How is Chrome Waste Produced?

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 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.

Chrome Waste Treatment Regulations

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.

Chrome Waste Treatment Process

Chromate waste rinse water is typically treated in 2 stages. 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)$_3$.

Hexavalent Chromium Reduction (Stage 1)

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$_2$S$_2$O$_5$). The following equation illustrates the reaction that takes place when sulfur dioxide is used:

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

pH Control to Promote Chromium Reduction

This reaction will progress rapidly between 2 and 3 pH. Therefore, facilities performing chrome waste treatment use a pH controller to add an acid, such as sulphuric acid (H$_2$SO$_4$), to adjust pH to this range.
ORP Monitoring to Gauge Reaction Progress

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.

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).

Percipitation of Chromium Hydroxide (Stage Two)

Once the first stage reaction is complete, calcium hydroxide, Ca(OH)$_2$, (lime), must be added to the wastewater to promote precipitation of chromium hydroxide. The precipitate can be easily separated and disposed of. The following equation illustrates this precipitate reaction:

\[ \text{Cr}_2\text{(SO}_4\text{)}_3 + 3\text{Ca(OH)}_2 \rightleftharpoons 2\text{Cr(OH)}_3 + 3\text{CaSO}_4 \]

pH Control to Promote Chromium Hydroxide Precipitation

The above reaction takes place at a pH of 8.0 or higher. A pH controller can be used to adjust chemical dosage to create the proper pH conditions.

Chrome Waste Treatment Systems

For a typical two-stage chromium destruct system as shown in the figure on page 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
- Two pH Sensors
- One ORP Sensor

Sensors and Instrumentation

The chrome waste treatment process exposes electrodes to very harsh conditions. Traditional combination sensors may fail quickly due to exposure to contaminants that cause reference junction fouling. Probes will need to be replaced frequently to maintain system operation. However, modular sensor packages and differential pH sensors may reduce the time and resources required to maintain a working chrome waste treatment system.

Modular Sensor Packages

Modular sensor packages consist of mounting hardware and cable assemblies that are purchased once and pH or ORP sensor cartridges that may be replaced as needed. This is a great solution for highly contaminated water treatment applications, including chrome waste treatment, because the overall cost of ownership is reduced. Additionally, the replacement pH and ORP sensor cartridges are designed for rapid and easy installation; they can be changed in seconds without the use of tools.

Differential pH and ORP Sensors

Another solution to sensor lifetime issues in chrome waste treatment applications is differential sensor technology. Differential sensors allow users to replace the electrolyte reference solution, so the sensor does not have to be replaced when fouling occurs. This extends the lifetime of a single sensor to as long as 5 years (compared to 1 year or less for combination sensors).