



Chemistry, Relationships and Trouble Shooting of Optical Media Electroforming Baths

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Introduction to Optical Media Stamper Electroforming

Electroforming is the production or reproduction of an article through electrodeposition of metal ions over a mold or mandrel. Like its parent technology, electroplating, electroforming employs direct current (DC) to transfer metal ions from an anode to a cathode via an aqueous medium containing electrolytes. While both technologies share vast similarities in process, chemistry and constituents, plating, whether functional (corrosion resistance) or decorative seeks to permanently modify the substrate. In contrast, the material deposited by electroforming must, by definition, be removable from the substrate. It is this critical difference, removability, which has created a new science and art which, in turn, has allowed for the advancement of many other technologies.

Historical Perspectives

Electroforming is perhaps the only technology that can deliver reproductions of great complexity, maintain fidelity and dimensional tolerances of the original and achieve detail at the submicron level by means of large scale production. From the production of mirrors to optical disc stampers, electroforming has changed the world we live in. The first seamless tubing was manufactured by electroforming around a core from which the deposit could then be removed. It was this technology which allowed for the production of rocket nozzles and jet engine components in which a seam would mean certain failure. With the ability to control the shape of deposition, intricate shapes, such as a radar wave guide, could be produced to change the way we saw the horizon. The ability to control the characteristics of the deposit, such as profile, allowed for the manufacture of items such as satellite telescope mirrors, ultimately changing the way we saw the universe.

Perhaps the most significant development in electroforming was its application to printing. Printing cylinders allowed for the detailed replication of print media on a scale available to all society. This technology was soon adapted into stamping operations for the manufacture of printing plates, phonograph recordings, holograms, and finally, optical media where billions of pieces of information can be replicated as an exact copy of the original in a matter of seconds.

Why Nickel Sulfamate?

Sulfamate nickel chemistries have become the electrolyte of choice for electroforming. While in and of itself nickel metal is ideal for producing the hard corrosion resistant surfaces which will become optical disc stampers, sulfamate nickel is unique in that it allows for greater control of the manner in which the nickel ions are deposited. This is especially true when it comes to the flatness of the electroform. Deposits obtained from sulfamate nickel solutions show a very small grain size without additives that may otherwise impact the internal stress of the deposit. As such, the ability to make very flat deposits that contain exceedingly fine details makes sulfamate nickel the ideal candidate for electroforming optical disc stampers.

GENERAL OPERATING PARAMETERS

The operating conditions of the electroform bath are established in order to maximize the control of the most significant characteristics. In the case of making optical disc stampers, parameters are maintained which control stamper flatness (stress), minimize finishing requirements, and maximize deposition rate. The following operating parameters are recommended on the basis of an understanding of the chemical and non-chemical relationships within the plating process, and the observed trends of optical disc stamper electroforming baths.

Anode Material	Nickel Metal (g/L)	Boric Acid (g/L)	Temp. (°C)	Surface Tension (dynes/cm) {%/vol. E-Imitate Pit}	Internal Stress of Deposit	Anode Corroder* (g/L as chloride)	Grain Refiner (as E-Line ** Refiner)
Use only sulfur depolarized nickel	76 – 105	Saturation by temperature	45 – 60	28 – 32 {0.2 – 0.4}	0 – 4000 PSI Tensile	1.5 – 3.0	0.02 – 0.15 % / volume

Components of Sulfamate Nickel Electroforming

The process of electroforming contains components which fall into two general categories: the physical (which includes the chemicals and the equipment) and the non-physical (such as temperature and solution flow). It may be argued that there is a third hybrid component comprising pH (i.e. hydrogen ions), which will be included with the physical for the sake of this discussion. Understanding the relationships between these components allows for the development of operating parameters and, more importantly, a means of controlling the process itself for ongoing reproducibility. In order to understand the relationships between the various process components we must first understand the function of the constituents themselves.

* Optional Component for improving cathode efficiency and preventing anode passivation

** Optional Component for improving back side finish, controlling stress and increasing hardness

Nickel Anodes (Nickel Source):

Nickel anodes are the source of nickel ions for deposition in sulfamate nickel electroforming. Electrical current from a rectifier is bussed to a titanium basket filled with nickel anodes. Nickel ions are dissolved and carried by the current to the cathode where they are deposited.

Several types of nickel anode materials are available, offering varying shapes and sizes. Whatever the choice may be, only sulfur depolarized nickel anodes should be used. All other anode material may be prone to passivation (polarization) in sulfamate nickel electroforming operations. Passivation occurs when the outer surfaces of the nickel anodes begin to lose their net positive charge. This may happen as the anodes undergo oxidation or other means by which they gain electrons. When this happens the nickel anodes are no longer dissolved by the input of current, causing the sulfamate nickel in solution to decompose instead. Because the anodes must supply the nickel in order to prevent breakdown of the sulfamate nickel electrolyte, it is essential that the anodes be kept in an active state where they are electron deficient. By incorporating a small amount of sulfur into the nickel during the manufacture of the anodes, the resulting anodes, once activated, tend to remain active as the nickel is dissolved around the insoluble sulfur. A second means of promoting anode activation, which will be discussed in more detail later, is through the addition of halogen salts to the bath which corrode the nickel.

Sulfur depolarized nickel anodes are available in two configurations: pellets and crowns (also called rounds). Pellets are generally preferred in optical disc mastering because their shape allows for ease of use and packing of the anode baskets. With regard to performance, crowns provide a much better surface configuration for uniform dissolution and, as a result, are less prone to passivation. A smaller version of the crown anode (Falconbridge Micro-D Crown) has recently become available as an alternative to the pellets¹.

Sizing of the anode basket is important as a 1:1 or greater anode to cathode ratio must be maintained to insure maximum anode efficiency, current distribution, and activation. The anode configuration should be positioned so that the baskets are parallel to the mandrel. Deposit thickness uniformity is achieved by minimizing the distance between the anode and cathode.

The anode basket must be bagged (Canton flannel inner bags and polypropylene outer bags, or comparable material is recommended) or utilize a micro-screen to prevent cathode nodule formation by anode particulates and to collect the sludge formed by the insoluble sulfur. No anode bags or any other equipment should be used until properly leached in a solution containing about 25% bath solution, 0.2% / volume wetting agent, at a pH 2.0 – 4.0. Leach for a 1 - 2 hours, then rinse thoroughly with DI water.

¹ The following anode materials are available from DisChem: INCO S-Rounds and S-Pellets, Falconbridge S-Pellets and Micro-D Crowns.

The anode material is maintained by adding crowns or pellets directly to the anode basket, keeping the basket full at all times. If large amounts of new anode material is to be added to a basket (i.e. > 10 kg.), the anodes should first be soaked in a 30g/L solution of sulfamic acid (technical grade, minimum) and 0.2% / volume wetting agent for one hour, then thoroughly rinsed with DI water. This procedure adequately activates the anodes for use.

Anode passivation resulting from inactive or polarized material is characterized by a steadily decreasing nickel metal concentration in conjunction with falling pH and increasing compressive stress. The phenomenon of falling pH occurs as nickel is plated from the solution rather than the anodes. As a result, oxygen is no longer generated at the anodes while hydrogen continues to form at the cathode. Passivation may occur through inadequate anode corroder, high pH, plugged anode bags/screens, or poor electrical contacts. Low bath circulation or insufficient boric acid can cause the formation of a pale green film on the anodes - nickel hydroxide. This can lead to plugging of the anode bags while insulating the anodes themselves, ultimately causing anode passivation. Should passivation occur, it is necessary to remove the anode material and reactivate the crowns or pellets as described above with sulfamic acid.

Electroforming Solution (Bath Electrolyte):

Sulfamate nickel, $\text{Ni}(\text{SO}_3\text{NH}_2)_2$, serves as the conductive electrolyte for carrying nickel ions from the anodes to the cathode for deposition in electroforming. This solution has a high efficiency (~ 98%) with few breakdown products resulting from normal use. Because of this, sulfamate nickel replenishment is seldom needed. For make-up and replenishment, the nickel metal is maintained by additions of liquid sulfamate nickel concentrate. While available in a variety of nickel metal concentrations, 180g/L nickel material is recommended for purposes of economy and storage. Use only OEM approved suppliers as purity varies dramatically between manufacturers. DisChem's ***E-Form² Electronic Grade Sulfamate Nickel*** is a highly purified concentrate, designed and manufactured specifically for optical disc mastering. Enough material should always be kept in stock for the worst case scenario: where all baths must be made-up new at the same time. Additions of ***E-Form*** may be calculated as follows:

$$\text{Addition volume (Liters)} = \frac{\text{g/L nickel metal needed} \times \text{bath capacity (L)}}{180 \text{ g/L nickel metal (E-Form)}}$$

$$\text{Gallons} = \frac{\text{Liters}}{3.785}$$

The nickel metal concentration may be determined either through E.D.T.A. titration or Baume', with titration being the preferred method. If Baume' is used, variables such as dissolved boric acid and temperature must be considered. When analyzing for the nickel metal concentration, it is important to note that bath level fluctuation may fluctuate

² *E-Form sulfamate nickel chemistries and additive are approved by all major optical media galvanics OEM's, and are recommended exclusively by Digital Matrix and ReynoldsTech.*

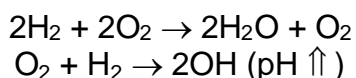
due to water evaporation, influencing the net result. For this reason, interpretations of the analyzed nickel concentration should be based on trends, and not singular readings. A sudden drop in the nickel concentration may indicate a loss of solution volume or dilution of the bath. A steady trend of decreasing nickel concentration over time suggests possible anode passivation, particularly if found in combination with declining pH and increasing compressive stress of deposit. During passivation, nickel metal is plated from the solution rather than the anodes. This causes a breakdown of the nickel sulfamate into nickel ions, ammonium ions and soluble sulfur compounds:



The sulfur compounds will co-deposit and cause a significant increase in compressive stress while the build-up of ammonium ions in the bath greatly lowers the efficiency, eventually poisoning the system. This subject is covered in greater detail in the section titled *Internal Stress of Deposit*. Heavy solution drag-out during mandrel removal may also show up as a gradual decline in nickel concentration. A trend showing a steady rise in the nickel concentration may indicate an excess of anode corroder, causing chemical dissolution of the anode material, especially if observed in combination with high tensile stress not readily reduced through carbon filtration.

Sulfamic Acid (pH Control and anode activation):

pH should be measured daily with an external temperature compensation probe at the actual bath temperature. Under normal circumstances, the pH of the bath rises with use. This occurs as oxygen (O₂) generated at the anode couples with hydrogen (H₂) generated at the cathode to form water (H₂O). The net reaction leaves uncoupled oxygen, which in turn, forms hydroxides:



Changes in pH are one of the best tools for evaluating the *health* of the bath. It is necessary to maintain the pH within the defined parameters for normal use: 3.8 - 4.4. The effect of pH on the internal stress of deposit follows a parabola, with high and low pH leading to increased tensile stress. pH provides the lowest stress of deposit at 4.0.

Bath trends showing a steady and gradual increase in pH over time indicate that the normal reaction shown above is occurring. As the pH reaches the specified upper limits for normal use (4.4), it is necessary to lower the pH using high purity sulfamic acid (***E-Line pH*** is a 99.9% high purity, low ammonium sulfamic acid available from DisChem). It should be noted that using acids other than sulfamic acid can cause rapid breakdown of the sulfamate nickel ion, producing detrimental ammonium and sulfur compounds. Sulfamic acid may be pre-dissolved in DI water for easier bath mixing, though never for more than twenty four hours prior to adding it to the bath, as sulfamic acid will undergo hydrolysis.



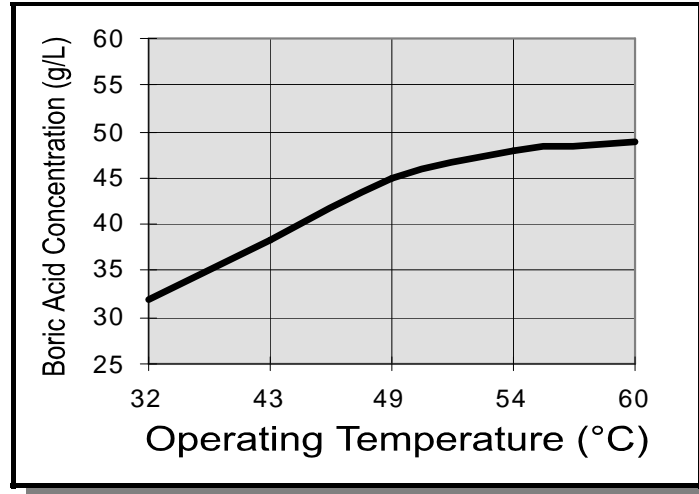
Trends in falling pH tend to suggest anode passivation, as oxygen is no longer being generated at the anodes to couple free hydrogen ions. Remedial action should be taken to rectify the cause of passivation. Such actions include cleaning and re-packing of the anode baskets and anode material, cleaning of the anode bags/screens, checking electrical contacts, and analysis of the anode corroder concentration. Should the pH fall below 3.8, it may be necessary to add nickel carbonate to the bath. As nickel carbonate is slow to dissolve, it should be partially pre-dissolved in DI water prior to adding it to the bath. Add the nickel carbonate slurry in small quantities, checking the pH after allowing each addition to completely dissolve, so as not to over add and raise the pH too high.

Below a pH of 3.8, the rate of anode corrosion and efficiency is increased. While these characteristics may be desirable in circumstances such as high-speed plating, they may cause increasing nickel metal concentrations as a result of chemical dissolution of the anodes. In addition, the increase of hydrogen ions (H+) at lower pH's may lead to an increase in pitting and burning of the electroform. A more serious problem that may occur when excessive hydrogen is present in the bath is an accelerated rate of hydrolysis of the sulfamate nickel ion, releasing ammonium and sulfur compounds into the bath. Problems resulting from low pH may be minimized by increasing the pH within the desirable range, running the bath at a higher temperature to increase cathode efficiency (i.e. more oxygen), increasing the boric acid to saturation, or by increasing cathode agitation to prevent localized pH changes.

High pH (> 4.4) should be avoided as it reduces anode dissolution and efficiency, allowing anode passivation to occur. Where metallic contaminants are present, high pH will also increase the likelihood of nodule formation as the contaminants are converted to insoluble hydroxide forms.

Boric Acid (pH Buffer):

Boric acid is maintained at the point of saturation, by temperature, to buffer hydrogen generated at the cathode during electrolysis. Without this buffering capacity, burning of the electroform may occur and may also lead to pitting as gas builds up around the cathode. The surest way to maintain saturation is to fill an anode bag (properly leached, as described above) with boric acid and allow it to dissolve as needed in the dummy compartment. A continuous drop in the boric acid concentration over the period of a week indicates the need to check and refill the boric bags. Only use boric acid with a minimum purity of 99.8%, such as DisChem's High Purity Boric Acid.

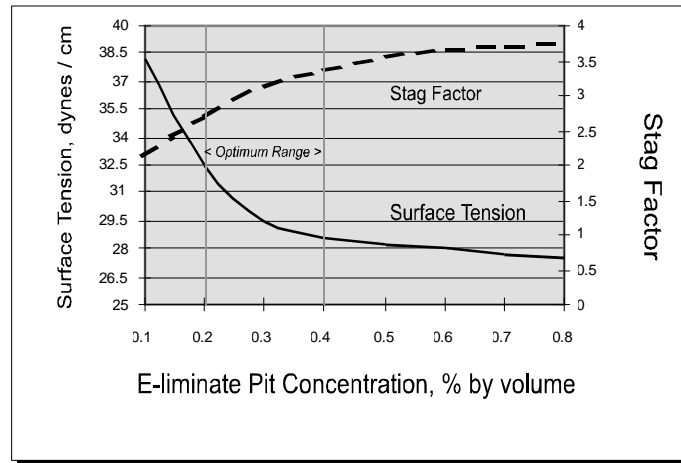


Note: Boric acid is operated at saturation by temperature to buffer pH changes. Temperature fluctuations will affect the solubility of the boric acid so that decreases in solution temperature will cause a precipitation or removal by filtration of the boric acid.

Wetting Agents (Pitting Inhibitor):

Wetting agents are organic surfactants added to the bath to help prevent hydrogen gas bubbles from clinging to the cathode. If not removed from the electroform, nickel will deposit around the gas bubbles, creating pits. While most CD electroforming baths have excellent agitation and are not prone to pitting, wetting agents should be added to the baths as preventative maintenance. The concentration of wetting agent in the bath is determined through measurement of the surface tension (dynes/cm) with the use of a tensiometer or stalagometer drop test. Organic wetting agents generally contribute only slightly to tensile stress and are readily removed by carbon filtration. The wetting agent concentration should be determined at least once a week, after carbon filtration, or when pitting is evident on the work. It is important to select a low foaming wetting agent because of the high rate of solution circulation used in stamper electroforming.

The choice of wetting agents should be carefully evaluated as they have typically been designed for uses other than optical disc electroforming and may contain additives that can deteriorate photoresist and NPR. Many of the proprietary wetting agents also use carcinogenic formaldehyde as a preservative. DisChem's ***E-eliminate Pit*** was designed to be 100% compatible with both positive photoresist and NPR and contains no formaldehyde. In addition, specialty wetting agents, such as E-Liminate Pit, can help in the removal of stubborn organic contaminants by acting as a "net" so that they are more easily removed by carbon filtration.



Comparison of wetting agent on surface tension. As can be seen, wetting agents tend to be very effective in small quantities. The relationship shown in this graph is specific to DisChem's E-Limitate Pit optical media wetting agent.

Grain Refiners / Leveling Agents

Grain refiners are added in small quantities directly to the electroforming bath in order to reduce the size of the crystalline structure of deposited nickel. Similarly, leveling agents are added to affect the directional growth of the crystalline structures, from columnar to laminar. While not new to the industry, grain refiners and leveling agents have traditionally been avoided in optical stamper electroforming because of their impact on stress. In addition, leveling agents containing certain sulfur compounds and organic agents such as butyne diol are not readily removed from the bath so that detrimental accumulation may occur with regular use. Still, the use of grain refiners can significantly reduce finishing requirements, maintain low stress and, may even increase the life of the stamper by increasing hardness.

With the developments of DVD and continuous groove recordable formats, such as CD-R and DVD-R, new attention is being given to additives that can offer a finer grain structure while increasing the life of the stamper.

DisChem's **E-Line Refiner** was designed to address both the stress and removability concerns of optical media electroforming, while refining the deposit grain structure for reduced finishing requirements, maintaining low stress and increased stamper hardness. Because grain refiners such as E-Line Refiner are deposited proportionally to the nickel, it is possible to calculate replenishment on an ampere hour consumption rate for consistent results.

Anode Corroder (Passivation Inhibitor):

Anode corroders, such as DisChem's high purity **E-fficiency Aid**, are added in low concentrations to the bath during make-up to inhibit anode passivation, particularly

where the frequency of operation is sometimes sporadic. The concentration of these halogen salts should be maintained between 1.5 and 3.0 g/L (as chloride). Above this concentration, the halogen can cause a significant increase in tensile stress of the deposit, even though the chloride is not co-deposited with the nickel. Under these circumstances, the stress will not be readily reduced by carbon filtration and the bath will have to be diluted. This component needs to be analyzed only when passivation is suspected (falling pH and decreasing nickel concentration) or when stress is not reduced by carbon filtration. Liquid nickel salt solutions of nickel chloride and nickel bromide may also be used when provided in sufficient purity.

Temperature (Cathode efficiency, rate of deposition):

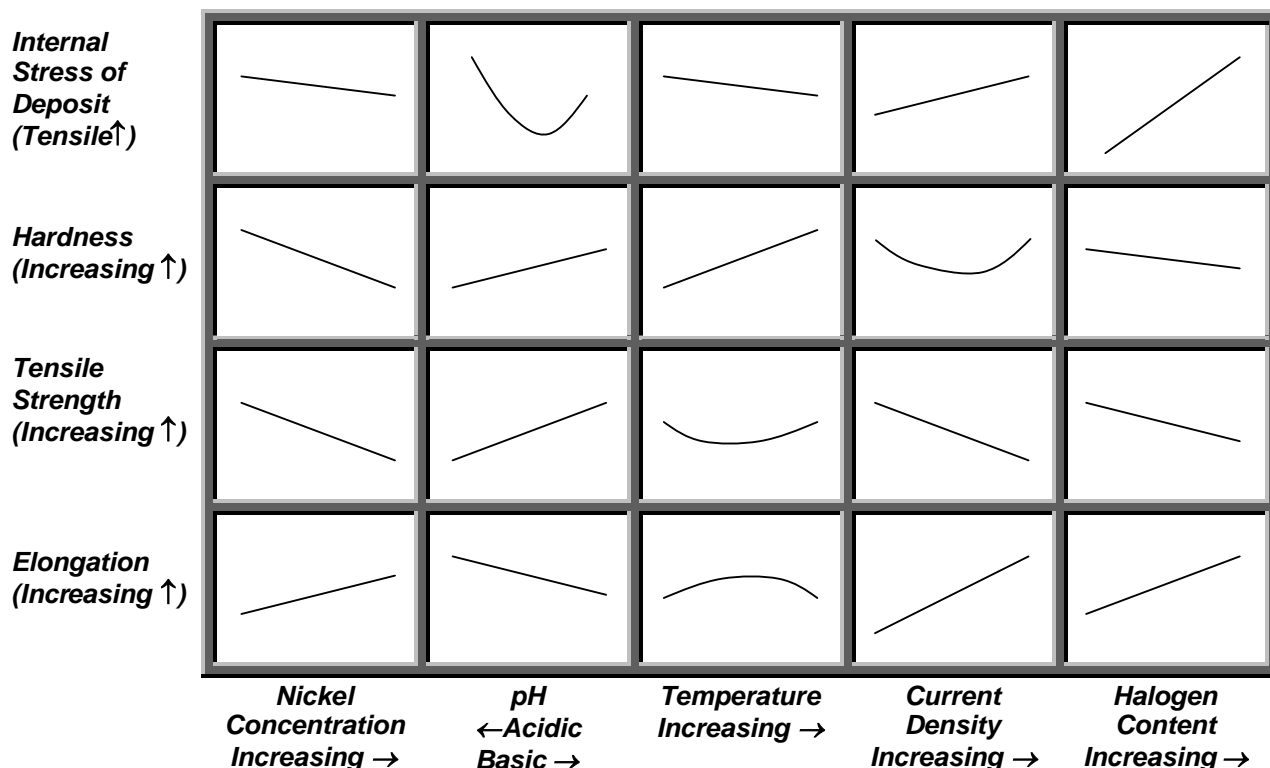
The operating temperature of the plating solution ultimately determines the cathode efficiency and the rate of deposition. At too low of a temperature (<30°C), cathode burning may occur where as, at too high a temperature (80°C), the nickel sulfamate begins to deteriorate. Temperature can be used as an effective tool in controlling internal stress of deposit. An inverse relationship exists between stress and temperature so that an increase in temperature will lower the tensile stress.

Filtration and Agitation

Adequate filtration and agitation are needed for high quality electroforming. Filtration flow rate should be sufficient to turn over the entire bath volume three or more times an hour. Filtration should be constant and involve pre and final filtration prior to returning the solution to the plating tank. As filtration and agitation rates are almost always specific to the equipment, especially with regard to the recent introduction of non-rotational cathode heads, these parameters should be obtained from your equipment manufacturer.

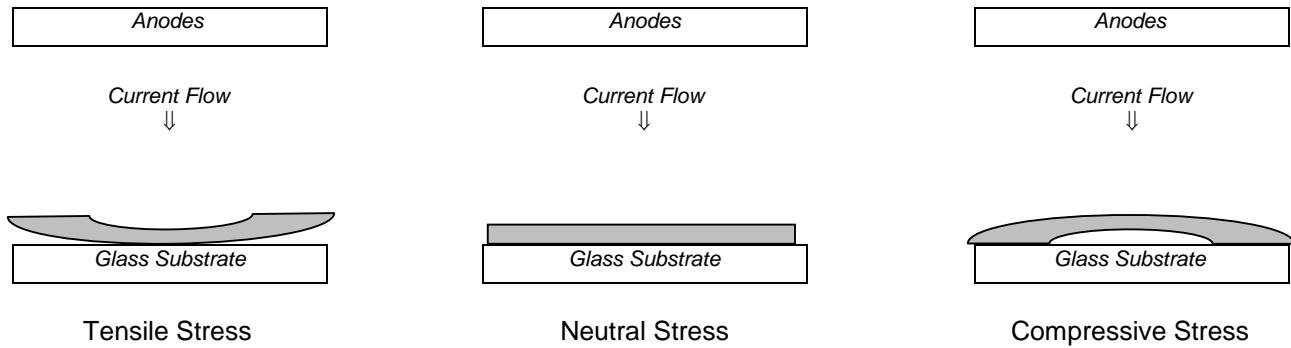
RELATIONSHIPS OF COMPONENTS AND PARAMETERS

Understanding the relationships of the various constituents and components operating within the electroforming process allows for the development and implementation of process controls. Five basic components within the electroforming process: nickel concentration, pH, temperature, cathode current density and halogen content (Cl^-), can be graphed to show their direct relationships to four major characteristics of the deposit: internal stress of deposit, hardness, tensile strength and elongation.



Internal Stress of Deposit:

Internal stress of deposit is a measurement of the relationship, or energy, between nickel crystals. Crystal growth is both columnar (vertical) and laminar (horizontal) during electrolytic deposition. The charge on the crystal groups, as well as their size and shape, creates varying forces of attraction and repulsion between these groups. Internal stress of deposit is a description of this phenomenon in terms of the net force exerted. The total of these forces create an overall internal stress of the deposit which is either neutral (zero stress / flat), tensile (positive: attracted crystals attempting to contract to relieve stress / edges bending away from the mandrel, toward the anodes), or compressive (negative: repelling crystals attempting to expand to relieve stress / center pushing away from the mandrel, toward the anode).



Internal stress of deposit is measured using a spiral contractometer. This instrument deposits plating solution onto a calibrated helix. Depending on the stress of the deposit, the helix will either contract or expand with the results typically expressed as pounds per square inch (lbs/in²), tensile or compressive. Through the spiral contractometer method, a quantitative analysis of these forces can be conducted within a reasonable degree of error and reproducibility. This quantitative analysis, in turn, provides a qualitative understanding of the expected stress of an electroformed deposit; in other words, the overall flatness of the electroformed stamper. As all bath parameters may influence fluctuations in stress, careful evaluation of bath trends must be done to control the ultimate stamper flatness.

While Spiral contractometer testing is sensitive and tedious, it provides the best understanding of the stamper flatness by manipulation of bath operating conditions. Warped or flexed stampers may cause pressing problems with regard to mounting and/or increased block error rate.

In general, the following results can be expected from manipulations in bath operating conditions with regard to internal stress of deposit:

- *Nickel Concentration*: Slight inverse relationship; higher metal provides lower stress.
- (More compressive) stress.
- *pH*: U-parabola relationship; lowest stress provided at pH 4.0, with increased stress above and below this point.
- *Boric Acid*: Negligible relationship.
- *Wetting Agent*: Negligible to slight increase in tensile stress.
- *Temperature*: Inverse relationship to stress; higher temperature provides lower stress.
- *Anode Corroder*: Increases tensile stress.
- *Grain Refiners / Leveling Agents*: cause either tensile or compressive stress, depending on composition.
- *Current Density*: Stress increases with current density. This is important in establishing an optimum current ramp.
- *Deposit Thickness*: A thicker deposit will generally show reduced tensile stress.
- *Soluble sulfur compounds*: Significantly reduce stress.

Under normal circumstances, the bath should provide a relatively consistent deposit stress. Fluctuation may result from inconsistent use of the bath, contamination, and changes in the operating conditions. Slight adjustments in bath temperature and pH are all that is normally needed to control stress in terms of stamper flatness.

Common Contaminants and Their Effects

Most common contaminants that may be encountered in an optical media electroforming bath are either metallic or organic. The acceptable limits on these contaminants vary greatly, as do their effects on the internal stress of deposit. The five most common metallic contaminants seen in stamper electroforming baths are Iron (Fe), Copper (Cu), Chromium (Cr), Lead (Pb) and Zinc (Zn). The tolerable limits for these elements, their effects on the deposit and possible sources of the contamination are listed below:

Effects of Common Five Metallic Impurities

<u>Metallic Impurity</u>	<u>Maximum Tolerable Limit (ppm)</u>	<u>Effects on the Deposit</u>	<u>Possible Sources of Contamination</u>
Iron (Fe)	0.15	Increased tensile stress (1000 psi / 300 ppm), increased hardness, reduced ductility.	Impure sulfamic and boric acids, impure sulfamate nickel concentrate, dissolution of equipment and tooling components, hard water, drag-in of impure cleaning solutions.
Copper (Cu)	0.04	Increased tensile stress (1000 psi / 200 ppm), reduced cathode efficiency, reduced ductility, darkening of the deposit.	Dissolution of copper bus bars and electrical contacts, impure sulfamic and boric acids, impure sulfamate nickel concentrate, impure anode material.
Chromium (Cr)	0.02	Significantly increased tensile stress (1000 psi / 1 ppm), reduced cathode efficiency, reduced ductility, darkening of the deposit.	Drag-in of chrome based stamper passivation solutions, impure sulfamic and boric acids, impure sulfamate nickel concentrate, impure anode material.
Lead (Pb)	0.02	Significantly increased tensile stress (1000 psi / 2 ppm), reduced hardness of the deposit.	Dissolution or leaching of plating equipment, impure sulfamic and boric acids, impure sulfamate nickel concentrate, impure anode material.
Zinc (Zn)	0.05	Increased tensile stress (1000 psi / 150 ppm), reduced cathode efficiency, streaked looking deposits, reduced ductility.	Impure sulfamic and boric acids, impure sulfamate nickel concentrate, impure anode material.

The effects of organic contaminants can vary significantly, but are usually characterized by dark or stained deposits, deposits that appear to stain very easily with fingerprints, solvents, etc., and increased tensile stress in the deposit. Fortunately, almost all organic contaminants are easily removed by carbon filtration.

A third category of contaminants are inorganic breakdown products resulting from hydrolysis and oxidation of sulfamate nickel and sulfamic acid. These include ammonium ion and sulfur compounds. Unfortunately, both of these contaminants are difficult to remove, with ammonium ion reduced only through dilution of the bath. Soluble sulfur compounds may exist in a variety of forms and co-deposit to reduce tensile stress (cause compressive stress) by as much as 1000 psi / 5 ppm. It should be noted that sulfur contamination is also possible from impure carbon and failure to leach any plastic components prior to use. Ammonium ion, while not the most drastic contaminant in its effects, is certainly one of the most serious as it may deem the bath unusable once the concentration approaches 2000 ppm. At 1000 ppm, high ammonium ion will begin to exhibit a darkening of the deposit, a slight increase in tensile stress, and a lowering of the cathode efficiency. These symptoms will continue to increase until the bath efficiency is reduced to the point where it is not possible to plate deposits without burning. Ammonium ion can not be removed from the bath and can only be treated through dilution until the remaining concentration is at an acceptable level.

Trouble Shooting Sulfamate Nickel Electroforming Baths

Understanding the function of chemical and operational parameters within an electroforming process provides a means of manipulating the relationships between various constituents to influence the end product. In short, once the pieces that make up the process are understood, it is possible to design and apply process controls. Furthermore, and just as important, knowledge of the system provides a means of systematically and logically solving problems, should they arise.

Below are listed the most common problems encountered during optical stamper electroforming, presented in the order of frequency of cause and the appropriate corrective action.

Trouble Shooting Common Problems

<u>Problem</u>	<u>Possible Cause</u>	<u>Corrective Action</u>
Pitting of the deposit	Low wetting agent	Analyze and replenish
	Low boric acid	Analyze and replenish. Maintain at point of saturation by anode bag method.
	High pH	Lower with sulfamic acid
	Organic contamination	Carbon filter
	Iron contamination	Treat with peroxide and filter
	Other metallic contamination	Dummy plate
Roughness / nodules	Dissolved air	Check system for leaks
	Insoluble matter in solution	filter, check for holes in anode bags or screens
	Iron hydrate	filter
	Iron contamination	Treat with peroxide and filter
Burning	Low boric acid	Analyze and replenish. Maintain at point of saturation by anode bag method.
	Low pH	Raise with nickel carbonate
	Low temperature	Check heating / chilling system, heat to operating range
	Low nickel content	Analyze and replenish
	Insufficient agitation	Check circulation system
	Ramp to fast	Evaluate and reprogram
Current too high	Reduce maximum current	
Dark, stained or streaked deposits	Metallic contamination	Dummy plate
	Organic contamination	Carbon filter
	Low boric acid	Analyze and replenish. Maintain at point of saturation by anode bag method.
High tensile stress	Organic contamination	Carbon filter
	Metallic contamination	Dummy plate
	Iron contamination	Treat with peroxide and filter
	High halogen content	Dilute

Trouble Shooting Common Problems, continued

Problem	Possible Cause	Corrective Action
High tensile stress	High ammonium ion concentration	Dilute. Check for signs of anode passivation.
High compressive stress	Sulfur contamination	Electrolyze solution at 3 – 5 amps / ft ² on corrugated plate giving 1:2 anode to cathode ratio. Dilute bath.
	Anode oxidation products (passivation)	Remove anode material and reactivate with sulfamic acid. Use only sulfur depolarized anode material. Use anode corroder, if necessary.
Poor initiation of premetallized (seed) layer	Seed layer passive	Activate by rinsing with solution of 10 g/L sulfamic acid just prior to lowering into electroform solution. Decrease transfer time between premetallization and electroforming.
Poor efficiency / slow plating rate	Electrical problems	Check current flow
	Low pH	Raise with nickel carbonate. Check anodes for passivation.
	Low nickel concentration	Replenish with concentrate. Check anodes for passivation.
	Passive anodes	Remove anode material and reactivate with sulfamic acid. Use only sulfur depolarized anode material. Use anode corroder, if necessary.
	Metallic contamination	Dummy plate
	High ammonium ion concentration	Dilute bath. Check anodes for passivation. When pre-dissolving sulfamic acid, never keep for more than 12 hours.
	Nitrate contamination	Dilute bath
	Hydrogen peroxide in solution	Heat to 65°C until removed
Falling nickel concentration in conjunction with falling pH	Anode passivation	Remove anode material and reactivate with sulfamic acid. Use only sulfur depolarized anode material. Use anode corroder, if necessary.

Specialized Treatments and Corrective Actions

It is occasionally necessary to employ specialized treatments as a means of averting or correcting problems within the electroforming system. The following treatments are provided as a means of correcting specific problems that may occur outside of the normal process control. It is important to note that it may not be possible to process work as normal while these treatments are being conducted.

Removal of Solublized Sulfur Compounds

As stated earlier, anode passivation causes a breakdown of the nickel sulfamate. As nickel is plated from the solution rather than the anodes, sulfur compounds and other by-products are left behind to contaminate the bath. Soluble sulfur compounds are extremely effective at reducing deposit stress (makes it more compressive). While difficult to remove, sulfur contamination can be treated by a number of different methods:

- Low pH High Current Density Oxidation: This method provides the fastest and most complete removal of sulfur contamination, but requires altering normal bath parameters and shutting down production. Lower the bath pH to 2.5 and dummy plate at 150 ASF with a 15:1 anode to cathode ratio. This provides an excess of oxygen to be generated to couple with the free sulfur compounds. Insoluble sulfates may then be easily removed by filtration.
- Idle Oxidation: If the bath is allowed to stand idle for a period of time, natural oxidation of the soluble sulfur will occur. This method is slow and may take several days to weeks depending on the concentration of sulfur to be removed.
- Dummy Plating: As soluble sulfur compounds co-deposit with the nickel plate, normal dummy plating at high current densities may be utilized for its removal. This method can be slow but can be run where production can not be impeded and the amount of contamination is minimal.
- Dilution: Remove a portion of the bath to reduce the concentration of soluble sulfur compounds.

Continuous Dummy Plating

Uncontrollable tensile stress may also result from metallic contamination, which is usually easily removed through low current density dummy plating. The current density on the dummy cathode should be run over an alternating range of 0.5 - 5.0 amps/ft² for a period of days, or until the stress is reduced. This procedure is also somewhat effective at breaking down organic contaminants.

Hydrogen Peroxide Treatment

A hydrogen peroxide treatment will effectively convert problematic iron contamination into insoluble iron hydrate. Once in this form, the iron contamination is easily removed by normal filtration. This treatment will also convert hexavalent chromium to trivalent chromium. Do not attempt to run production during this procedure.

1. If possible, pump the solution to a treatment tank or common sump.
2. Raise temperature to 55°C
3. Add 0.1 to 0.25% by volume of 30% hydrogen peroxide while agitating the solution. The peroxide solution should be diluted in water (1 part peroxide, 10 parts water) prior to adding it to the tank. Continue agitation for 1 – 2 hours.

4. Raise pH to 5.0 – 5.2 using a slurry of technical grade or better nickel carbonate. Nickel carbonate dissolves slowly so it is important to add the slurry in small quantities, monitoring the pH, so as not to over add. Good agitation is essential for thorough mixing.
5. Raise solution temperature to 65°C and maintain at temperature for 1 to 2 hours to drive off any excess peroxide.
6. Cool to 55 – 60°C and begin normal filtration. Filter for a minimum of 4 - 8 hours.
7. Cool to normal operating temperature and check solution level, replenishing any water that may have evaporated during the treatment.
8. Lower pH to 3.8 – 4.2 using sulfamic acid. Filter for 1 to 2 hours before running production.

Back to Back Carbon Filtration

In order to remove stubborn organic, a back to back carbon filtration procedure may be required. The back to back carbon filtration process uses two stages of carbon filtration in combination with a peroxide breakdown process. Please note that the use of hydrogen peroxide will not cause an appreciable increase in the ammonium ion content as long as the peroxide is not used in quantities greater than list herein. This process may also be used for the removal of stubborn organic contaminants, but is not recommended as part of a normal bath maintenance procedure. Do not attempt to run production during this procedure.

1. Carbon filter bath, 2 – 3 hrs, at normal operating temperature. All residual wetting agent will have been removed when the surface tension is greater than 65 dynes / cm.
2. Heat to 57°C (135°F) and change carbon filters.
3. Add 0.25 % by volume hydrogen peroxide (30%) and filter with agitation for 2 – 3 hours.
4. Heat to 65°C (150°F) and maintain temperature for 1 hour to drive off residual peroxide. Caution: Exceeding 70°C for several hours may cause a breakdown of the sulfamate nickel solution, releasing ammonium ion into the bath.
5. Cool to normal operating temperature. Remove carbon filters and replenish wetting agent.

Important Note:

The information contained in this bulletin is provided for use in training and general guidelines for operation. Optimum results will be obtained when using the mentioned product within the recommended parameters and with the consensus of the applicable OEM. As final use of this information is beyond the control of the authors, we assume no responsibility for misuse of the information provide herein, product applications discussed, or for use which may infringe upon third party patents.

Products mentioned in this article available from DisChem:

- **E-Form** Electronic Grade Sulfamate Nickel
- **E-Line pH** Refined Electronic Grade Sulfamic Acid, 99.9%
- **E-eliminate Pit** Wetting Agent
- **E-fficiency Aid** Anode Agent
- **E-Line Refiner** Grain Refiner / Hardening Agent
- DisChem Boric **Acid**, 99.8% Minimum Purity
- INCO anode materials

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