Bright Nickel Plating

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I have had a number of inquiries about troubleshooting bright nickel plating in the last few months, so I decided to contribute the following. It is based on notes from a talk I gave a few years ago, and includes a trouble shooting chart.

Bright nickel plating solutions are based on a Watts nickel formulation, sometimes with variations.

	Watts Nickel	High chloride
Nickel sulfate	40 oz/gal (298 g/L)	15 oz/gal (112 g/l)
Nickel chloride	8 oz/gal (60 g/L)	25 oz/gal (60 g/L)
Boric Acid	6 oz/gal (45 g/L)	6 oz/gal (45 g/L)
pH	3.5 - 4.5	3.5 - 4.5 (Optimum 4.0)

High chloride baths have higher electrical conductivity than Watts nickel, can operate at lower temperatures (energy saving) and have slightly better throwing power than the Watts solution. However, not all brighteners can operate under conditions of high chloride.

Brighteners

Among Class I, or Primary Brighteners are anionic sulfonic acids, sulfonamides, sulfonimides and (saccharine + sulfonimides). These compounds are adsorbed on the nickel surface, and give up sulfur to the deposit (up to 0.04%). They thus act as grain refiners, reducing stress (toward compressive). Certain compounds tolerate zinc more than others (sulfinic acid, for example).

Among Class II, or Secondary Brighteners are cationic compounds, acetylinic (C=C), pyridine and sometimes both. These compounds are strong inhibitors. Cathode polarization increases, an increase in tensile stress occurs and carbon is incorporated into the deposit. They are used in the lowest concentration and have the highest consumption rate. They deposit preferentially in low current density areas.

Among Class I Leveling Agents are sulfones and unsaturated carbon groups (C=C). Coumarin is an example. These compounds function as both primary and secondary brighteners. They move stress toward the compressive, increase cathode polarization and concentrate less in valleys than peaks found in the microtopography of the substrate surface. The nickel ion is small compared with levelers and can pass through into valleys. A low concentration of levelers allows secondary brightener into valleys inhibiting leveling.

While the organic additives promote desirable properties in the deposits, there are advantages to having the total organics in solution as low as practicable. Among the advantages are:

- Low occluded organics in the deposit, leading to better ductility
- Improved chromium reception and appearance
- Reduced flaking and blistering
- Better "mileage," *i.e.*, organic usage
- Easier to treat when necessary, and usually less often.

Stress and ductility

Typical bright nickel stress is about 4,000 lb/in^2 (27.6 MPa) compressive. Sulfamate nickel is about 300 to 4,000 lb/in^2 (2.1 to 27.6 MPa) tensile. However, the elongation of a bright nickel is about 4% while that of sulfamate deposits is 25% or better. Elongation is one way to judge ductility. Zero stress does not mean that the deposit is ductile. It often means the deposit is brittle because both tensile stress-causing and compressive stress-causing materials are present.

Maintenance

Brighteners, leveling agents and wetting agents should be added in small amounts and often. The preference is to make automatic additions based on ampere-hours.

Continuous filtration is strongly recommended through a filter with high capacity (4 to 20 turnovers per hour, the more the better) through a suitable distribution piping system. Agitation is necessary. Solution agitation is most efficient when it is uniformly distributed toward the parts to be plated. Air agitation is used, but it has many problems and is not as uniform or efficient as solution movement using spargers and/or eductors. Mechanical agitation is the least efficient method. Filtration through a carbon pack or cartridge is recommended for many bright nickel systems. As a rule of thumb, one pound of carbon per week per 1000 gallons of solution is often used. It should be kept in mind however, that some brighteners are removed or lowered in concentration by carbon filtration.

Impurities

Chromium. As little as 2 ppm can cause serious problems, including extremely high tensile stress, dark streaked deposits and no coverage in low current density areas. 5 ppm can cause the deposit to crack spontaneously.

Zinc, copper and lead. Dark deposits form in low current density areas, Streaks, increased tensile stress (Zn and Pb) and brittleness can develop.

Organics. All of the above can result.

Treatments

Carbon treatment

Heat to 150°F; pump into a storage tank; add 2 to 4 lb of activated carbon per 100 gal of solution. Stir well for 30 min or more. Add 2 lb of filter aid per 100 gal. Let solution settle for 2 to 4 hours and filter back into the plating tank. Keep the intake hose just below the surface while filtering to minimize clogging the filter. When the filtration-transfer is complete, check for any carbon that may have passed through the filter. Extract a sample and pour through a white filter paper in a funnel). Add brighteners, check the analysis, and make other additions as necessary. Lower temperature to normal. Filtering tests are recommended periodically during the filtration process.

Peroxide high pH treatment

This treatment is performed for organic contamination and iron removal. In the storage tank containing the nickel solution, add 3 gal of 30 vol% hydrogen peroxide. Heat to 150°F and stir for 30 min. Add nickel carbonate (2 to 7 lb/100 gal), using a hot water slurry, to raise the pH to 4.5 to 5.0; then add carbon. Stir with a mixer for one hour. Add filter aid as with the carbon treatment above and allow the bath to settle for 8 hr to destroy excess peroxide. Filter back into the plating tank. Adjust by analysis and add brighteners and surfactants.

Permanganate treatment

Heat solution to 150°F. Add 2 to 4 lb of potassium permanganate per 100 gal of nickel solution dissolved in hot water to solution in a storage tank. Stir for 30 min. Add carbon, stir for a further 30 min. Add filter aid. Allow to settle for 2 to 4 hr. Filter back into the plating tank. Test for excess permanganate. If found, add small amounts of hydrogen peroxide until no permanganate remains.

Electrolytic purification (Dummy plating)

The procedure removes copper, zinc, cadmium, lead and some organics. Add 1 gal of hydrogen peroxide per 1000 gal. Adjust pH to 2.5 to 3.0 using sulfuric acid. Plate on as large a cathode area as possible (usually corrugated sheet steel with 3" corrugations) at 2 to 6 A/ft^2, with good agitation. The dummy time is usually 8 to 16 hr. Finally, readjust pH to the operating value of 4.0.

Chromium removal

In a storage tank, lower the pH to 3.0 to 3.5 using sulfuric acid. Add 5 gal of hydrogen peroxide per 1000 gal. Raise temperature to 150°F. Stir for 2 hr. If there is no iron in the solution, add a small amount of ferrous sulfate, about 0.1 g/L. Peroxide aids the iron, which then reduces chromium. Add a slurry of nickel carbonate to adjust the pH to 5.0 to 5.2. Nickel carbonate can be added through the filter followed by recirculating the nickel solution through the filter. Stir for 30 min. Add 4 to 6 lb of carbon per 100 gal and stir for 1 hr. Add filter aid and allow to settle for 2 to 4 hr and filter back into the plating tank. Adjust pH and add brighteners (The procedure also removes iron).

Plating calculations

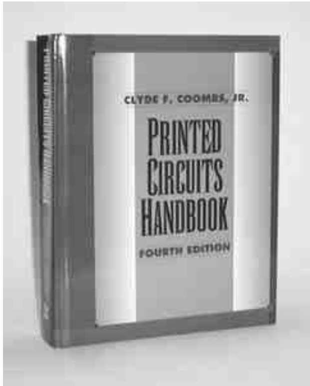
At 97% efficiency, 1.06 g of nickel will deposit per A-hr. For example, 100 A for 12 min will deposit 0.001 in. on a square foot of surface area.

The plating thickness will not be uniform on most parts plated. Current flows to the point nearest the anode. Anode-to-cathode spacing should be 6 in. or more. Robbers and shielding are often necessary to make the deposit thickness more evenly distributed. *P&SF*

References

1. M. M. Beckwith, *Proc. Am. Electroplaters Soc.*, **29**, 80 (1941).
2. W.A. Wesley and W.H. Prine, *Practical Nickel Plating*, International Nickel Co., New York, 1952; p. 30.
3. N.V. Mandich, *Plating & Surface Finishing*, **85** (12), 91 (1998).

Note: The preceding column was adapted from an online article written by Mr. Baudrand for the Technical Library in the website *Plateworld - A Directory of Surface Finishing Suppliers & Plating Shops*, www.plateworld.com — *Ed.*



Nickel Plating Troubleshooting Chart

Dull Deposit (Bright nickel baths)

Possible source of trouble	*Suggested cure*
pH out of proper range	The pH should be adjusted to an optimum value.
Secondary brightener low	Analysis, if available, would indicate the required addition. The bath should be tested with a Hull Cell for the optimum bright range.
Temperature out of range	The temperature should be kept at the proper range within ± 20°F.
Brightener additions out of balance	Where two or more addition agents are used, the proper proportions must be present. Adjustments should be made to the correct values.
Organic impurities	The bath should be tested with a Hull Cell for the presence of organic impurities from rack coatings, tank linings or buffing compounds. When found, they are removed by carbon treatment, with or without preliminary oxidation, as tests may indicate.
Metallic impurities	The bath should be analyzed for presence of copper, zinc, lead and cadmium. Dummy plating, precipitation and/or filtration remove these impurities.
Drag-in contamination	The bath should be checked for contaminating drag-in from cleaners, acid dips, dirty rinses, etc., by cracked or loose tank linings and plating rack coatings or by improper rinsing of recessed work. The source of trouble should be eliminated.

Dark Deposits (Semi-bright nickel baths)

Possible source of trouble	*Suggested cure*
Metallic impurities	Excessive amounts of copper, zinc, lead or cadmium may be present. They are removed by dummy plating.
Concentrations not in proper range	A dull nickel plate may plate dark when used diluted and at higher current densities. The bath should be analyzed to test for this condition and it then should be adjusted.
pH too high	A dull nickel bath will plate dark at a high pH where basic nickel salts will plate out. Adjustment of pH to proper level corrects the difficulty.

Lack of Adequate Adhesion and Peeling

Possible source of trouble	*Suggested cure*
Cleaning cycle	Cleaners should be tested routinely for concentration, temperature, current density, chromic acid or other contamination. When hexavalent chromium is found, it may be overcome by sodium hyposulfite ($Na_2S_2O_4$) treatment.[1] Water rinses should be checked for cleanliness.
Weak or lack of acid dip	A proper concentration acid dip and a clean water rinse should be used as final steps before the work is plated to neutralize any residual alkalinity or remove any oxides present on the surface.
Current interruption	Breaking of current should be avoided, as the laminated deposit may not be adherent, especially when the plated ware is bent.
Repair work (replating)	Repair work should be stripped clean before it is replated, or the old nickel surface must be activated. Activation of the work is accomplished in either of two ways. The preferred method is cathodic treatment in sulfuric acid for a few seconds up to two min.[2] Activation can also be done in the Woods nickel strike. The other involves an obsolete, but effective, cyanide activator; the work is made cathodic for 30 to 60 sec at 70 to 80°F in a 12 oz/gal NaCN solution. At least 6V are needed to produce vigorous gassing on the work being activated.
Over-cleaning	The surface of the work should be checked after cleaning for films or stains from an over-concentrated cleaner. Excessive current density, especially in anodic cleaning, should be avoided.
Under-cleaning	Water breaks from an under-concentrated cleaner indicate under-cleaning. Current density, concentration or temperature may be too low.
Improper acid dipping	Inspection should be made for stains or films from an over-concentrated acid dip, or lack of neutralization from an under-concentrated acid dip. Muriatic (hydrochloric) acid may be more suitable than sulfuric, or vice versa, for the particular job.
Impurities	The plating bath should be tested for metallic impurities such as lead, chromium, or for foreign organics. Metallics such as lead are removed by dummy plating. Chromium is removed by a high pH treatment and sometimes with the additional use of potassium permanganate and lead carbonate.[3] Organics are removed by carbon treatment, either with or without previous oxidation with potassium permanganate, hydrogen peroxide or sodium hypochlorite, as indicated by tests.
Passive basis metal	Alloys, such as stainless steel, heat-treated steel and nickel alloys, may have to be activated by use of the Woods strike or by cathodic acid treatment.[2]
Porosity of basis metal	Thorough rinsing is required to remove entrapped cleaner, acid, etc.

Deposit Lacks Ductility

Possible source of trouble	*Suggested cure*
pH too low	The pH should be tested and adjusted with nickel carbonate. Never use ammonia or alkali carbonates in bright nickels for this adjustment.
Peroxide in excess	Where hydrogen peroxide is being used for removal of organic impurities, excesses should be avoided. When accidental excess occurs, it is removed by heating the bath. Hydrogen in excess may cause pitting or may result in a deposit that is passive to subsequent chromium plate. Also, the ductility of the deposit may be impaired.
Low boric acid	Boric acid may be very much below normal. Analysis will indicate the additions that are required.
Organic contamination	Organic impurities should be checked and removed. The effect of organic impurities should be determined by use of Hull Cell tests. They are removed by carbon treatment, with or without preliminary oxidation, as tests may indicate.
Excess brighteners	Lack of ductility in bright Ni baths results from excess brighteners, especially the secondary (leveling) type. The amount of excess should be determined and then reduced to the proper level. Secondary brighteners are those that give the greatest brightness as well as leveling. They require more frequent additions and normally are present in small concentrations as compared to the other additives. They require frequent Hull cell testing in order to be kept in the optimum range.

Streaky Deposits

Possible source of trouble	*Suggested cure*
Concentrations in the nickel bath not normal	The solution should be tested for low concentrations of nickel, chloride and boric acid and adjusted to the correct values.
Gassing due to dirt in crevices and holes	Adherent buffing compounds and dirt should be eliminated.
Contamination present	Cleaner may be retained in holes or crevices through improper rinsing. Steps should be taken to eliminate such a condition if they are found.
Foreign material suspended in bath	Acid may be retained in holes or crevices due to improper rinsing. Thorough rinses will help to avoid this condition
Localized low pH	Acid may be retained in holes or crevices due to improper rinsing. Hydrogen gassing may cause vertical streaks. Agitation, redesign of racks and other steps may be taken to correct this. Thorough rinses will help to avoid this condition.
Excess of brightener	After additions of brightener, the bath should be thoroughly mixed.

Spotty Deposits

Possible source of trouble	*Suggested cure*
Defect at bottom of work	The bath should be stirred well or agitated to avoid stratification, non-uniform temperature layers or both.
Foreign solid material in the bath	Filtration of the bath eliminates this contamination. Calcium sulfate is less soluble in a hot bath than in a cold one and may precipitate out to cause roughness.
Poor rinsing	Cleaners not thoroughly rinsed off, not neutralized by acid dip or silicates precipitated on the work will cause spotty deposits. Thorough rinses are advised. Additional spray rinsing may be required.
Undissolved boric acid	Heat the bath to dissolve the boric acid crystals formed when the bath is cooled.

Deposit Dark in Recesses and Low Current Density Areas

Possible source of trouble	*Suggested cure*
Metallic contaminants present in bath	The bath should be tested for contamination by copper, zinc, cadmium and lead. If found, they are removed by dummy plating. Hull Cell tests indicate these impurities on the backside of the panel.
Organic impurities	Hull Cell tests indicate these impurities as dark streaks. They are removed, if found present, by carbon/peroxide treatment.
Low current density	Increased current density, as high as possible without burning, is advised.

Poor Throwing Power and/or Poor Metal Coverage

Possible source of trouble	*Suggested cure*
Nickel metal content low	Analysis for nickel concentration and increases to the proper level are in order.
Conductivity poor	A check of chloride content and an increase to the proper level is indicated.
Current density low	An increase in current, as high as possible without burning, is advised. Bipolar or auxiliary anodes may be needed.
Impurities present	The bath should be tested for metallic impurities (Cu, Zn, Cd and Pb) and organic impurities. These are removed, if found present, by dummying to eliminate the metals and by carbon treatment to remove organics.

Loose contacts	A check of all electrical connections to tank, rack and anodes is advised. Cleanliness to insure full flow of current is a must.
Anodes	An inspection of anodes for adequate number, spacing and proper anode area is suggested. Normally two or three anodes per foot of anode bar are sufficient. Check anodes for a black adherent polarized film. Clean anodes.
Burnt Edges or Frosty Plate	
Possible source of trouble	*Suggested cure*
Excessive current density	A reduction of current or an increase of agitation and a higher temperature are in order. Work should not be too close to the anodes.
Bath concentrations low	The bath should be routinely analyzed and built up to the prescribed limits.
Ammonium salts present	Ammonium salts limit the maximum current density and never should be introduced, as they can only be reduced by drag-out.
Excess brighteners	Brighteners in excess may limit maximum practical current density, and should be kept within proper limits.
Chemical contaminants	A test for chromates or nitrates is advised. Chromium is removed by a high pH treatment.[2] Dummy plating at 50 to 60A/ft^2, at a pH of 2 to 3 reduces nitrates. Aluminum and iron are removed by high pH treatment.
Organic contaminants	Hull Cell tests and contaminant removal as per treatment noted earlier are in order.
Excess iron in bath	Analysis for iron in solution should be done. It is removed by increasing the pH and followed up with filtration of the solution.
Pitting	
Possible source of trouble	*Suggested cure*
Antipitting agent out of concentration range	If a surfactant is used, pitting may occur if the concentration is too low, but in some cases also if too high. Operators have a tendency to keep them at high levels. Avoid excesses if possible.
Antipitting agent low	If a proprietary antipitting agent is used, the concentration may be adjusted.
Organic contamination	Organic contaminants may cause pitting and are removed with activated carbon treatment.
Rough deposit pits	Foreign solid materials, such as precipitated iron, dirt or carbon, are removed by filtration.
Air pits	If the pH and concentrations are normal and the bath is clean, inspection for air being introduced by the leaking filter should be done. Also, when everything else is normal, air pits can be obtained from the bath by a large addition of cold water while plating is underway.
Gassing while plating	Zinc basis metal, not completely covered with copper, will be dissolving along with hydrogen evolution and contamination of the bath.
Low pH	Too low a pH will attack the zinc basis metal through a thin copper plate. Adjustment to best operating level is recommended.
Low temperature	Adjustment of temperature to the optimum range is necessary.
Low boric acid	Analysis for boric acid and a build-up to the proper concentration are required for proper buffering of the solution.
Excessive Current	Reduced current, increased agitation and/or increased temperature are suggested.
When heating up bath	A cold bath, especially if not used for some time, will have absorbed air within it that will be released after the bath is heated.
After raising pH	Carbon dioxide, produced when the pH is raised with nickel carbonate, is removed by heating the bath.
Deposit Roughness	
Possible source of trouble	*Suggested cure*
High current density	Adjustment of the current density is required, as excessively high current may cause co-deposition of minute solid particles suspended in bath. Each nickel bath has its intrinsic limiting maximum current density.
Low bath concentration	Too low a concentration of nickel, chloride and boric acid will promote rough deposits. Analysis of the bath and adjustments are in order.
Low temperature	Very low temperature, below about 60°F, depending on current density, will cause roughness. The bath temperature should be adjusted to a practical value.
High pH	A pH above 5.0 may promote inclusion of basic nickel salts in the deposit, depending on current density. A pH adjustment to a proper level is advised.
Iron and aluminum	An excess of dissolved iron and aluminum will promote precipitation under electrolysis at high pH. High pH precipitation plus filtration remove the impurities.
Solids in bath	Filtration of the bath is recommended. Avoid the presence of anode sludge, dirt, buffing compounds, filter-aid and activated carbon in solution. For best performance, continuous filtration with a properly sized filter is a must.
Note: a bright pit with a vertical tail characterizes hydrogen pits. Very fine pits with no tails characterize gas pits from air or carbon dioxide. Rough deposits are sometimes confused with pitting.	