

EN Process Performance: Effect of Agitation, Loading and Stabilizer Level

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Abstract

Numerous articles have been published and studies conducted on the chemistry of electroless nickel and its relationship to deposit performance^{1,2}. The main core of this published work to date concentrates on mechanical and physical properties, such as wear and corrosion resistance of the coatings. Reviews of EN chemistry, mechanisms and solution operation are also available and beyond the scope of this paper^{3,4}. There is, however, limited information on the combined effects of agitation, loading and stabilizer levels on the performance of an electroless nickel process and the resulting deposit. The purpose of this paper is to present the results of such a study.

An experimental matrix consisting of nearly 200 experiments were conducted on a typical high phosphorus electroless nickel process. Type and intensity of agitation, workload to solution volume ratios and stabilizer levels all were varied and the synergistic effect was evaluated for critical process characteristics or what will be referred to as the *six P's*.

- 1.) Deposit *porosity* and inherent corrosion protection
- 2.) Deposit *passivity*
- 3.) *Pitting* of thick deposits
- 4.) Edge *pullback* phenomena
- 5.) *Plating* rate
- 6.) *Plate-out* or solution stability

Results of all experiments will be presented along with recommended process modifications and improvements. An EN plater can implement the practical suggestions with immediate success regardless of electroless nickel type or supplier.

Introduction

Discovered in 1946, electroless nickel by hypophosphite reduction has grown from a lab curiosity to one of the most reliable coatings available in our industry. The broad commercial acceptance of EN is due, in part, to a wealth of beneficial properties that are widely recognized and known. Along with the commercial success came major technological advancements. Many of the common problems with electroless nickel that a plater encountered 20 years ago have become a thing of the past. Through a concerted effort from platers and suppliers, process traits such as solution turbidity, decomposition and short solution life are for the most part gone. Marginal performing processes based loosely on the original "Kanigen" style chemistries have all but been replaced by a myriad of specialty electroless nickel systems that offer properties unique for many of today's demanding applications.

Proprietary systems available today, are, for the most part, easy to make up and operate. Concentrates are properly balanced and variations in chemistry are minimal when operated properly. Having said this, modern electroless nickel still has its technical flaws.

EN is a process that is in a state of perpetual conflict. On one hand a pure, stabilizer (poison) free solution is desired to produce a deposit with ideal properties such as low stress and porosity as well as high passivity and zero pitting. On the other hand, the EN process must offer performance benefits such as reduced plate-out, high plating rates and in some cases, bright deposits. Most often a balance exists between the two, but not without problems.

Poor corrosion protection due to high **porosity**; inferior chemical resistance due to inadequate **passivity**; **pitting** of thick deposits; edge **pullback** with small workloads; slow **plating** rates; **plate-out**. At some point, all of us have encountered one or more of these afflictions. A summary of each these follows:

1.) *Deposit porosity and inherent corrosion protection*

Porosity of electroless nickel deposits determines corrosion protection for a vast majority of applications. To follow this line of reasoning we must begin with the galvanic series. When two dissimilar metals are coupled, in this case substrate and coating and are placed in an ionic solution of some kind (saltwater for example) one metal must be the anode and the other a cathode. The anode oxidizes, releasing electrons and in effect corrodes. In the case of sacrificial coatings such as zinc or cadmium they are most often anodic to the substrate and preferentially corrode, thus protecting the cathodic substrate.

With barrier coatings like electroless nickel the opposite holds true. Electroless nickel is most often the cathode^(A) and corrosion of the anode (the substrate) occurs through the pores and voids of the EN deposit. It is rare when the corrosion resistance of the actual electroless nickel deposit comes into play.

Over the past decade much has been made of methods to improve corrosion protection of electroless nickel deposits by reducing porosity. This has been accomplished through improved pre-treatment⁵, various heat treatments⁶ and in depth chemistry modifications⁷. Even with this work there remains a certain amount of obscure practices used to attain consistent corrosion performance of electroless nickel deposits. An objective of this study is to provide methods to minimize porosity through modified solution operation techniques.

2.) *Deposit passivity*

Passivity is defined as “A condition in which a metal, because of an impervious covering of oxide or other compound, has a potential much more positive than that of the metal in the active state.”⁸ As it relates to electroless nickel, passivity has been a quick and somewhat reliable method to test relative purity of a particular deposit. It has been used in the past as a rough measure of phosphorus content^(B), although a direct correlation is highly suspect.

^(A) 77% of EN applications are on steel or aluminum. R.N. Duncan, Electroless Nickel: Past, Present and Future, EN Conference 95,

^(B) RCA Nitric Acid Test. The deposit when applied to a thickness of .0001 in shall withstand an immersion for 30 seconds in concentrated nitric acid at 65-75°F, without any significant discoloration.

The blackening of the deposit has less to do with the stripping of nickel but rather the formation of nickel sulfide and nickel oxide on the surface⁹. Factors that contribute to accelerated attack of EN deposits by nitric acid include co-deposition of heavy metals such as cadmium and lead as well as the presence of co-deposited sulfur, typically found in low and medium phosphorus systems.¹⁰ In our set of experiments we will be utilizing a sulfur free, organic compound stabilized, high phosphorus process that contains a trace amount of heavy metal as a complimentary stabilizer. We will be utilizing the nitric acid test as a measurement of deposit purity and will use it as a gauge for comparing corrosion performance of electroless nickel deposits plated under different conditions.

3.) *Pitting of thick deposits*

Although surface condition and substrate pretreatment play a role in pitting of EN deposits¹¹, it is one of the most notable defects to emanate from the plating solution itself. Pitting is very common in low and medium phosphorus deposits and in thick deposits of all EN types. High phosphorus processes are less susceptible to pitting for a number of reasons. Lower stabilizer levels, both heavy metal and sulfur-organic type, result in less co-deposition of impurities and a more homogenous deposit. The high phosphorus chemistry also plates slower. The significance of this is that it is believed that the most common cause of pitting is the attachment of hydrogen gas bubbles at the substrate-solution interface during plating. As the gas bubbles form on the plating surface they inhibit deposition until the gas bubble releases into the surrounding solution. The pit grows larger in size as the deposition process continues.

The hydrogen gas attachment process and subsequent formation of pit pre-cursors can be brought on by a number of factors. Substrate morphology and adsorption of microparticles are both considered suspects.¹² High-speed EN processes are very susceptible to pitting because the plating continues to grow rapidly while the hydrogen gas bubble adheres to the trouble spot. Slower plating speeds, like those found in high phosphorus processes allows time for the hydrogen gas bubble to release before a significant amount of nickel can be deposited in the surrounding area. Wetting agents that lower surface tension and promote a quicker gas bubble release help to an extent, however the pits remain and the source is not eliminated.

We will be monitoring the effect of loading, agitation and stabilizer level on deposit pitting. Efforts will be made to identify sources of pitting and methods to minimize them through operation techniques.

4.) *Edge pullback phenomena*

Edge pullback is a condition produced by high concentrations of stabilizers, brighteners or metallic poisons. While this is only postulated, it is believed that stabilizers act by preferentially adsorbing at the surface of colloids or near colloidal micelles thus preventing random formation of catalytic particles and subsequent solution instability.¹³ These stabilizers and/or poisons also readily co-deposit. It is this characteristic that can lead to edge pullback as well as other deleterious deposit characteristics

This co-deposition process can be accelerated by excessive agitation and/or low workload to solution volume ratios. The performance of most stabilizers are governed by diffusion. That is to say that the more solution that passes over a surface, the more stabilizer can be adsorbed at that site. Areas of high solution movement, i.e., edges and holes are the first locations to be

affected. Stabilizers also tend to adsorb on sharp points and threads and can lead to skip plating, high porosity or poor passivity. By monitoring mixed potential, Mallory found that increased solution agitation shifts the critical point of a stabilizer (the point at which it poisons the reaction) to a lower concentration.¹⁴ For example, a high phosphorus solution that operates at 1.0 ppm of heavy metal stabilizer under optimum loading and agitation might require ½ that amount for low loading and/or high agitation conditions. If not taken into consideration edge pullback or related edge effect problems may occur.

Effect of various solution loading, agitation and stabilizer levels on edge effect phenomena will be evaluated during this matrix and noted as it occurs.

5.) *Plating Rate*

Plating rate is a critical process characteristic and in many cases determines the commercial viability of a particular chemistry. Various studies have found that specific organic acids offer significant advantages in terms of stress and corrosion protection only to be eliminated from commercial consideration due to very slow plating rates.^{15,16}

It is widely accepted that plating rate is a function of the following factors:

- 1.) Operating temperature
- 2.) Operating pH
- 3.) Solution age
- 4.) Type and amount of organic acid
- 5.) Sodium hypophosphite concentration (most chemistries)
- 5.) Presence of rate exaltants
- 6.) Stabilizer type and level

Others have reported:

- 7.) Agitation¹⁷
- 8.) Workload to solution volume¹⁸

Our studies will focus on the last three. Numerous studies have shown that both stabilizer type and level have a profound effect on plating rate.^{19,20} In most cases, the research found that Class II (oxy-anion), Class III (heavy metal) and Class IV (unsaturated organic acid) stabilizers all reduced the plating rate as their levels approached the critical value (the point which plating stopped altogether). In our experiments we will monitor plating rate as a function of stabilizer level within a tight range, one that an EN plater would typically encounter between 80%-120% solution activity.

Stallman²¹ found that deposition rate increased with an increase in flow velocity. He found that several low intensity stirrings produced better results than one and recommended pumping solution through numerous outlets. It is believed that higher agitation increases plating speed by intensifying rates of diffusion of reacting species at the plating interface. Fresh reactants (nickel, sodium hypophosphite) are brought in and by-products (H₂, etc.) are removed, both at faster rates. Some studies found that that certain types of agitation can actually decrease the plating rate.^{22,23} Feldstein, et. al. found a sharp decrease in plating rate with excessive stirring agitation and associated it with suppression of the nucleation sites as plating initiated. He found that if agitation was introduced after an initial layer of nickel was deposited, it had little or no effect on

plating speed. He also varied rotation speed from 0 to 1200 RPM and found a significant increase up to 300 RPM at which point plating rate dropped until no plating occurred. In this segment of our matrix we will evaluate plating rate as a function of stirring speed (580 RPM, 900 RPM), air and nitrogen agitation.

A correlation between workload to solution volume ratio and plating rate has been claimed in the past.²⁴ Riedel referenced an Allied Kelite study that showed a clear connection between higher loading and slower plating rates.²⁵ The flaw in this experiment lies in the fact that replenishment was made every 60 minutes and at a loading of 0.25 ft²/gal and 0.55 ft²/gal respectively it is quite possible the solutions were in a constant state of low pH and reactants.

Gutzeit and Kreig found faster plating rates were realized with higher workloads.²⁶ Effect of solution loading in the range of 0.05 to 1.0 ft²/gal will be evaluated while chemistry is maintained at or near optimum levels.

6.) *Plate-out or solution stability*

There are a number of reasons equipment plate out occurs. Troubleshooting guides that list the possible culprits are readily available and in the interest of brevity will not be noted here. In short, solution chemistry (stabilizer type/level and complexing agent), operating parameters (temperature, pH) and equipment (tank condition, agitation amount, filtration) are several of the key players.

During our research we will observe the effect stabilizer level, agitation and workload has on solution stability and the propensity to plate-out on the bottom of a glass beaker. All other variables that could play a role in instability (equipment, etc.) will be kept fixed and can therefore be discounted.

Experimental Procedure

General Preparation

The total number of experiments in the matrix was determined and lab made lots of make-up and replenishment chemistry were set aside to guarantee all solutions were made from the same raw materials. Critical stabilizers were not added to these stock solutions so that their levels could be adjusted during specific experiments. A 50% solution of ammonium hydroxide was also prepared and saved. All electroless nickel plating solutions utilized were of the high phosphorus type (10.5-12% b.w.) and all were processed through a 1-micron absolute filter prior to use. In each case, 800 mls of electroless nickel solution was prepared and heated to operating temperature in a 1,000 ml Pyrex beaker No.1060. All beakers were cleaned and passivated in 30% nitric acid prior to use.

Unless otherwise noted, all electroless nickel solutions were aged to 0.5 metal turnovers before initiation of tests.

Panels used for passivity tests, plating rate and pitting analysis were all polished 1010 carbon steel 3" x 4" zinc coated (removed during cleaning cycle). When necessary, panels were cut to size for certain workload requirements.

Standard 1" x 1/4" zinc plated 1010 mild steel hex bolts were used for porosity measurement as well as dummy bolts to meet certain workload requirements.

Plating rate was determined by weight gain on a Mettler AT 261 balance and confirmed at regular intervals by X-Ray on a Fischerscope Model# XA-1550.

Solution agitation (unless noted otherwise) and heating were performed on a series of identical hot plate/stirrer units. A 1" teflon coated magnetic stir bar was used in conventional agitation experiments. Rotation speed was set to "5", approximately 580 RPM. For excessive agitation a 1.5" teflon coated stir bar was used and the rotation speed was increased to "5.5", approximately 900 RPM.

Air and nitrogen agitation were supplied by regulated compressed gas cylinders and run through Airco 754 flowmeters, 1/4" tygon tubing and a 1.25" fritted glass disc with a 6" glass stem. Flow rates were maintained at approximately 100 mls/minute.

Heavy metal stabilizers were monitored on a Buck Scientific Model #210-VGP AA Spectrophotometer and results were periodically confirmed by ICP (inductively coupled plasma).

A Baush & Lomb Stereo Zoom Microscope at 20x power was used for evaluation of deposit pitting.

Ferroxyl test

Solution was prepared and all tests were conducted per ASTM B733. Hex bolts (1" x 1/4") were plated to 0.4 mils of high phosphorus EN and tested for porosity. Visual examination was performed after 5 minutes air dry.

Pitting test

Panels (1"x 0.75") were plated to 2.0 mils and grids were applied with permanent ink. The deposit was then evaluated under 20X for appearance of round, "fish eye" type pits. This type of pit has a distinct oblong center and is typical of pits brought on by the electroless nickel process. All other pits due to roughness and/or surface imperfections were not counted.

Passivity test

Panels (1"x 0.75") were plated to 0.2 mils, dried and immersed in concentrated reagent grade nitric acid at 70° F. Two variables were monitored. The time required for the edges to turn black was considered a qualitative measurement of the stabilizer adsorption process. The time for the entire panel to turn black was also documented.

Plate-out/instability

Solution stability was measured by two (2) methods. Monitoring for extraneous nickel consumption and/or evidence of plate-out on the bottom of the glass beaker was one method used. The other was a palladium stability test that was run in all cases except for loading experiments. This test requires the addition of a dilute solution of palladium chloride to a hot electroless nickel solution over a set period of time until the solution decomposes. The higher number of mls of palladium chloride required, the greater the solution stability.

Standard cleaning cycle

The following is the cleaning and activating cycle followed for both panels and bolts (rinses omitted).

- 1.) Immersion in 50% hydrochloric acid at ambient temperature for 30 seconds to remove the zinc coating.
- 2.) Anodic electroclean (12 oz/gal) at 180° F for 2 minutes at 3 volts.
- 3.) Immersion in 50% hydrochloric acid until uniform gassing is evident.
- 4.) Repeat step #2
- 5.) Repeat step #3

The purpose of the double cleaning cycle is to minimize variation in results due to poor cleaning. C.F. Beer²⁷ reported that anodic electrocleaning in highly alkaline cleaners was far superior in promoting reduced porosity than either soak cleaning or cathodic electrocleaning. Although claims have been made that chlorides from hydrochloric acid activation can “accelerate” corrosion²⁸ we have been unable to find any correlation between type of activating acid used and porosity of thin high phosphorus deposits²⁹. More important factors include complete soil and oxide removal as well as adequate rinsing.

Preparation of high phosphorus solutions for testing

- Preparation of 800 ml bath
- 1.) 36 mls of high phosphorus nickel component
120 mls of high phosphorus make-up component
 - 2.) Required addition of stabilizer
 - 3.) Adjust to volume with deionized water
 - 4.) Filter through 1 micron absolute filter
 - 5.) Adjust pH to 4.8 with 50% b.v. ammonium hydroxide
 - 6.) Heat to 190° F and begin plating 2-3"x4" steel panels
 - 7.) Monitor solution concentration per standard EDTA titration and replenish as needed up to 0.5 metal turnovers.
 - 8.) Cool solution, analyze, replenish and adjust pH to 4.8
 - 9.) Plate 30 minute rate panel.

Solution activity was maintained between 90-100%, temperature (+/- 2 °) and pH (+/- 0.1 units) by constant monitoring.

Standard testing procedure

The following procedure was followed for each of the 160 plus experiments and was designed to maintain constant workload throughout the test. (The only time this procedure was not followed was for evaluation of workload effects.)

- 1.) Plate bolt for approx. 60 minutes to a thickness of 0.4 mils along with a 1" x 0.75" pit panel.
- 2.) After 60 minutes of plating, remove bolt for ferroxyl evaluation, replace with a new 1" x 0.75" plating rate panel (to maintain workload) and continue plating pit panel to 2 mils.
- 3.) Remove rate panel after 30 minutes and replace with dummy bolt; determine rate of deposition by XRF.
- 4.) Remove dummy bolt and pit panel after 2 mils is deposited.

Results and Discussion

A.) Standardization of substrate effects and pre-treatment for ferroxyl and pitting tests

The purpose of this set of 12 experiments was to uncover any substrate defects or pre-treatment conditions that would contribute to inaccurate results during ferroxyl and pit evaluation.

Twelve (12) EN solutions were made and operated as set forth above. The heavy metal stabilizer was modified to determine consistency of results over a range of plating conditions. The experimental matrix and results are tabulated below:

Heavy metal stabilizer level (ppm)	Pitting Panel (# of pits)	Ferroxyl bolts (# of blue spots)
0.3	4	14
0.3	3	8
0.3	5	9
0.3	3	10
0.1	---	0

Although the statistical sample is small the results do indicate that the conditions of our experiment are repeatable and should not be subject to variations due to pre-treatment and substrate effects. This creates a solid foundation for data evaluation based solely on the variables we are monitoring.

The Six P's

During each of the following 4 sets of experiments six (6) critical variables were monitored: **porosity, pitting, passivity, plating rate, pullback and plate-out.**

B.) Effect of solution age

An 800 ml high phosphorus solution was operated out to 5 metal turnovers. Filtration through a 1 micron filter was performed at each metal turnover. Plating rate, deposit porosity, pitting and passivity were monitored. In addition, solution stability and edge effect were evaluated and levels of hypophosphite and orthophosphite recorded.

MTO	Ni (g/l)	Hypo (g/l)	Ortho (g/l)	Specific gravity (g/cc)	Plating rate (mils/hr)	HM stabilizer (ppm)	Passivity ¹ (minutes)	Pores	Pits	Plate out
0	6.0	30.0	-	1.052	.55	.35	8	4	11	
1	6.0	29.4	41	1.080	.52	.37	Not available	7	8	
2	5.9	30.3	61.7	1.094	.48	.31	Not available	5	15	light plate-out
3	6.1	30.3	85.1	1.118	.46	.38	Not available	15	5	
4	5.7	29.4	124.4	1.141	.42	.41	Not available	12	5	light plate-out
5	5.8	31.5	157.5	1.168	.40	.44	Not available	22	8	light plate-out

There were not many surprises here. Nickel metal and sodium hypophosphite levels were maintained near optimum. Although inconsistent from turnover to turnover the increase in orthophosphite concentration is in agreement with published results and the specific gravity increased linearly with solution age. As expected, the plating rate did decline and is due primarily to the increased level of orthophosphite³⁰ although the higher levels of complexor required to maintain phosphite tolerance also plays a role. All panels maintained a semi-bright, clear appearance throughout the 5 metal turnover life test.

The stabilizer concentration remained consistent which allowed us to accurately evaluate the effect bath age had on pitting and porosity independent of heavy metal stabilizer level.

Comprehensive passivity data vs. solution life was not unavailable at this time and will be presented at a later date. Initial data was in agreement with previous studies, indicating that passivity increased after the first 0.5 metal turnovers and then slowly declined with solution age.³¹

In agreement with several studies, porosity increased with bath age.^{32,33} Although the test was stopped at 5 metal turnovers, the continued increase in porosity with solution age is expected to continue. Deposit pitting did not appear to be solution age related, at least up to 5 metal

¹ Results for passivity tests vs. solution age were unavailable and will be presented during EN Conference 1999

turnovers. Evaluating roughness or nodular features of the deposit vs. solution age were beyond the extent of this study.

Slightly more plate out was evident as the solution aged. Beside the obvious introduction of shop dust and metal fines, some postulate that decreased stability with increasing solution age is due to the presence of insoluble nickel phosphide and/or gelatinous metal hydroxides that can cause localized reduction of nickel ions.²⁶ The build up of “micro” gelatinous metal hydroxides is most likely from dissolution of substrates during the initial displacement reaction. Phosphite intolerance and precipitation as the solution ages is another likely contributor to instability.³⁴

C.) Effect of heavy metal stabilizer level

Four(4) high phosphorus solutions were prepared and plated to 0.5 metal turnovers. A heavy metal stabilizer was added to each of the solutions in varying amounts and the effects summarized below in Table1. The testing parameters were:

Solution pH	4.8
Temperature (°F)	190
Agitation	1” stir bar set at “5” (560 RPM)
Loading	0.4 ft ² /gal
Stabilizer level (ppm)	<i>variable</i>

Table 1

HM stabilizer level (ppm)	Pores	Pits	Passivity ^A (minutes)	Plating rate (mils/hr)	Pullback	Plate-out (mls Pd)
0.1	0	0	1 / 8	.51	No	6 mls
0.3	13	4	1 / 8	.54	No	12 mls
0.6	20	21	0.75 / 5	.47	Yes	16 mls
1.0	25	24	0.33 / 4	.47	Yes	26 mls

^A minutes to black edges/ minutes to blackening of entire panel

The results in Table 1 clearly indicate a correlation between heavy metal stabilizer level, pitting and porosity. All other variables held constant, higher concentrations of heavy metal stabilizers promote higher porosity and pitting. Passivity was also inversely related to stabilizer level. The time to black was cut nearly in half for the higher levels of stabilizer.

Plating rate was independent of stabilizer level in the range tested. Edge pullback was encountered at 0.6 and 1.0 ppm levels. This is a common level of stabilizer for many commercial high phosphorus systems and may account for the “break in” period required for some of them. Although this was not tested and/or confirmed during our experimental matrix, the stabilizer concentration has been found to be less critical in terms of edge pullback as the solution ages.

Palladium stability increased with an increase in stabilizer level. Little plate out was observed, however the group of experiments above were not run over a extended period of time and the opportunity for plate out to initiate was minimized.

D.) Effect of workload to solution volume

Four(4) high phosphorus solutions were prepared and plated to 0.5 metal turnovers. All variables were held constant except various workload to solution volumes were evaluated. The results are summarized in Table 2 below. The parameters were as follows:

Solution pH	4.8
Temperature (°F)	190
Agitation	1” stir bar set at “5” (560 RPM)
Loading	variable
Stabilizer level (ppm)	0.3

Table 2

Solution loading (ft ² /gal)	Pores	Pits	Passivity (minutes)	Plating rate (mils/hr)	Pullback	Plate-out (mils Pd)
0.05	36	39	10 seconds / 2	.54	yes	N/A
0.1	20	15	40 seconds / 3	.46	no	N/A
0.4	13	4	1 / 8	.54	no	N/A
1.0	36	5	2 / 8	.56	no	N/A

The results do show a causal effect on loading and pitting. Higher loading appeared to substantially reduce pitting. An explanation for this phenomenon is most likely that the heavy metal stabilizer was co-deposited uniformly and distributed over a larger surface area. This same thinking applies to the deposit passivity that showed a similar improvement as the workload increased.

The same effect might have been expected for porosity but that was not the case. Further studies may be necessary to determine the reasons for this.

Plating rate was unaffected by workload to solution volume which contradicts other studies.^{24,25,26} This did not surprise us, however, since in our experiments solution chemistry was maintained at or near optimum for the entire test. Previous researchers allowed the reactants to deplete well below current industry recognized operating levels.

E.) Effect of solution agitation

Five(5) high phosphorus solutions were prepared and plated to 0.5 metal turnovers. Variable types and amounts of agitation were introduced into the solution. The results are summarized in Table 3 below. The parameters were as follows:

Solution pH	4.8
Temperature (°F)	190
Agitation	variable
Loading	0.4 ft ² /gal
Stabilizer level (ppm)	0.3

Table 3

Agitation	Pores	Pits	Passivity (minutes)	Plating rate (mils/hr)	Pullback	Plate-out (mls Pd)
Moderate stir bar	13	4	2 / 8	.54	no	12 mls
No agitation	6	8	2/10	.52	no	8 mls
Excessive	16	2	1 / 5	.60	no	10 mls
Moderate air	16	2	1 /10	.61	no	22 mls
Moderate nitrogen	15	2	2 / 10	.53	no	22 mls

At first glance, the results appeared random and insignificant. Upon closer examination the data does indicate a pattern. No agitation provided the best results for porosity and the worst for pitting. Based on this as well as the data generated from our workload experiment it appears there is a distinctly different mechanism that controls pitting and porosity. Low porosity deposits under conditions of no agitation supports earlier claims that adsorption and co-deposition of stabilizers is diffusion controlled. Less agitation, less adsorption, less porosity. Upon introduction of agitation, all porosity patterns disappear with no clear benefit derived from any type or amount.

It appears as though interdependence exists between pitting and agitation. Higher agitation, regardless of type or amount promotes lower pitting. This is in agreement with many of the EN troubleshooting guides available in our industry.³⁵

Passivity was affected by agitation. No agitation and moderate nitrogen produced the best results. Excessive agitation produced the worst. Again, this appears to be a diffusion and distribution phenomena where high agitation, especially rotational, promotes high adsorption of stabilizer into the deposit.

Although the data points are limited, higher agitation did tend to promote higher plating speeds. The average plating rate for the 11 experiments in this set (not including excessive and air) was 0.516 mils/hr. The plating rate increase for excessive agitation and moderate air is 16% and 18% respectively, well above our margin of error.

A marked improvement in solution stability was observed with an increase in agitation, regardless of type. This is in agreement with field observations that show a noteworthy decrease in equipment plate out when solution movement is increased by various means.

Most of the data presented thus far supports our earlier statements on electroless nickel process conflicts. High rotational agitation promotes higher porosity and less corrosion protection, yet faster plating rates. Increased stabilizer levels increase solution stability but reduce passivity and contribute to high porosity and pitting.

Synergy

Up to this point all experiments were conducted with only one operating parameter varied. Operating conditions of an EN process in the real world are not nearly as static. **Optimum performance of an electroless nickel process is very often a direct result of combining ideal operating conditions.** Low stabilizer levels may be fine for low loading applications but what

happens when loading is substantially increased and/or excessive agitation is introduced? This next group of approximately 120 tests will evaluate the synergistic effect of loading, agitation and stabilizer concentration on deposit porosity and pitting.

Each group is comprised of 16 different experiments where one parameter (i.e. solution loading) was held constant while all others were varied. For simplicity sake, the entire experimental matrix along with results were tabulated and can be found as table A.

Due to the volume of data, operating trends were difficult to ascertain from table A. For this reason an ascending sort was executed for the results of both deposit porosity and pitting. This simplified the data analysis and permitted easier recognition of effects a particular parameter had on the results. Sorted porosity and pitting data can be found as table B and C respectively.

Analysis of synergy experiment results

The first group of experiments compared the effect heavy metal stabilizer had on porosity and pitting. Again, due to the volume of data, the average of all experimental results were utilized and the results presented below in Figure 1.

Figure 1

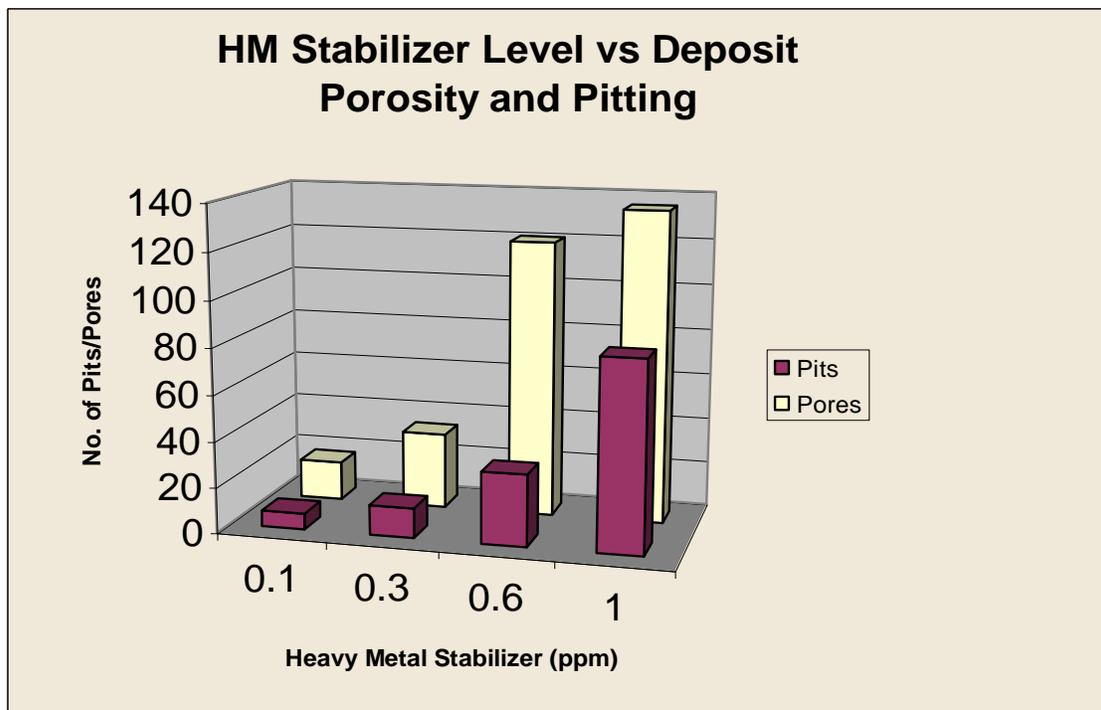


Figure 1 illustrates the effect that heavy metal stabilizer levels have on both porosity and pitting. Over the sequence of 120 synergy experiments the results clearly indicate a direct relationship between increased stabilizer level and increased deposit pitting and porosity. This relationship held independent of workload and agitation.

In table B, ascending sort of porosity data, 13 of the 16 experiments utilizing the lowest level of heavy metal stabilizer (0.1 ppm) were found in the top 1/3 of the table. The only time a higher stabilizer level produced low porosity results was with higher workloads and moderate nitrogen

agitation (exp.# 7). This is in agreement with our results in table 2 that indicated higher loading reduced porosity.

In table C, ascending sort of pitting data, 12 of the 16 experiments utilizing the lowest level of heavy metal stabilizer were also found at the top 1/3 of the table. Again, the only time that higher stabilizer concentrations produced lower pitting was with increased workloads. (see experiments # 66, 68, 70, 77 and 85 in table C).

Of the 16 experiments run at the highest stabilizer level (1.0 ppm), 15 experienced edge pullback. (see table A, exp. # 49-64). It is interesting to note that of the experiments that resulted in edge pullback, a number of them had little or no pitting and very little porosity (exp.# 66-# 70 in table C). This was surprising considering that pitting is often a pre-cursor to step plating and edge pullback. A review of the data did not yield a possible mechanism for this.

The second group of synergy experiments compared the effect of solution loading on deposit porosity and pitting. Again, an average of all experimental results were utilized and the results presented below in Figure 2.

Figure 2

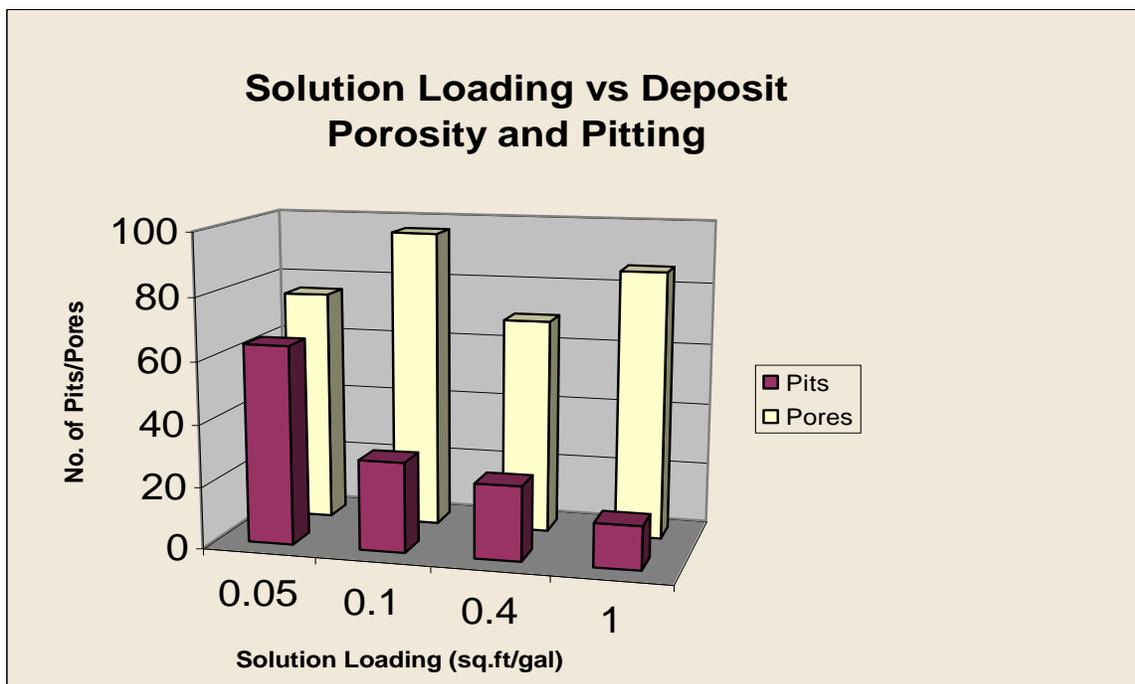


Figure 2 illustrates the effect that workload to solution volume has on both porosity and pitting over a wide range of experimental conditions. The results are in agreement with earlier tests that show a decrease in deposit pitting with an increase in loading. Exp.# 107 and # 128 in table C were run under identical operating conditions, except #107 was run at 1.0 ft²/gal and # 128 at .05 ft²/gal. The former produced a deposit with 29 pits, the latter 300, a ten-fold increase. Similar results were found for exp.# 77 and #119 as well as # 85 and #114. Again, the most likely reason for this is greater distribution of pit inducing stabilizers over a larger surface area.

In terms of deposit porosity, the results of our synergy experiments are similar to earlier trials that indicated no real consistent effect of solution loading.

The third group of synergy experiments compared the effect of solution agitation on deposit porosity and pitting. Averages of all experimental results were utilized and the results presented below in Figure 3.

Figure 3

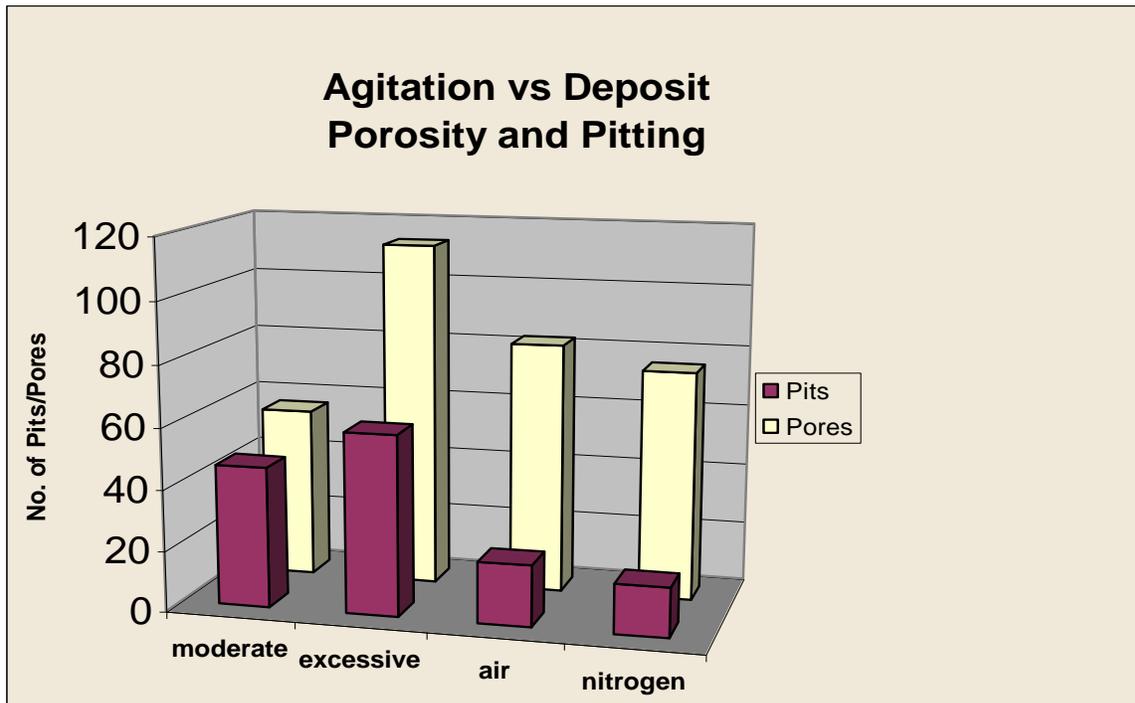


Figure 3 illustrates the effect that agitation has on both porosity and pitting over a wide range of experimental conditions. Overall, pitting was reduced when air or nitrogen agitation was introduced. A comparison of Exp.# 32 with # 25 and #27 in tableA highlights our findings. All three experiments were run under identical conditions except agitation was varied. Similar patterns can be found throughout the data.

By comparison, excessive rotational agitation (900 RPM) resulted in a 50-fold increase in pitting. This may be explained by the uniformity of high-speed rotational agitation. A vortex develops in the solution, creating a uniform flow pattern. This pattern of solution flow may deposit stabilizers onto fixed sites resulting in high pit areas. This may also explain the high incidence of skip plating under excessive agitation conditions. In contrast to rotational agitation, air or nitrogen agitation is not homogenous. The panels and bolts are not held in place as they are by the vortex and solution movement is irregular. This type of agitation appears beneficial to pit reduction and may do so by facilitating release of hydrogen gas bubbles.

Porosity also increased with agitation. A comparison of the results in table A from experiments #2, #3 and #4 with experiment # 16 show a dramatic increase in porosity with an increase in rotational agitation. This phenomenon is exaggerated with low solution loading. These results are in agreement with earlier tests that show an increase in deposit porosity with an increase in agitation (see table 3).

Conclusions

Our conclusions based on the experimental data have been drawn after much consideration. We were careful not to formulate these based solely on individual experiments but incorporated an in depth review of trends in tables B and C. Based on this information we offer the following summary, some of which simply confirms what has previously been reported.

Effect of solution age

- 1.) Deposit porosity increases & inherent corrosion protection is reduced as the solution ages.
- 2.) Deposit pitting was unrelated to solution age, at least up to 5 metal turnovers.

Effect of heavy metal stabilizer

- 1.) Increased levels of heavy metal stabilizer resulted in higher deposit porosity and pitting.
- 2.) Plating rate was independent of stabilizer level within a specific operating range.
- 3.) Deposit passivity was reduced with an increase in stabilizer concentration.
- 4.) Solution stability increased with a concomitant increase in stabilizer.
- 5.) Edge effect phenomena were more prevalent with increased stabilizer concentrations.

Effect of workload to solution volume

- 1.) Higher loading resulted in reduced deposit pitting and increased passivity.
- 2.) Plating rate was independent of solution loading.

Effect of solution agitation

- 1.) Deposit pitting was reduced with moderate air or nitrogen agitation.
- 2.) High rotational agitation led to an **increase** in deposit pitting and reduced passivity.
- 3.) Deposit porosity increased with agitation.
- 4.) Plating speed increased with high rotational or air agitation.
- 5.) Solution stability was substantially improved with an increase in agitation.
- 6.) No real benefits from nitrogen agitation were realized.

Note: The effect of agitation on sodium hypophosphite consumption will be presented during EN Conference 1999

Suggestions

- 1.) Pay close attention to solution loading and make efforts to operate within the specified process guidelines.
- 2.) When operating below minimum loading recommendations reduce all types of solution agitation and operate the solution chemistry below 85% activity (this effectively reduces stabilizer levels). Monitor any adverse effect this may have on equipment plate out.
- 3.) Parts requiring optimum corrosion resistance should be plated between 0.2 (“break in period”) and 5.0 metal turnovers.
- 4.) For heavy build applications (deposits in the range of 2-50 mils) operate the solution chemistry below 85% activity and utilize air agitation to minimize pitting.
- 5.) If experiencing stability problems maintain chemistry at or near optimum, increase solution agitation (bigger pump for example) and introduce air if not already present.
- 6.) If experiencing edge effect problems operate at lower solution activity and reduce all types of agitation. Increase workload if possible.
- 7.) To increase plating speeds, increase agitation. Monitor for edge effect problems.
- 8.) If experiencing poor corrosion resistance due to high porosity, reduce agitation and operate solution below 85% activity.
- 9.) If experiencing poor passivity, make sure plating speed is at or below 0.5 mils/hr, reduce agitation, increase workload and operate chemistry below 85% activity.
- 10.) Work closely with your supplier. The effect that stabilizer type and level have on the performance of an EN process can not be stressed enough . This information is easily ascertained and should be provided to you along with recommended pH, nickel and sodium hypophosphite concentrations.
- 11.) Talk to your supplier about “designer” electroless nickel processes. Off the shelf chemistry works fine for most applications, however, there are instances where using a standard EN process just doesn’t meet requirements. Ask your supplier about adjusting an existing process or developing one specifically suited for your unique application or operating conditions.

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Table A

Synergy Data

Exp.#	Stabilizer level (ppm)	Workload (sq. ft/gal)	Agitation	Pores	Pits	Comments
1	0.1	0.4	moderate	0	0	(C2)
2	0.1	0.05	moderate air	4	15	light plate-out
3	0.1	0.05	mod. nitrogen	6	12	light plate-out
4	0.1	0.05	moderate	6	15	light plate out
5	0.1	0.1	moderate	9	n/a	rough deposit
6	0.1	0.4	moderate air	10	4	
7	0.1	0.4	mod. nitrogen	11	4	
8	0.1	0.1	moderate air	12	4	
9	0.1	0.1	excessive	12	n/a	severe plate-out
10	0.1	1.0	moderate	13	30	
11	0.1	0.4	excessive	16	0	edge pull back
12	0.1	0.1	mod. nitrogen	16	1	
13	0.1	1.0	moderate air	21	2	
14	0.1	1.0	mod. nitrogen	35	1	
15	0.1	1.0	excessive	100	0	roughness on one side
16	0.1	0.05	excessive	100	n/a	very rough deposit
17	0.3	0.4	moderate	13	4	(C1,D1,E1)
18	0.3	0.4	mod. nitrogen	15	2	(E5)
19	0.3	0.4	excessive	16	2	edge pull back (E3)
20	0.3	0.4	moderate air	16	2	(E4)
21	0.3	0.1	moderate	20	15	(D3)
22	0.3	0.05	mod. nitrogen	23	6	slight edge pullback
23	0.3	1.0	moderate	36	5	(D4)
24	0.3	0.05	moderate	36	39	edge pullback (D2)
25	0.3	0.1	moderate air	57	3	
26	0.3	1.0	excessive	59	0	Frosted deposit appearance
27	0.3	0.1	mod. nitrogen	62	3	
28	0.3	0.05	moderate air	65	10	slight edge pullback
29	0.3	1.0	mod. nitrogen	79	4	
30	0.3	1.0	moderate air	100	3	
31	0.3	0.05	excessive	100	6	edge pullback
32	0.3	0.1	excessive	175	100	edge pull back
33	0.6	1.0	mod. nitrogen	11	0	slight step plating
34	0.6	0.4	moderate	20	21	edge pullback (C3)
35	0.6	0.05	moderate air	22	35	
36	0.6	1.0	moderate air	32	0	step plating
37	0.6	0.05	mod. nitrogen	42	40	slight edge pullback
38	0.6	0.4	mod. nitrogen	63	5	
39	0.6	1.0	excessive	83	0	no pits but step plating
40	0.6	1.0	moderate	100	4	
41	0.6	0.1	moderate	100	50	severe edge pullback
42	0.6	0.1	excessive	140	25	severe edge pullback
43	0.6	0.1	mod. nitrogen	200	5	
44	0.6	0.1	moderate air	200	6	
45	0.6	0.4	moderate air	200	12	
46	0.6	0.05	moderate	200	100	severe edge pullback
47	0.6	0.05	excessive	200	100	severe edge pullback
48	0.6	0.4	excessive	300	100	edge pullback

Table A (cont.)

Synergy Data

	Stabilizer level (ppm)	Workload (sq. ft/gal)	Agitation	Pores	Pits	Comments
49	1.0	0.4	moderate	25	24	edge pullback (C4)
50	1.0	0.4	excessive	30	45	edge pull back, step plating
51	1.0	0.05	mod. nitrogen	100	48	edge pull back
52	1.0	0.1	moderate air	100	65	edge pull back
53	1.0	0.05	moderate air	100	98	edge pull back
54	1.0	0.1	moderate	135	50	severe edge pullback
55	1.0	1.0	excessive	135	150	severe edge pullback
56	1.0	0.1	excessive	140	100	severe edge pullback
57	1.0	0.1	mod. nitrogen	150	35	edge pull back
58	1.0	0.4	moderate air	165	70	edge pull back
59	1.0	1.0	mod. nitrogen	190	3	slight edge pullback
60	1.0	1.0	moderate	190	29	
61	1.0	1.0	moderate air	200	1	slight edge pullback
62	1.0	0.4	mod. nitrogen	200	100	slight edge pull back
63	1.0	0.05	excessive	300	200	severe edge pull back
64	1.0	0.05	moderate	400	300	severe edge pullback

Notes: Letters and numbers in the parentheses denote experiment run in another section of the matrix
Under comments, edge effects was noted as were other characteristics of each experiment

Table B

Ascending Sort of Porosity Data

Exp.#	Stabilizer level (ppm)	Workload (sq. ft/gal)	Agitation	Pores	Pits	Comments
1	0.1	0.4	moderate	0	0	(C2)
2	0.1	0.05	moderate air	4	15	light plate-out
3	0.1	0.05	mod. nitrogen	6	12	light plate-out
4	0.1	0.05	moderate	6	15	light plate out
5	0.1	0.1	moderate	9	n/a	rough deposit
6	0.1	0.4	moderate air	10	4	
7	0.6	1.0	mod. nitrogen	11	0	slight step plating
8	0.1	0.4	mod. nitrogen	11	4	
9	0.1	0.1	moderate air	12	4	
10	0.1	0.1	excessive	12	n/a	severe plate-out
11	0.3	0.4	moderate	13	4	(C1,D1,E1)
12	0.1	1.0	moderate	13	30	
13	0.3	0.4	mod. nitrogen	15	2	(E5)
14	0.1	0.4	excessive	16	0	edge pull back
15	0.1	0.1	mod. nitrogen	16	1	
16	0.3	0.4	excessive	16	2	edge pull back (E3)
17	0.3	0.4	moderate air	16	2	(E4)
18	0.3	0.1	moderate	20	15	(D3)
19	0.6	0.4	moderate	20	21	edge pullback (C3)
20	0.1	1.0	moderate air	21	2	
21	0.6	0.05	moderate air	22	35	
22	0.3	0.05	mod. nitrogen	23	6	slight edge pullback
23	1.0	0.4	moderate	25	24	edge pullback (C4)

Table B (cont.)

Ascending Sort of Porosity Data

Exp.#	Stabilizer level (ppm)	Workload (sq. ft/gal)	Agitation	Pores	Pits	Comments
24	1.0	0.4	excessive	30	45	e.pull back,step plating
25	0.6	1.0	moderate air	32	0	step plating
26	0.1	1.0	mod. nitrogen	35	1	
27	0.3	1.0	moderate	36	5	(D4)
28	0.3	0.05	moderate	36	39	edge pullback (D2)
29	0.6	0.05	mod. nitrogen	42	40	slight edge pullback
30	0.3	0.1	moderate air	57	3	
31	0.3	1.0	excessive	59	0	Frosted deposit appearance
32	0.3	0.1	mod. nitrogen	62	3	
33	0.6	0.4	mod. nitrogen	63	5	
34	0.3	0.05	moderate air	65	10	slight edge pullback
35	0.3	1.0	mod. nitrogen	79	4	
36	0.6	1.0	excessive	83	0	no pits but step plating
37	0.1	1.0	excessive	100	0	roughness on one side
38	0.3	1.0	moderate air	100	3	
39	0.6	1.0	moderate	100	4	
40	0.3	0.05	excessive	100	6	edge pullback
41	1.0	0.05	mod. nitrogen	100	48	edge pull back
42	0.6	0.1	moderate	100	50	severe edge pullback
43	1.0	0.1	moderate air	100	65	
44	1.0	0.05	moderate air	100	98	edge pull back
45	1.0	0.1	moderate	135	50	severe edge pullback
46	1.0	1.0	excessive	135	150	
47	0.6	0.1	excessive	140	25	severe edge pullback
48	1.0	0.1	excessive	140	100	
49	1.0	0.1	mod. nitrogen	150	35	
50	1.0	0.4	moderate air	165	70	
51	0.3	0.1	excessive	175	100	edge pull back
52	1.0	1.0	mod. nitrogen	190	3	slight edge pullback
53	1.0	1.0	moderate	190	29	
54	1.0	1.0	moderate air	200	1	slight edge pullback
55	0.6	0.1	mod. nitrogen	200	5	
56	0.6	0.1	moderate air	200	6	
57	0.6	0.4	moderate air	200	12	
58	0.6	0.05	moderate	200	100	severe edge pullback
59	0.6	0.05	excessive	200	100	severe edge pullback
60	1.0	0.4	mod. nitrogen	200	100	
61	0.6	0.4	excessive	300	100	edge pullback
62	1.0	0.05	excessive	300	200	severe edge pull back
63	1.0	0.05	moderate	400	300	severe edge pullback
64	0.1	0.05	excessive	400	n/a	very rough deposit

Notes: Letters and numbers in the parentheses denote experiment run in another section of the matrix
Under comments, edge effects was noted as were other characteristics of each experiment

TableC

Ascending Sort of Pitting Data

Exp.#	Stabilizer level (ppm)	Workload (sq. ft/gal)	Agitation	Pores	Pits	Comments
65	0.1	0.4	moderate	0	0	(C2)
66	0.6	1.0	mod. nitrogen	11	0	slight step plating
67	0.1	0.4	excessive	16	0	edge pull back
68	0.6	1.0	moderate air	32	0	step plating
69	0.3	1.0	excessive	59	0	frosted deposit
70	0.6	1.0	excessive	83	0	step plating
71	0.1	1.0	excessive	100	0	
72	0.1	0.05	excessive	100	0	very rough deposit
73	0.1	0.1	moderate	9	0	rough deposit
74	0.1	0.1	excessive	12	0	rough deposit, bad plate-out
75	0.1	0.1	mod. nitrogen	16	1	
76	0.1	1.0	mod. nitrogen	35	1	
77	1.0	1.0	moderate air	200	1	slight edge pullback
78	0.3	0.4	mod. nitrogen	15	2	(E5)
79	0.3	0.4	excessive	16	2	edge pull back (E3)
80	0.3	0.4	moderate air	16	2	(E4)
81	0.1	1.0	moderate air	21	2	
82	0.3	0.1	moderate air	57	3	
83	0.3	0.1	mod. nitrogen	62	3	
84	0.3	1.0	moderate air	100	3	
85	1.0	1.0	mod. nitrogen	190	3	slight edge pullback
86	0.1	0.4	moderate air	10	4	
87	0.1	0.4	mod. nitrogen	11	4	
88	0.1	0.1	moderate air	12	4	
89	0.3	0.4	moderate	13	4	(C1,D1,E1)
90	0.3	1.0	mod. nitrogen	79	4	
91	0.6	1.0	moderate	100	4	
92	0.3	1.0	moderate	36	5	(D4)
93	0.6	0.4	mod. nitrogen	63	5	
94	0.6	0.1	mod. nitrogen	200	5	
95	0.3	0.05	mod. nitrogen	23	6	slight edge pullback
96	0.3	0.05	excessive	100	6	edge pullback
97	0.6	0.1	moderate air	200	6	
98	0.3	0.05	moderate air	65	10	slight edge pullback
99	0.1	0.05	mod. nitrogen	6	12	
100	0.6	0.4	moderate air	200	12	
101	0.1	0.05	moderate air	4	15	light plate-out
102	0.1	0.05	moderate	6	15	light plate out
103	0.3	0.1	moderate	20	15	(D3)
104	0.6	0.4	moderate	20	21	edge pullback (C3)
105	1.0	0.4	moderate	25	24	edge pullback (C4)
106	0.6	0.1	excessive	140	25	severe e. pullback
107	1.0	1.0	moderate	190	29	
108	0.1	1.0	moderate	13	30	

Table C (cont.)

Ascending Sort of Pitting Data

Exp.#	Stabilizer level (ppm)	Workload (sq. ft/gal)	Agitation	Pores	Pits	Comments
109	0.6	0.05	moderate air	22	35	
110	1.0	0.1	mod. nitrogen	150	35	Edge pullback
111	0.3	0.05	moderate	36	39	edge pullback (D2)
112	0.6	0.05	mod. nitrogen	42	40	slight edge pullback
113	1.0	0.4	excessive	30	45	edge pull back, step plating
114	1.0	0.05	mod. nitrogen	100	48	moderate rust, edge pull back
115	0.6	0.1	moderate	100	50	severe edge pullback
116	1.0	0.1	moderate	135	50	severe edge pullback
117	1.0	0.1	moderate air	100	65	edge pull back
118	1.0	0.4	moderate air	165	70	edge pull back
119	1.0	0.05	moderate air	100	98	edge pull back
120	1.0	0.1	excessive	140	100	severe edge pull back
121	0.3	0.1	excessive	175	100	pitting and edge pull back
122	0.6	0.05	moderate	200	100	pitting and edge pullback
123	0.6	0.05	excessive	200	100	pitting and edge pullback
124	1.0	0.4	mod. nitrogen	200	100	sl. Edge pullback
125	0.6	0.4	excessive	300	100	edge pullback
126	1.0	1.0	excessive	135	150	severe edge pull back
127	1.0	0.05	excessive	300	200	severe edge pull back, step pl.
128	1.0	0.05	moderate	400	300	edge pullback, pitting & porosity

Notes: Letters and numbers in the parentheses denote experiment run in another section of the matrix

Under comments, edge effect was noted as were other characteristics of each experiment

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