ANODIC PASSIVATION OF ELECTROLESS NICKEL PLATING TANKS

By

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ABSTRACT

Historically, electroless nickel plating tanks have been constructed of polypropylene or stainless steel, and have been passivated periodically with diluted nitric acid to protect their surfaces against unwanted plating. This practice limits the amount of plating which can be produced, and usually requires that at least two plating tanks be available for production. Its use also increases the amount of waste and its associated treatment costs.

In 1990, an electrochemical system was introduced in the United States which produces a passive film on stainless steel by carefully controlling its potential. This technique, called anodic passivation, prevents plate-out in electroless nickel solutions and avoids the need to strip the tank on a daily basis. During the last seven years, the acceptance of this system has grown dramatically, and today there are more than one hundred instruments in use.

This paper describes this system and its theory of operation. Several case histories showing the system's value are also presented, along with the economic justifications for its use.

INTRODUCTION

Anodic passivation is an electrochemical system for continuously passivating the stainless steel components in electroless nickel plating baths. Its use helps prevent plate-out and avoids stripping the tank with nitric acid on a daily basis. The system also reduces the disposal of spent nitric acid solutions and the cost of their waste treatment.

The system is based upon the electrochemical technique of anodic protection, which has been used for many years to prevent corrosion in the chemical industries. Anodic protection produces a passive film on the stainless steel by discharging a small impressed current from it at a carefully controlled potential. This film is very similar to that produced by nitric acid passivation and prevents deposition of electroless nickel, while also avoiding corrosion.

The difference between this technique and the *reverse current* method used in the past, is that with *deplating* the potential of the stainless steel is not controlled. Instead a large current is discharged from the metal to keep it from plating.[1] This current, however, also causes the stainless steel to corrode and become etched, especially at the welds. With anodic passivation only the amount of current needed to maintain the potential of the metal within a desired range and to prevent plate-out is discharged.[2] In addition, at the proper potential, most current is discharged through oxygen evolution rather than by metal dissolution.

Not only will anodic passivation protect the plating tank, but it will also reduce plate-out in the stainless steel pumps and heat exchangers electrically connected to it. Because protection is not dependent upon current flow, passivation does not change significantly with distance. In one installation, passivation was found to extend more than 60 feet inside a 1 inch diameter pipe while its potential varied by only 0.3 mv.[3]

Hundreds of anodic protection systems have been used on electroless nickel plating tanks in Europe, some for more than twenty-five years.[4] During the past four years, more than one hundred systems have been installed in North America. These instruments have been very successful and have allowed the plating baths to remain in the same tank for as long as four months without nitric acid passivation.

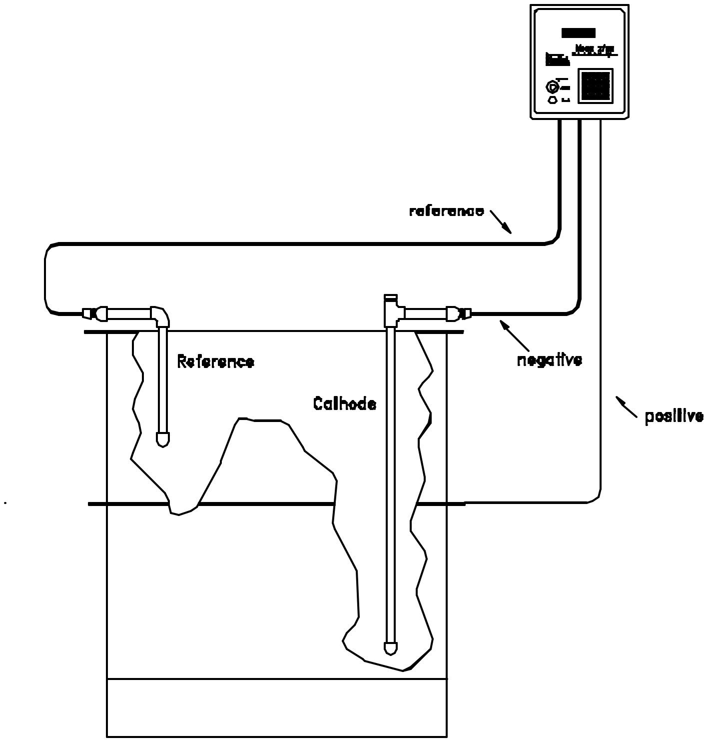
HOW IT FUNCTIONS

Clean stainless steel is normally passive in electroless nickel plating solutions and not susceptible to either corrosion or to the deposition of plating. Passivity, however, is lost by galvanic coupling with plating parts, by the present of dirt or debris on the metal, or by either mechanical or chemical abrasion.

Anodic protection prevents chemical reactions, like corrosion or plating, by controlling the potential of the metallic surface. In electroless nickel solutions it serves to prevent the break down of stainless steel's natural passivity. It strengthens the oxide film upon the surface of the metal and reduces its solubility, in much the same way as does nitric acid passivation.

To use this technique, a potentiostat is connected to the tank, and a cathode and a reference electrode installed in it, as illustrated by Figure 1. The potentiostat will then maintain the tank at a constant potential (with respect to the reference electrode) by passing a small current between it and the cathode.

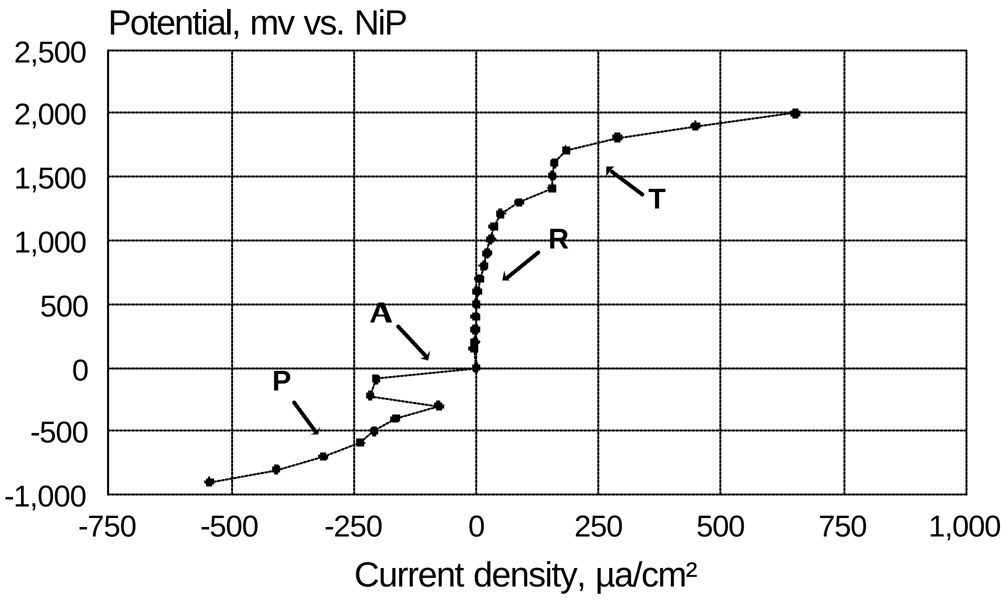
Figure 1
System Layout



Anodic protection is only possible for those materials and those solutions whose electrochemical behavior follows the classic active/passive pattern illustrated by Figure 2. Fortunately this behavior is typical for stainless steel and titanium in electroless nickel plating solutions.

Polarization diagrams of this type are generated by plotting the current density received or discharged from a metal (which is directly proportional to its plating or corrosion rate) when its potential is controlled versus a reference. The polarization diagram shown in Figure 2 was developed for passivated stainless steel in the traditional Kanigen plating solution (0.1 mole/L $NiSO_4$, 0.3 mole/L NaH_2PO_2, 0.3 mole/L lactic acid, 0.03 mole/L propionic acid and 1 mg/L lead at 5 pH and 90°C), but is typical for acid electroless nickel baths.

Figure 2
Potentiostatic Behavior of Stainless Steel
In Electroless Nickel Solutions



Point *A* on this diagram represents the potential of freshly activated stainless steel (versus a reference of the electroless nickel reaction) just before it begins plating. This is also the active region where corrosion of the metal would occur lacking other influences. As the potential is increased negatively (cathodically) toward Point *P*, current is applied to the stainless steel and nickel will be electroplated upon it. This is the reaction which occurs on the cathode.

If the potential is forced in the positive (anodic) direction, however, current is reduced and electroplating slows. At Point *R* the plating reaction is in equilibrium and the oxidation of hypophosphite equals the reduction of nickel.

Point *R* is also the rest potential of passivated stainless steel in an actively plating solution. Stainless steel will remain at this state, without plating, while its passivation is maintained. If, however, it loses its passivity, its potential will shift toward Point *A* and plating will begin.

As the potential is increased further in the positive direction, current will decline to zero or negative values, and will stay at this level until the potential reaches approximately one volt. This range is the passive region for stainless steel. Here the metal's surface is covered by a tenacious oxide film which retards corrosion and where plating cannot occur. In this region, most current discharges from the tank through oxygen evolution rather than by metal dissolution. Above Point *T* is stainless steel's transpassive region where current rapidly increases and where severe corrosion can occur.

Accordingly, if the potential of stainless steel can be controlled within the passive region, both plating and corrosion can be prevented. If not enough current is applied, however, the passivity of the stainless steel will be lost and plating will occur. If the tank discharges too much current, it will be forced into the transpassive region and severe corrosion will occur. Thus, for anodic protection to be successful, careful control of potential instead of current is mandatory.

EASY TO OPERATE

Anodic passivation systems are very easy to use. To install the system, it is only necessary to locate the cathodes and the reference electrode in the tank, and to connect the instrument's cables to them and to the tank as illustrated in Figure 1.

The cathodes should have an exposed area equal to approximately one half percent of the area of the tank and its components. Typically, two 1/4 inch diameter stainless steel rods, extending from the top lip to 6 inches above the tank bottom at opposite corners, are adequate for current collection. Because anodic protection is dependent on potential and not current, passivation does not depend on distance and current distribution is not important.

The cathodes and the reference electrode, however, must be insulated from the tank. This is usually accomplished by enclosing them inside a perforated, 1 inch diameter CPVC pipe. If they are not shielded with a pipe, the cathodes and reference electrode must be separated by at least 6 inches from each other and from the tank's walls.

Before the anodic protection system is energized, the tank should be passivated with 30 percent nitric acid. This action will ensure a clean surface for the instrument to protect and will reduce the current required. Then after the electroless nickel solution has been transferred into the tank and heated to at least 150°F (65°C), the cathodes and reference electrode should be carefully cleaned and activated with a nickel strike. The strike is necessary to ensure that they begin plating and to provide good adhesion.

Next, the anodic passivation system should be adjusted to control the potential of the tank to between +0.6 to +0.8 volt versus the electroless nickel reference. The actual current needed to maintain a tank's passivity will depend upon its size and upon the amount of dirt and debris in it, but typically is one to three amperes. Once the reference set point has been established, no further adjustment by the operator is necessary. The instrument will automatically change its current output to maintain the tank's potential at the set point.

Once the anodic protection system has been energized, it should always remain turned on, and the tank should remain filled with solution, even when it is cold. Otherwise, protection may be lost. The instrument should only be turned off when the bath is transferred and the tank is filled with nitric acid for cleaning. Leaving it energized when nitric acid is present, can result in severe corrosion.

The current supplied to a tank may temporarily increase if a part is dropped into it, but will return to its normal level after the part is passivated. The system will also passivate any dust or dirt which settles onto the bottom of the tank. The presence of parts or dirt will not cause the stainless steel to start plating, and so the solution does not have to be transferred to allow the part to be retrieved or the tank to be cleaned. As debris collects on the tank's bottom, however, the current required to maintain passivity will increase, and may be used as a measure of the tank's condition.

Anodic passivation does not stop dust, dirt or metal particles from accumulating in the solution. Thus, it is good practice to periodically clean and passivate the stainless steel with 30 percent nitric acid. The frequency of cleaning depends upon the quantity of soils introduced and upon solution filtration. Most electroless nickel plating systems, however, can be operated for three weeks or more between passivation treatments.

The cathodes and reference electrode also require periodic cleaning to remove the plating built up on them. Provided they are large enough and have been properly cleaned, they should only need stripping every few weeks. They should be visually inspected weekly, however, to check for buildup and for flaking. Poorly adherent deposits falling onto the bottom of the tank will increase the current required from the instrument and may affect plating quality.

ECONOMIC JUSTIFICATION

Historically, it has been necessary to transfer the bath from electroless nickel plating tanks and passivate them with nitric acid after one to five days of operation. The frequency of transfer depends upon the type of bath used and how well it is maintained. With an anodically protected, stainless steel tank, however, this period can be extended to three or four weeks or even longer. This is illustrated by the following table, showing the experience of some facilities that have converted to this type of tank.

Facility	**Tank Size**	**Transfer Period**	
		Before	**After**
L	225 gallons	<1 day	>5 days
F	300 gallons	1 day	2-3 weeks
U	450 gallons	5 days	12 weeks
M	1100 gallons	2 days	3-4 weeks
K	2000 gallons	2-3 days	4 weeks
T	2200 gallons	2 days	3-4 weeks

On average, facilities using this system have extended the time between passivation from about two days to almost 3½ weeks.

Every transfer results in a cost to the plating facility. The operator's labor to transfer the bath to a second tank, rinse and fill the tank with nitric acid, then pump the nitric out after passivation, and finally rinse and neutralize the acid requires time. This time also results in lost production, when the tank could be plating work and generating revenue.

Another direct cost of passivation is the nitric acid or plating solution lost during transfer. Typically, 1/2 inch or more of solution is left in the bottom of tanks after transfer. Not only does this solution have to be collected and waste treated, but the lost plating solution effectively depletes the bath and must be replenished. Along with the solutions lost during transfer, the water used to rinse and neutralize the tank between steps must also be waste treated.

The cost of making up and disposing of the nitric acid passivation solution can also be significant. A 30 percent by volume solution is most commonly used for passivation. The life of this solution depends on how often the tank is passivated. Where tanks are being passivated every few days, the nitric solution will last about six months. With anodic passivation, this solution can last for several years.

A survey of 73 electroless nickel facilities was recently conducted to establish their operating and waste treatment practices.[5] This survey found the following mean times, losses and waste treatment costs for transferring the bath in an electroless nickel tank.

Transfer Time	13 minutes/100 gallons
Transfer Losses	0.5 gallon/100 gallons
Transfer Rinses Losses	13 gallons/100 gallons
Waste Treatment Cost	$0.08/gallon
Nitric Acid Disposal Cost	$2.62/gallon

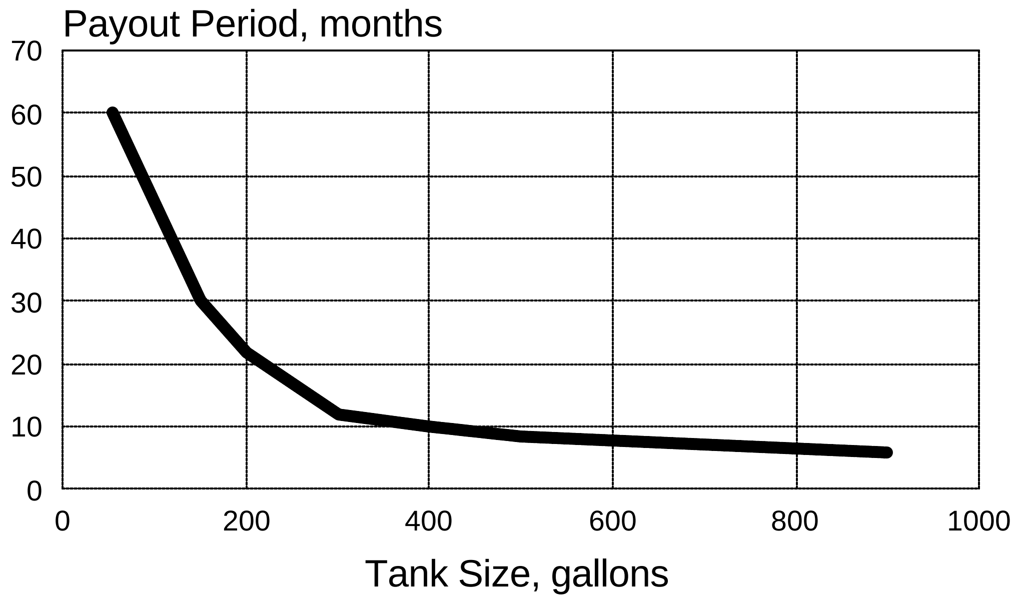
This data, combined with the typical costs of $12 per hour for labor, of $18 per gallon for replenishers, and of $2 per gallon for nitric acid, allows the cost of a transfer to be calculated. The following table compares the transfer costs of a polypropylene lined and an anodically protected stainless steel, 300 gallon plating tank for a one year period.

Item	**Polypropylene**		**Stainless Steel**	
	Loss	**Cost**	**Loss**	**Cost**
Number of transfers	130		15	
Man-hours of labor	84	$1,008	10	$117
Gallons of bath lost	221	$558	26	$64
Waste treatment		$17		$2
Gallons of nitric lost	221	$129	26	$15
Waste treatment		$17		$2
Gallons of DI rinse lost	10,140	$1,014	1,170	$117
Waste treatment		$811		$94
Number of nitric acid makeups	2	$360	1/2	$90
Disposal of spent nitric	600	$1,572	0	0
Total		**$5486**		**$501**

Thus, anodic passivation can save almost $5,000 each year in labor, chemicals and waste treatment for a 300 gallon tank. The same spreadsheet approach can calculate the savings for any size tank. Typically, the annual savings will range from $1,000 for 50 gallon tanks to $15,000 for 900 and 1000 gallon facilities. Of course, costs will vary with individual conditions and should be calculated based on the facility's costs and practices.

Such savings can easily pay to purchase and install a potentiostat and its cathodes. Frequently the payback for this investment is less than one year. This is illustrated graphically in Figure 3, which shows the period of return for different anodically protected, plating tanks.

Figure 3
Payout Period For Anodically Protected Stainless Steel Construction



CONCLUSION

Anodic passivation is an easily operated and highly effective method of preventing unwanted plate-out of stainless steel tanks and components in electroless nickel plating solutions. It allows the plating system to be operated for extended periods without the need to transfer the bath and passivate the tank, while reducing the disposal of spent nitric acid solutions and the cost of their waste treatment. Anodic passivation can increase productivity and reduce the cost of operating electroless nickel plating systems.

REFERENCES

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3. Wolfgang Frick, *Protektostat, anodischer Schutz metallischer Behälter beim außenstromlosen (chemischen) Metallisieren*, **Metalloberfläche**, Vol. 41, No. 12 (1987) p. 578.

4. Walter Anke, private communication, 20 August 1989.

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Ronald N. Duncan

BIOGRAPHICAL SKETCH

In Memory of Ron Duncan

Ron Duncan served as Vice President of Palm International, Inc., where he led the company's technical and educational initiatives. Prior to joining Palm, he was Director of Research at Elnic, Inc., focusing on electroless nickel formulation and materials research.

Before entering the metal finishing industry, Ron spent 12 years in the oil sector with Exxon and Caltex Petroleum Corporations, tackling materials and corrosion challenges. His work took him across the globe—including the United States, Middle East, Europe, South America, and Africa—where he developed a reputation for his deep expertise and practical problem-solving.

Ron held a BE in Mechanical and Metallurgical Engineering from Vanderbilt University. He was a Registered Professional Engineer and a certified Corrosion Specialist through NACE. A leader in technical standards, he chaired NACE task groups T-1G-19 and T-6A-53, contributing to authoritative reports on electroless nickel and other metallic coatings. He also served on the AESF's Electroless Committee.

Throughout his distinguished career, Ron authored more than fifty technical papers on corrosion, coatings, and electroless nickel. His work appeared in Materials Performance, Plating and Surface Finishing, Metals Progress, Products Finishing, and Finishers Management, as well as in numerous industry conferences. He was the principal author of the electroless nickel chapter in Volume 5 of the Metals Handbook and was honored with the AESF Gold Medal in 1996 for the best paper published in Plating and Surface Finishing.

Ron also directed the Electroless Nickel School, a comprehensive four-day seminar presented by Palm, which educated professionals in all aspects of electroless nickel technology.

Ron Duncan passed away on December 15, 2006. He is deeply missed by his family, colleagues, and the broader surface finishing community. His legacy of innovation, mentorship, and integrity continues to inspire all who had the privilege of working with him.