Analysis Methods for Zinc Plating Brighteners

By David Crotty and Kenneth Bagnall

The usefulness of high performance liquid chromatography (HPLC) for the analysis of a number of organic zinc brighteners cited in this paper has been screened. Results detailed herein show that HPLC is helpful for controlling the concentrations of several of these brighteners and some breakdown products.

Electroplated zinc has long been an important surface finish for decorative and functional purposes. Unlike other finishes, such as decorative copper-nickel-chromium, the importance of zinc has not diminished in recent times. The economy of deposition and the excellent corrosion protection provided by zinc coatings are obvious reasons for their popularity.

With the continued importance of zinc, there now is a greater emphasis on quality. Users are demanding stricter compliance with thickness, adhesion, and corrosion performance specifications, as well as better brightness uniformity.

This emphasis on quality requires electroplates to have close control of all stages in the plating line, with special attention to both the inorganic compounds and the organic brighteners in the plating bath. However, published information on brightener analysis has been limited, despite the importance of electrodeposited zinc for corrosion protection.

The methods of analysis of organic compounds in zinc baths are discussed in this paper. High performance liquid chromatography (HPLC) is considered, in particular. HPLC can be applied to many brighteners commonly used in cyanide, alkaline noncyanide, and acid zinc solutions. However, this report focuses on a few compounds reported for cyanide and alkaline noncyanide baths.

Analytical Methods

Although methods for the analysis of organic additives are well developed for some plating processes such as acid copper,[1,2] this is not the case for organic agents used for zinc plating. Electroanalytical methods applicable to copper have not been applied to zinc, for example. Spectrophotometric methods[3-5] that take advantage of the ultraviolet light absorbance exhibited by many brighteners are used for determining the concentrations of brighteners in copper and nickel. Ultraviolet photometry can track zinc plating compounds, but because the breakdown products of most additives also absorb ultraviolet light, a buildup in their concentrations makes the determination of the active compounds difficult. Therefore, photometry is usually limited to the quality control of brighteners during their manufacture.

Methods that use gas and thin layer chromatography (TLC) also have been reported. Benzoic acid, a breakdown product in acid chloride zinc baths, was analyzed’ by using TLC to separate the acid from the plating solution and ultraviolet photometry to determine the concentration. Gas chromatography was used’ to analyze anisaldehyde and vanillin in zinc solutions and acetylenic alcohols in nickel baths.[7-9] Although gas chromatography is readily applicable to volatile compounds, many plating additives are nonvolatile, high-molecular-weight reaction products.

Polarography is used for the quantitative determination of several nickel plating bath constituents,[10,11] as well as vanillin used in alkaline noncyanide zinc solutions.[12]

HPLC is particularly useful for the separation of organic addition agents from plating baths. Immel[13] discussed the determination of some compounds in bright nickel solutions, and Bocker[14] studied the effect of some aromatic sulfonamides on the properties of electroformed nickel.

Lamcione[15,16] described the equipment needed for HPLC and ion chromatography and noted several applications in electroplating. Equipment manufacturers frequently supply notes on applications to assist the user in methods development.

Zinc Plating Additives

The identity of a brightener component need not be known in order to use HPLC. Knowledge of the general nature of the additive in question usually suffices. Although the types of compounds likely to be encountered in alkaline cyanide and noncyanide solutions have been documented in the literature, only a few reports on specific organic compounds have appeared recently. Furfural in acid zinc baths was discussed by Morisaki,[17] for example. Other information appears in patents that unfortunately do not always characterize the relevant compounds or give details on their effects. However, the patent literature does provide information on the general classes of compounds that produce desirable zinc electrodeposits.

The carrier provides a smooth but not necessarily bright deposit. A black powdery electroplate is characteristic of alkaline noncyanide baths containing no additive, whereas addition of the carrier results in a smooth, smoky deposit. A complete additive system prevents burning at areas of high current density and improves throwing power. Most carriers do not absorb ultraviolet light, as a rule, and cannot be detected by using the standard UV detectors supplied with HPLC instruments. Optional refractive index detectors make it possible to separate and analyze carrier compounds using HPLC, but such detectors are very expensive.

Carriers cited in the literature include polyvinyl alcohol (which is sometimes oxidized before use),[18] polyethylene imines,[19] and their quaternized[20] and sulfonated[21] derivatives. Other polymeric amines claimed in patents include the reaction products of amines with epichlorohydrin or other polymerization agents.[22-26]

Brightener components add clarity and brilliance to the deposit. The brightener concentration is critical. Although a loss of brightness is the result of a low brightener concentration, the deficiency is easily detected and corrected by performing Hull Cell tests. However, an excessive brightener concentration will reduce thickness in low-current-density areas and trigger delayed blistering.

Aldehydes [18,27] such as anisaldehyde, pyridine derivatives such as nicotinic acid,[19] and benzyl pyridinium 3-carboxylate [28] are well-known zinc brighteners. Several reaction products of nicotinic acid[29-31] have been cited in patents. Many aromatic compounds containing more than one nitrogen atom (e.g., imidazole) and their reaction products have been patented,[22-38] usually as products of epichlorohydrin, the N-heterocyclic compound of choice, or a third reactive species. (Because some of the imidazole reaction products do not absorb ultraviolet light, it is believed that the aromatic character of such products is lost.) A number of thio compounds have also been patented. [39-41]

Experimental Procedure

The chemicals used in this study generally were of the same grade as those used for production. However, reagent-grade chemicals also were used when available to verify that ultraviolet spectra were not dominated by impurities.

Ultraviolet absorption spectra between 230 and 400 nm were recorded using a dual-beam spectrophotometer* and a recorder. Deionized water was used as the solvent and blank. Samples were characterized by using an HPLC gradient and integrator system consisting of dual pumps, an injector, an automatic gradient controller, a programmable detector, a computing integrator, and a Cl 8 reverse-phase column. The detector was set at 254 nm, a wavelength typical of fixed wavelength instruments. The sample volume was 25 *µL.* Test chemicals were diluted to concentrations recommended in the literature and then further diluted to 2 percent by vol and acidified with sulfuric acid. The resulting sample was then filtered through a 0.45-µm filter before injection. Each sample was eluted with a flow rate of 1.0 µL/min using a mobile-phase gradient initially set at 20 percent methanol and 80 percent water and linearly changed during a 10-min period by the gradient controller to 60 percent methanol and 40 percent water.

Results and Discussion

Table 1 lists the ultraviolet-absorbing compounds selected from the literature for this study. The table includes two proprietary materials designated P1 and P2. Absorption maxima and absorption coefficients are given in the table. All of the Table 1 compounds were strong ultraviolet light absorbers at 254 nm, although the maxima were not necessarily close to this wavelength.

Figure 1 is an HPLC chromatogram of a mixture of several chemicals commonly found in zinc brightener systems. The horizontal axis represents the elapsed time since injection into the column, and the vertical axis is the

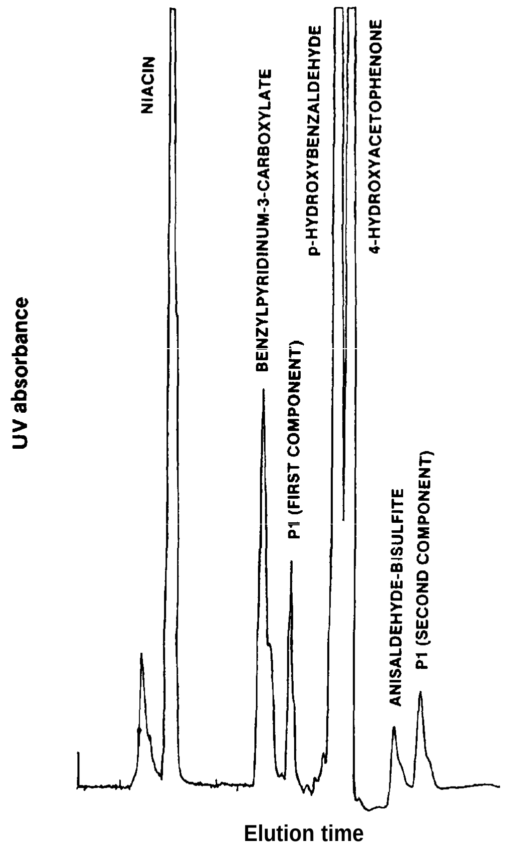

Fig. 1 —HPLC chromatogram of some organic brightener cited in the literature for zinc plating.

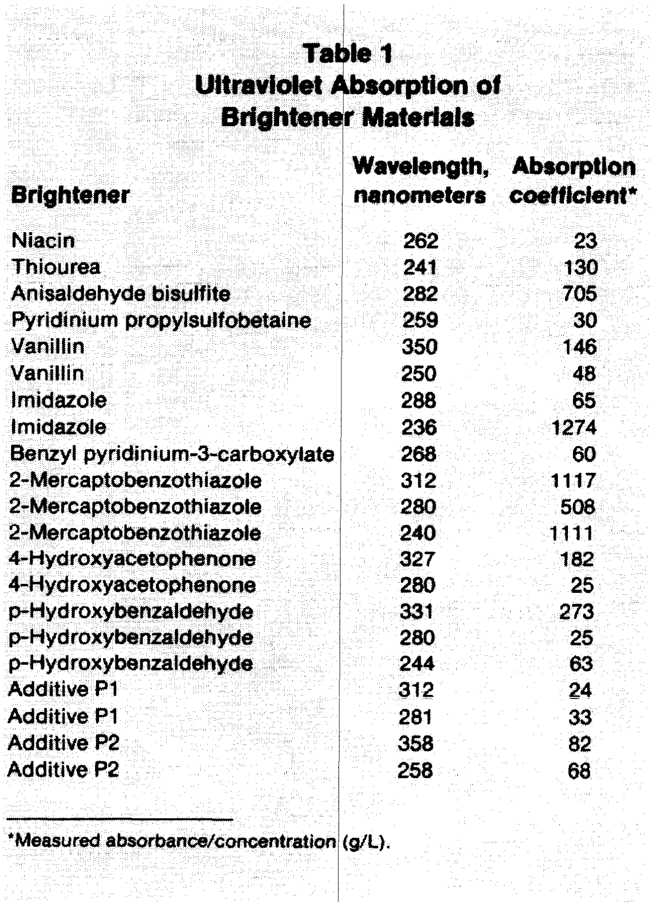

Table 1
Ultraviolet Absorption of Brightener Materials

Brightener	Wavelength, nanometers	Absorption coefficient*
Niacin	262	23
Thiourea	241	130
Anisaldehyde bisulfite	282	705
Pyridinium propylsulfobetaine	259	30
Vanillin	350	146
Vanillin	250	48
Imidazole	288	65
Imidazole	236	1274
Benzyl pyridinium-3-carboxylate	268	60
2-Mercaptobenzothiazole	312	1117
2-Mercaptobenzothiazole	280	508
2-Mercaptobenzothiazole	240	1111
4-Hydroxyacetophenone	327	182
4-Hydroxyacetophenone	280	25
p-Hydroxybenzaldehyde	331	273
p-Hydroxybenzaldehyde	280	25
p-Hydroxybenzaldehyde	244	63
Additive P1	312	24
Additive P1	281	33
Additive P2	358	82
Additive P2	258	68

*Measured absorbance/concentration (g/L).

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*Beckman DBG, Beckman Instrument Co., Fullerton, CA.

response from the ultraviolet detector. As the sample passes through the column, the packing material retains each component of the mixture for a different amount of time resulting in a separation. As the components exit the column, an ultraviolet detector and a computing integrator permit quantitative analysis of each component.

The data in Table 2 show that elution time varies sufficiently to distinguish several brighteners from others. However, some compounds eluted closely to another compound. For example, vanillin, p-hydroxybenzaldehyde, and 4-hydroxyacetophenone would not be separated adequately if they were used together in the same additive system. It is of interest to note that the proprietary product, PI, contains two components that elute with different retention times.

Several compounds included in this study eluted quickly through the column, indicating that they had not been retained by the packing material under these conditions. These compounds subsequently were separated by using an isocratic (constant eluent) mode with an eluent consisting of 98 percent water and 2 percent methanol (Table 3). If chemicals of this type are encountered in a mixture, a separate procedure that starts with pure water (rather than 20 percent methanol) may be appropriate.

During the development of an analytical procedure for a mixture, it is especially important to observe the detector response to increasing concentrations of each component. The response of anisaldehyde at 254 nm is shown in Fig. 2. The plot of peak area vs. concentration is linear only up to about 10 mg/L. Because anisaldehyde generally ranges from 100 to 1000 mg/L, dilution would be required before a zinc bath sample could be analyzed.

A fresh, noncyanide zinc plating bath was prepared for a study of brightener breakdown products. The 1-L bath contained 7.5 g/L zinc ions, 110 g/L sodium hydroxide, and 30 g/L sodium carbonate. A commercial brightener system comprised of three components separable by the HPLC method was selected because the authors had acquired considerable knowledge about the relationships of the individual components to plating performance. Component A is a divalent sulfur compound, and Components B and C are aldehydes. Performance deteriorates as their concentrations drop below certain limits.

A panel of 4 x 10 cm was cleaned and plated at 3 A/dm^2 for 2 hr before brightener components were replenished with a brightener addition. The current density was normal, but the load per unit volume of solution (A/L) was much larger than that used in typical industrial practice. Figure 3 shows changes with time in the Concentrations of all three components. The concentrations were determined using the "method of standard additions,"[42] which involves adding known amounts of each component directly to the sample to observe the detector response. The method of standard additions is the best way to obtain an accurate analysis when using methods like HPLC, atomic absorption, and polarography where detector response may vary markedly with small changes in conditions. Although the brightener

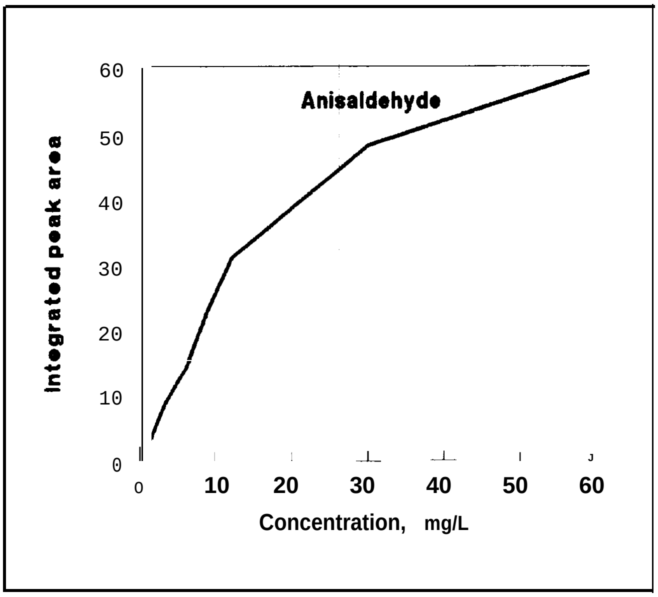

Fig. 2—integrated area under the curve of UV absorbance as a function of anisaldehyde concentration.

Table 2
Brightener Retention Time
With Reverse-Phase Chromatography

Brightener	Retention time, min	K'*	Minimum detection limit
Niacin	4.04	0.55	5
Benzyl pyridinium-3-carboxylate	8.36	2.22	10
P1 (first component)	9.71	2.73	25
p-Hydroxybenzaldehyde	11.65	3.48	0.5
Vanillin	12.08	3.65	2
4-Hydroxyacetophenone	12.25	3.71	0.5
Anisaldehyde bisulfite	14.65	4.63	5
2-Mercaptobenzothiazole	15.42	4.93	0.5
P1 (second component)	15.88	5.11	25

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*$K' = (V_s - V_o)/V_o$, where V_s = sample retention time and V_o = void volume retention time.

was replenished at the normal rate, the concentration of two components never returned to optimum values. Consequently, the performance of the bath deteriorated dramatically.

Figures 4a-b are the chromatograms of bath samples removed at makeup and after 8 hr of plating. Peaks for the breakdown products of components A and B appear as A’ and B in Fig. 4b. The breakdown product for component C is not UV active at 254 nm.

This brightener system is an excellent example of one that lends itself to routine analysis by HPLC. One of the components is packaged with the carrier, and the other two are combined in a second package. The procedure used included monitoring all three components. Similar procedures have been adopted for cyanide, acid chloride, and other noncyanide systems. Usually at least two components of the brightener system are monitored because circumstances may cause one to be depleted preferentially.

Regular HPLC analyses are beneficial for tracking breakdown products during bath use, especially baths used for rack plating where dragout is low. Frequent assays can be helpful for determining if a batch purification is required or if regularly scheduled purification procedures have been effective. Some purification agents such as polysulfides for cyanide baths and hydrogen peroxide for acid chloride solutions destroy some brighteners without affecting others. HPLC can remedy the imbalance that occasionally occurs from overuse of purifying agents.

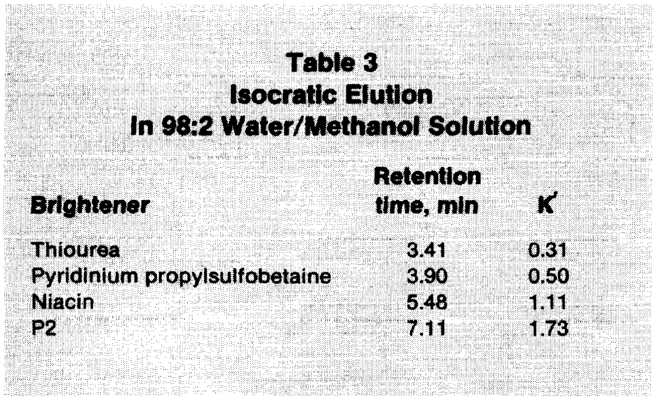

Table 3
Isocratic Elution
In 98:2 Water/Methanol Solution

Brightener	Retention time, min	K'
Thiourea	3.41	0.31
Pyridinium propylsulfobetaine	3.90	0.50
Niacin	5.48	1.11
P2	7.11	1.73

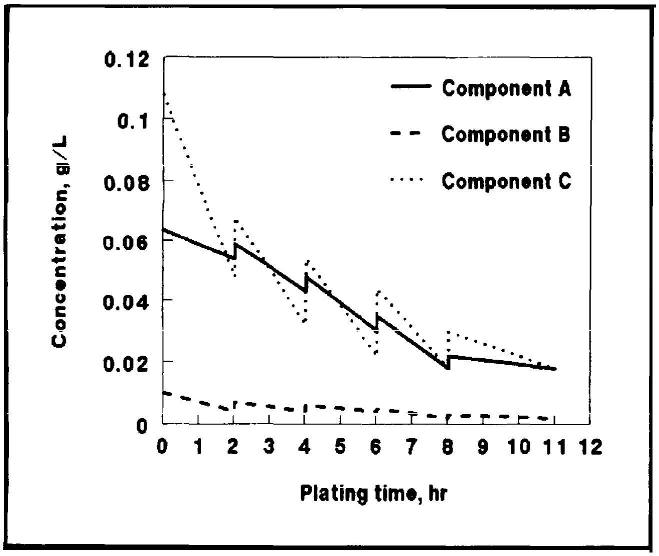

Fig. 3—Changes in the concentration of brightener components A, B and C as a function of plating time.

The exact identity of the additive components need not be known for the successful use of HPLC analysis of brightener components. A sample of concentrated proprietary brightener may be used to judge the relative concentration of its components, and a method can be adopted to check the relative concentrations in plating bath samples as the plating bath is used.

Closing Comment

Hull Cell testing has been, and still is, the chief method for tracking brightener performance, but Hull Cell tests cannot detect some important process Parameters. A few analytical methods have been adopted over the years for a few specific brighteners, but none has been as useful as HPLC. Increasing use of instrumentation, such as HPLC, for controlling brightener systems will find more use in the plating industry as the demand for high-quality products increases.

Acknowledgments

The authors would like to thank Carl Steinecker, senior development chemist at Allied Kelite, for helpful discussions and the Allied Kelite Division, Witco Corp., for providing the time and resources for the preparation of this paper.

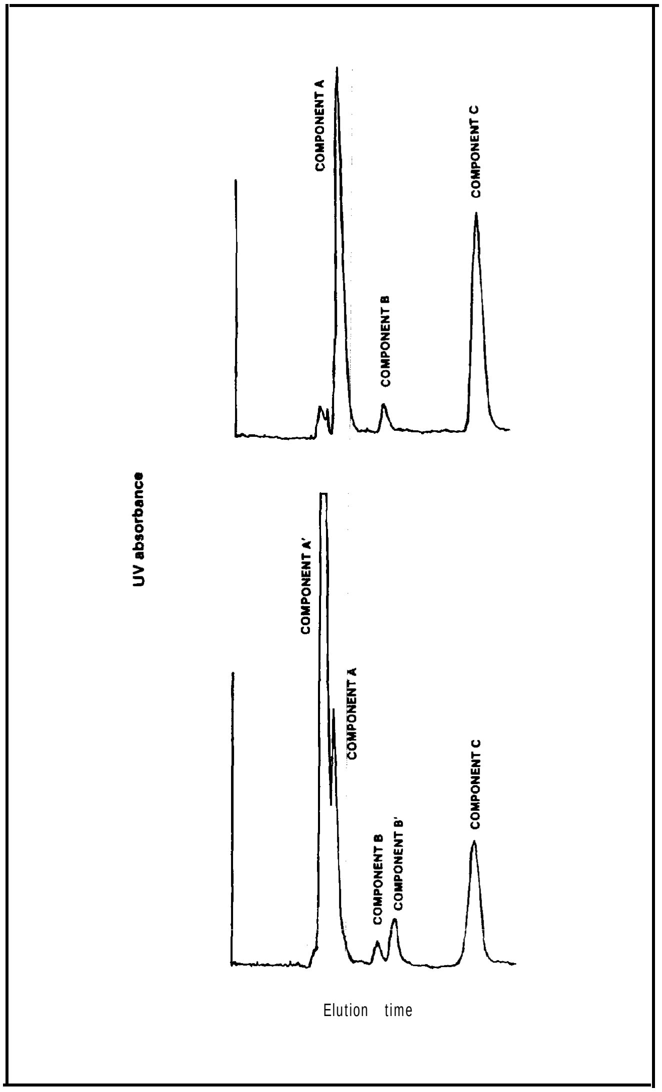

Fig. 4—HPLC chromatograms of brightener components A, B and C in a fresh plating bath (top) and the same bath after 8 hr of operation (bottom). Components A and B are brightener breakdown products.

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