Electroless Nickel Treatment Process Model

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Many companies have successfully managed electroless nickel plating wastes using a variety of "plate out" methods. Typically, these involve using proprietary liquid additives to maintain bath activity so that nickel will deposit on either steel wool or aluminum plates. The nickel level that remains in the waste bath ranges from 70 – 150 ppm, far less than the 2 – 3 oz/gal in the spent bath, but not low enough to meet discharge standards. The objective this treatment process model development project was to determine if and how the "plate out" method could be optimized to reduce nickel level to the local discharge standard of 5 ppm. The objective was achieved using precise process control over temperature, solution flow, pH and hypophosphite additions. Process parameters and equipment design will be presented.

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Background

IMC Magnetics manufactures specialty solenoids for aerospace customers. The plating operation uses electroless nickel to provide corrosion protection on a variety of cold rolled steel and stainless steel composite parts. An assessment of the plating and waste water processes, conducted by TNT Technology Company, identified electroless nickel waste treatment for waste reduction and process improvement. It was recommended that the existing "plate out" tank and method be reviewed for why it was abandoned and how best to revive its use. This would significantly reduce sludge waste generation, hauling costs, time and labor for batch treatment of the chelated and high metal content of waste electroless nickel baths and drag out rinse.

The old "plate out" tank had been abandoned due to excess labor and cost of proprietary chemistry used. In order to re-implement this process, the tank and method would need to be updated and sized to accommodate the new, modern plating and waste water treatment plant that IMC is planning to implement in the near future. The focus of this process model development project focused on reducing time, labor and cost of running a "plate out" process, which included sufficient automation to achieve consistent and reliable results before the move to the new facility. The existing waste water treatment system is a manual, batch treatment operation and requires dedicated labor to keep running. If the plate out process could only reduce nickel to 70-150 ppm, then the remaining nickel would need to be removed in this batch treatment system.

Thus, an additional goal was to determine if the "plate out" process could be optimized to remove nickel to discharge standard of 5 ppm,. This would eliminate a waste stream from the batch treatment system., saving time, labor and cost.

Initial Investigation

The first step was to research the literature and consult with other plating shops that had successfully used a "plate out" method. The vendor and other literature reviewed all described a similar process. Each adds reducing agent and adjusts pH, and conducts the plate out process at 190+ degrees F. [1-7] Each vendor literature reference [1,5-7] indicated that the plate out method for their proprietary baths required a proprietary additive which would not work for any other vendors bath. Several cited the ability to reduce nickel levels below 50 or below 10 ppm with process times of 4 – 8 hours.

Conversations with the manager of the Hughes Aircraft Space & Communications Plating Center (now Boeing) confirmed that the plate out method they implemented in 1993 regularly achieved nickel reduction to approximately 100 ppm. The lowest level achieved was 75 ppm. Hughes has used aluminum plates for nickel removal since it is a readily available commodity in their shop. Hughes runs Fidelity electroless nickel process and uses the Fidelity plate out method and chemistry.

Conversation with Doug Vogel of Fidelity in 1991 identified the ability to achieve < 5 ppm residual nickel with a process chemical cost of $.40-.50/treated gallon for a proprietary additive.

A conversation with IMC personnel that had run the old electroless nickel plate out system confirmed that nickel removal down to a range of 100-150 ppm was normal.

The next step was to identify the process variables that could be automatically controlled. Electroless nickel plating methods were reviewed.[8] These are:

Temperature
Solution flow
pH
Reducing agent concentration
Time
Contaminants

At this point, it was known that controlling pH and reducing agent would enable nickel levels to be reduced below 75 ppm. The economics of the process also needed to be addressed. Using generic chemicals was chosen as opposed to proprietary chemicals. Although proprietary chemicals offer simplicity of addition and control, the generic chemicals offered lower cost and the challenge of designing a simple addition and control system. Crystalline sodium hypophosphite and 50% caustic are the two chemicals that were readily available on the plant site. Some of the references cited

recommended ammonia hydroxide for pH adjustment and pre-activation of the steel wool using hydrochloric acid dip and rinse. Neither of these were tested since the objective was to keep the waste treatment process simple.

Bench Scale Test Methodology

First a qualitative set of bench scale tests were run to determine how the two different spent electroless nickel baths would behave. IMC uses both medium phosphate as well as high phosphate electroless nickel baths. It was also important to determine if a regular spent bath would plate out similarly to one that had auto decomposed due to contamination.

Each bath was analyzed for nickel and hypophosphite levels using wet chemical method. pH was measured using a Durafet L&N pH Controller. The amount of hypophosphite needed to achieve 100% in a bath was calculated. First, the pH of the sample waste bath was adjusted to 6.8-7.0 using caustic. This causes the solution to turn cloudy, as reported in the literature. Since test results were good, ammonia hydroxide was not used. Then the sample was heated. As the bath heated up to 185-190 degrees F., the first addition of hypophosphite was made. pH must be adjusted before the addition of hypophosphite. A simple wire frame was formed that fit into the 4000 ml beaker. It was wrapped once with 3" wide steel wool. The steel wool was not activated in hydrochloric acid as is typically recommended. When the solution reached 185 degrees F., the steel wool was lowered into the beaker. After approximately 30 seconds, the bath activity was observed and plating started. Plating started faster when temperature was 190 degrees F. The steel wool on the wire frame was agitated in the beaker constantly. As the steel wool rubbed along the sides of the beaker, black nickel deposit was formed. pH was readjusted to 7.0 several times as listed in Fig. 1 below. Each addition of caustic increased bath activity. In one test, hypophosphite was added during the plate out process as a 25g/l solution. In the other test it was added as a solid. In both cases, the addition caused an increase in bath activity. Nickel level was tested periodically throughout the test using Hach test strips.

Qualitative Test Results

Time (min)	pH	Grams hypophosphite	Nickel ppm
0	4.52	85	2028
19	6.13		100-250
28	7.1		100
95	7.2		<10

Rig. 1

After 90 minutes, the nickel level was approximately 10 ppm by semi-quantitative analysis (test strips). The color of the solution was a very pale yellow-green. The series of qualitative test showed the need to maintain pH and hypophosphite levels in order to maintain bath activity. It also demonstrated that a residual nickel level below 75 ppm could be achieved and that bath activity was the key process parameter for obtaining low residual nickel levels.

A phenomenon of nickel going back into solution was discovered when the nickel plated steel wool was left overnight in the cooled bath sample. The nickel level increased and the solution returned to a pale green color . this confirmed the need for solution filtration and immediate removal of steel wool racks at the end of the plate out process.

The same tests were repeated to obtain the quantitative data that would identify potential process costs and automated controls needed. The same steel wool and wire frame were used with no activation. Typically the steel wool can be reused three times before it becomes brittle. The data in Fig. 2 below shows a repeatable pattern of additions and reduction of nickel level.

Quantitative Test Results

Time	50% caustic mL	Hypophosphite g	Nickel ppm
0	125	24.5	3200
16	25	25	100
30		16	~10
44	25	6	~25
60		12	~10
90		25	3.7

Fig. 2

Final nickel level was determined by using a HACH DR2000.

The addition of hypophosphite is more convenient as a liquid of known concentration rather than weighing and adding the solid manually. The maximum solubility of commercial grade hypophosphite in deionized water was determined to be 816g/l at 75 degrees F. A hypophosphite makeup tank with mixer then was added to the equipment design to keep the system as fully automated as possible.

An average of 125 mL of 50% caustic and 70 grams or 86 mL of 816 g/L concentrated hypophosphite were added per 3500 ml of spent EN plating solution.

Two further quantitative tests were conducted. One was a 50:50 blend of waste electroless nickel bath and immersion drag-out rinse water. The second was a simulated spray drag-out rinse which is designed into the new plating facility.

The 50:50 blend started with a nickel level of 2.54 g/l and a hypophosphite level of 9.073 g/l. 100 g. of hypophosphite were added to bring the mixture up to the activity of a regular bath. This turned out to be too active and caused plateout on the sides of the beaker. A total of 24.94 g. of very spongy nickel plated on the steel wool used. pH was adjusted up to 6.7 using caustic. For this blend, the gassing of plate-out started approximately 5 minutes after immersion of the steel wool.

50:50 Blend Test Results

Time	50% caustic mL	Hypophosphite g	Nickel ppm
0	35.9	100	2540
20	-	-	25-100
36	18.45	-	<10
50	-	-	~10
67		3.2	~10
97	-	12	14

Fig. 3

Approximately 1000 mL of the solution had evaporated during this test. If the 1000 mL had not been lost, the concentration of nickel would have been 10 ppm.

The new plating facility will incorporate a spray drag-out rinse after electroless nickel. A simulation using scrap parts determined that the approximate nickel content of a spray drag–out rinse would be 300-500 ppm. A waste of mixed medium and high phosphate baths was used to create a 500 ppm simulated drag-out rinse for testing. The expected optimum hypophosphite concentration in the waste bath of 38 g/l was used to adjust the hypophosphite concentration of the simulated rinse. Since the previous experiment showed that using the full amount of 38 ga/l caused over activity of the plate-out process, only half or 19 ga/l were added to this sample. During the plate-out process, additional hypophosphite was added using 800 g/ l liquid.

The solution was observed to take longer to achieve gassing with this lower concentration of nickel. Approximately 25 minutes elapsed from the immersion of the steel wool until the start of gassing. Within 30 minutes the solution was clear with dark particles and showed approximately 10 ppm of nickel in the filtered sample. 500 mL of solution evaporated during the test. The steel wool increased in weight by 1.91 grams as compared to the theoretical content of 1.75 grams of nickel in the test sample. Moisture is probably the cause.

Quantitative Test Results

Time	50% caustic mL	Hypophosphite g	Nickel ppm
0	10.4	63	500
28	-	11.44	10
42	-	-	4.8

Fig. 4

The above two tests demonstrated that the highest volume waste for electroless nickel in the new plating facility; namely the drag-out rinse would be easy to treat and achieve less than discharge standard.

Equipment Design

The design process started with scale up of the bench level tests. The expected waste volumes in the new IMC plating operation are 200 gallons per day of spray drag out rinse bath and 200 gallons per month of spent electroless nickel bath. The polypropylene plate out tank size was calculated to be 250 gallons of solution to be treated. The actual size of the tank was designed to accommodate bottom stainless steel heaters and provide a

minimum of 6 inches of free board for the hydrogen gas formation during plating.

Tank components include heater and controller, circulation/transfer pump, CPVC bag filter, rack supports and level controls to protect the heater and the pump. The heater was sized to heat up the bath during the rare cool weather of Phoenix within 2 hours to 190 degrees F. The heater placement above the sloped tank bottom was designed for maximum solution flow over the heater as solution is drawn from the bottom to the circulation pump. A circulation / transfer pump was sized for 7 turnovers of the solution per hour with a pump curve which accommodate the head loss for transfer to a remote location and keep the flow rate in the tank at a high level (30 gpm). Solution return to the tank after the bag filter is directed through the sides of the tank. With multiple ports of entry aimed at the racks of steel wool, it is expected that solution flow through the steel wool will be enhanced. As the amount of nickel dwindles, the turnover of the tank will be important. This becomes a surface area game similar to removal of low levels of metal using ion exchange. This is one of the parameters of optimizing this plate out process.

The number of racks wrapped with steel wool needed to load the spent bath to remove nickel quickly was determined from the bench scale tests. Using 2 pounds of steel wool per gallon[6] was identified by only one reference. Using typical plating bath loading of 0.5 to 1.0 surface sq. ft. per gallon, a rack area of approximately 4 sq. ft. wrapped with 3" wide steel wool "ribbons" was devised. Actual surface area is difficult to determine.

The control over the chemical additions and temperature are expected to maintain the bath activity more than surface area of steel wool.

A Durafet pH probe on a Honeywell pH controller tied to a metering pump is used to maintain pH at 7.0 + or – 0.4. (Durafet was originally developed by Leeds & Northrup, which was purchased by Honeywell.)

A hypophosphite makeup tank with a mixer will meter hypophosphite solution into the plate out tank using a metering pump calibrated to deliver 1 mL per minute of 816 g/L concentrated solution. Time for additions will be used to maintain control over the total hypophosphite added.

[NOTE: Full scale test results and photos of the system will be available for the Conference, since equipment fabrication is not yet complete at this time. Data available by the Nov. 6th deadline for the paper will be included.]

Process Economics

One of the goals of this project was to demonstrate a lower cost system compared to standard batch treatment. The following calculations are based upon the quantitative bench scale results and will be verified during full scale testing. All figures are for a batch size of 250 gallons.

a) Hypophosphite: av. 40 pounds
(40 lb x $ /lb)/250 gal = **$___/treated gal**

b) 50% Caustic: av. 12.5 gallons
(12.5 gal x $1.53/gal.)/250 = **$.077 /treated gal**

c) Energy: 12KW heater on for 4 hours
(12KW x .08/kWhr x 4 hr.)/250
= **$.015 / treated gal**

d) Labor: Load / unload racks and makeup Hypo tank (~2 hours / day). ($15/hr fully burdened labor rate)
(2 hr x $15/hr)/250 = **$0.12/treated gal**

TOTAL Cost per Treated Gallon: **$0.21+**

This compares very favorably with Fidelity's chemical cost of $0.40-.50/treated gallon and to current operations for proprietary precipitant and coagulant used by IMC.

Summary / Conclusions

Using a plate out method for treating spent electroless nickel plating bath and drag out rinse is both economical and has a low labor content. The time and cost to achieve typical 75-100 ppm residual nickel levels may be sufficient for some shops. The ability o optimize the process to meet local discharge limits was also demonstrated. The development project essentially identified the same process parameters as those used to maintain an elelctroless nickel bath for plating. These include: constant small additions of reducing agent and pH adjustment; solution agitation and filtration, surface

area loading, and temperature. Obviously, the plate out process is not concerned with streaky, or dark plating. But the process must be controlled well enough to avoid “run-away” plate out on the tank walls. Organic and non organic contamination is minimized by using deionized water for makeup of the hypophosphite and by minimizing the time the steel wool is in contact with the bath.

References

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