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Electroless nickel (EN) plating is used to apply a protective coating to a substrate without the use of an electric current. Following a catalytic activation step, a nickel phosphorous alloy (NiP) is deposited through chemical reactions on the surface of the part. The advantages over other metal coatings include: coating uniformity, corrosion resistance, wear resistance, desirable magnetic and electrical properties, and indifference to part shape. The most common nickel source is nickel sulfate. Nickel ions are reduced to nickel metal by accepting electrons from an electron donor, typically hypophosphite, present in solution as sodium hypophosphite. Some of the hypophosphite is reduced to phosphorous, and is co-deposited with nickel to form a NiP alloy. As the nickel is plated onto the part, the concentrations of nickel and hypophosphite in the bath decrease. Nickel sulfate and sodium hypophosphite are periodically added to replenish these losses. When 100 percent of the original nickel has been replaced, this is termed a metal turnover (MTO).

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ADDITIONAL PAPERS

ELECTROLYTIC REGENERATION OF CONTAMINATED ELECTROLESS NICKEL PLATING BATHS

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INTRODUCTION

The Naval Facilities Engineering Service Center (NFESC) working under the direction and support of the Strategic Research and Development Program has been tasked to develop technologies that can be used to maintain and extend the service life of metal preparation and finishing baths. The effort is being conducted in partnership with Air Force's Wright Laboratory and EPA's National Risk Management Research Engineering Laboratory. The overall project will address removal of contaminants from several types of solutions. This paper reports work done in evaluating and developing an electrodialytic (ED) process for removing contaminants from electroless nickel plating baths.

ELECTROLESS NICKEL PLATING

Electroless nickel (EN) plating is used to apply a protective coating to a substrate without the use of an electric current. Following a catalytic activation step, a nickel phosphorous alloy (NiP) is deposited through chemical reactions on the surface of the part. The advantages over other metal coatings include: coating uniformity, corrosion resistance, wear resistance, desirable magnetic and electrical properties, and indifference to part shape[1,2]. The most common nickel source is nickel sulfate[1]. Nickel ions are reduced to nickel metal by accepting electrons from an electron donor, typically hypophosphite, present in solution as sodium hypophosphite. Some of the hypophosphite is reduced to phosphorous, and is co-deposited with nickel to form a NiP alloy. As the nickel is plated onto the part, the concentrations of nickel and hypophosphite in the bath decrease. Nickel sulfate and sodium hypophsphite are periodically added to replenish these losses. When 100 percent of the original nickel has been replaced, this is termed a metal turnover (MTO).

Simultaneous, to the deposition reaction, a portion of the hypophosphite is converted to orthophosphite, a contaminant to the process, and hydrogen. Alkaline material must be added to the solution in order to maintain acceptable pH. Other contaminants that are by-products of the reaction are dissociated sulfate anions, and sodium cations. As the plating continues to high MTOs, the deposition rate slows, and the internal stress of the deposited plate begins to change from compressive to tensile. Compressively stressed deposits are required for good adhesion and structural stability of the deposit[3,4]. Typically after 6 to 8 MTOs, depending on the required plating quality, the bath becomes unusable and is discarded. Although the effect of sulfate and sodium on EN baths has not been well characterized, it is generally concluded that orthophosphite is the primary species responsible for the decrease in plating rates and the other deposit quality problems experienced after several MTOs[3,4].

REGENERATION TECHNOLOGIES

The three most viable technologies for removing contaminants from electroless nickel plating solutions are: 1) chemical precipitation; 2) chemical precipitation (CP) combined with ion exchange; and 3) electrodialysis[5]. The Environics Division of Armstrong Laboratory has completed a project at the Air Logistic Center Oklahoma City to develop an EN regeneration system, working with a proprietary CP process (Stapleton Company, of Long Beach, California). Martin Marietta Energy Systems, Inc. operator's of the Oak Ridge National Laboratory in Tennessee for the Department of Energy, developed a process that combines CP with ion exchange[6]. This process has not been demonstrated outside the laboratory.

Electrodialysis (ED) is an electrochemical membrane separation technology that can potentially be used to remove contaminants from certain plating and cleaning baths. A typical ED system consists of alternative pairs of cation and anion, charge selective membranes, that separate the cathode and anode of an electrolytic cell pair. A diagram of an ED process consisting of a single membrane pair for this application is shown in Figure 1. The number of membranes can be increased as a function of required system capacity. Contaminated EN solution is fed on the outside of each pair of membranes, and a dilute salt solution circulates between them. When the cell is energized, orthophosphite and sulfate ions migrate toward the anode. The anions pass through the anion charge selective membrane, but are rejected by the cation charge selective membrane, and accumulate in the salt solution. Sodium ions are transfered to the salt solution in a similar manner. Two effluent streams are produced: a concentrate that contains the ionic contaminants originally present in the feed stream, and a diluate stream which can be used for subsequent plating operations. The success of this technology depends on the preferential removal of the contaminants over necessary bath components (nickel and hypophosphite) by the ED process.

LABORATORY TEST PROGRAM

The goal of the test project was to evaluate the feasibility of an electrodialytic process to remove contaminants from, and reuse spent EN plating baths. The evaluation was based on three criteria: 1) the capability of ED to remove bath contaminants; 2) the ability to add the proper replenishment chemicals; and 3) determination of plating quality with a regenerated bath. The two most common EN bath chemistries used at Navy activities, hereafter referred to as Vendors A and B, were selected for the test project.

Test Methods

Contaminated EN solution was obtained by plating carbon steel test panels (1 ft^2 in area) in a nine step laboratory scale EN plating line that consisted of: 1) alkaline cleaning in a heated (150°F) sodium hydroxide solution (10 oz/gal); 2) rinse; 3) acid activation in a 10 percent (by volume) hydrochloric acid bath; 4) rinse; 5) nickel strike (NiCl, HCl); 6) rinse; 7) DI water rinse; 8) electroless nickel plate (180°F); 9) rinse. The EN bath size was 5 gallons. A one mil thick deposit was plated on the test coupons until 4 MTOs were reached (based on a Ni concentration of 7.8 g/l), or until the plating rate, or quality significantly declined. Titration techniques were used to monitor nickel, hypophosphite, and orthophosphite concentrations during the plating operations. Metallurgical testing was performed in order to characterize the resulting deposit.

A total of 12 plating runs were conducted. Afterwards, each contaminated bath was allowed to cool, and was subsequently processed in the ED unit. The objective in dialysizing the spent baths from the first 8 plating runs was to optimize the process. The primary operating parameters (rectifier current/voltage, flow rate, and processing time) were varied while recording total dissolved solids (TDS) concentration, current, and voltage, and collecting performance samples for laboratory analysis. Samples were collected at regular intervals to determine the change in concentration with respect to time of nickel, hypophosphite, orthophosphite, sulfate, and sodium. Plating rate was established by periodically measuring deposit thickness with a micrometer. Once the optimized operating parameters were determined, the spent bath from the eighth plating run was dialysized at the optimized operating conditions. This same bath was subsequently replenished and used through four additional plating and regeneration cycles. Metallurgical testing was performed on four test coupons plated with the bath prior to dialyzation, and after each of the five ED regenerations. As with the first plating runs, 10 samples were collected during plating operations conducted with the regenerated baths and analyzed for the parameters above. In addition, the EN vendor analyzed samples collected from the bath at the beginning and end of 3 of the 5 regeneration runs for any other components (stabilizers or inhibitors) that would require replacing. Optimal operating conditions were determined to be a current density of 0.15 amps/in^2, with a flow rate of 0.4 gpm.

ED Processing

The ED test apparatus consisted of a 9 pair membrane stack, 20 in^2 cathode, a 20 amp rectifier, EN and salt solution holding tanks, and feed pumps. Contaminated EN and salt solutions were continuously circulated through the membrane stack until the desired processing time was reached. Optimal processing time was determined by weighing adequate contaminant removal against the increased losses in necessary bath components experienced with longer processing times. It was further observed that changes in orthophosphite concentration tracked very closely with reduction in TDS concentration, as seen in Figure 2. TDS was subsequently used to control the process. Based on the stoichiometry of the reaction, each MTO results in approximately 30 g/l orthophosphite present in solution, a concentration that corresponds to approximately 180,000 to 200,000 g/l TDS present at the end of a plating run. Contaminated EN baths were dialysized until TDS concentration was reduced to approximately 60,000 g/l; which is equivalent to a bath at 1.0 MTOs, based on orthophosphite concentration.

RESULTS

Contaminant Removal

Figure 3 is a plot of change in concentration with respect to time of orthophosphite, sodium, and sulfate. Initial and final orthophosphite, sodium, and sulfate concentrations were 170 and 28 g/l, 54 and 10.5 g/l, and 67 and 14 g/l respectively. The process was very selective for sodium over nickel. Nearly 75 percent of the original nickel present was retained in the plating bath. The ED system was run with a rectifier setting of 0.15 $amps/in^2$ for 56 hours, with a flow rate of 0.4 gpm.

Bath Replenishment

Standard chemicals supplied by the EN vendors were used for bath replenishment throughout the test project. Replenishment chemicals contain nickel sulfate, and sodium hypophosphite to replace material that is deposited, and stabilizers and inhibitors make up for dragout losses. In addition to these losses, when regenerating an EN bath, it is necessary to make up for any bath components that are removed by the ED process. The bath composition prior to and after subsequent ED processing is contained in Table 1.

Deposit Characteristics

During the entire test program approximately 360 test coupons were plated. These plating operations served two purposes: 1) generate contaminated EN solution; 2) characterize plating characteristics with a fresh bath and regenerated bath. Metallurgical testing was conducted on 4 test coupons from each plating run. One plated with a fresh bath (or immediately following regeneration), one plated at 6 MTOs, and 2 plated at the midpoints. Metallurgical testing consisted of analyzing the coating thickness, phosphorous content, hardness, corrosion resistance, and internal stress. A micrometer was used to measure coating thickness and establish plating rate. Phosphorous content was measured by scraping off a portion of the deposit and analyzing it with a high pressure liquid chromatagraph. ASTM Standard B578 was used to measure microhardness. A 100g load was used and converted to Knoop hardness. Corrosion resistance was tested by exposure in a salt spray chamber in accordance with ASTM B117 for a period of 10 days. Internal stress was measured using a spiral contractometer. The results of these tests performed on coupons plated in Vendor B chemistry, with a fresh bath, and following four regeneration cycles are summarized in Table 2. Results of hardness, salt spray, and phosphorous content tests are averaged values for the four test coupons analyzed from each plating run. Test coupons plated with a regenerated path displayed corrosion, and hardness properties, and had a phosphorous content close to those plated with a new bath. Internal stress levels were tensile on all test coupons and the stress levels were slightly higher in deposits from the regenerated bath, however, internal stress lower than 1000 psi are considered acceptable. Based on these results the EN deposit plated with a regenerated bath are as good as those plated in conventional EN plating.

ECONOMICS

Data generated at the laboratory scale was used for scale up to a 300 gallon bath size. Economic data was based on an assumed annual production rate of 328 kg of nickel deposited. Vendor B chemistry plates 8.86 kg of nickel per MTO and the total MTOs per year required to plate 328 kg would be 37 . Chemical procurement, and utility costs for conventional and regenerable bath systems were calculated based on this amount. Frequency required for bath disposal was calculated based on a minimum plating rate criteria. Plating rate continually deteriorates in an EN bath due to the increasing levels of orthophosphite in the bath. It was assumed that the bath would be either discarded and replaced or regenerated with ED whenever the plating rate fell below this level. Using Vendor B chemistry in the conventional mode, plating rate falls below 0.3 mils per hour after approximately 3 MTOs. A regenerated bath falls below the minimum threshold after 2 MTOs. Based on these assumptions a conventional plating bath would be discarded 12 times per year, and a regenerable bath would require ED processing 18.5 times per year.

A brief economic comparison between conventional and regenerable EN plating with electrodialysis is presented in Table 3. Chemical procurement costs are proportional to the quantity of nickel plated and are therefore essentially the same. Slightly lower chemical cost are realized with ED due to the ability of the ED process to salvage a significant portion of the nickel and a portion of the hypophosphite and return them to the bath. The comparison includes ED alone and ED combined with an evaporation step to reduce waste disposal. Capital equipment unit costs for labor, electricity, and waste disposal are contained in the table. Capital equipment costs for ED alone are $35,874, and ED with evaporation are $49,409. The comparison assumes that with the exception of waste disposal and the slight difference in chemical procurement. the other production costs associated the actual plating operations will be the same.

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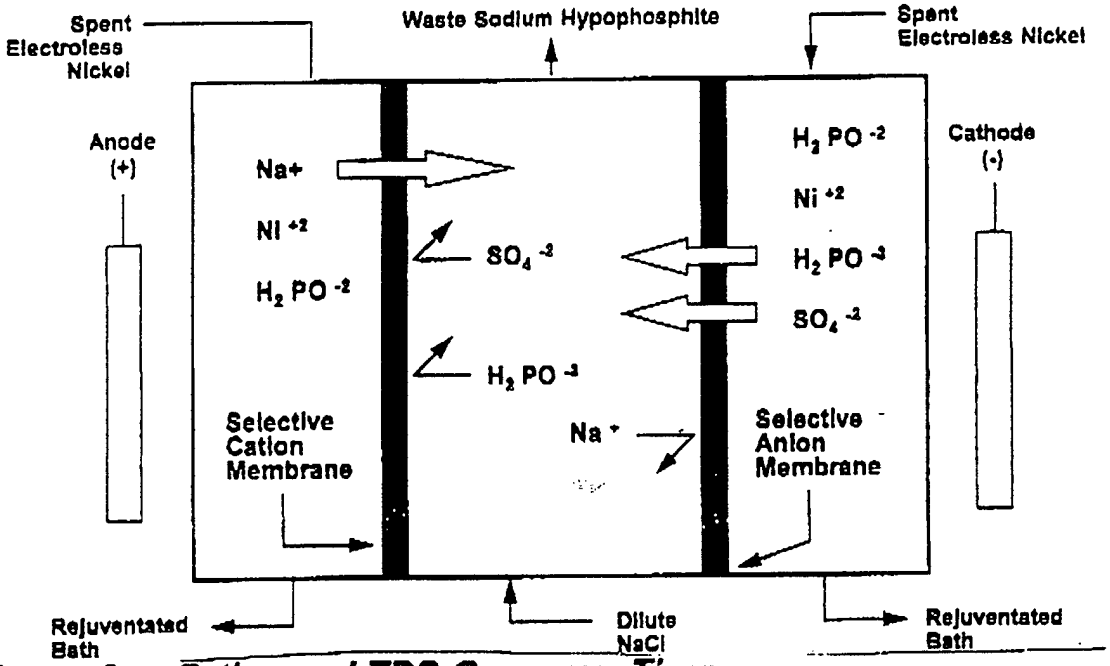

Figure 2 - Ortho and TDS Conc. vs. Time

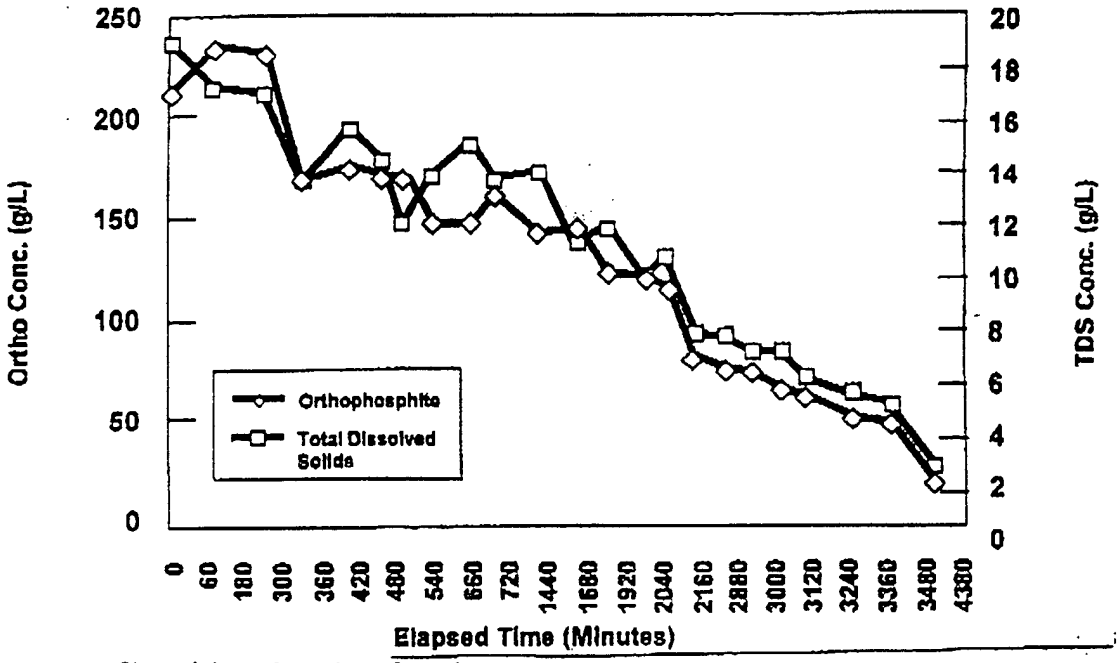

Figure 3-3 - Contaminant Removal

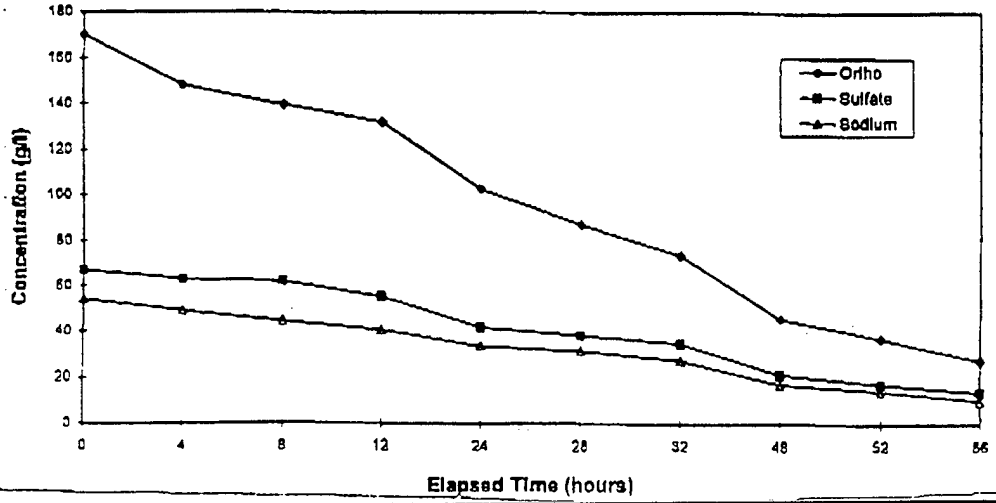

Table 1 - EN Bath Composition (Vendor B Chemistry)

Parameter	Complexors % of Original	Ortho-phosphite (g/l)	Nickel (g/l)	Hypo-phosphite (g/l)
New Bath	100	0	7.8	38-42
After 6 MTOs	107	165-185	7.2	13-17
Dialysized Bath	54.9	41	4.9	2.8
Replenished Bath	100	41	7.8	38-42

Table 2 - Plating Characteristics

Physical Parameter	Fresh Bath	After 6 MTOs	End ED Run 1	End ED Run 2	End ED Run 3	End ED Run 4
Corrosion (ASTM D610)	4.5	---	6.8	7.5	3.0	3.2
Phosphorous Content (%)	10.0	---	10.0	9.4	10.3	10.2
Hardness (Avg. KHN)	409.8	---	401	403.5	402.5	407.5
Internal Stress (psi)	220	220	450	400	340	220

Table 3 - Economic Comparison

Cost	Conventional EN	ED Regeneration	ED w/ Evaporation
Chemicals	$68,645	$65,700	$65,700
Disposal ($2.46/kg)	$44,246	$23,183	$2,218
Capital Equipment	N/A	$35,874	$44,915
Elec. ($67.50/MW-hr.)	N/A	$713	$1,412
Labor ($79.80)	N/A	$12,000	$12,000
Maintenance	N/A	$1,000	$1,000
Payback Period (yrs.)*	N/A	0.8	0.4

* Assuming a ten year equipment useful life, and a 5 percent discount rate