop that etches copper foils, has been purified, using the process described previously. Results of solution analysis before and after purification are listed in Table 3. For the two solutions (polluted and purified) the pH is the same: about 0.4. For highly acidic solutions, the pH measurement is difficult because of standardization of the apparatus.

#### **Economic Aspects**

A (very) rough estimation of the different costs follows; this economic estimate is made for these two cases:

- 1. Bath is sent to be destroyed.
- 2. Purification and recycling of the bath for hexavalent chromium plating solutions.

#### Generalities

In this estimate, the carrying cost of the bath is not included (about the same in the two cases). This estimate is made following the French hexavalent chromium market and, more particularly, chromium electroplating. It would be easy to apply this estimate in Europe, the U.S. and Japan ...Currently, about 800 tons/yr (t/y) of chromic acid are bought and used in France for chromium plating. Following information from chromium platers, about 400 (t/y) after use are sent from shops to be destroyed (polluted solutions). Calculation for estimation of purification costs is done by supposing that only half the rejected hexavalent chromium is to be rejuvenated or destroyed. In France, about 200 t/y (from 400 t/y) are to be purified and recycled.

#### Estimate of Actual Destruction Costs

Using the same estimate for volume to be destroyed, this is equivalent to about 800 m<sup>3</sup> of solution (250 g/L). Currently, the cost for destruction is about \$300/m<sup>3</sup>, so the total cost of destruction is 800 x 300 \$/m<sup>3</sup> = \$240,000. For 200,000 kg (200 tons) of CrO<sub>3</sub>, the destruction cost for one kg is \$240,000/200 t = \$1.2/kg. This permits calculation of the total cost for replacement of one kg of CrO<sub>3</sub> when the bath is too polluted. The total cost for one kg is the sum of destruction cost and cost of commercial CrO<sub>3</sub>. Actually, the cost for commercial CrO<sub>3</sub> is about: \$2.5/kg, (to replace a used bath of CrO<sub>3</sub>. The total cost will be  $1.2 + 2.5 = $3.7/kg CrO_3$ 

#### **Estimate of Purification Costs**

To compare, we have evaluated the cost (approximately) to purify and recycle a volume (or a mass) equivalent by chemical purification process. It is possible to estimate the costs to purify 1000 liters (250 kg of chromic acid). The various costs are:

• \$250 (Chemical reagents)

• \$320 (Labor)

thus,  $\frac{570}{250}$  kg =  $\frac{2.28}{\text{kg}}$ .

The cost of the installation is about \$400,000 with a duration of about three yr. If it is possible to treat 200 t/y, the resulting cost is about 66 ¢/kg. The total cost is then 2.28 + 0.66 = \$2.94/kg. Accordingly, we must compare \$2.94/kg to \$3.7/kg: the difference is favorable to the recycling process (about 25% savings). This result is increased by the environmental aspect.

#### **Findings**

The results of this investigation of this chemical purification and recycling process indicate that:

- Purification and recycling of hexavalent chromium solutions 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 revealing, compared to renewal of a polluted solution (about 25% savings: \$3.7/kg vs. \$2.95/kg). Usually in France and Europe, the true destruction cost is more important because in the different costs used in our estimate, until the present, there have been government grants for encouraging environmental aspects. These grants will be decreased (or withdrawn) shortly.
- The chemical products cost could be reduced by using large quantities.
- The treatment and valorization of sludges (for instance, by heat treatment under hydrogen atmosphere) is not included in this estimate (valorization of metallic hydroxides).

This process is interesting because it does not necessitate a very technical process and apparatus like electrodialysis or IER, and it allows recycling of one of the most polluting agents (Cf. the different regulations worldwide).

*Editor's note:* Manuscript received, January 2000; revision received, March 2000.

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