Introduction

Cyanide has been used extensively in the surface finishing industry for many years. Metal deposits produced from cyanide plating solutions are finer grained than those plated from an acidic solution. In addition, cyanide-based plating solutions tend to be more tolerant of impurities than other solutions, offering preferred finishes over a wide range of conditions.

Environmental, health and safety requirements and competitive pressures have forced metal finishers to adopt better process management practices.

To manage cyanide effectively, the chemistry of the cyanide system must be controlled so that little is lost from the system.

Cyanide plating chemistry

Cyanide readily joins with a variety of metals. Electrochemically, the formation of a metal-cyanide complex can alter the required potential (voltage) for metal deposition to occur in plating. In electrolytic plating cells, the metal with lowest potential (most negative) will typically plate first. If the electrical potentials are close, alloy plating can occur. Cyanide use in brass plating shifts the potentials of copper and zinc from a difference of greater than one volt to a difference of approximately 0.1V that allows brass plating to occur.

The problem

Cyanide is a hazardous substance that must be handled with caution. Cyanide-based metal finishing solutions usually operate at basic pH levels to avoid decomposition of the complexed cyanide and the formation of highly toxic hydrogen cyanide gas.

When the pH of the system is lowered, free cyanide will combine with the available hydrogen ions and form hydrogen cyanide gas (HCN) that has the propensity to escape from solution. Some processes exhibit small releases of hydrogen cyanide during plating, such as acid cyanide gold plating. Many variables govern the quantity released; however, actual hydrogen cyanide measurements above the tank have shown HCN concentrations in the range of 3-5 ppm.

Most cyanide plating solutions are operated at alkaline pH to prevent the potential release of hydrogen cyanide gas. Alkaline operation causes the solution to slowly absorb carbon dioxide from the air, forming carbonates. Carbonates are generally not an interference at low concentration (below 60g/l), but as the concentration increases they will begin to precipitate, which can interfere with the quality of the plated deposit. Consequently cyanide solutions, and other alkaline solutions, are generally not air-agitated since solution aeration would introduce more carbon dioxide to the system and increase the rate of carbonate build-up.
The solution

Step 1
The incoming cyanide effluent is first held in a holding tank to stabilize the cyanide content. It is then transferred to a stir mixing tank where the dosing of sodium hydroxide (NaOH) via a solenoid valve is controlled by an AX460 pH meter/controller. An AP300 sensor electrode system is sited near the overflow to the next treatment tank.

Step 2
In this tank, hypochlorite is dosed by a solenoid valve which is actuated by the AX460. The treated effluent is then transferred to a large holding tank to allow the hydrated metal oxides to precipitate out and to let the hydrolysis of the cyanogen chloride approach completion. The holding time is usually 30 minutes, but can be as much as two hours.

By using an AX466 dual input analyzer, it is possible to have just one analyzer control these two steps, receiving inputs from the two AP300 sensors and actuating the sodium hydroxide and sodium hypochlorite dosing processes.

Step 3
The treated effluent which is very alkaline has now to be pH adjusted before it can be discharged. This is carried out in a stirred mixing tank where the addition of acid, again via a solenoid valve, is controlled by a dip electrode system connected to the AX460. The signal output from this meter is connected to a two channel recorder, the second channel accepting a signal from the hypochlorite dosing redox controller.

Benefits:
- Ensures that the effluent is at the optimum pH level for the destruction by hydrolysis of the chlorination product, cyanogen chloride.
- Allows the hypochlorite to be dosed so as to achieve a small excess of chlorine and thus ensure complete cyanide destruction. Saves on chemicals, thus keeping costs to a minimum.
- Produces an effluent suitable for discharge into Local Authority drainage systems. A record is kept of the discharge pH level and also an indication as to the efficiency of the hypochlorite dosing section.
What can ABB offer?

Analyzers:
Ax460 pH/Redox (ORP) analyzer and AX466 dual pH/Redox (ORP) analyzer
The AX460 analyzer can be used with glass or antimony pH electrodes and also metal redox sensors to provide measurements with exceptional accuracy and performance.

The AX466 enables two continuous measurements of pH or Redox (ORP) with simultaneous local display and retransmission. A dual input unit offers a cost-effective, lower investment compared to installing separate instruments.

Key features & benefits:
- Wall, pipe and panel-mount versions which are rated to IP66/NEMA 4X ingress protection
- Continuous in-line diagnostics providing reduction in operating costs
- Auto-Water wash/chemical clean – significantly reduces maintenance
- Integral P, PI, PID Control: pulse frequency, pulse-length and analog signals (AX460)
- Real-time clock and log book records alarm events and electrode status
- 2 to 4 current outputs and 3 to 5 relay contacts
- Versatile power supply options – 85 to 265V AC or 12 to 30V DC
- High visibility, multi-language display

Both analyzers are ideal for a range of applications including water and waste-water treatment and process lines in water, power, chemicals, pharmaceuticals, pulp & paper and food & beverage industries.

Sensors:
AP300 pH/Redox (ORP) sensors
The AP300 range of pH/Redox sensors combines measurement, reference and temperature compensation elements in a single unit, making it suitable for a wide range of standard industrial applications including water, food, textiles and chemicals. Rugged construction enables the sensors to operate at up to 105°C and 6bar. Within the robust outer casing, the electrolyte is a media-resistant gel, which is faced with a PTFE liquid junction. The PTFE junction is ideal for most applications and is especially resistant to fouling when used in conjunction with a flat glass element.

Key features & benefits:
- User-customizable for Insertion, Flow-through, Immersion and Hot-tap Retractor
- Economical investment, powerful performance
- Combination sensor complete with measuring, reference and temperature elements
- Bulb and Flat Glass options
- High stability PTFE reference junction
- Gel-filled disposable sensor
- Process-resistant gel electrolyte