Application Note AN-PR2

Hexavalent Chromium Waste Treatment

This application note is an introduction to hexavalent chromium waste treatment in the plating industry. Basic application and treatment methods are described along with recommended instrumentation.

Application

In the plating industry, electrolytic deposition of metals is essential. The process increases corrosion-resistant properties, corrects dimensions for finishing, and improves wear qualities. After electroplating is completed, the plated parts are rinsed with water in one or more rinse tanks. Eventually this rinse water becomes too contaminated with plating solution "drag-out" to be effective, and must be replaced. This presents a serious environmental problem since the rinse water is highly concentrated in toxic chromates. The abatement of pollution from such wastes includes recovery of raw material or total destruction in a waste treatment system.

Treatment

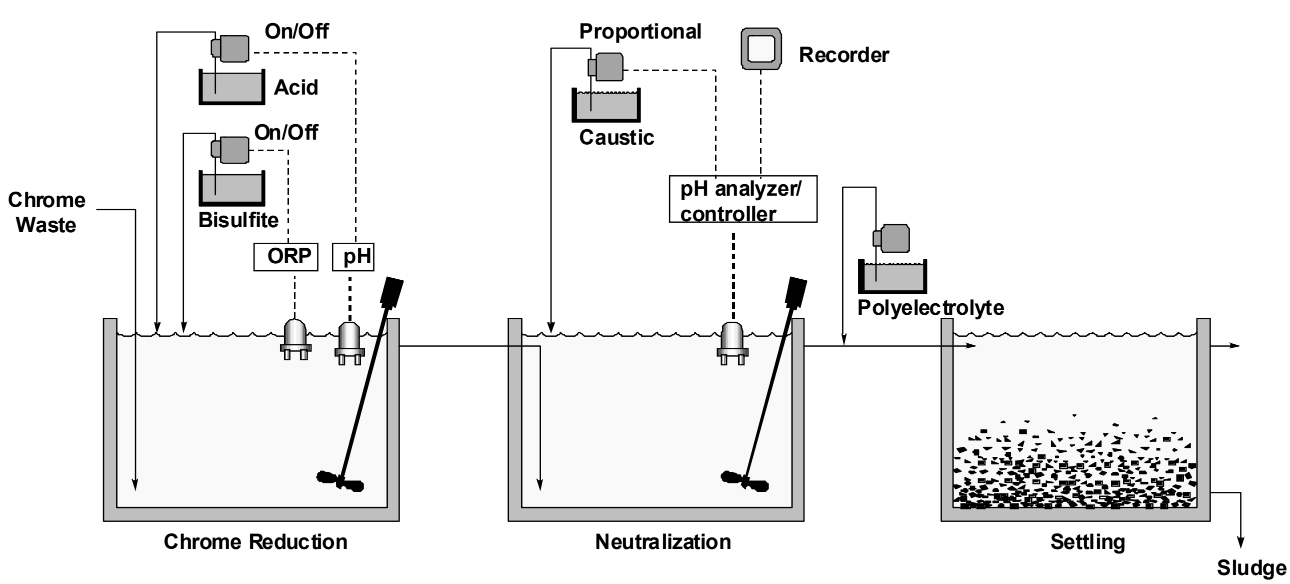
Rinse water with chromium wastes is usually treated with a two-stage process (Figure 1). The first stage changes hexavalent chromium (CR^{+6}) to a chemically unstable state known as trivalent chromium (CR^{+3}). In this interim state, trivalent chromium freely bonds to hydroxide in the second stage of the treatment process. The final result is a non-toxic precipitate; chromium hydroxide $CR(OH)_3$.

First Stage

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:

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

Figure 1 Typical Two-stage Hexavalent Chromium Destruct System



This reaction will progress rapidly between 2 and 3 pH. Retention time can be minimized by keeping the wastewater within this pH range. This is accomplished using a pH controller to add an acid such as sulphuric acid (H_2SO_4).

After achieving the proper pH, an ORP (oxidation reduction potential) setpoint must be established. Typically, it is in the range of 200 to 300 mV. 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. Therefore, tight pH control is necessary 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

After the first-stage reaction is complete, calcium hydroxide, $Ca(OH)_2$, commonly known as lime, must be added to the wastewater using a second pH controller to increase and maintain an 8 pH or higher value. This is necessary for the precipitation of chromium hydroxide to occur. The precipitate can be easily separated and diverted for disposal. The following equation illustrates this precipitate reaction:

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \Leftrightarrow 2Cr(OH)_3 + 3CaSO_4$$

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 to between 2 and 3 pH to assure a rapid reduction rate. The 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

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

A typical control system supplied GLI International consists of:

- Two pH Sensors and Analyzers
- One ORP Sensor w/Platinum Electrode
- Three Sensor Mounting Hardware Assemblies

Conclusion

Each application is unique, so it is highly recommended that each waste stream be properly analyzed to insure correct treatment.

References

Cushnie, *Electroplating Waterwater Pollution Control Technology,* Noyes Publications.

Marin, *Methods for Neutralizing Toxic Electroplating Rinsewater – Part One.*

Hach Company, *Cyanide Waste Treatment,* Application Note No. AN-PR1.

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