No More Activated Carbon Treatments Required

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Kuntz Electroplating Inc., a large OEM 'job shop' located in Kitchener, Ontario, was faced with a unique situation. The configurations of their customers' products required extensive use of inert auxiliary anodes in order to meet OEM quality standards. The extent of use resulted in a significantly higher amount of organic breakdown products occurring as a result of numerous electrochemical reactions within the electroplating cell and at the auxiliary anode. These organic breakdown products remain within the operating bath and have the potential to alter the structure and physical properties of the deposit. These organics are controlled by regular and frequent activated carbon maintenance which is very costly due to issues such as downtime requirement, degree of solid and liquid waste generated, loss and replenishment of organic constituents, inefficiencies in established treatment method, employee contact with activated carbon, etc. As a result, Kuntz began investigating alternative methods for control and purification of nickel baths.

The company had for years used a combination of hydrogen peroxide and activated carbon powder to undertake batch treatments of their nickel plating solutions during scheduled maintenance periods. In certain cases, a more aggressive treatment had to be used whereby the hydrogen peroxide was replaced with potassium permanganate. The success of the hydrogen peroxide and permanganate chemicals is based on their oxidative potentials in addition to the adsorptive ability of the activated carbon powder. A comparison of the oxidative potentials of other oxidants indicates that other oxidants, such as fluorine, hydroxyl radicals and ozone have high oxidizing potentials (Figure 1). Of these three oxidants, hydroxyl radicals are relatively simple to produce. The use of hydroxyl radical principals for organic compound destruction in aqueous environments is known as 'Advanced Oxidation Technologies' or AOT. Currently, there are a number of proven methods for generating these hydroxyl radicals in solutions.

Reactive Species	Relative Oxidation Power
Fluorine	2.23
Hydroxyl Radical	2.06
Atomic Oxygen	1.78
Hydrogen Peroxide	1.31
Perhydroxyl Radical	1.25
Permanganate	1.24
Chlorine Dioxide	1.15
Chlorine	1.00
Bromine	0.80
Iodine	0.54

Figure 1: Oxidative potentials, in volts

As with most oxidants, the hydroxyl radical is indiscriminate in nature and will ultimately oxidize all organic constituents within the electroplating solution. The organic brighteners, carriers and surfactants along with their breakdown products, as a result of electrolysis, will as a result of the interaction of the hydroxyl radical be oxidized through various intermediates and if given sufficient reaction time, will ultimately be converted to carbon dioxide.

These individual organic compounds can be measured within the treatment process using analytical methods such as HPLC however, due to oxidation reactions these compounds are difficult to quantify and track. An alternative method to monitoring the process is by measuring the Total Organic Carbon content or TOC. This analytical procedure was used and provided the following results (Figure 2).

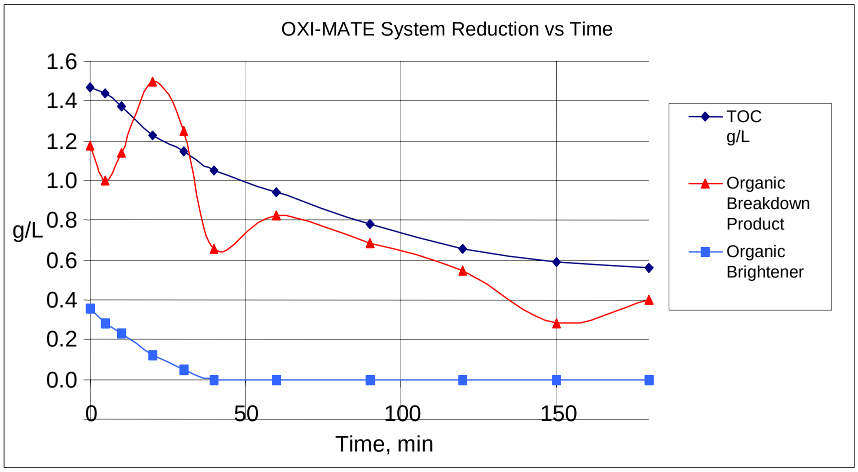

Figure 2. Reduction of organics using catalyzed hydrogen peroxide system.

Initial observations indicated that the catalyzed hydrogen peroxide system, removed the organic constituents as well as the conventional hydrogen peroxide/activated carbon system. However, the major improvement lay in the ability of the catalyzed hydrogen peroxide system to remove substantially more of the unwanted and detrimental organic breakdown products. Based on the TOC levels of semi-bright plating solutions which were about to be treated, due to ductility and internal stress concerns, it was determined that reduction of TOC was economical to TOC levels of 0.3 – 0.5 g/l. Organic constituents concentrations during the treatment period were monitored by conventional testing methods such as UV Spectrophotometer and HPLC. The hydrogen peroxide concentrations were monitored and maintained using a simple wet titration method. Hull Cell testing was used to evaluate completed process solution.

As a result of the efficiency of removal of TOC using the catalyzed hydrogen peroxide system, it was determined that compared to the regular weekly volume of solution requiring hydrogen peroxide/activated carbon treatment, a smaller faction of the original plating bath solution would actually require treatment using this new process.

A long term trial was developed which yielded very positive results. TOC levels gradually were lowered to level around 1 g/l and maintained at this level. Hull cells were done on the treated semi-bright nickel solution and the resulting foils tested for ductility, sulphur content and tensile strength. All parameters were within acceptable limits. The results indicated that the catalyzed hydrogen peroxide system continued to be effective in maintaining and controlling all physical deposit characteristics in a plating process which required high amount of inert auxiliary anode use.

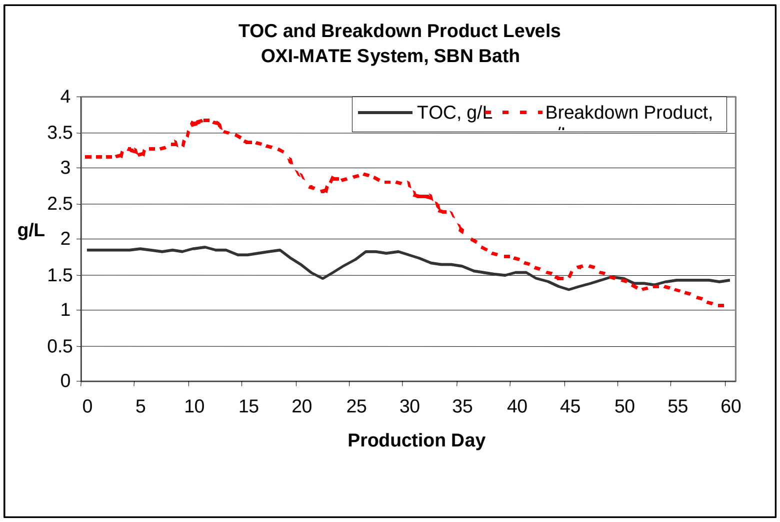

Figure 3; In process testing results

The observed advantages using the catalyzed hydrogen peroxide system in comparison to the conventional hydrogen peroxide/activated carbon treatment method were:

- ✓ Overall lower TOC values within bath
- ✓ Less replacement chemistries required
- ✓ No solid waste handling required
- ✓ Reduction of nickel plating solution losses due to adsorptive nature of carbon
- ✓ Reduction of human exposure to potentially toxic materials
- ✓ Safe controlled storage and dispensing of hydrogen peroxide
- ✓ Reduction in volume requiring treatment on regular basis
- ✓ Continuous bath treatment possible
- ✓ Significantly shorter treatment time required
- ✓ Easy method for monitoring and controlling treatment process
- ✓ Affective organic control allows for greater flexibility for recycling drag-out rinse waters back to process tanks
- ✓ Lower overall treatment cost
- ✓ Effective on organic containing nickel and copper based electroplating solutions

The treatment process continues to be used on a regular basis yielding cost savings and assuring increased process stability. The research and development of this process by Kuntz Electroplating Inc has also resulted in a U.S. patent for this treatment process, known as Oximate. (‘Method and Apparatus for Treating an Aqueous Electroplating Bath Solution’ U.S. Patent N. 6,884,332)