Analysis of an Aqueous Photoresist

by Robert E. Smith

An aqueous-processable photoresist can be used without fear of damaging the tin-lead bath, even if there is unusually high leaching.

series 9000 computer from Hewlett-Packard (Avondale, PA). An HPLC grade acetonitrile from J.T. Baker (Philipsburg, NJ) was also used.

A column packed with polystyrene/divinylbenzene (PS/DVB) was used in the study to analyze the fluoroboric acid-based tin-lead plating solution for photoresist content. The different chemicals present in a photoresist before it is exposed to UV light can be retained on the PS/DVB for different lengths of time and produce different peaks when detected with a diode array detector. After exposure to UV light, the photoresist produces one peak, the size of which is directly proportional to the photoresist's concentration. Therefore, reverse-phase HPLC with a PS/DVB column was used to quantitate the photoresist in the tin-lead bath.

To determine the concentration of photoresist in the bath, four standards ranging in concentrations from 1.59 to 8.0 grams per liter were injected into an NG1 guard column. This column was connected to an NS1 (a column packed with PS/DVB) separator column pre-equilibrated with 90’% acetonitrile plus 10’% water, flowing at 1.0 ml per min. Channel one on the diode array detector was set at 252 nanometers (rim), and the peaks produced (eluting at 3.4 min.) were integrated. The peak areas were plotted vs. photoresist concentration,

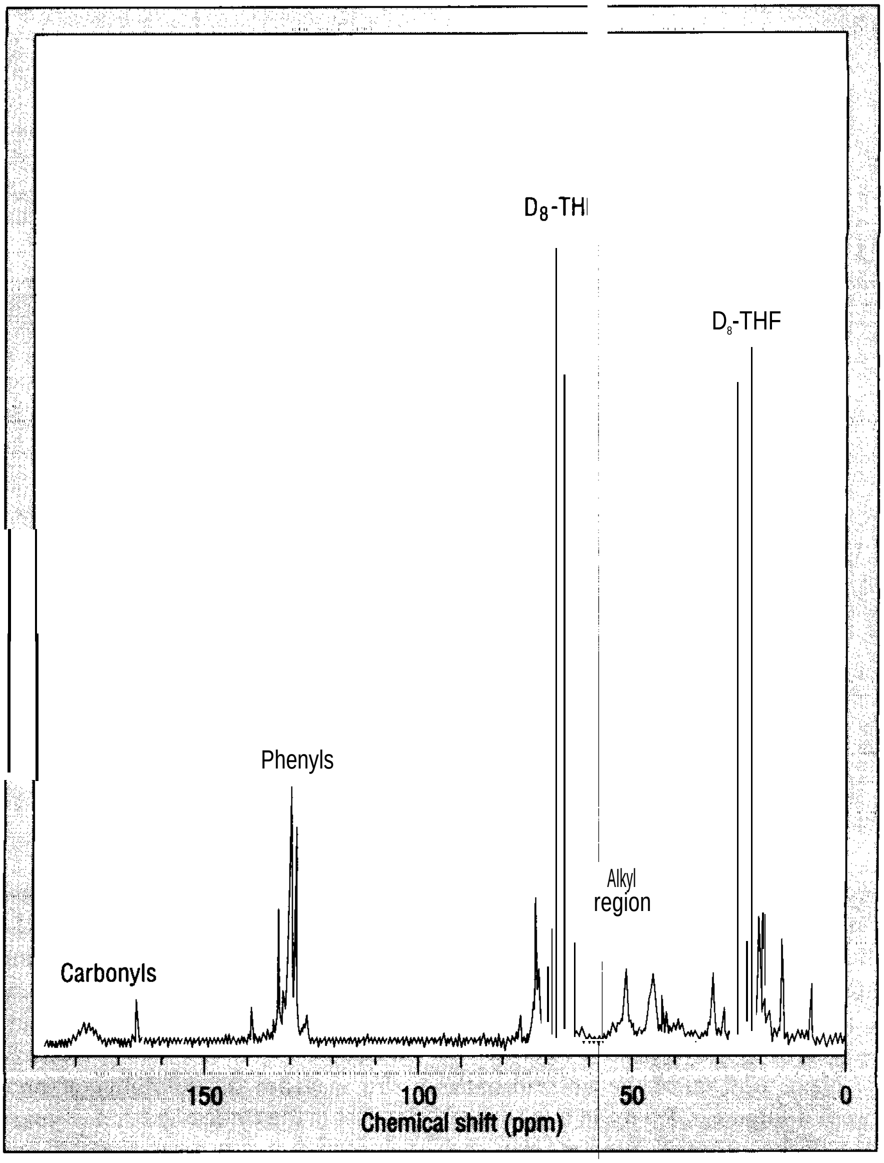


Figure 3. *Carbon-13 NMR spectrum of aqueous-processable photoresist.*

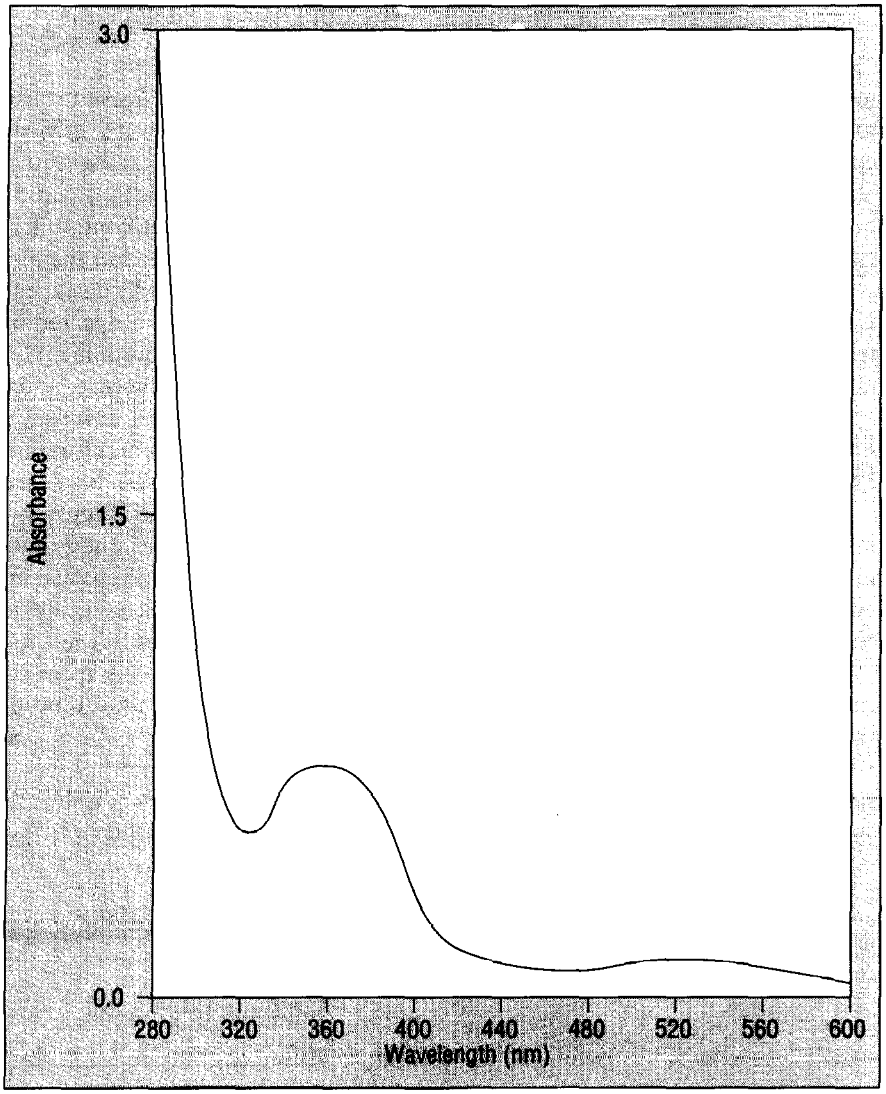


Figure 1. *UV spectrum of aqueous-processable photoresist before exposure to UV light.*

An industry-wide effort is currently underway to reduce the use of chlorinated hydrocarbon (CHC) solvents because of their hazardous effect on the environment. In the past, negative photoresists were usually processed with CHCs, but now the availability of aqueous-processable photoresists offers an alternative to CHC use.

One such product is developed in aqueous sodium carbonate, which dissolves the photoresist on the areas of a PCB that are not exposed to ultraviolet (UV) light. In exposed areas, the UV light cross-links the low-molecular-weight, water-soluble chemicals to form a higher-molecular-weight polymer that is insoluble in the sodium carbonate solution.

Although it is important to reduce the use of CHCs, it is also important to ensure the quality of PCBs produced with aqueous-processable photoresists. In this attempt, the aqueous sodium carbonate product was chemically analyzed using three methods: ultraviolet spectrophotometry, nuclear magnetic resonance (NMR) spectroscopy, and high-performance liquid chromatography (HPLC). These and other test types are defined in the sidebar "Description of Analytical Methods,"

ANALYTICAL FINDINGS

Ultraviolet spectrophotometry revealed that the negative aqueous photoresist contains the same bis azo groups found in most negative photoresists commercially available.[1] NMR spectroscopy identified an acrylate polymer an ethoxylate, and phenyl groups in the photoresist. Finally, reverse- base HPLC analysis indicated t at the photoresist contained three components before exposure to UV light , but only one after exposure.

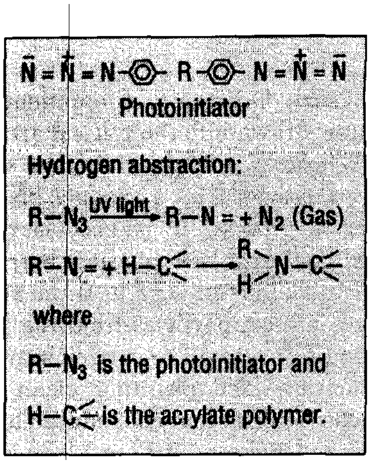


Figure 2. *The reactive nitrene formed by exposure to UV light can abstract a proton from a carbon in the p polymeric component to create a covalent bond.*

One of the processing solutions the photoresist will encounter is a tin-lead bath, which deposits a tin-lead alloy as an et h resist on the copper circuitry. Photoresist can leach into this bath, but the amount of damage, if any, it could do to the quality of the electrodeposit was undetermined.

To test how aqueous photoresist leaching would affect a tin-lead bath, 12 square feet of photoresist were shredded and put into a three-liter tin-lead solution. After agitation, a sample 'of the bath was taken for HPLC analysis to determine how much photoresist had dissolved. In addition , the appearance of the electrodeposit was evaluated with a Hull cell test. Then, the alloy composition and thickness on the Hull cell panel were measured using X-ray fluorescence. he HPLC and Hull cell analyses were repeated during the next several days.

THE EXPERIMENT

The equipment used in this experiment included a model 4000 liquid chromatograph from Dionex (Sunnyvale, C), equipped with a model 1040A diode array detector and a

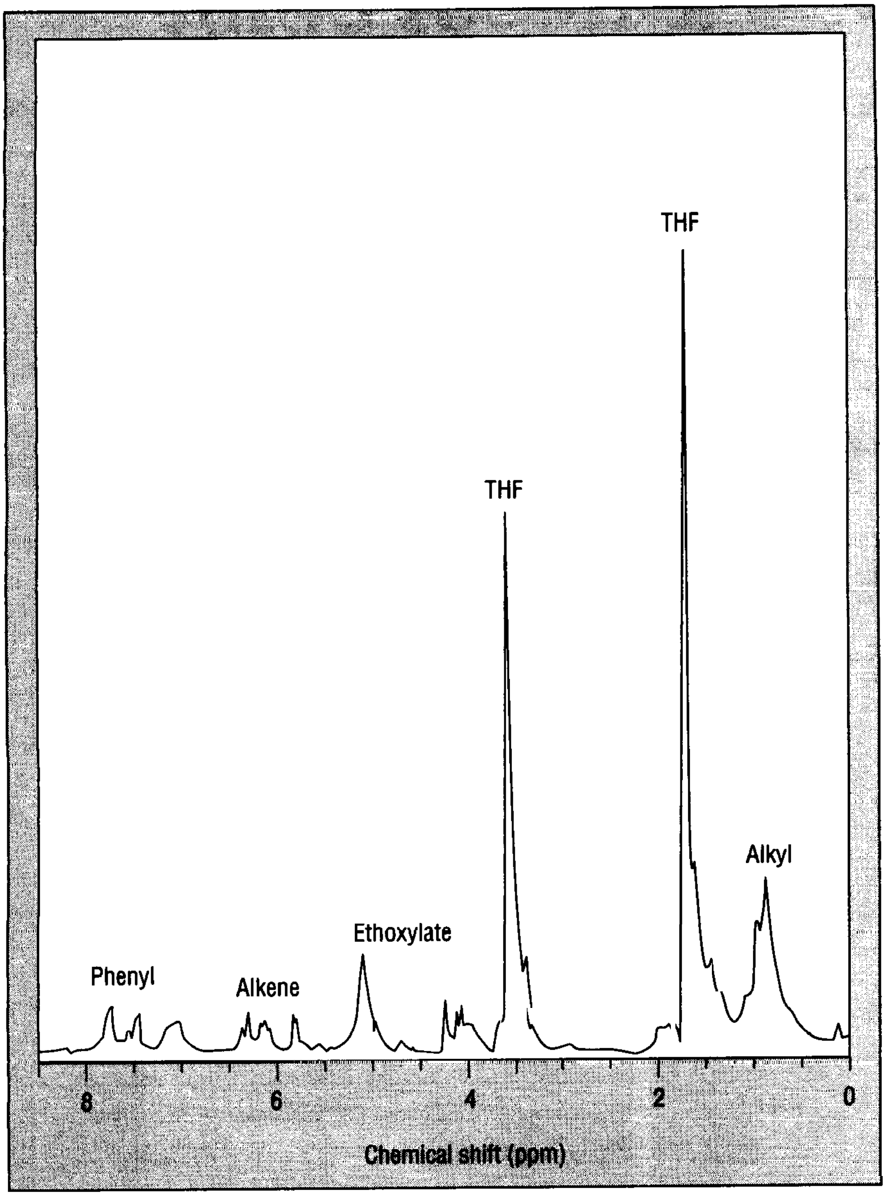


Figure 4. *Proton NMR spectrum of aqueous-processable photoresist.*

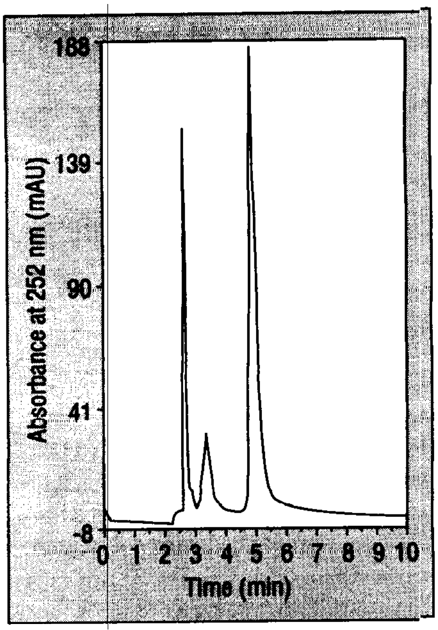


Figure 5. HPLC *of aqueous-processable photoresist before exposure to UV light.*

and the data were fit to a straight line using least squares analysis. The standards were prepared by diluting aliquots of a 159-grams-per-liter stock solution of exposed photoresist dissolved in tetrahydrofuran (THF).

Next, 10.0 ml of the tin-lead bath were diluted to 25.0 ml in a volumetric flask and then injected into the same NG1 plus NS1 columns. The area of the peak at 3.4 min. was measured and substituted into the straight line equation, obtained using the standards, to determine the concentration of photoresist in the diluted bath.

To measure the volubility of photoresist in the tin-lead bath, 12 square feet of photoresist were shredded and stirred into three liters of a used bath, which had plated 24 12“ X 12“ PCBs. After the undissolved photoresist settled out, an aliquot was taken for analysis. After sitting for three days, the bath sample was agitated thoroughly and another aliquot was taken for analysis once the undissolved photoresist settled out. This procedure was repeated each day for five days. The HPLC analysis procedure was then performed.

A GN300 spectrometer from General Electric (Fremont, CA) procured NMR spectra. **A** 90° pulse width, an eight-second pulse dela y, and 32 transients were obtained for proton spectra of photoresist dissolved in deuterated THF(d_8 — THF). A 300 pulse width, a 0.5-second pulse delay, and 4,000 transients were obtained for the carbon-..3 spectrum of photoresist in d_8–THF.

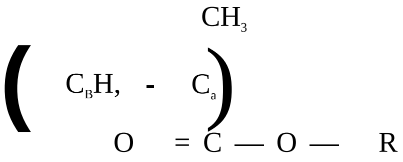
UV-visible spectra were recorded using a model 320 spectrophotometer from Perkin-Elmer (Overland Park, KS) with 0. l-nm resolution and photometric accuracy of 0.001 ‘%. Quartz cuvettes with a 1-cm path length were used.

RESULTS AND DISCUSSION

The Uv-visible spectrum of the photoresist before exposure to light is shown in Figure 1. Negative photoresists typically contain a bis azide compound that acts as a photoinitiator and exhibits the characteristic peak at 360 nm. Ultraviolet light causes a reactive nitrene to form, which can abstract a proton from a carbon in the polymeric component to create a covalent bond (Figure 2).

In previous negative photoresists, the polymeric component was usually a polyisoprene that was soluble in the chlorinated solvents used in developing the resist.

Carbon-13 NMR analysis of the aqueous processable photoresist revealed the presence of alkyl, phenyl, and carbonyl carbons (Figure 3). The small, broad peaks from 45.3 to 46.5 ppm and 51.6 to 55.0 ppm are due to Ca and C_BH_2 carbons of polymethacrylate, for example:



$$\left(\mathrm{C_BH,}\ -\ \overset{\mathrm{CH_3}}{\mathrm{C_a}} \right)$$
$$\mathrm{O = C — O — R}$$

where the carbonyl carbon produces the peak from 175.5 to 180.0 ppm and the a-methyl carbon produces a peak at 20 ppm. In addition, the peaks near 73 ppm are due to ethoxylate carbons, for example, $–CH_2–\ CH_2–\ O–$.

The ethoxylate carbons and the polymethacrylate are soluble in aqueous sodium carbonate. In addition, there are sharp peaks at 19.7, 20.1, 31.3,31.6,64.0, and 64.3 ppm, which arc due to butyl and other alkyl groups corresponding to the – R in the polymethacrylate structure being shown.

The chemical composition of the photoresist is further elaborated by the proton NMR spectrum (Figure 4). The peaks at 1.7 and 3.6 ppm are due to the THF solvent. The peaks from O ‘.0 2 ppm are due to the $CH_3–CH_2–CH_2$ protons from butyl and the B—CH$_2$— of the acrylate. The peaks from 3.9 to 4.2 ppm are due to ethoxylate protons. The peak at 5.1 ppm is due to an acrylate – CH$_a$–; thus, there are acrylates that do not have an attached methyl group. The peaks from 5.8 to 6.4 ppm are due to – CH = groups, and the peaks from 7.1 to 7.8 ppm are due to phenyl protons.

Table 1. Photoresist Content of Tin-Lead Bath.

Date	**Photoresist (g/l)**
September 29	0.0
October 2	3.3
October 3	4.7
October 4	5.6
October 5	7.1
October 6	8.9

To summarize, the photoresist contains a bis azide, polyacrylates, and alkyl phenol ethoxylate groups. Before exposure to light, these materials are present in at least three components that are separable by reverse-phase HPLC on the PS/DVB-based NS1 column (Figure 5). The absorbance at 252 nm, due to phenyl groups, was monitored in the chromatogram. After exposure to light, only one peak is seen (Figure 6), indicating that the three components have been cross-linked.

Using the same chromatographic conditions, the tin-lead bath (diluted from 10 to 25 ml) showed no interfering peaks (Figure 7). After adding photoresist, however, the peak at 3.6 min. appears (Figure 8). The relative standard deviation from five replicate injections of this bath sample was 4.63%. No photoresist was detected immediately after adding shredded resist (Table 1). But after sitting for three days, 3.3 grams per liter of photoresist were detected. During the following days, more photoresist dissolved until 8.9 grams per liter were found.

Hull cell analysis of the electrodeposit showed the desired matte grey appearance. In addition, X-ray fluorescence showed that the thickness of the electrodeposit was greater than the required minimum of 300 microinches and the composition was within 2% of the 6390 tin and 37% lead requirement for the desired infrared reflow process.

CONCLUSION

Ultraviolet-visible and NMR spectra were useful when analyzing the chemical composition of the aqueous-processable photoresist. The UV-visible peak at 360 nm identified the photoresist as a bis azide material, and the NMR spectra signaled the presence of polymethacrylate, alkyl phenol ethoxylate, and alkene groups.

The reverse-phase HPLC process, using a PS/DVB-based column and UV detection, quantified the amount of photoresist in the fluoroboric acid-based tin-lead bath. Hull cell and X-ray fluorescence analysis showed that the presence of unusually high levels of the aqueous photoresist studied (8.9 grams per liter) did not adversely affect the quality of the electrodeposit.

Therefore, it is possible to produce quality PCBs while minimizing the use of hazardous CHC solvents. ■

DESCRIPTION OF ANALYTICAL METHODS

Hull Cell. Hull cells are used throughout the PCB industry to help evaluate the quality of an electrodeposit, which can be markedly affected by the presence of organic contaminants. In this study, a 2.5- X 4.5-in. brass panel was placed into a 260-ml Lucite Hull cell containing a sample of the bath being evaluated. The current density varies from 2 to 80 amps per square foot (A/sq. ft.) along the brass panel.

When evaluating a tin-lead deposit, a matte grey color is desired. The appearance of any burning or a shiny silver color in the 15 to 50 A/sq. ft. region would indicate that the electrodeposit is unsatisfactory. The tin-lead deposit must have a minimum thickness of 300 microinches and an alloy composition of 63% tin and 37% lead.

Ultraviolet-Visible Spectrophotometry. This technique measures the absorbance of UV and visible light by a chemical dissolved in a suitable solvent. The wavelength of light is decreased from 850 to 195 nm. A photometer compares the amount of light transmitted at each wavelength that passes simultaneously through a reference cuvette containing only solvent and another cuvette containing the dissolved sample. A plot of the amount of light absorbed vs. wavelength is obtained when the microprocessor on the spectrophotometer converts the percent of light transmitted to the amount of light absorbed. This conversion is described by $Abs = log (T_0/T)$, where Abs is the absorbance, T_0 is the amount of light transmitted through the reference cuvette, and T is the amount of light transmitted through the sample. The exact wavelengths of light absorbed depend on the chemical structure of the sample. The amount of light absorbed is directly proportional to the concentration of absorbing molecules, as described by the Beer-Lambert law $Abs = abc$, where a is the molar absorptivity of the molecule, b is the path length of the cuvette (1 cm in this study), and c is the concentration of the absorbing molecule in molecules per liter. The UV-visible spectrum indicates the type of molecules present (by looking at the exact wavelengths at which maximum absorbance occurs) and their relative amounts.

Nuclear Magnetic Resonance (NMR) Spectroscopy. When an organic compound or polymer is placed in a strong magnetic field, the ^{13}C and ^{1}H nuclei process about the magnetic field at a frequency dependent on the chemical environment of the nucleus. The chemical environment depends on the structure of the molecule. With a magnetic field strength of 7.1 Tesla, ^{13}C nuclei absorb radio frequencies around 78.5MHz and ^{1}H nuclei absorb in the region of 300MHz.

Unlike UV-visible spectra, which produce broad peaks and can provide only a general description of the structure of a molecule, NMR spectra, especially ^{13}C spectra, produce sharp peaks, providing significant detail about the structure of the molecule. The relative intensity of radio frequencies absorbed by each nucleus depends on the amount of that kind of nucleus present in the sample. Thus, the relative abundance of each type of atom in the molecule can be estimated.

Reverse-Phase High-Performance Liquid Chromatography (HPLC). HPLC is a technique in which a sample is dissolved in a suitable solvent and injected on a column packed with a solid material that selectively absorbs the sample for a limited period of time. The sample is eventually washed off the column (eluted) with a solution called the mobile phase and detected using a UV-visible spectrophotometric detector. A diode array detector consists of hundreds of photodiodes, each sensitive to different wavelengths. A computer interface monitors the spectral region from 190 to 400 nm and stores the data.

Originally, the column was packed with a relatively polar substance, such as silica or alumina, and a relatively nonpolar mobile phase, such as hexane or chloroform, was used. This technique was called normal-phase HPLC. Today, it is much more common to use a column packed with a relatively nonpolar material such as polystyrene/divinylbenzene (PS/DVB) or octadecylsilica (ODS). The mobile phase is relatively polar, usually containing water. This technique is called reverse-phase HPLC. Columns packed with ODS are extremely popular, but ODS is not stable at extremes of pH. A strong acid or base will dissolve the silica in the ODS. A column packed with PS/DVB, called the NSI or MPIC, is stable to acids and bases and has been used to analyze corrosive processing solutions.[2] ■

REFERENCES

[1] Stein, A. ***The Chemistry and Technology of Negative Photoresists,*** Palisades Park, NJ: Philip A. Hunt Chemical Corp., 1978.

[2] Annable, P.L. and R.E. Smith. ***Plating and Surface Finishing,*** Vol. 73, 1986, pp. 126-129.

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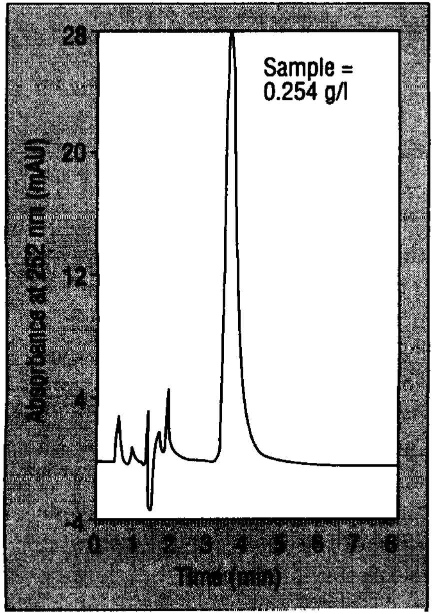

Figure 6. *HPLC of aqueous-processable photoresist after exposure to UV light.*

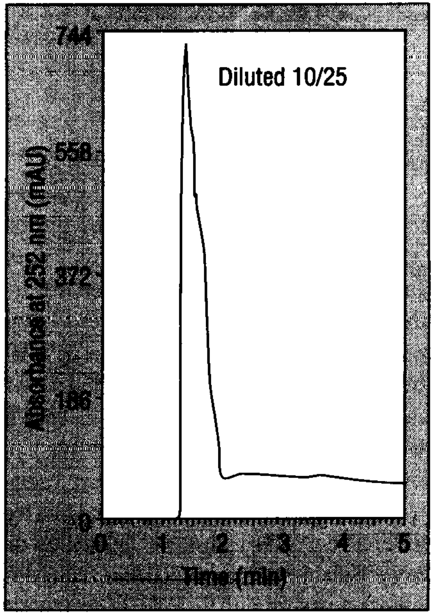

Figure 7. *HPLC offresh tin-lead bath.*

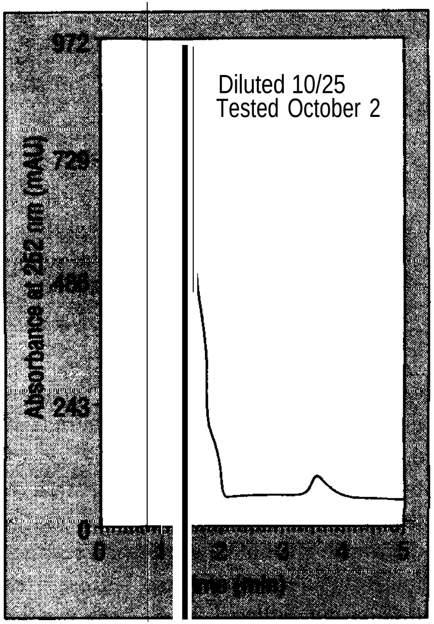

Figure 8. *HPLC of tin-lead bath after the aqueous-processable photoresist has*