Advances in the Electrodialysis of Electroless Nickel Baths

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Electroless nickel processes build salt content during use because the nickel ion must be replenished with a nickel salt and the reducing agent produces a salt as well. When the salt content reaches a certain level, the bath must be discarded. One method that has been used to extend the life of electroless nickel processes is electrodialysis. Generally, electrodialysis of electroless nickel solutions is a batch process that is expensive and time consuming. This paper will discuss the advancements that have been made to allow electrodialysis to be a continuous on-line process that operates while the bath is being used to maintain the plating solution at a true steady state. The continuous method eliminates the processing time required for the batch process.

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Introduction

Electroless nickel processes build salt content during use because the nickel ion must be replenished with a nickel salt and the reducing agent produces a salt as well. When the salt content reaches a certain level the bath must be discarded. One of the methods that has been used to extend the life of electroless nickel process is electrodialysis.

Generally, electrodialysis of electroless nickel is a batch process [1,2]. A bath is worked until it is close to being spent and then the technique is used to regenerate the bath. While the batch method works well there are three operational problems that can be improved on. First, the batch method is somewhat time consuming since it may take 3-5 days for the electrodialysis system to remove the salts. Second, this method requires that several baths be kept in inventory: a bath being used, a bath being treated, and one or more baths that have been rebuilt and ready to use. Third, the electrodialysis stack must be rather large so that the treatment time is reasonable.

Modifications of the batch process have been proposed. In these modifications a portion of the operating plating bath is removed from the tank temporarily, cooled to near room temperature, and treated with the electrodialysis unit. During the treatment time the plating bath continues to operate. Once the portion of the bath has been treated and rebuilt it is heated and returned to the production line and another portion of the bath is taken. This type of cycle can be used to keep the production bath close to steady state and the three operational problems mentioned above are corrected. The only operational problems that might remain with this method is that the equipment needed to automate the process might be rather complicated and there will be some energy losses in cooling and reheating the bath.

A true continuous electrodialysis operation would reduce the energy losses and could be used to simplify the operation. Advances have been made that allow electrodialysis to be a continuous on-line process that operates while the bath is being used. The continuous process is used to maintain the production bath at a true steady state. This paper will discuss these advancements.

Introduction to Electrodialysis

The methods used today for electrodialysis of electroless nickel are the offshoots of R&D work from the 1960's and 1970's to find practical ways for desalination of sea water and brackish waters from streams and wells. Examples of reports of government funded work include those by Davis and Lacey [3,4] where the available membranes were screened for their suitability for this type of work and were then tested in brackish wells in the southern United States. Reports of this type are not kept in libraries and thus are not readily available. However, there are discussions in a number of texts including works by Korngold [5] and Shaffer and Mintz [6] that explore the technology and provide some details.

The electrodialysis membranes are made of resins that are very similar to those used for ion exchange or deionization beds. The major difference is that for electrodialysis the resins are molded into thin sheets over a cloth support rather than into the beads used for ion exchange and deionization. The chemistry of the resins is shown in Figure 1 [5]. The cationic exchange resin contains numerous sites occupied by the $-SO_3^=$ group that can form a weak chemical association with positively charged cations. Likewise, the anion exchange resin contains numerous sites occupied by positively charged quaternary nitrogen groups that can associate with negatively charged anions.



Figure 1 Structures of Cationic Resin and Anionic Resin

The mechanism that causes an ion to move through a membrane includes the application of a DC current and the

nature of a membrane. Under an applied DC potential an ion, such as a positively charged sodium ion for example, will be attracted toward a negatively charged cathode. If the sodium ion meets an anionic membrane the positively charged groups in the membrane impede its transfer through the membrane despite the sodium ion's attraction to the charged cathode. However, if the sodium ion meets a cationic membrane the negatively charged functional groups will form a weak association with the sodium ion. The ion will be driven to move from one functional group to another by the direction of the DC polarity until it passes completely through the membrane into the solution on the other side. Similarly, negatively charged anions, like orthophosphite, will be attracted to the positively charged anode and will be allowed to pass through the anionic membrane but a cationic membrane will keep it from migrating further.

Several membrane properties are important in choosing the proper material for an application, including the following:

- 1. Mechanical Strength. The cloth that is used to support the resin can withstand a certain pressure.
- 2. Chemical Resistance. The resin and the support must be able to withstand the chemical environment.
- 3. Permselectivity. The ability of a membrane to be selectively permeable to certain anions or cations.

Figure 2 Electrodialysis Cell



- 4. Limiting Current. The current density at which water splitting and precipitation of salts occurs.
- 5. Water Transport. Water is naturally transported through a membrane with an ion. There is also a tendency for water to be transported by osmosis if there is a large concentration difference on either side of a membrane. Some membranes transport water more readily by osmosis than others.
- 6. Temperature Stability.

A more complete discussion of these properties can be found in Korngold [5] and Shaffer and Mintz [6].

A membrane stack is constructed with alternating anionic and cationic membranes as in Figure 2. Gaskets placed between each membrane pair are designed to distribute two solution steams into alternating channels between the membranes. Through the one channel flows the electroless nickel solution and through the other channel flows the waste salt solution. Electrodes are placed a both ends of the stack. The anode is usually platinized titanium (or a similar conductive coating) and the cathode is usually stainless steel [3,4,5,6]. The distance between the two membranes affects the solution flow and electrical conductivity [4]. Finally, between each pair of membranes is placed a layer of woven polypropylene netting that keeps the membranes separated and helps to cause a turbulent flow inside the channel.

The subject of electrodialysis applied to electroless nickel baths has been discussed by Kuboi [5], Kingenberg and Schario [6], Steffani and Meltzer [7], Bellemere [1] and Crotty [2]. All of these authors describe similar equipment and list the advantages, with processing details and costs, for electrodialysis use in the recycling of electroless nickel baths.

The Continuous Process

The application of electrodialysis in a continuous high temperature mode requires that all parts of the equipment

be capable of operating at high temperature. This includes items like valves, pumps, tubing, flow meters, and the electrodialysis stack. All the plumbing parts of the system are easily found made from temperature resistant materials. However, the most commonly used electrodialysis membranes are rated at a maximum temperature of about 55°C (120°F) while electroless nickel baths typically operate around 88°C (190°F). A suitable membrane has been obtained and built into a stack

While most electrodialysis stacks used for electroless nickel use a two chamber design, one for the electroless nickel and one for the orthophosphite salt waste, a three chamber design is used for a wide variety of electrodialysis applications. The third chamber is the electrode wash chamber, which contains fresh conductive solution that washes both the cathode and the anode. For the continuous high temperature application the three chamber design is best because the electrode wash helps to separate nickel containing solution from the cathode, thus preventing nickel buildup on that electrode.

A pilot laboratory sized electrodialysis unit was designed with a 57 L electroless nickel tank, a pumping system that provides about 3-4 L/min of solution flow, and a stack with 20 membrane pairs having a total surface area of 0.2 m² of cathodic membrane. A DC voltage was applied across the membrane stack to drive the electrodialysis transfer of ions.

The electroless nickel feed entered the electrodialysis unit at a temperature of about $88^{\circ}C$ (190°F) and exited the unit

at about 77°C (170°F). This feed was returned to the plating tank where the tank's heater easily took care of keeping the bath at operating temperature

A sample of a proprietary midphosphorus electroless nickel solution was obtained from a metal finishing shop. This bath had been worked in normal production for about 4 MTO. The sample was placed in the 57 L tank and heated to 88°C (190°F). A load of parts was placed into the electroless nickel solution and the electrodialysis unit was started. As the work pieces were plated with electroless nickel the bath was maintained with normal components for the proprietary EN process. The two components are A, the nickel component, and C, the hypophosphite component. The addition ratio of the two components is 1:1. During this pilot laboratory run it was found that a ratio of 1:1.2 of the two components is needed to compensate for the fact that hypophosphite ions as well as orthophosphite ions pass through the electrodialysis membrane stack into the waste stream. Table 1 lists the analysis results of the run.

Table 1 shows that as the run proceeded the hypophosphite was maintained at the usual 30 g/L and the orthophosphite concentration was maintained at about

		Table 1 High Temperature ED						
Load	Amps	ED Amp.Hrs	MTO	Plating Rate	Ni Used	Hypo Used	Hypo g/L	Ortho g/L
				Mil/Hr	g	g		
0			0				33.9	117
1*	3	19	0.3	0.58	121	709	32.1	110
2*	3	24	0.55	0.56	103	865	26.0	113
3*	3	25	0.85	0.59	123	743	30.5	112
4	7	35	1.24		160	958	28.5	112
5	7	64	1.87	0.60	262	1573	27.8	113
6	7	52	2.34		194	1158	28.8	110

*Bath loading 0.1 ft²/gal. All other loads were 0.2 ft²/gal

110 g/L. The amperage drawn by the stack will be largely proportional to the amount of material that passes through the membranes.

During this portion of the test about 2.3 MTO of work was obtained from the plating tank while the nominal "age" of plating bath remained at about 3-4 MTO (about 110 g/L of orthophosphite).

During three of the work loads the concentration of materials was allowed to build up in the ortho waste tank. Table II shows the concentrations of nickel metal ions, sodium hypophosphite and sodium orthophosphite. After about 180 amp.hours of operation, 650 g of nickel was plated and 53 g (8.2%) of nickel was lost to the salt tank. Also, during this time 3894 g of hypophosphite was added to the tank, of which 907 g (23%) is lost to the salt tank. The rest of the hypophosphite was transformed into sodium orthophosphite by the electroless nickel plating process.

One important consideration is the size of the cell used for this work. When compared with cells used for the normal batch operation, the continuous operation requires a much smaller cell.

	Table II
]	Materials Transferred to
	Ortho Waste Tank

Material	Weight
	Transferred
Nickel	53.2 g
Sodium Hypophosphite	907.2 g
Sodium Orthophosphite	3100 g

Conclusions

The use of an electrodialysis stack that has been designed to tolerate high temperatures makes it possible to maintain an electroless nickel bath continuously at a steady state, where the bath remains at the same "age", or essentially at the same concentration of sodium orthophosphite.

As with the batch treatment method, there are losses of nickel, sodium hypophosphite and other components of the electroless nickel bath. However, the losses from the two methods are equivalent in magnitude.

The continuous method allows the user to operate with a single bath, while the batch process requires three or more baths be kept in inventory at all times. The continuous high temperature method reduces the heating losses expected by the modified batch process.

The processing time for the batch processing is eliminated since the electrodialysis unit runs concurrently with the electroless nickel bath and can be designed to keep up with production in most cases.

Most significantly, the size of the electrodialysis stack, the most expensive part of the system, can be much smaller than the stack needed for batch processing.

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