Closing the Loop on Bright Nickel Electroplating; 2nd-Year U.S. Status

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With seven years of global experience and two years of U.S. experience, the value of using a regenerable 'absorber polymer' to purify bright nickel electroplating solutions has been demonstrated. This has eliminated periodic carbon treatments for bright nickel baths. The system can be used in conjunction with membrane anodes to almost totally recover the bright nickel rinses. Experience in the U.S. has shown more interest in solution purification than closed loop operation, however. The value of TOC (total organic carbon) as a measurement of bath performance has also been demonstrated.

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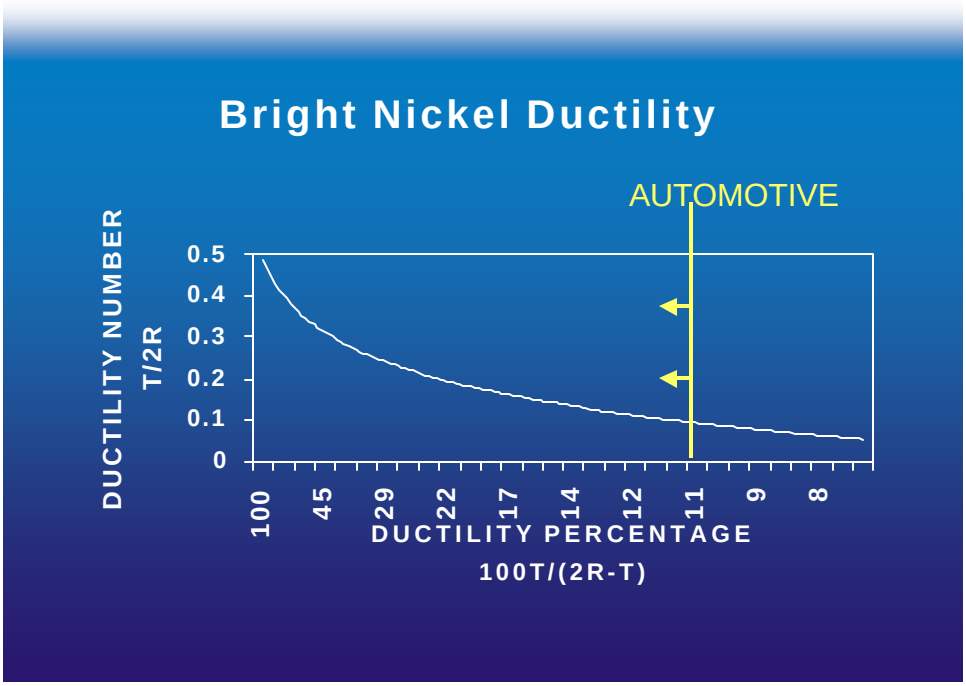
During AESF Week in 1999, the authors presented a paper describing the advantages of a virtually closed loop bright nickel plating system. This system was based on 2 technologies: first the use of membrane anodes to balance cathode and anode plating efficiencies as well as compensate for nickel being added back from rinse waters; and second, an 'adsorber polymer' to preferentially remove organic contamination in the bath while leaving behind most of the functional additives (especially the expensive brighteners).

This system is now in use in 13 countries. There are 54 adsorber polymer units working, predominantly for rack applications where drag-out is lower. There are also 5 membrane anode systems working with 4 on bright nickel and 1 on acid zinc. Usage of the membrane anode portion of the system to close the loop by returning the nickel rinses to the plating tank has had limited success. This is not due to any technical problem, but to economics:

- Nickel prices have been low for the last several years making the value of recovered nickel less than in earlier times
- the membrane anodes are costly as the proper selective membrane assures a multi-thousand dollar price per anode and usually 5-10% of all nickel baskets must be replaced with the membrane anodes
- the cost of nickel waste disposal has not risen over the past few years as regulatory agencies have not increased their requirements

Three of the adsorber polymer units are in the USA. This paper will show data from Meridian Automotive Systems Inc., a large OEM bumper plater in Ionia, Michigan who has been using this system since October 20, 2000. Data collection used in this paper ended November 12, 2001. The system continued operating and additional data is being recorded. Meridian has one 300 liter tank of adsorber polymer resin and switches that between 4 bright nickel tanks to keep a total of 38,400 gallons of solution delivering very consistent deposits. These are separate tanks with the adsorber polymer unit being used sequentially on the four different solutions about 1 time/day. One of Meridian's major concerns was consistently meeting the automotive OEM elongation specification for bright nickel of 11% (approximately equivalent to a Chrysler Bend Test value of 0.1, as in ASTM B490). Since use of the adsorber polymer began, this has been consistently obtained without the use of batch carbon treatments.



Meridian has not had a single batch carbon treatment since use of the adsorber polymer began. Consequently there has been no need for peroxide or permanganate treatments. Since the adsorber polymer operates by diverting a small fraction of the plating bath continuously for treatment, production has never been interrupted. This means that Meridian is able to maintain its 20 hour/day, 5 day/week, 50 week/year operation.

The thickness specifications at Meridian are 33 µ total nickel of which 8 µ is bright nickel. During the approximate one year period being reported here, there were about 2,000,000 automobile bumpers plated in these tanks. Current used was 42,000 amps/hour in 38,400 gallons. From this you can extrapolate to 5,469 amps/gallon per year. At 94% cathode efficiency this suggests about 481,000 lbs (241 tons) of bright nickel were plated during the year with no batch carbon treatment. With an anode efficiency of close to 100%, about 31,000 lbs of unplated nickel was lost from the plating solution. This would have been through drag-out predominately. If this had been recovered from the rinse water, nickel would build in concentration in the plating solution. Membrane anodes could have been used to balance the plating efficiencies.

In batch carbon treatment the usual preference for the carbon is to take out the wetting agent first, brightener second, and then break down products along with saccharine. For adsorber polymers that order is rearranged. They take out the break down products first, saccharine second, wetting agent third, and then

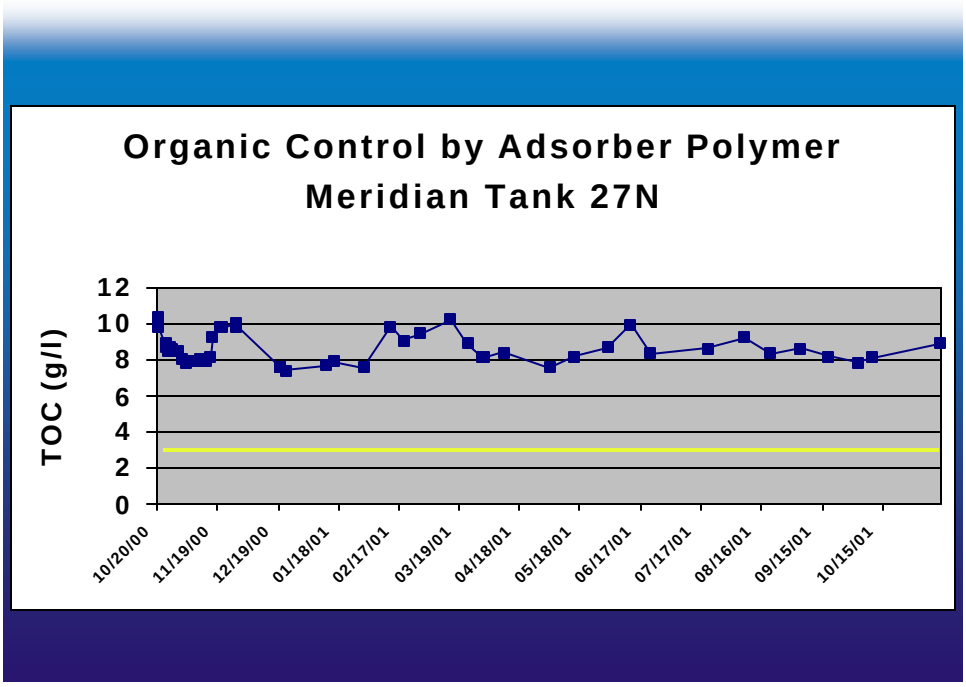
brightener. This means that the most expensive material has the least preference from being removed.

The system is not 100% closed. Every regeneration cycle requires rinsing the adsorber polymer. Despite the very best efforts to minimize loss of solution, about 10-11 gallons is lost. This contains nickel. In the case of Meridian this is a loss of about 42 gallons/day from 38,400 gallons in the tanks. This is modest compared to normal drag-out losses from the average 5,556 bumpers being processed/day.

Analysis of nickel plating baths, additive by additive, is not cost effective. A measurement of total organics (TOC or Total Organic Carbon) is a good alternative. Many shops run their own TOC for waste treatment compliance, so the methodology is well known. Freshly made up bright nickel baths run from about 3 to 6 g/l TOC. The lower range is preferred for high drag out situations, like bumper plating or barrel plating, to save on nickel additive losses. Once a bright nickel bath reaches about 20 g/l TOC, deposit properties begin to deteriorate. It is almost impossible to maintain deposit properties once TOC reaches 25 g/l.

The adsorber polymer operates quite effectively in the range of 8-12 g/l TOC. Baths held in this range give excellent and consistent deposit properties. Operating the adsorber polymer to hold TOC below about 8 g/l leads to higher losses of expensive nickel additives and more hours of operation of the polymer per thousand gallons of solution without any improvement in deposit properties.

Meridian gave their bright nickel plating solutions their last batch carbon treatment a few days before October 20, 2000. A freshly made-up bath would have about 3 g/l TOC that is shown on the following graphs. Looking at Meridian's 4 plating tanks:


Organic Control by Adsorber Polymer
Meridian Tank 27N
TOC (g/l)
12
10
8
6
4
2
0
10/20/00
11/19/00
12/19/00
01/18/01
02/17/01
03/19/01
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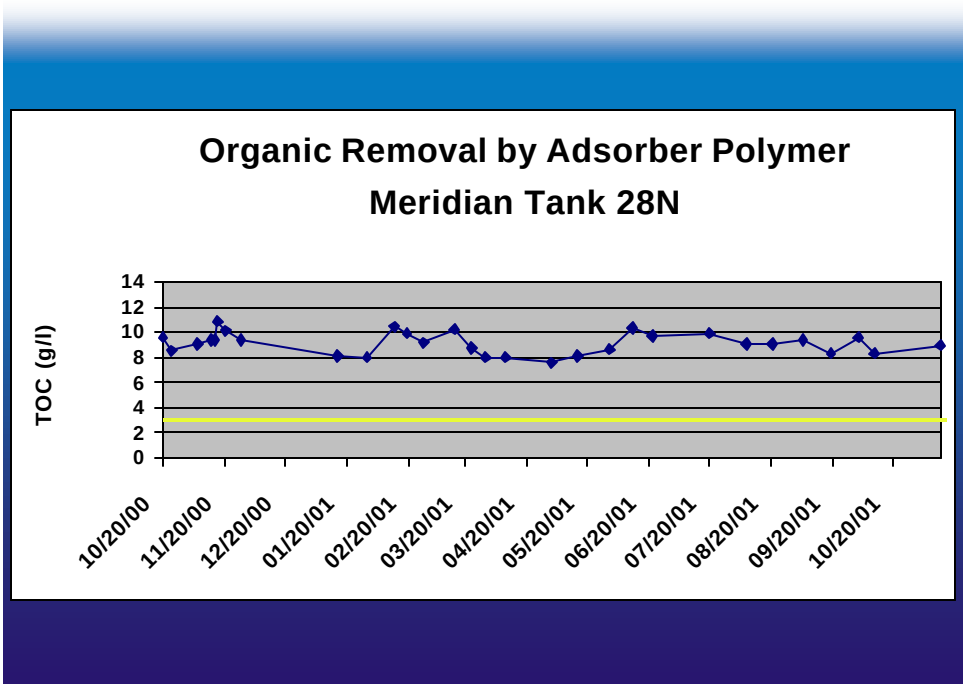
Organic Removal by Adsorber Polymer
Meridian Tank 28N
TOC (g/l)
14
12
10
8
6
4
2
0
10/20/00
11/20/00
12/20/00
01/20/01
02/20/01
03/20/01
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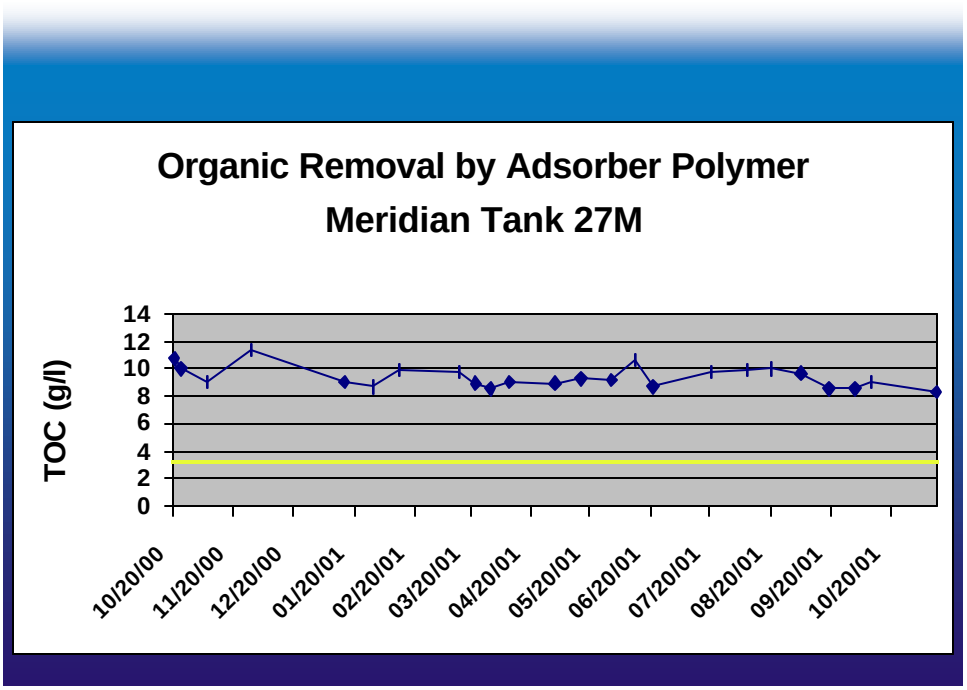
Organic Removal by Adsorber Polymer
Meridian Tank 27M
TOC (g/l)
14
12
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8
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10/20/00
11/20/00
12/20/00
01/20/01
02/20/01
03/20/01
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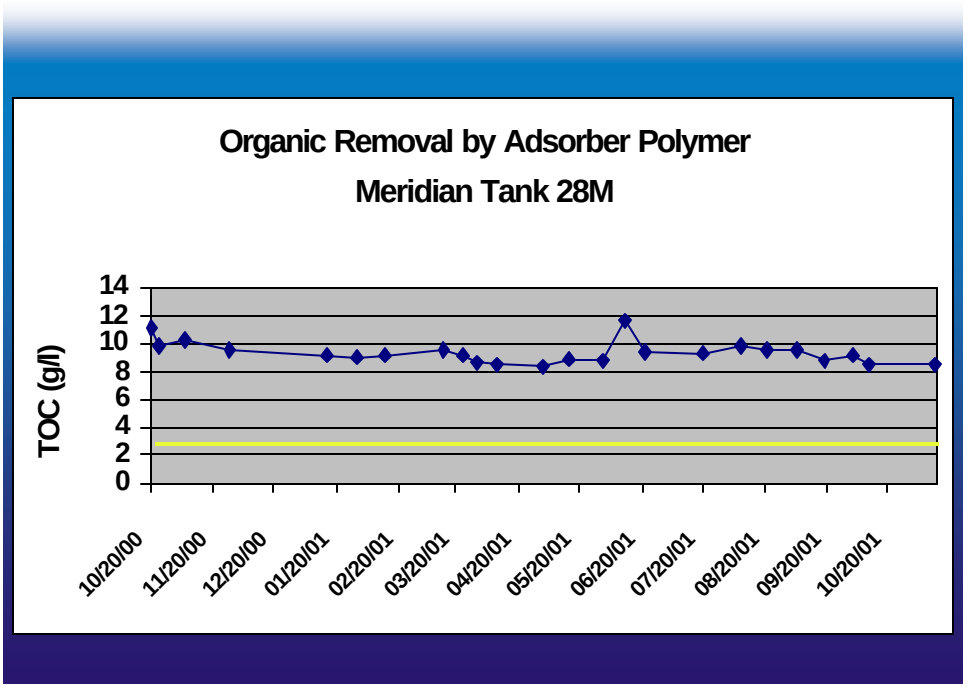
Organic Removal by Adsorber Polymer
Meridian Tank 28M
TOC (g/l)
14
12
10
8
6
4
2
0
10/20/00
11/20/00
12/20/00
01/20/01
02/20/01
03/20/01
04/20/01
05/20/01
06/20/01
07/20/01
08/20/01
09/20/01
10/20/01

As can be seen, the TOC was held between 8 and 12 g/l. Throughout this time the deposit ductility specification of 11% or greater was never violated. No F006 waste from batch carbon treatment was created because no batch carbon treatments were performed. The solutions from the regeneration of the adsorber polymer are easily treated in Meridian's waste treatment system for nickel plating.

Some cost estimates from Meridian show annual labor and material cost of batch carbon treatment at about $2600/tank plus another $5200/tank for filter changes. The total being spent before the use of adsorber polymer was about $31,200/year. Meridian estimates the cost of replacing the solution lost with the carbon or filter media at about $21,600/year.

An additional advantage of the adsorber polymer relates to pyridine, usually added with PPS (pyridinium sulfo-betain) in systems based on this secondary brightener. Despite over almost 20 years excellent experience with very clean PPS (under 60 ppm free pyridine in PPS) being used in nickel brighteners, there is still a small segment of the industry that worries about this class of brighteners. The adsorber polymer removes short chain PPS impurities and break down products without removing the active longer chain compounds, which are such an excellent source of brightening and ductility in the nickel deposit.

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