Hexavalent Chrome Waste Teatment

Application

Electroplating metals onto surfaces increases corrosion-resistant properties, corrects dimensions for finishing, and improves wear qualities of products. While pH and ORP are often used to control plating by adjusting bath chemistries, these applications will be discussed in other application notes. The focus of this application note is the monitoring and control of plating rinse water. After electroplating is completed, the plated parts are rinsed with water in one or more rinse tanks. When this rinse water becomes too contaminated with plating solution to be effective, it must be replaced. However, this presents a serious environmental problem since the rinse water is highly concentrated with toxic chromates. Treatment includes recovery of raw material or total destruction in a waste treatment system.

Treatment

Chromate waste rinse water is typically treated in 2 stages.(Figure 1). Stage 1 changes hexavalent chromium (Cr^{+6}) to trivalent chromium (Cr^{+3}). Trivalent chromium freely bonds to hydroxide in Stage 2 of the treatment process. The final result is a non-toxic precipitate: chromium hydroxide $Cr(OH)_3$.

First Stage

(Hexavalent chrome reduction) The most common treatment method for reducing hexavalent chromium to trivalent chromium is by using chemical reducing agents such as sulfur dioxide (SO_2), sodium bisulfite ($NaHSO_3$) or sodium meta-bisulfite ($Na_2S_2O_5$). The following equation illustrates the reaction that takes place when sulfur dioxide is used:

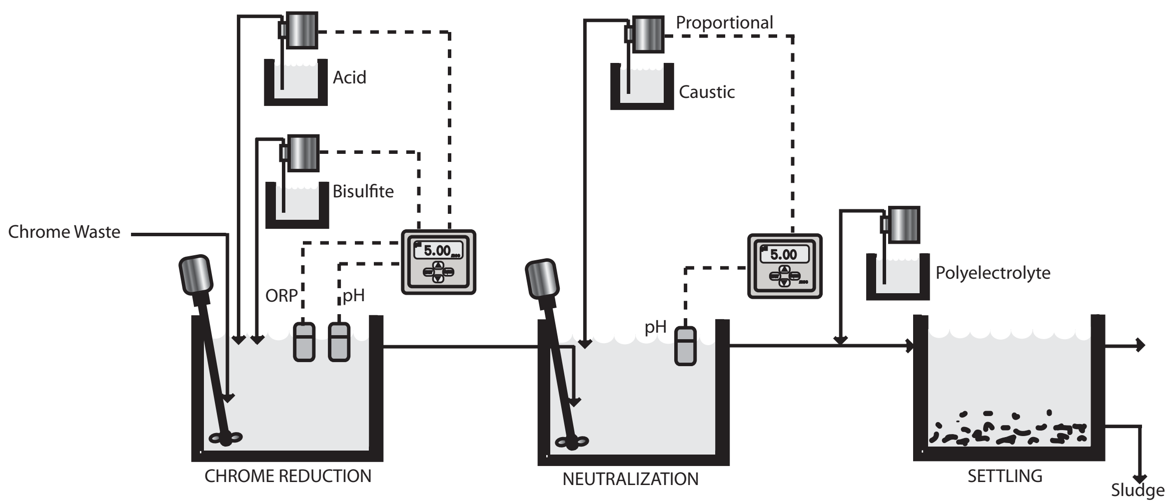
$$3SO_2 + 2H_2CrO_4 + 3H_2O \longleftrightarrow Cr_2(SO_4)_3 + 5H_20$$

This reaction will progress rapidly between 2 and 3 pH. This is accomplished using a pH controller to add an acid such as sulphuric acid (H_2SO_4)via proportional control.

Once the pH range has been reached, an ORP (oxidation reduction potential) setpoint must be established. The typical range is from 200 to 300 mV. Keep in mind that the absolute ORP value will vary from process to process and with pH changes.

NOTE: A shift of up to 150 mV can occur with a change of just one pH unit, so tight pH control is critical during this stage. The actual ORP setpoint must be specifically determined for each application.

When the reaction is completed, a sudden drop in the ORP value will occur (typically 20 to 50 mV).



Stage Two

Once the first-stage reaction is complete, calcium hydroxide, $Ca(OH)_2$, (lime), must be added to the wastewater using a second pH controller to increase and maintain a pH of 8.0 or higher., for the precipitation of chromium hydroxide to occur. Then the precipitate can be easily separated and dispose. The following equation illustrates this precipitate reaction:

$$Cr_2(SO_4)_3+3Ca(OH)_2 \longleftrightarrow 2Cr(OH)_3+3CaS0_4$$

Summary

The Environmental Protection Agency has established standards for the plating industry that require the destruction of chromates. Compliance is usually achieved by reducing hexavalent chromium to trivalent chromium with precipitation to chromium hydroxide - - a harmless, non-toxic substance.

The main disadvantage of this treatment method is the need to reduce the wastewater pH to between 2 and 3, to assure rapid and complete reduction. Unfortunately, this acidic wastewater must then be neutralized before discharge. These steps consume large amounts of chemicals and tend to significantly increase the volume of sludge with unreacted precipitants.

Instrumentation and Electrodes

For a typical two-stage chromium destruct system as shown in Figure 1, two pH control systems and one ORP control system are suggested. All three controllers should be the on/off type that have a control relay with adjustable dead band. It is recommended that the controllers also have alarm relays to alert the operator of conditions outside the normal range. A typical control system consists of:

- Three pH/ORP Controllers (your choice)
- Two pH Sensors (Model S650CD-HT)
- One ORP Sensor w/Platinum Electrode (Model S650CD-ORP-HT)

The use of flat-surface, self-cleaning pH & ORP electrodes are recommended. Cleaning frequency is reduced and much time can be saved.

Products for Chrome Wastewater Treatment

Submersible pH Sensors:

Sensors require no tools to install and can be changed in seconds. Reusable cable assembly with integral temperature sensor for ATC saves money!

Submersible ORP Sensors:

Sensors require no tools to install and can be changed in seconds. Available in Platinum or Gold measuring surface.

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