

Autopsy of an Acid Copper Plating Bath: Dangers of Recycling

by Jim Economus and Ron Barauskas of EMS Analytical Labs

Being an independent laboratory, we do quite a bit of periodic monitoring for our customers. It is usually routine and the variation we observe is as expected. Occasionally though, we catch an anomaly that gets alarm bells ringing and calls for further investigation. The story that follows is one such instance.

We perform acid copper plating bath analysis, TOC analysis, and tensile strength and elongation testing for a particular customer on a regular schedule. TOC is an acronym for total organic carbon and the analysis is good way to monitor the build-up of organics in a plating solution. When a maximum amount is reached the plating solution can then be carbon treated or replaced. In this particular case, the TOC levels in the customer's plating baths had risen slowly over a long period of time as expected, but then suddenly increased more dramatically. The customer determined that they would carbon treat each of three baths, one at a time. The first tank was treated and a sample was taken for TOC analysis. The sample which had a TOC concentration of 2681 ppm before treatment now tested at 2362 ppm. The maximum recommended concentration for this particular bath is 2500 ppm.

For reference, a bath matrix, consisting of copper sulfate, sulfuric acid and a very small amount of hydrochloric acid typically has a TOC value of less than 10 ppm. A properly carbon treated bath should be less than 100 ppm after carbon and 500 to 800 ppm after adding back the organic additives. After double-checking the result, the customer was contacted and, needless to say, he was upset. We reviewed the carbon-treatment procedure with the customer and the service that had performed the procedure and found that everything had been executed properly.

We decided to try carbon treating the remaining sample in our laboratory. This consisted of adding 0.5% v/v of organically stabilized 50% hydrogen peroxide, allowing it to mix for 1 hour at room temperature; heating the bath to 140°F to drive off the excess peroxide; adding 8 lbs/100 gal (10 g/l) of Darco G-60 powdered carbon and allowing it to mix hot for 3 hours; filtering out the carbon; cooling it down to room temperature and finally adding DI to restore the original volume. We were very surprised to see that the TOC level had only dropped to 1839 ppm. We then treated the same sample with more aggressive treatments of potassium permanganate, peroxide, and carbon followed by a third treatment using bleach and carbon. There was no further significant decrease in the TOC concentration, so then we knew that nothing had gone wrong at the customer's site, but that we had a chemically stable organic in the plating bath.

Acid copper plating baths can run at these elevated levels of TOC without experiencing detrimental effects to the copper deposit, but that was not the case here. We had foils plated for tensile strength and elongation testing at this time and saw a significant drop in the copper elongation after the TOC levels had risen. Previously, the customer was

obtaining elongations in the 25 – 28% range, but now they dropped to approximately 16%. While these numbers pass acceptance criteria, they were much lower than what is expected from this particular plating process. The customer decided to replace the baths but wanted to identify the organic contaminant in order to prevent this from occurring in the future.

We visited the customer to perform an audit and to discuss possible sources of this type of contamination. There are very few organic additives, mainly wetting agents, which survive in extremely oxidizing environments. Process chemistries that would use them include permanganate desmear, anti-foams, alternative oxide, and hole prep solutions. When the vendors of those chemistries were identified, they were contacted and asked to provide information on the types of organics that were used in those processes that fit the above description. This resulted in these possibilities: p-toluene sulfonic acid, phosphate ester, and silicone antifoam emulsion. Samples of the suspect bath components were provided. The treated acid copper bath was sent to another laboratory for FTIR (Fourier Transform Infrared) analysis of the residue remaining after methylene chloride extraction and evaporation of the solvent. The result was consistent with an ethoxylated surfactant (Figure 1) – match #1, Index 783. This eliminated the silicone emulsion and the p-toluene sulfonic acid but left the phosphate ester as a possibility.

To match the phosphate ester, NMR (nuclear magnetic resonance) analysis was suggested. The results of that analysis eliminated the phosphate ester but provided a fingerprint for a poloxamer (Figure 2) that came from the sample. This is a family of non-ionic block copolymer surfactants that have high molecular weights. BASF manufactures a series of these compounds under the Pluronic[®] trade name. This information allowed us to identify one of the alternative oxide wetting agents as the closest match (Figure 3).

The NMR analysis served to make sense of what had occurred. The TOC data proved to be real, since an organic species was identified that survived peroxide, permanganate, and carbon treatment. Nonionic copolymers would not be removed by a system design to remove ions. The compound was not amenable to carbon. Therefore, this material was slowly increasing in concentration in the acid copper baths or was introduced by accidental addition. But where did it come from?

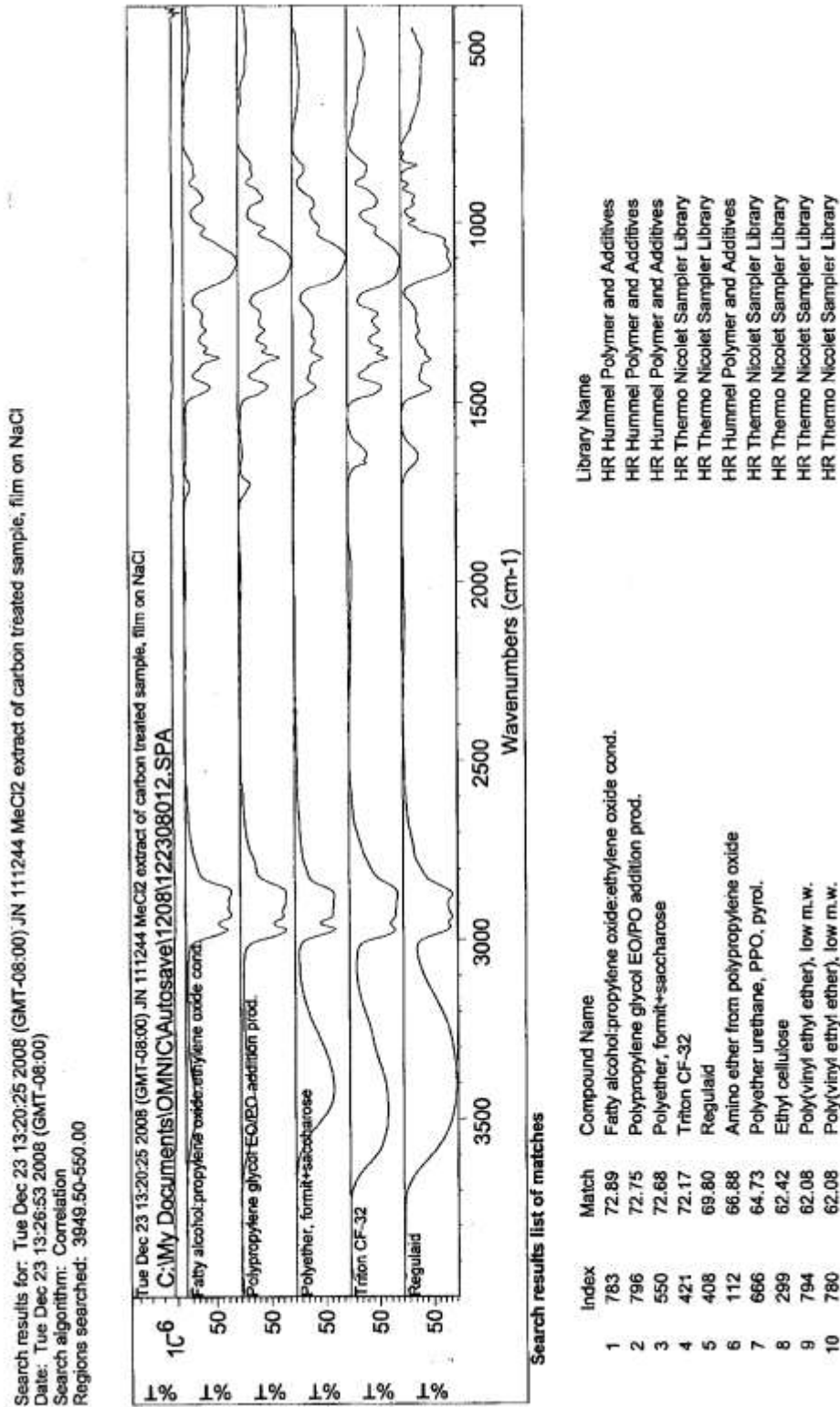
It was revealed during this period of time that the customer had installed a water recycling system just a few months prior to the development of this problem. In setting up this system, they had included rinses following solutions containing surfactants. This is not recommended. Paul Petruna of Sirco, who installs water treatment systems, discourages the use of recycled water for making up or replenishing plating baths for the following reasons. Weakly cationic resins do not effectively remove all cations, and definitely will not remove non-ionic compounds. And although it would not have helped in this case, he recommends using ozonation following deionizing columns or reverse osmosis units for treating recycled water. RO water cannot be used for the acid copper bath make-up because of the high chloride levels and algae formation also becomes an issue.

The customer installed fresh D.I. water lines to replenish the plating tanks and all three of the acid copper baths were replaced. The TOC levels are back to normal and they have no plating issues at this time. Several months later the same customer was having a skip plating issue on the electroless nickel line which was also traced back to the recycled water.

Conclusion: We strongly suggest performing carbon treatment of acid copper baths on small (1 liter) samples in the laboratory to evaluate the standard treatment's effectiveness before having it performed on a production scale. Periodic TOC analysis can be performed to determine carbon treatment schedules. This can save considerable time, money, and aggravation as opposed to schedules based only on time or amp-hours/gallon. TOC analysis is an excellent tool for monitoring of organic build-up in acid copper and other types of plating baths. When viewed with the physical testing data from the plated foils it becomes an invaluable tool. Recycling water is a necessity in today's manufacturing environment but it needs to be set-up correctly and used only in processes where it does not create detrimental effects. Apparently, not all of these scenarios are yet clear.

We would like to give a special thank you to Tim Kramer who performed most of the bench work on this project.

FIGURE 1



Extract of Carbon Treated Sample in CDCl3
 JN 111504 EMS Analytical Labs
 Standard 1D 1H experiment (zg30)
 Ambient temperature (~298K)
 01-08-09 DJN

BRUKER
 111504 Extract of Carbon Treated

```

NAME          JN111504
PROCNO        1
INSTRUM       spect
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
DE            1
DS            4
SWH           10330.978 MHz
F2          0.147612 MHz
AQ           3.3719323 sec
RG           128
IN           48.430 uMWC
DE           4.30 uMWC
TE           297.9 K
SI           1.6000000 sec
TO           1
===== CHANNEL f1 =====
NUC1          1H
P1           12.00 usec
PL1          -0.00 dB
PC1          12.00184655 W
SFO1         500.1300120 MHz
SI           65536
SF           500.1300120 MHz
SSB          0
LB           0.00 Hz
GB           0
PC           1.00
  
```

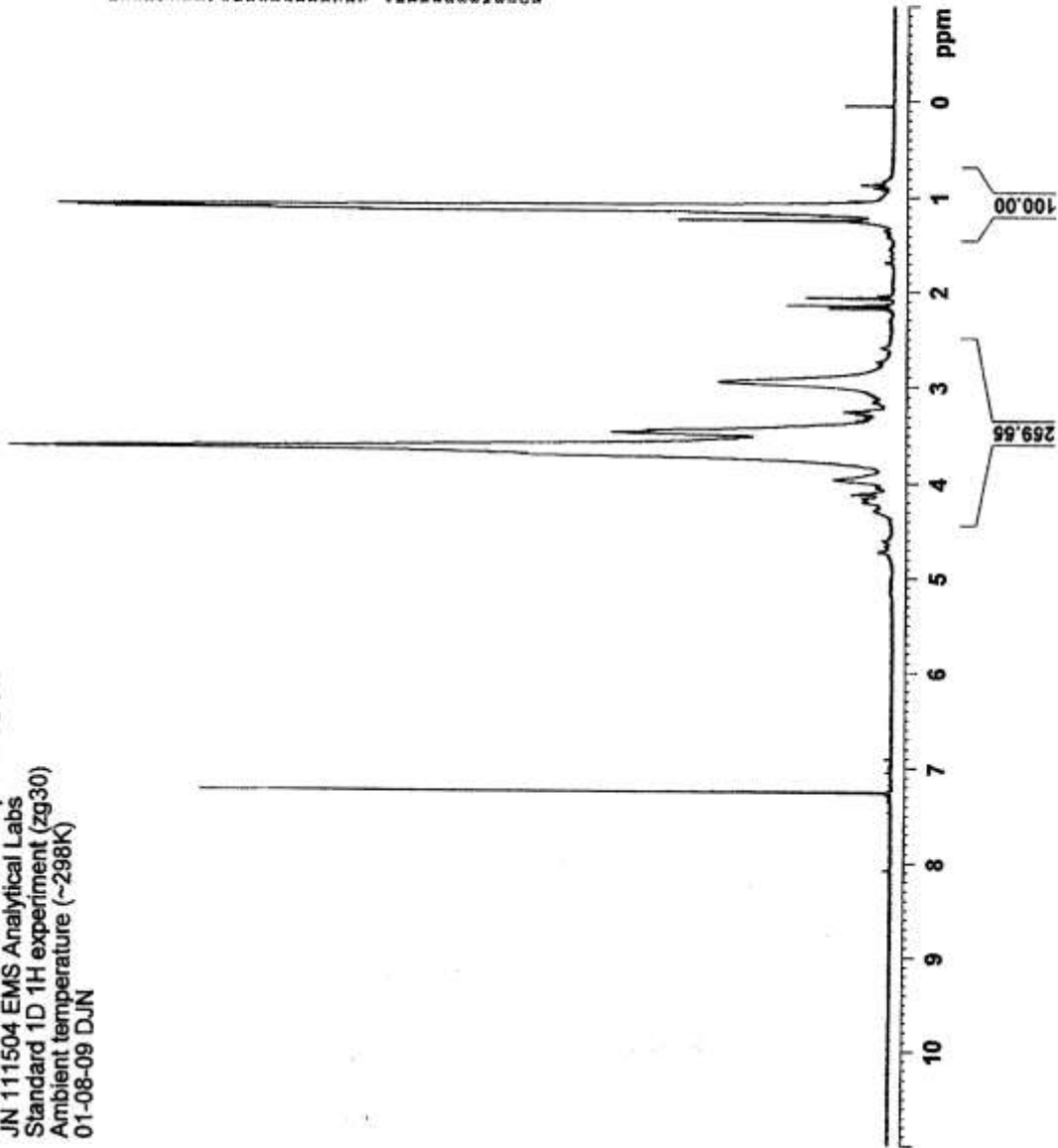


FIGURE 2



USP Poloxamer Solid RS Lot# F0G283
(83 mg in 1 mL CDC13, drop D2O, 3 uL TMS)
Standard 1D 1H experiment (zg30)
Ambient temperature, Spinning
01-12-09 HVH

```
NAME 111484 DSP Poloxamer Solid 1
EXPNO 1
PROCNO 1
Date_ 20090112
Time 10.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 4
SMH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.171923 sec
RG 20.2
DW 48.400 usec
DE 6.50 usec
TE 296.4 K
D1 1.0000000 sec
TD0 1
***** CHANNEL f1 *****
NUC1 1H
P1 15.00 usec
PL1 -0.56 dB
PL1W 12.00188065 W
SFO1 500.130888 MHz
SI 65536
SF 500.1300133 MHz
WDW DO
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
```

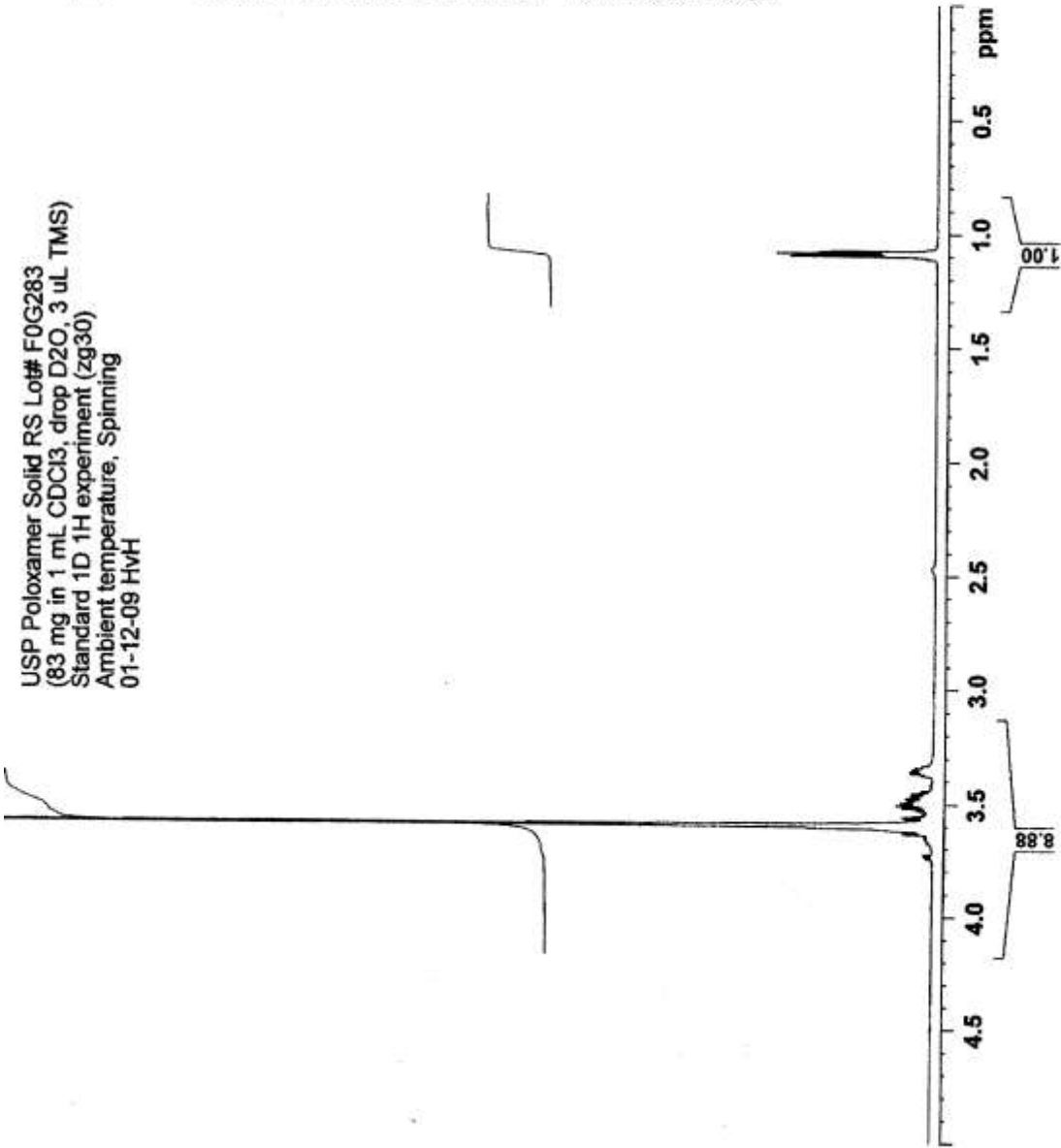


FIGURE 3