Consistency of Electrolytic Nickel Processes for Optimum Performance

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As the cost of electroplating nickel increases, it becomes even more important to improve the performance of the nickel plating operation. Obtaining the best physical properties from the nickel deposits improves the performance of the plated part. Increased corrosion resistance, brightness, leveling, and chromium receptivity are some of the benefits of optimizing the performance of the nickel solution. Consistent solution purity and nickel concentration, even while recovering dragged out solution, is critical for process performance. A proven method to accomplish this is reviewed.

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One characteristic of quality nickel electroplaters is that they want the best possible performance from their nickel processes at the lowest possible cost. This is especially true when nickel prices increase. Quality and performance are important when plating to a specification, either their customer's or in house. Automotive specifications contain examples of some challenging requirements but the plumbing, hardware, furniture, etc. industries all have their nickel/chromium specifications even if it is only for appearance or coverage. Choosing high performance nickel processes and operating them at their optimum level of performance goes a long way in meeting these requirements.

Maintaining the purity of the plating solution is required if the nickel process is going to consistently perform at its optimum level. No matter how clean the plating line is maintained, contaminants will build in an operating nickel electroplating solution due to breakdown products formed during plating. Excess organics (even additives) are also contaminants to the process. These contaminants interfere with the performance of the additives and the physical properties of the deposit. The appearance of the part declines and the part's long-term performance in service is reduced. If the physical properties such as ductility, stress, quantity of co-deposited sulfur, adhesion, and stress are not within specification, premature corrosion failure of the part is common. Many times additional additives can be added to cover up a loss of appearance due to contamination but this adds additional organics to the solution and can further reduce the deposit's physical performance.

Traditionally, maintaining an adequate amount of fresh carbon on the solution's filter and periodically batch treating the nickel solution were the only means to maintain purity. Batch treatments usually use carbon or carbon and peroxide depending upon the concentration and type of contaminants being removed. Performed frequently enough with enough reaction time, filtering, carbon and peroxide, these treatments usually remove a sufficient quantity of organic contaminants to maintain the deposit's physical properties. Depending upon such variables as the volume of solution, part, amp-hours, plant operations, bath chemistry and type of nickel process (bright, semi-bright, etc.) these batch treatments might have to be repeated once, twice of even twelve or more times per year to maintain optimum performance. Another set of procedures and treatments are necessary for metallic contaminants.

Adsorber Polymer Eliminates Batch Carbon Treatments

In 1996, a unique and very effective nickel electroplating solution purification system was introduced in Europe. It includes a piece of equipment that looks like an automatically controlled ion-exchange unit. However, instead of containing ion-exchange resin, the column is filled with a custom made polymer designed to adsorb organic contaminants directly from a nickel electroplating solution. Part of its uniqueness is that it is customized to purify bright nickel processes formulated around PPS. PPS baths are the highest performing bright nickel processes available today. They require much less total additives to produce better deposits than non-PPS processes. This is especially noted in the low current density areas and in overall brightness and leveling. Most suppliers of bright nickel electroplating processes have PPS type formulations. They are the most common type of high performance process used worldwide.

One problem with some improperly designed PPS bright nickel formulations is that the standard carbon and carbon/peroxide batch treatments will not purify the solution enough to maintain the optimum physical properties required for plastic substrates and automotive specifications. If the plater used one of these formulations they have to choose between the best possible appearance and optimum physical properties. However, properly formulated PPS baths can be purified by batch carbon treatments but the treatments have to be performed more frequently than many platers would like. Bath carbon/peroxide treatments are time consuming (loss of production or overtime pay), a substantial amount of nickel solution can be lost, and they generate a large amount of "hazardous" waste. Quality shops have accepted this as part of what is required to meet their tight specifications and arrange their production schedule around treatments.

The adsorber polymer unit has eliminated the need for batch carbon/peroxide treatments. The unit continuously maintains the purity of the nickel solution at its near-new condition. In many cases, this is cleaner than what is obtainable through batch carbon/peroxide treatments. Even poorly formulated PPS bright nickel baths can now be purified because of the adsorber polymer's affinity to PPS contaminants and break down products. Today, there are over 20 adsorber polymer units operating in North America with the oldest dating back to October 2000. There are over 60 units worldwide.

Just like batch carbon treatments, the adsorber polymer will remove some additives along with the organic contaminants. However, an easy method is used to keep this to a minimum. In practice, repeated analytical analyses demonstrate that for the amount of organic contaminants removed, the adsorber polymer removes less additives than batch carbon treatments. This is attainable because of how the polymer was formulated. Table 1 lists the removal preference for carbon and adsorber polymer. In order for carbon to remove a sufficient amount of break down products, carrier also has to be removed. The adsorber polymer cycle time can be adjusted so that very little carrier and no brightener additives are removed. The adsorption time is determined by monitoring the total consumption of carrier. HPLC analysis, Figure 1, verifies that the break down products are removed without a significant amount of carrier or other additives.

Table 1- Removal preference for organics from nickel electroplating solutions

Carbon Treatment	Adsorber Polymer
Wetting Agents	Break Down Products
Carrier	Carrier
Break Down Products	Wetting Agent
Brightener	Brightener

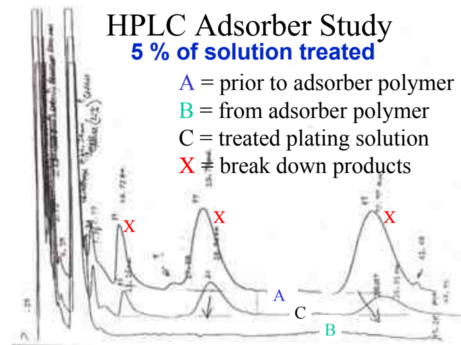


Figure 1-HPLC curves showing the effects of the Adsorber Polymer on break down products

PLC curve A in Figure 1 denotes the presence of break down products in a bright nickel electroplating solution in need of batch carbon treatment. These contaminants caused the physical properties of the nickel deposits to not meet specification, especially the ductility. Curve B shows that the adsorber polymer removes all the impurities detectable by HPLC. Curve C in Figure 1 is the HPLC curve for the solution after 5% of the bath was passed through the adsorber polymer in one two-hour adsorption cycle. The ductility and other deposit properties are now well within range. Nickel plating solutions do not have to be completely purified to operate at their optimum. This treatment and regeneration was performed by a push of a button on the automatic unit. One cycle per week is usually sufficient to maintain this level of purity. And, in contrast to batch carbon treatments, the purity level of the plating solution is almost constant. When batch carbon treatments are used, the contamination level can rise to an almost unsatisfactory quantity before treatment. In order to remove shop oils etc., carbon is still recommend on the solution's filter. However, much more carbon filtering is required when batch carbon treatments are used than when the adsorber polymer is used.

Consistently Maintaining Automotive Specifications

The longest operating adsorber polymer unit in North America is located at Meridian Automotive Systems Inc. in Ionia, Michigan. Like all large OEM bumper platers, they frequently batch carbon treat and continuously carbon filter their bright nickel solutions in order to continuously meet automotive specifications. Prior to using the adsorber polymer unit, Meridian calculated that they spent $31,200 a year to batch carbon treat their four 38,000 liter bright nickel tanks. *(Products Finishing, December 2002)* They also spent $21,600 between October 20, 2000 and November 12, 2001 to replace the solution lost along with the carbon and filter media. The adsorber polymer unit required $12,500 to operate during this time period. This gave them a savings of over $40,000 per year. During this period, Meridian operated 20 hours per day, five days per week at an average of 42,000 amperes per hour.

More important than the savings in expense was that their solutions were consistently at a high level of purity that helped them to continuously meet their automotive specifications. This was accomplished without any batch carbon treatments and with greatly reduced carbon filtering. The unit has now been operating for over 3.5 years with no batch carbon treatments and no increase in additive consumption. One adsorber polymer unit is more than sufficient to treat their four bright nickel solutions. One treatment per tank per week is usually sufficient to maintain the purity of the solutions. One treatment can usually be completed during one shift but since it is automatic, no one has to be available when the cycle is finished.

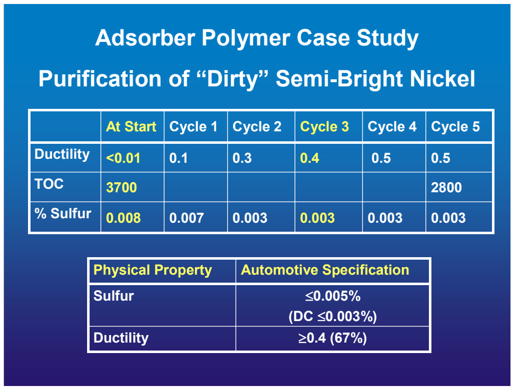
Semi-Bright Experience

The initial evaluation in 1996 established the selectivity of the adsorber polymer with a Watts based nickel baths. Solutions were prepared and single bright nickel additive components were added and tested after ½, 1, 8 and 16 hours of circulation through the adsorber polymer. Most of the selectivity work was conducted on single ingredients proprietary wetting agents, carriers, levelers and brighteners to understand what types of materials are absorbed, how fast, and at what percentage.

Introducing this technology to the North American decorative market, the comment from plating shops needing duplex nickel was that the semi-bright nickel was key to their operation, would the adsorption technology have the same effect on the semi bright organic values, which would be approximately 1/3 the amount compared to a bright nickel.

To evaluate the use of the adsorber on a proprietary semi bright nickel process, a bath in poor condition was chosen. The solution was dark in color, with poor ductility and stress and high sulfur content. The goal was to eliminate long-term carbon treatment by maintaining organic levels in “new bath” properties. Lab tests showed improvements in stress, ductility and sulfur content, considering only 15% of the bath was run through a small column, the indication was that the adsorber prefers to remove the most detrimental organics. The relatively small reduction in total organic carbon (TOC) highlights that it is the type of organics removed, not the absolute reduction that is important.

In August of 2002 a production trial revealed similar results to the lab evaluation, Figure 2. The unit ran once a week with a three-hour adsorption cycle/ 6 hr regeneration cycle. The most significant improve-ment was the increase in ductility of the deposit (T/2R) from less than measurable initially, the foil shattered, to a ductility of 0.5 after four cycles. Sulfur in the deposit was reduced from 0.008% to 0.003%, Figure 3.



Adsorber Polymer Case Study

Purification of "Dirty" Semi-Bright Nickel

	At Start	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Ductility	<0.01	0.1	0.3	0.4	0.5	0.5
TOC	3700					2800
% Sulfur	0.008	0.007	0.003	0.003	0.003	0.003

Physical Property	Automotive Specification
Sulfur	≤0.005% (DC ≤0.003%)
Ductility	≥0.4 (67%)

Figure 2 – Purification of a "dirty" semi-bright nickel with the adsorber polymer

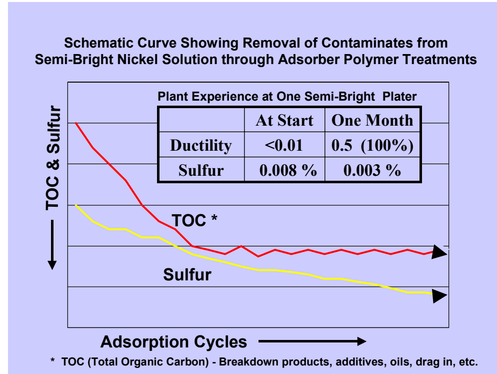


Figure 3 – Removal of sulfur and total organic carbon with adsorber polymer

Since the initial field evaluation, three facilities have installed a unit on their semi bright baths and another unit on their bright baths. The units are capable of maintaining numerous tanks of the same solution. It is not recommended to try to maintain a bright nickel and semi bright nickel with the same unit, due to possible contamination to the semi bright. The adsorption cycle for semi bright is usually longer than for bright, with the regeneration solutions and times the same. A qualitative HPLC program, Figures 4 and 5, is available to determine the cycle that will minimize the loss of carrier, matching the adsorption cycle with frequency to run the unit per week, Figures 6 and 7. It is required to run a polishing carbon filter to remove drag out, shop oils, etc that are not removed by the adsorber polymer system.

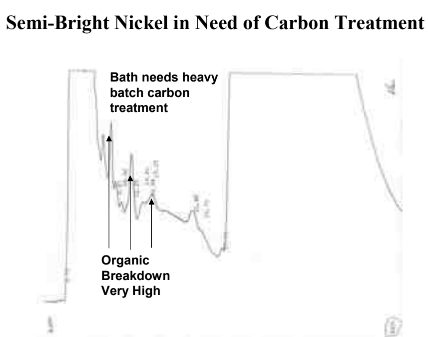


Figure 4 – Contaminated Semi-Bright nickel prior to carbon treatment

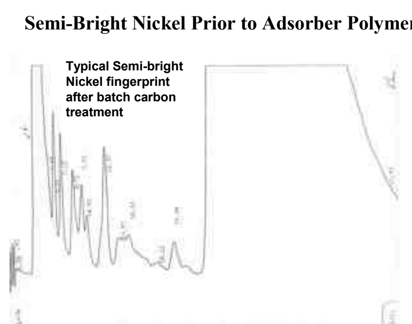


Figure 5 – Contaminated Semi-Bright nickel prior to Adsorber Polymer

After 1 Month Using Adsorber Polymer

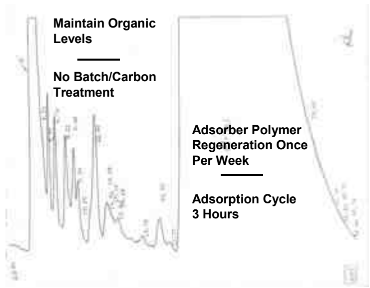


Figure 6 – Semi-Bright nickel after one month using Adsorber Polymer

After 2 Months Using Adsorber Polymer

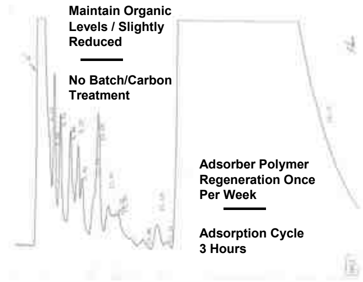


Figure 7 – Semi-Bright nickel after two month using Adsorber Polymer

A Versatile Technology

The adsorber polymer unit originally designed only for bright nickel electroplating solutions has proven to be far more versatile. Semi-bright nickel baths are now being purified with no need for additional batch carbon treatments. A unit will be placed on a particle nickel solution very soon. It might even be useful for high potential nickel processes.

For both the semi-bright and bright electroplating processes, production experience has demonstrated that the adsorber polymer unit consistently maintains the solution purity at the almost near-new level. The deposit's physical properties are therefore at their optimum levels without the need for batch carbon treatments. The nickel additives are also consumed at a more constant rate based upon amp-hours without any increase in additive consumption.

The adsorber polymer brings the nickel electroplater closer to a closed loop operation. Less plating solution is lost and far less waste is generated that has to be treated and disposed of. But most of all, platers can concentrate on their production with less concern about the operating conditions of their nickel solutions.