Determination by Ion Chromatography Of Ethylene Glycol Degradation Products In Chromium Plating and Electropolishing Baths

By Sam Sopok

Ion chromatography exclusion and conductivity detection were used to determine the degradation products of ethylene glycol in chromium plating and electropolishing solutions. As expected, the products were glycolic, oxalic and formic acids. Leaks in cooling systems can be detected by the chromatography method described in this paper.

thylene glycol from cooling system leaks can adversely affect the results of chromium plating and electropolishing. These leaks can be monitored by quantitatively determining the degradation products of ethylene glycol, using ion chromatography. Ion chromatography separates solution analytes into component bands and detects each individually. This instrumental method has been shown to be useful for metal finishing solutions.^{1,2}Ion chromatography exclusion (ICE) is used for determining the concentration of organic acids

is used for determining the concentration of organic acids and has been applied for identifying the degradation products of ethylene glycol used in solar energy collectors.³⁴

The degradation products of ethylene glycol, formed by the oxidation effects of chromium plating and electropolishing baths, compromise plating and polishing quality.⁵⁶ Hexavalent chromium is reduced to trivalent chromium, which also can affect plating quality.⁶ A method is described below for monitoring the organic degradation products resulting from ethylene glycol coolant leaks into chromium plating and electropolishing solutions.

Experimental Procedure

A chromatography and associated integrator* with an attenuation of 1024 was used for this study. The system flowstream consisted of an eluent reservoir (0.001 M hydrochloric acid), an eluent delivery system (1.0 mL/min), a separator column** and a conductivity detector (10 μ S full-scale). Calibration standards were composed of glycolic, oxalic and formic acids—the expected oxidation products of ethylene glycol. These standards contained 10, 20 or 30 mg/L of each organic acid.

Samples of contaminated chromium plating and electropolishing solutions were prepared with 25 mL of reagent grade ethylene glycol and 975 mL of chromium plating or electropolishing solution. The chromium plating bath contained 250 g/L of chromic acid and 2.5 g/L of sulfuric acid, and the electropolishing bath contained 680 g/L of phosphoric acid and 840 g/L of sulfuric acid. The used electropolishing solution also contained small amounts of several metals. The sample solutions were allowed to react with ethylene glycol for 2 hr and were stirred to allow gases to evolve. Although vigorous evolution of carbon dioxide subsided after about 10 min, the samples were stirred for an additional 2 hr to equilibrate the degradation products. Each sample was diluted 1:250 before analysis.

Results and Discussion

Figure 1 shows the conductivity values corresponding to the concentrations of glycolic, oxalic and formic acids contained in the calibration standards. The curves are based on the average of three measurements. The relative standard deviation was three to four percent.

Table 1 shows the concentrations of glycolic, oxalic and formic acids found in chromium plating and electropolishing solutions after reaction with ethylene glycol, based on the conductivity data for the calibration standards in Fig. 1. In addition to the above analyses, there was a small peak with a height of 0.1 μ S at 15.3 min, which later was confirmed to correspond to carbonic acid when a known carbonic acid injection was made into a calibration standard. (Although a great deal of carbonic acid is liberated during the oxidation process, it is reasonable to assume that some remains under weak acid conditions.)

As suggested elsewhere,³⁶ the oxidative degradation of ethylene glycol leads to the formation of glycolic, oxalic, formic and carbonic acids. In chromium plating solutions,



Fig. 1—Calibrated conductivity values of hexavalent chromium solutions containing glycolic, oxalic or formic acids.

^{*}Model 2020i Dionex ion chromatograph, Sunnyvale, CA.

^{**}Dionex high performance ion chromatography separator (HPICE-AG-1).

Table 1Conductivity Data and Concentration ofEthylene Glycol Degradation Products			
Acid	Finishing bath	Conductivity, μS	Conc., mg/L
Glycolic	Chromium	0.40	2
Oxalic	Chromium	4.85	12
Formic	Chromium	5.41	15
Glycolic	Electropolishing	1.11	4
Oxalic	EP	7.62	19
Formic	EP	9.10	26

trivalent chromium is a by-product of the oxidation of ethylene glycol. The composition of the degradation products depends on acid composition, acid concentration, retention time and temperature.

ICE does not retain sulfate, phosphate or chromate ions. Furthermore, no interaction exists between these nonretained species and the retained organic acid analytes. These are factors that contribute to the success of ICE.

The separator column selected with the ICE system keeps the analytical time below 20 min with an acceptable level of analyte band resolution. An hour or less was needed to complete triplicate samples, not including the standards.

Conclusion

The method described above provides baseline resolution of analyte peaks and accurately determines the concentration in mg/L of glycolic, oxalic and formic acids in chromium plating and electropolishing baths.

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