Monitoring Acidic Zinc Electroplating Bath Conditions

Description
Casters are wheels that are mounted on the bottom of a larger object, in order to enable the object to be easily moved. Heavy-duty versions of these wheels are found in numerous industrial applications, including platform trucks, carts, and tow lines. Industrial casters are commonly made of steel. Due to the wide range of environments casters are found in, corrosion prevention is a major concern in the caster industry. In order to improve the longevity and prevent corrosion, steel casters are often plated with zinc.

Zinc is an abundant metal found in Earth’s crust. Zinc is a popular metal for plating industrial parts due to its appearance, affordability, and corrosion resistance. In zinc electroplating, a thin layer of zinc is bonded to steel by applying electrical current through a salt/zinc solution (electrolyte) with a zinc anode and steel cathode. The applied current drives reduction at the cathode, depositing solid zinc onto the steel cathode. Because of this, electroplated parts make up the cathode. Zinc coating over ferrous metals acts as a corrosion barrier, sealing the steel off from the outside environment. Zinc corrodes slower than steel would, increasing the durability of the plated item. Zinc further protects the steel by providing a sacrificial coating: salts and oxygen react more readily with zinc than iron, causing the plating layer to degrade while the base steel remains intact.

Application
A zinc electroplater contacted Hanna Instruments to inquire about automating their titrations for their acidic zinc bath. The company was primarily plating casters and other small hardware, and had recently obtained a large contract. They were looking to increase their throughput by maintaining better bath efficiency and reduce the frequency of refreshing their baths. Their plating bath was comprised of a mixture of zinc chloride, ammonia chloride, and boric acid. The components needed to be present in strict ratios for optimal plating time and finish quality. Accordingly, the customer was performing manual titrations for boric acid, chloride, and zinc. They were using color indicators for each endpoint.

For their boric acid titration, the customer was adding mannitol to their sample before performing a titration with NaOH. Because boric acid is a very weak acid, the titration endpoint can be difficult to detect. The addition of mannitol contributes to the release of protons from boric acid, making the reaction more pronounced. For chloride determination, the customer was performing a titration with silver nitrate (AgNO₃). For zinc determination, the customer was first adding an ammonium hydroxide-ammonium chloride buffer to raise the pH of the sample to 10, and then directly titrating with EDTA.

Hanna Instruments recommended the HI902C with HI1131B pH electrode, HI4115 Silver Sulfide ISE, and HI4108 Cupric ISE for their titrations. The customer appreciated the ability to seamlessly switch between their three titrants with the Clip-Lock™ exchangeable burette system. The completely customizable methods options allowed the customer to set a pre-titrination volume to dose a set amount of titrant at the beginning of each titration, to decrease the time per titration.

The customer appreciated the method support provided by Hanna Instruments’ technical experts. Because an electrode to detect zinc directly is not available, Hanna worked with the customer to modify their existing standard operating procedure (SOP) in order to automate the titration. Their new SOP utilizes an indirect titration, in which the titration of one metal is monitored with the activity of another metal. Before titrating for zinc, a few drops of Cu-EDTA are added to the sample. At pH 10, EDTA has a higher affinity for zinc than copper. As a result, the Cu-EDTA dissociates, forming Zn-EDTA and free copper as seen in the following reaction:

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\text{Cu-EDTA} + \text{Zn}^{2+} \rightarrow \text{Zn-EDTA} + \text{Cu}^{2+}
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The sample is then titrated with EDTA. The EDTA titrant preferentially reacts with zinc, and only once all of the zinc is complexed, the EDTA then complexes the free copper. Due to the Cu-EDTA addition, a copper ISE can be used to detect this reaction equivalence point. Overall, the customer was pleased with how easy Hanna Instruments and the HI902C made their transition from manual to automatic titrations.