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Ion chromatography in the manufacture of multilayer circuit boards

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ABSTRACT

Ion chromatography (IC) has proven useful in analyzing chemical solutions used in the manufacture of multilayer circuit boards. The manufacturing process is described briefly and previously published IC methods are reviewed. Then, methods are described for determining chlorate and chlorite in a brown oxide solution; salicylic acid in an epoxy cure agent; formate, sulfate and tartrate in an electroless copper bath; anionic detergents in a tin–lead brightener and in a cleaning solution; and aqueous photoresist and non-ionic brightener in a tin–lead bath. Anion exchange, reversed-phase high-performance liquid chromatography on a poly(styrene–divinylbenzene) column and two-dimensional liquid chromatography are described. Chemically suppressed conductivity and photometric detection are used.

INTRODUCTION

Manufacturing process

Multilayer printed wiring boards are manufactured in a multi-step procedure. One starting material is usually a polyimide/glass covered with a copper foil. This is treated with a brown oxide solution, which contains sodium hydroxide and sodium chlorite, which can be converted to sodium chlorate in time. When making rigid circuit boards, the other starting materials are an epoxy pre-polymer, which usually consists mostly of the diglycidyl ether of bisphenol A (DGEBA) and a cure agent consisting of a tetraethyl methylene dianiline plus about 1% salicylic acid. After polymerization, the copper foil is laminated onto the epoxy, which is put on a polyimide-based flexible cable, which is put onto another layer of epoxy/copper foil/polyimide/glass. This pattern is repeated until the desired number of layers are obtained.

Next, holes are drilled in the laminate and the surface is cleaned and prepared for copper plating. If an epoxy laminate is used, the process starts with a chromic acid etchback. The surface is then lightly roughened by wet-blasting. Next, the conductive copper layer is electrodeposited. Initially, 20 microinches are deposited using an electroless copper bath which contains a strong reducing agent, formaldehyde. After

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applying this copper strike, a 0.001-in. layer of ductile copper is electrodeposited using an acid copper tank.

Next, photoimaging is performed. A negative photoresist is added and a photographic image of the desired circuitry is applied. Exposure to UV light induces the production of a reactive nitrene which cross-links the three components of the resist to form a polymer. The areas of the circuit boards which were not exposed to light are soluble in aqueous sodium carbonate developing solution, and is so removed. The photochemically reacted photoresist now covers selected regions of the copper conductor.

The exposed, undesired copper is removed in an acid etch, exposing the epoxy, which acts as a dielectric. The cross-linked photoresist is then removed using an aqueous sodium hydroxide stripping solution, leaving the desired bare copper circuitry on an epoxy substrate. When panel plating, the finished board is dipped into molten solder, then a hot air leveler is used to evenly distribute the solder. When pattern plating, a tin–lead bath is used. In either case, there is a solderable alloy to which other devices can be attached.

Solution analysis

Ion chromatography has been used to monitor the concentrations of anions in many of the tanks used in the manufacturing process. Chromic acid was analyzed for chloride and sulfate [1], water rinses for chloride and sulfate, alkaline cleaners for chloride, phosphate and sulfate [2], ammonium bifluoride–HCl etchback tanks for fluoride and chloride and electrolytic acid copper for trace chloride [3].

The anion-exchange columns used are made of surface sulfonated poly(styrene–divinylbenzene), or PS–DVB, to which aminated latex beads have been attached. This polymeric core is resistant to extremes of pH, enabling the analysis of corrosive baths. Fluoride, chloride and sulfate have been separated on older columns such as the AS-1, AS-3 and AS-4 (Dionex, Sunnyvale, CA, U.S.A.). The more efficient columns, AS-4A and AS-5A, are now available and can be used for these separations. To minimize analysis time, there is even a fast run anion separator (for samples with few anions), but to obtain maximum column efficiency, the AS-5A can be used. Chromate, though, is strongly retained on the AS-1, AS-3, AS-4 and AS-5A columns. In the original report, the AS-5 column was recommended because it has a lower selectivity coefficient for chromate, which can be eluted using the standard 3 m*M* sodium bicarbonate plus 2.4 m*M* sodium carbonate eluent [1]. Since the publication of this report, the AS-4A column became available, and chromate can be eluted from it also. When analyzing a plating bath (or any other sample) for a trace anion in the presence of another anion (such as ppm levels of chloride in chromic acid etchback bath), it is important to prepare the standards in the same matrix as exists in the sample [1]. It is important also to use a PS–DVB-based column because it is resistant to damage by low (or high) pH and by corrosive samples such as chromic acid, which can partly hydrolyze silica-based columns.

In addition, mobile phase ion chromatography (MPIC) can be used to monitor the non-ionic organic brightener content in plating baths [4]. Using automated procedures, applied labor can be minimized and sample throughput maximized.

Transition metals

The concentration of the major metal in a bath (copper or tin and lead) can be determined using a cation-exchange column and an eluent containing a mild chelating agent such as oxalate or citrate, followed by post-column reaction and visible detection [5–7]. The metals are converted to a chromophore by post-column reaction with 4-(2-pyridylazo)resorcinol (PAR). In the original reports, the CS-2 cation-exchange column was used, and the technique was capable of separating and detecting ppm levels of divalent copper, lead, cadmium, cobalt, zinc and nickel; it could also differentiate between ferrous and ferric ions [5,6]. Since then, a more efficient cation-exchange column, the CS-5, has become available. This, together with advances in post-column reaction, has enabled the determination of stannous and stannic ions in samples including the tin–lead alloy bath [7]. In addition, low ppm levels of zinc and nickel were determined in acid copper baths [5]. Thus, the transition metals can be routinely determined.

EXPERIMENTAL

Chromatograms were obtained with an automated Dionex Model 4000 ion chromatograph equipped with a Hewlett-Packard 9000 computer and AI-300 software from Dionex. Chemically suppressed conductivity detection was accomplished using an anion micromembrane suppressor (AMMS-II) which was continuously regenerated with 0.0125 *M* sulfuric acid.

Salicylic acid was determined in the amine cure agent by dissolving about 0.5 g of the sample in 25 ml of methylene chloride, then extracting this with 40 ml of 17 m*M* 4-cyanophenolate, pH 9.1. The aqueous extract was transferred to a 50-ml volumetric flask, then diluted to mark. The 50-ml sample was diluted 1/10 with 17 m*M* 4-cyanophenolate, pH 9.1, then injected on an AG-4A plus AS-4A column pre-equilibrated with the same 17 m*M* 4-cyanophenolate, pH 9.1, flowing at 1.6 ml/min. Detection was accomplished by chemically suppressed conductivity using an AMMS-II. Quantitation was done by injecting five different standards of salicylic acid, also dissolved in the eluent, integrating peak areas, then plotting areas *vs.* concentration. Data were fitted to a straight line using linear regression analysis (correlation coefficient was at least 0.999). Peak areas of samples were substituted into the straight line equation to obtain sample concentrations.

Chlorite and chlorate in brown oxide were determined by diluting the sample 1:1000, then injecting it on an AG-4A plus AS-4A pre-equilibrated with 1.9 m*M* sodium carbonate plus 1.5 m*M* sodium carbonate at 2.0 ml/min. Detection and quantitation were performed as in salicylic acid determination, except that standards contained chlorite plus chlorate and calibration lines were calculated for both.

Formate, sulfate and tartrate were determined in electroless copper by diluting the sample 1/1000 then injecting it onto an AG-4A plus AS-4A pre-equilibrated with 2.4 m*M* sodium bicarbonate plus 1.9 m*M* sodium carbonate flowing at 2.0 ml/min. Detection and quantitation were performed as described above, except that standards contained formate, sulfate and tartrate and three calibration lines were calculated.

Aqueous photoresist was determined in a tin–lead bath by diluting the sample 10:25 and injecting it onto a PS–DVB-based MPIC 5 μm column pre-equilibrated with acetonitrile–water (9:1, v/v) at 1.0 ml/min. A Model 1040M diode array detector

(Hewlett-Packard, Kansas City, MO, U.S.A.) had one channel set at 252 nm. The area of the photoresist peak observed was compared to that of photoresist standards (linear regression analysis) to obtain concentrations in tin–lead baths.

Brightener in a tin–lead bath was determined by injecting a 10:25 diluted sample onto a MPIC 5 μm column pre-equilibrated with 77 m*M* NaOH in methanol–water (2:8) at 1.0 ml/min. Chemically suppressed conductivity detection was used.

Retention of ethano-, propano-, butano-, pentano- and hexanophenones on an MPIC 5 μm, PAX-500 and an octadecylsilica (ODS) column was measured using different proportions of acetonitrile in water at 1.0 ml/min. Diode array detection at 246 nm was used. The capacity factor, k', was calculated as follows [8]:

$$k' = (V_r - V_0) / V_0 \quad (1)$$

where V_r is the retention volume of the alkylphenone and V_0 is the column void volume.

Detergent-containing cleaner used to prepare printed wiring boards for copper plating was analyzed by diluting the sample 2:1000 into 0.96 *M* sodium hydroxide in acetonitrile–water (18:82, v/v) and injecting it onto a PAX-100 column pre-equilibrated with the same 0.96 *M* sodium hydroxide in acetonitrile–water (18:82, v/v). Diode array detection at 227 nm was used.

RESULTS AND DISCUSSION

The amine cure agent used to react with DGEBA-containing epoxy must contain the proper amount of salicylic acid to enable proper reaction kinetics. The salicylic acid is ionized at pH 9.1, so it is selectively extracted into the aqueous solution containing 4-cyanophenolate. Salicylate elutes at 2.69 min, as shown in Fig. 1. Any tetraethyl methylene dianiline extracted into the aqueous phase is removed by the suppressor and is not detected. In a single blind experiment, seven samples were submitted for analysis, and the results (Table I) showed an average percent error of 3.99%. This was calculated by first computing the percent difference (or error) between the observed and expected values. The absolute values of the percent differences for each sample were added together, then divided by seven to get the average percent error.

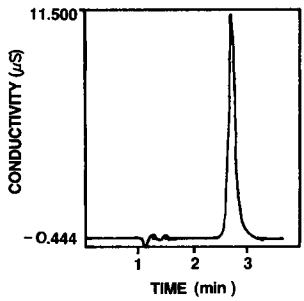

Fig. 1. Salicylic acid determination. Column: AG-4A plus AS-4A. Eluent: 17 m*M* 4-cyanophenol, pH 9.1, 1.6 ml/min. Detection: chemically suppressed conductivity.

TABLE I

PERCENT SALICYLIC ACID

Column: AS-4A; eluent: 17 m*M* 4-cyanophenolate, pH 9.1; detection: chemically suppressed conductivity.

Added	Found
1.77	1.68
2.06	2.14
2.53	2.49
2.53	2.45
2.53	2.39
2.72	2.60
3.10	2.97

The diluted brown oxide sample produced four peaks (Fig. 2). Chlorite (at 1.2 min) is the active ingredient, as it promotes a strong bond between the internal copper circuitry and the epoxy layer. It is easily quantitated, together with chlorate (at 3.2 min) using computerized data analysis in which the chromatograph can be expanded and baselines drawn using menu-driven software. Monitoring chlorite and chlorate informs the electroplator about the strength and age of the bath.

An electroless copper tank deposits 20 microinches of copper on the holes drilled through the multi-layer boards. It uses formaldehyde to reduce the cupric ion to the elemental copper electrodeposit. In the process, the formaldehyde is oxidized to

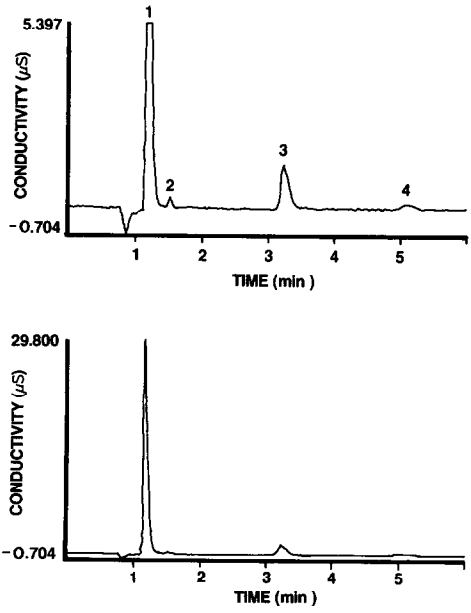

Fig. 2. Brown oxide anion analysis. Column: AG-4A plus AS-4A. Eluent: 1.95 m*M* $NaHCO_3$ + 1.56 m*M* Na_2CO_3, 2.0 ml/min. Detection: chemically suppressed conductivity. Peaks: 1 = chlorite, 2 = chloride, 3 = chlorate, 4 = phosphate. The top is a re-plot of the bottom chromatograph in which the conductivity scale is expanded.

formic acid. In addition, the bath contains sodium tartrate, which forms a slightly dissociated complex with the cupric ion, keeping it in solution despite the high pH of the bath. Tartrate, sulfate and formate can be separated by using the AS-4A column and a 2.4 m*M* sodium bicarbonate plus 1.9 m*M* sodium carbonate eluent as shown in Fig. 3. As the electroless copper tank is used, the formate concentration increases. This can be monitored, so the age of the bath can be observed and bath performance predicted.

Recently, there has been an emphasis on decreasing the use of chlorinated hydrocarbons, so new aqueous-processable photoresists have been developed. Though one wants to protect the environment, it is still important to produce good circuit boards. Thus, a method was developed to measure leaching of an aqueous photoresist.

The material being evaluated is a negative photoresist, meaning that when it is exposed to light, it becomes insoluble in the developing solution. A major manufacturer of photoresists, Hunt Chemical Company, published a report stating that all negative photoresists contain a bis azide compound as a photoinitiator [9]. UV light causes the formation of a reactive nitrene, which can abstract a proton from a carbon in the polymeric component of the photoresist, causing the formation of a covalent bond, as shown below. Hydrogen abstraction:

$$\text{R–N}_3 \xrightarrow{\text{UV}} \text{R–N:} + \text{N}_2\ (\text{gas})$$
$$\text{R–N:} + \text{H–C}\lessgtr \rightarrow \text{N–C}\lessgtr$$

where R–N_3 is the photoinitiator and H–C$\lessgtr$ is an acrylate polymer.

In previous negative photoresists, the polymer was a poly(isoprene) which was soluble in chlorinated solvents; these solvents were used to develop the resist after exposure to UV light. On the other hand, the new aqueous processable photoresist contains a water soluble acrylate-based polymer, eliminating the need for hazardous chlorinated solvents.

In pattern plating, a subsequent step after developing the photoresist and washing the circuit board is tin–lead electroplating. Thus, it was necessary to develop a

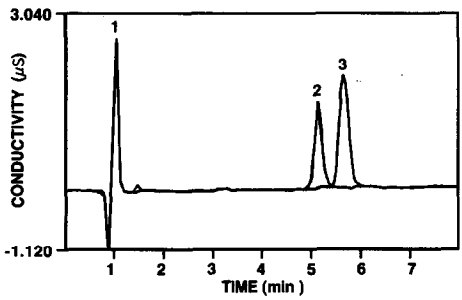

Fig. 3. Ion chromatograph of two week old electroless copper bath. Column: AG-4A plus AS-4A. Eluent: 2.4 m*M* $NaHCO_3$ + 1.9 m*M* Na_2CO_3, 2.0 ml/min. Detection: chemically suppressed conductivity. Peaks: 1 = formate, 2 = sulfate, 3 = tartrate.

method to measure leaching of this aqueous photoresist in the fluoroboric acid-based bath. Because of the low pH of the sample, it was necessary to use the corrosion-resistant MPIC column, which is based on PS–DVB, as opposed to standard reversed-phase HPLC silica-based columns. Using an eluent consisting of acetonitrile–water (9:1, v/v) flowing at 1.0 ml/min, the photoresist can be separated from the other chemicals in the tin–lead bath as shown in Fig. 4. In this case, UV detection was used. Diode array detection provides an UV spectrum of each peak, which helps to confirm its identification. It should be noted that no photoresist was detected in the tin–lead bath after plating 24 circuit boards.

To obtain this chromatogram, the sample was spiked with a solution of UV-curved photoresist in tetrahydrofuran. In addition, the plating performance was mea-

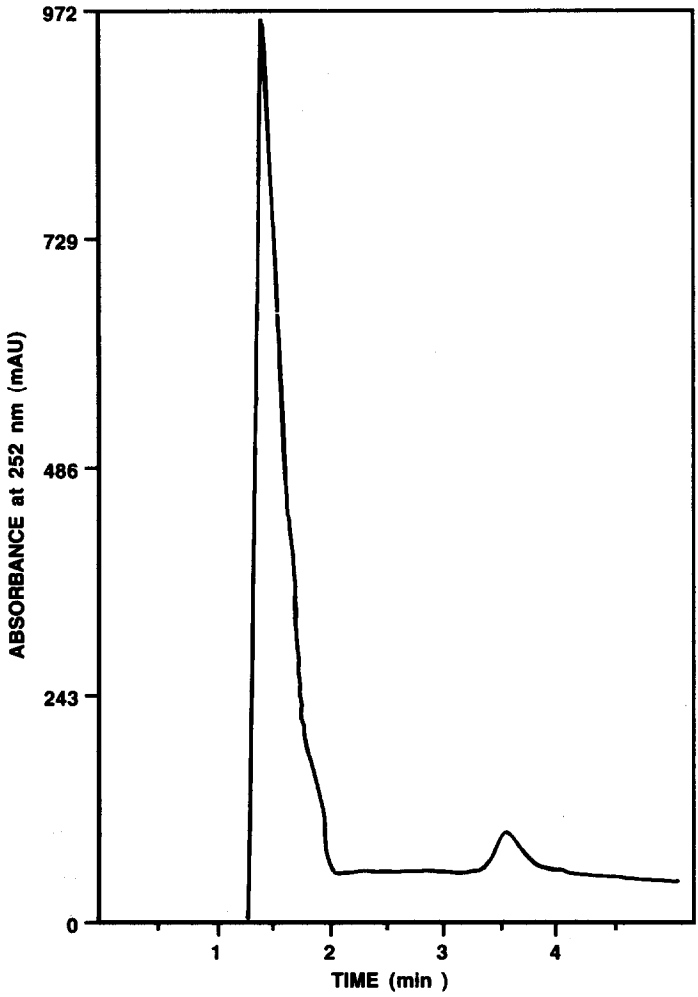

Fig. 4. Analysis of photoresist solubility in 2:5 diluted tin–lead bath. Column: MPIC 5 μm. Eluent: acetonitrile–water (9:1, v/v), 1.0 ml/min. Detection: diode array set at 252 nm. The peak at 3.5 min is due to aqueous photoresist.

sured using a Hull cell test for brightness, and it was found that baths spiked with up to 8 g/ml of photoresist still had the desired matte-gray appearance. X-Ray fluorescence of the Hull cell panel indicated an acceptable plating thickness (minimum of 300 microinches) and composition (63% Sn and 37% Pb) at current densities between 20–30 A/ft.^{2}. Thus, it was demonstrated that not only did normal production operations fail to produce measureable photoresist leaching, but that even if there was photoresist contamination in the tin–lead bath, it did not harm the product. Thus, circuit board manufacture now utilizes this aqueous photoresist.

In addition, surface active organics are added to the acid copper and tin–lead tanks to reduce the particle size of the electrodeposited metals, brightening their appearance. Quite often poly(ethylene glycols) or alkyl phenol poly(ethoxylates) of the Triton or Igepal class are used. These organic materials are non-ionic, so they cannot be detected by conductivity. Instead, a UV detector is used. Conventional reversed-phase HPLC techniques using silica-based columns cannot be used to analyze the highly acidic bath samples. Instead, an acid-resistant PS–DVB-based column is recommended. The non-ionic organics are retained on this column based on non-ionic interactions with the PS–DVB. As shown in Figs. 5–7, the MPIC column was

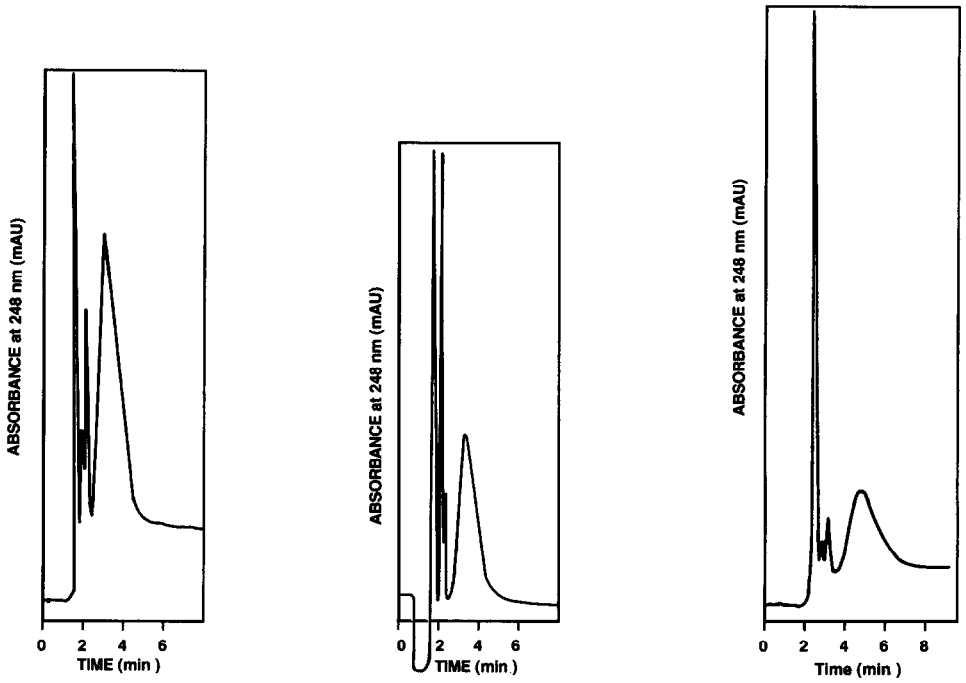

Fig. 5. MPIC of two week old tin–lead bath. Note the comparative sizes of the peaks at 1.8, 2.0 and 3.2 min. The peak at 1.8 min is a breakdown product.

Fig. 6. MPIC of three month old tin–lead bath. Note the increased size of the breakdown product's peak at 1.8 min.

Fig. 7. MPIC of three month old tin–lead bath after carbon treatment. Note the decrease in breakdown product at 1.8 min.

used to monitor the concentration of brightener in the tin–lead tank. After 2 weeks, little break-down product (the peak at 2.0 min) is seen, but after 3 months, it becomes the predominant peak. Carbon treatment removes this break-down product and some of the alkyl phenol poly(ethoxylate) detergent brightener (the peak at 3.5 min). Using MPIC, the electroplator can determine how much of the original brightener solution to add after carbon treatment. Thus, MPIC can monitor the concentration of non-ionic organics in highly corrosive plating tanks.

There is no reason to assume that all brighteners contain only non-ionic organics. Spectroscopic methods such as ^{13}C NMR can identify ethoxylates, alkyl phenols and other organics, but they cannot easily distinguish between non-ionic and ionic compounds. Ion chromatography should be the ideal method for doing this. In the past, though, anion-exchange columns would strongly retain ionic detergents.

Because the detergents were not eluted, they could poison the column. Recently, new polymeric anion-exchange (PAX) columns have become available. These columns are based on surface sulfonated poly(ethylvinylbenzene–divinylbenzene), or EVB–DVB, to which aminated latex beads are covalently attached, so they are also resistant to extremes of pH. Unlike the older anion-exchange columns, though, the covalently attached anion-exchange sites enable the use of 100% organic solvents, which would destroy an AS-4A, AS-5A and other anion separators.

In the past, when attempting to characterize a new brightener, ^{13}C NMR would identify the types of carbons present. Injection of a diluted brightener sample on an AS-4A column would identify the presence of low levels of chloride or perhaps other inorganic anions. Analysis by MPIC would show that there was an organic component that would bind with the non-ionic PS–DVB. Many anionic detergents, though, contain a large non-ionic tail and a small ionic head group. This would have little effect on the MPIC chromatogram or NMR spectrum of the detergent, but the physical properties of an anionic detergent are quite different from a non-ionic detergent.

To distinguish between them, an anion-exchange column compatible with organic solvents is needed. There are two such columns available now [10,11], a PAX-100 and PAX-500. They both contain the same quaternary ammonium anion-exchange sites present in the AS-5A column, but they are attached to latex beads which are covalently attached to the EVB–DVB core particle, making them solvent compatible. The EVB–DVB in the PAX-500 has 60 Å pores with 300 m^2/g adsorption surface area, enabling retention of analytes by the same non-ionic interactions as in MPIC. The EVB–DVB in the PAX-100 is microporous, though, so there is little such interaction with non-ionic compounds. However, anionic organic compounds can interact with the poly(vinylbenzylchloride–divinylbenzene) of the latex beads.

The PAX-500 column can be used exactly as the MPIC column for separating non-ionic compounds. One set of compounds often used to characterize a reversed-phase HPLC column is the alkylphenones. Ethano-, propano-, butano-, pentano- and hexanophenone can be separated on an octadecylsilica (ODS) column and an MPIC column using an acetonitrile–water eluent. Reversed-phase HPLC retention is often described by the equation [12]:

$$k' = k'_0 c^{-m} \tag{2}$$

where c is the concentration of organic solvent in the eluent and k' and m are con-

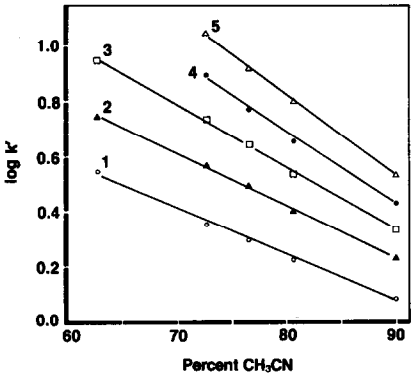

Fig. 8. Plots of log k' of different alkylphenones *vs.* percent acetonitrile in the eluent. The column was a PAX-500. Data were fit to straight lines using linear regression analysis. 1 = Ethanophenone, 2 = propanophenone, 3 = butanophenone, 4 = pentanophenone, 5 = hexanophenone.

stants. Thus, a plot of the log k' *vs.* percent acetonitrile produces a straight line for a wide variety of analytes on the ODS and PS–DVB-based columns. The PAX-500 column produces a similar straigth line, as shown in Fig. 8. However, anions are not retained on an ODS or MPIC column without an ion pair reagent in the eluent, but they are retained and separated on a PAX-100 or PAX-500. With the PAX-100, if an organic compound has a negative charge, its retention can be controlled by varying the concentration of organic solvent as described by eqn. 2.

With a PAX column, then, anionic detergents can be easily identified. One such brightener produced a ^{13}C NMR spectrum similar to most brighteners; that is, it had ethoxylate carbons, phenyl groups and some alkyls. Analysis on an AS-4A indicated low levels of chloride, nitrate, phosphate and sulfate. This provided little useful information, and most likely, the main constituent, the organic detergent, was strongly

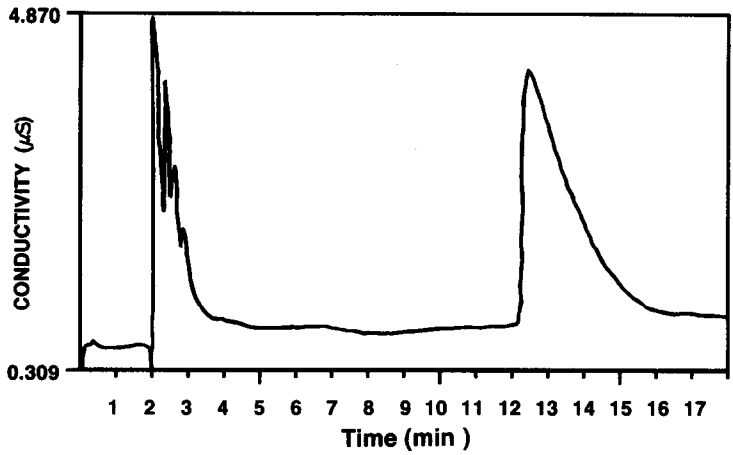

Fig. 9. Analysis of a tin–lead brightener used in pattern plating and infrared reflow. Column: PAX-100. Eluent: 77 mM NaOH in methanol–water (2:8) at 1.0 ml/min. Detection: chemically suppressed conductivity.

retained on the AS-4A. This same brightener was injected on a PAX-100 and 65% of the total peak area (chemically suppressed conductivity detection) was due to a peak eluting much later than the inorganic anions, as shown in Fig. 9. This detergent has an anionic head group, making it more water soluble and causing retention by anion exchange on the PAX-100. As is the case with other anions, increasing the concentration of sodium hydroxide in the eluent causes this detergent to elute sooner.

A cleaning solution used to prepare boards for copper plating was found to contain phosphate using an AS-4A column with 2.4 m*M* sodium bicarbonate plus 1.9 m*M* sodium carbonate eluent and chemically suppressed conductivity detection. The cleaner also contains detergents which were not eluted off the AS-4A column. Using an ODS column with 54% aq. acetonitrile eluent and diode array detection at 227 nm, one peak with a k' value of 0.9 was obtained. Using an MPIC column and acetonitrile–water (18:82, v/v) eluent, three partly resolved peaks were obtained. Using the PAX-100, though, with 0.96 *M* NaOH in 18% aq. acetonitrile as eluent, six different peaks were resolved as shown in Fig. 10. The concentration of sodium hydroxide in the eluent was lowered to 0.80 *M*, then 0.70, then 0.60 *M* and k' values for the first four peaks were measured. Plots of the log k' *vs.* log NaOH concentration produced straight lines for the peaks that appeared at 1.994, 3.715 and 6.182 min in Fig. 10. Slopes were -0.82, -0.83 and -1.73, suggesting that the peaks are due to anions with a charge of -1, -1 and -2, respectively as predicted by the equation [13]:

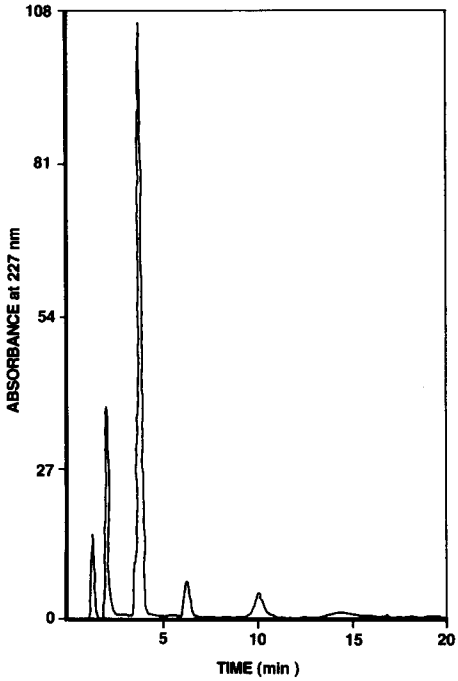

Fig. 10. Analysis of a cleaning solution. Column: PAX-100. Eluent: 0.96 *M* NaOH in acetonitrile–water (18:82) at 1.0 ml/min. Detection: diode array at 227 nm.

$$\log k' = (-Z/E)\log C + \log I$$

where E is the charge on the eluent (-1 for NaOH), I is an isocratic constant and Z is the effective charge (or Z number) of the analyte. The first peak remained in the void volume, indicating that it is due to a non-ionic compound.

Thus, the PAX columns enable two-dimensional chromatography with one column and one injection, whereas older two-dimensional techniques required columns switching or (as in thin-layer chromatography) two completely different runs. With the PAX columns, one can take advantage of retention based on non-ionic interactions by varying the concentration of organic solvent in the eluent, just as one does with reversed-phase HPLC or MPIC. At the same time, one can take advantage of retention based on anion exchange by varying the concentration of ionic (sodium hydroxide, sodium carbonate, etc.) in the eluent, and from the slope of plots of log k' *vs.* log NaOH (or other ionic eluent) one can estimate the charge on the analyte. This promises to be a powerful new tool in helping control the manufacture of high quality circuit boards.

The chromatographic methods have been partly validated. The determination of salicylic acid had an average percent error of 3.99%, obtained in a single blind experiment using seven samples. The absolute value of the percent error for each sample was divided by seven to get the average percent error. Reproducibility was evaluated in each method by injecting at least five replicate samples and calculating the percent relative standard deviation, which varied from 0.95% for salicylic acid to 5.6% for photoresist determination.

An AG-4A guard column will last for about 50 analyses before it needs to be replaced. An MPIC guard column also lasts for about 50 analyses. The AG-4A and MPIC 5 μm separator columns will last for about 200 analyses, and the PAX columns have not degraded after about 100 analyses. It should be noted that the PAX columns should always have at least 10% organic solvent on them (especially during storage), but that the AS-4A (and other AS separator columns) should never have more than 5% organic solvent, and function quite well with no organic solvent. The AS-4A and AG-4A are routinely stored in dilute aqueous sodium hydroxide.

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