

## Treatment and Control of Nickel Electroplating Baths Using Catalyzed Hydrogen Peroxide

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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.

Most Watts electrolyte solutions are a mixture of nickel salts and depending on their direct application, a group of specifically formulated organic constituents, used to modify the crystalline electroplated structure. At Kuntz (KEI) the nature of our challenge indicated that focusing on the ‘coumarin’ based semi-bright nickel solution would be the most advantageous. The bath make-up is as follows (Table 1);

Contents		Optimum Ranges	Units
pH		3.7 to 4.0	
Nickel Sulphate	NiSO <sub>4</sub> .6H <sub>2</sub> O	150 to 450	g/L
Nickel Chloride	NiCl <sub>2</sub> .6H <sub>2</sub> O	37.5 to 150	g/L
Boric Acid	H <sub>3</sub> BO <sub>3</sub>	37.5 to 60	g/L
Coumarin	C <sub>9</sub> H <sub>6</sub> O <sub>2</sub>	0.15 to 0.3	g/L
Organic Surfactants		0.045 to 0.055	g/L

Table 1: Typical semi-bright electrolyte make-up

These particular semi-bright solutions contain organic constituents that are non-sulfur bearing. A view of the organic structure (Figure 1 ) indicates that coumarin is an aromatic compound, without the presence of sulfur.

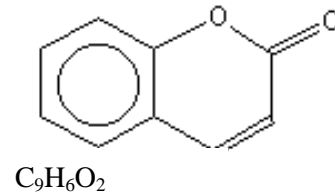


Figure 1. Chemical structure of coumarin.

These semi-bright process tanks as well as most other nickel plating baths contains wetting agents or surfactants, which are normally long straight chained organic compounds. The deposit from a semi-bright plating tank yields a semi-dull high leveling and ductile deposit (Figure 2. ). This deposit is an essential component in a multilayer nickel deposit. It is followed by a thin layer of ‘high sulfur’ bearing nickel, a layer of sulfur containing ‘bright’ nickel and finally with a thin layer of ‘particle’ nickel prior to hexchrome plating. This system of nickel layering is the preferred sequence in order to maximize the corrosion resistance of automotive bright products. All nickel plating processes used are proprietary processes.

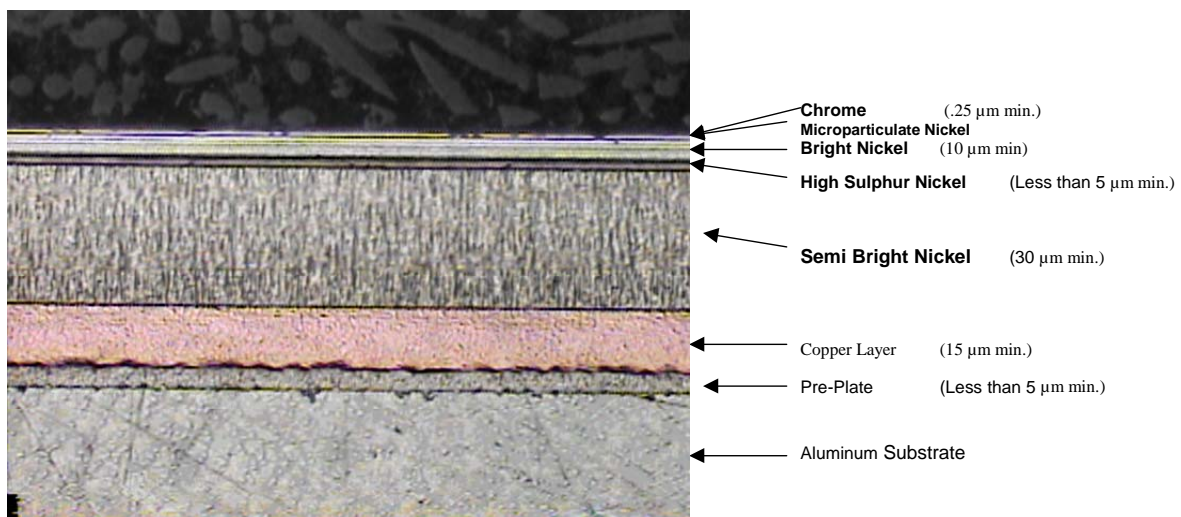


Figure 2: Cross-sectional view of typical multi-layer system

As the semi-bright nickel process is a ‘sulfur-free’ system, it is essential to maintain a comprehensive testing protocol to ensure that the physical characteristics of the deposit are maintained. Main areas of concern would be ductility, tensile strength and sulfur content. These are normally measured by plating a semi-bright nickel foil and bending it using the measurement ductility =  $T/2R$  and by plating a strip on a spiral contractometer. Sulfur levels are measured by burning a semi-bright plated foil in a specially designed furnace. When fluctuations occur in these parameters the regular course of action would be to expose the semi-bright plating solution to a continuous activated carbon pack or undertake a batch treatment in the next scheduled downtime period. Solution treatment using activated carbon alone or in combination with hydrogen peroxide has been the

mainstay in the nickel plating industry, for most organic containing solutions including many non-nickel type systems.

The success of the conventional batch hydrogen peroxide/activated carbon treatment system is based on two factors: the oxidative potential of hydrogen peroxide and the adsorptive ability of activated carbon for specific organic compounds. 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 3). Fluorine, due to its nature, is impractical for use. Ozone, requires the use of a ‘generator’ unit in order to produce this compound. This is used in a commercial environment in many municipal water purification facilities. Due to the capital cost of such equipment, we did not investigate this as an oxidant. However, hydroxyl radicals are far more economically produced.

<u>Reactive Species</u>	<u>Relative Oxidation Power</u>
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 3: Oxidative potentials, in volts

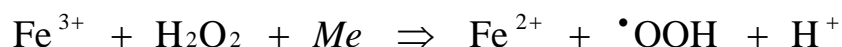
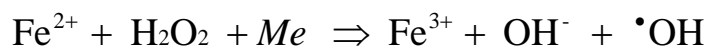
The use of hydroxyl radical principals for organic compound destruction in aqueous environments is known as “Advanced Oxidation Technologies” or AOT. There are a number of proven methods for generating hydroxyl radicals such as:

- ❑ Catalytic ozonation
- ❑ Anodic oxidation
- ❑ UV Light treatment with Hydrogen Peroxide
- ❑ Chemical oxidation
- ❑ Titanium dioxide Photocatalysis
- ❑ Fenton’s Reaction

The principals of AOT have been developed in commercial use over the last 5 – 10 years. Their primary use has been for purification of drinking water; however, documented data indicates success in soil remediation of difficult to treatment organic contaminants. Other developing applications are for the odour control, NO<sub>x</sub> control from power generating stations and nitric acid stripping solutions, and for producing paint and glass surfaces which stay clean regardless of environment.

Investigating some of the practical methods of generated hydroxyl radicals resulted in the awareness that hydroxyl radicals could be economically generated using chemical oxidation within nickel and copper plating solutions through the use of hydrogen peroxide. Trials of this principal and its subsequent technical investigation indicated that the hydroxyl radical was being generated through a metal catalyzed hybrid Fenton reaction. The reaction is shown below:

This reaction process not only yielded the oxidant hydroxyl radical but also a second



oxidant known as perhydroxyl radical. In combination, under the proper operating conditions, these oxidants are very powerful for the oxidation of most organic compounds. The chemical reactions of the hydroxyl radical in aqueous solutions are of four types:



Where the hydroxyl radical adds to an unsaturated compound.



Formulation of organic free radical and water

**Electron Transfer:**  $\text{Fe}^{2+}$  converts to  $\text{Fe}^{3+}$  and metal catalyst ion converts to a higher valence state



Hydroxyl radicals and perhydroxyl radicals react with each other to combine or disproportionate

As with most oxidants, the hydroxyl radical is indiscriminate in nature and will ultimately oxidize all organic constituents within the plating solution. The virgin organic brightener and surfactant along with its 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 enough reaction time will ultimately be converted to carbon dioxide. Our intention was not to proceed to this final stage of carbon dioxide but reduce the organic components to a lower than normal level within the semi-bright process.

Individual organic compounds can be measured within the treatment process using analytical methods 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(TOC). This analytical procedure was used and provides the following results(Figure 4).

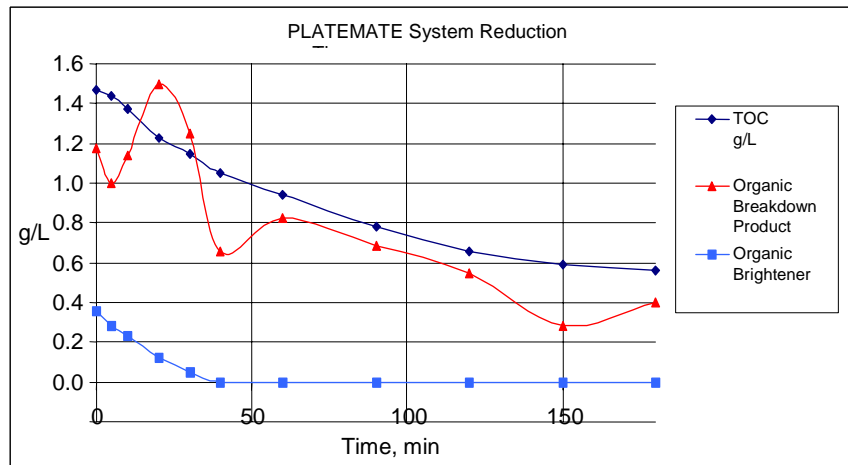


Figure 4. Reduction of organics using OXIMATE system.

Multiple trials within the lab environment demonstrated repeatability in results. The next stage in development of the process involved the construction and assessment within a 500 litre 'pilot' unit. A comparison between the conventional treatment method and the OXIMATE system is provided (Table 2).

	<b>Conventional H<sub>2</sub>O<sub>2</sub> / Carbon Treatment</b>	<b>OXIMATE System</b>
TOC Reduction	29%	66%
Organic Brightener Reduction	100%	100%
By-product Reduction	21%	38 to 50%

Table 2: Comparison of reduction efficiencies

Initial observations indicated that the catalyzed hydrogen peroxide system, OXIMATE, removed the virgin organic constituents as well as the conventional hydrogen peroxide/activated carbon system. However, the difference lay in the ability of the OXIMATE 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 OXIMATE Process, it was determined that compared to the regular weekly volume of solution requiring hydrogen

peroxide/activated carbon treatment, a smaller fraction of the original plating bath solution would actually require treatment using this new process. 'Full' scale testing commenced to evaluate this observation and also to ensure no detrimental side effects. This trial continued for six months in a segregated 'working' semi-bright nickel plating solution environment. All standard and routine testing was completed in addition to monitoring TOC levels (Figure 5).

The trial 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 SBN solution and the resulting foils tested for ductility, sulphur content and tensile strength. These parameters were within acceptable limits. The results indicated that the OXIMATE Process 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.

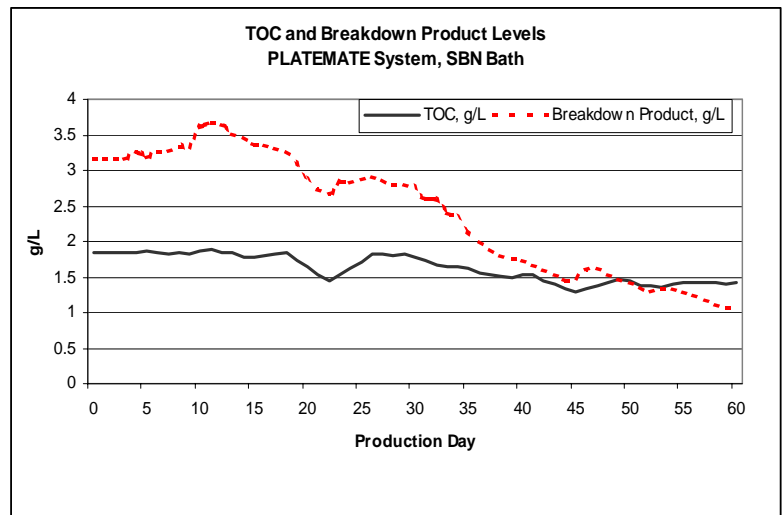


Figure 5; In process testing results

The advantages documented using the OXIMATE Process in comparison to the conventional hydrogen peroxide/activated carbon treatment method are as follows:

- ✓ 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

Optimization of the treatment operating parameters, has resulted in the development of a simple controlled equipment setup, Figure 6, which can be automatically controlled so that a minimum of operator interaction is required. Once specific plating bath operating conditions are investigated and understood the OXIMATE reaction process can be monitored using a simple wet titration method.

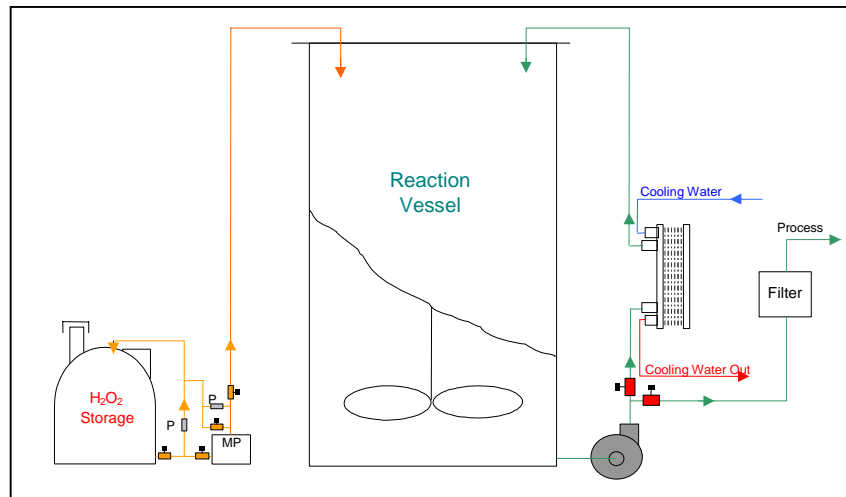


Figure 6; OXIMATE System configuration.

Understanding the chemical reactions occurring within the OXIMATE Process has led to further investigative work for the treatment of the following plating solutions:

- ◆ Non-coumarin based semi-brights
- ◆ Bright nickel solutions, including SAS and Pyridine based
- ◆ Acid Copper solutions, dye and non-dye based

To date, this work has yielded positive results which would suggest that these and many other organically based electroplating solutions are candidates for controlling their organic breakdown products using this simple and effective OXIMATE Process.

### References:

- Nickel Plating*, George A. DiBari, Metal Finishing Guidebook 2001.
- Nickel Plating*, Louis Gianelos, Metals Handbook Volume 5, Surface Cleaning, Finishing, and Coating.
- Carbon Treatment & Filtration*, Fred Mueller, Hands-on Management, Plating and Surface Finishing, June 2000.
- The Properties of Electrodeposited Metals and Alloys, A handbook*, William Safranek
- Electroplating*, Frederick A. Lowenheim, Technical Reference Publications.
- Stress*, Joseph B. Kushner, Electroplaters' Process Control Handbook.
- Ductility*, D. Gardner Foulke, Electroplaters' Process Control Handbook.
- Advanced Oxidation*, Hydroxyl Radical Technology, Calgon Carbon Corp. Web site
- Fenton's Reagent*, Industrial Wastewater Reference Library.
- Soil Treatment*, In-situ chemical oxidation of contaminated soils using hydrogen peroxide, Industrial Wastewater Reference Library.
- Maintenance of Nickel Plating Baths with the help of UV/H<sub>2</sub>O<sub>2</sub> Oxidation*, M. Sorensen and J. Weckenmann, A.C.K.

*Maintenance of Bright Nickel Electrolytes*, A. Mobius, Enthone-OMI, LpW.  
*Advanced Oxidation Technologies, Fundamentals, Applications and Economics*, Hussain  
Al-Ekabi, Presentation Paper at AOT Conference June 2001.