SURPASSING CHROME PLATING WITH
COMPOSITE ELECTROLESS NICKEL COATINGS

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Abstract: Electroless nickel is a key segment of the metal finishing industry. Its properties are widely recognized and utilized in a broad array of industrial applications. The inclusion of certain particulate matter within electroless nickel deposits can be a powerful enhancement of the coating's inherent characteristics, and, in many instances, adds entirely new properties to the nickel layer. While composite electroless nickel coatings have increased in notoriety and commercial acceptance, there are an ever growing number of applications which may benefit from these coatings; especially as productivity, quality, and environmental concerns continue to expand at an increasing rate coupled with the ongoing development of such composite coatings. This paper demonstrates how the inclusion of certain particles within electroless nickel coatings surpass chromium plating for hardness, wear resistance, impact resistance, lubricity, uniformity, thermal transfer, and economy. Moreover, composite electroless nickel coatings are truly non-line of sight coatings. Attention is given to variables such as particulate matter used, particle size, particle density, coating thickness, friction, wear resistance and other unique properties. Also presented are descriptions of the newest advances in the field of composite electroless plating.

Electroless plating has grown to be a mature segment of the metal finishing industry. Its characteristics and distinction from other coating methods including electroplating are well known and widely utilized. Numerous metals and alloys are capable of being deposited electrolessly. Electroless nickel (EN) processes, discovered in the 1940's, are the most commercialized in this field. Composite EN coatings are an established and still a developing field in the EN industry.

These properties make composite EN coatings increasingly advantageous for:
1. Ever more demanding usage conditions requiring less wear, lower friction, etc.
2. Facilitating use of new base materials such as titanium, aluminum, low cost steels, ceramics, and plastics.
3. Allowing higher productivity of equipment at greater speeds, less wear, and less maintenance downtime.
4. Replacing environmentally problematic coatings such as electroplated chromium.

Electroless Nickel: Electroless nickel is an alloy of 88-99% nickel and the balance with phosphorous, boron, or a few other possible elements. EN coatings, therefore, can be tailored to meet the specific requirements of an application with the proper selection of the nickel's alloying element(s) and their respective percentages in the plated layer. EN is commonly produced in one of four alloy ranges: low (1-4% P), medium (6-8% P), or high (10-12% P) phosphorous, and electroless nickel-boron with 0.5-3% B. Each variety of EN thus provides properties with varying degrees of hardness, corrosion resistance, non-magnetism, solderability, brightness, internal stress, and lubricity.

All varieties of EN, including composite EN coatings, can be applied to numerous substrates including metals, alloys, and nonconductors; with outstanding uniformity of coating thickness to complex geometries. It is this last point which most commonly distinguishes electroless from electrolytic plating methods such as electroplated chromium and electrolytic nickel. When chromium plating parts with complicated geometries

such as extrusion screws, molds, gears, and many more; the chromium must often be applied with uneven thicknesses from one area of the part to another. While the thinnest areas of the coating may meet the specification, the remainder of the plating is too thick and must be re-worked with a mechanical post plating method to achieve the specified coating thickness. After plating, EN and composite EN coatings do not need to be ground, re-machined, or otherwise re-worked to get the part into proper tolerance. This benefit translates into cost, time, and material savings.

Electroless nickel is produced by the chemical reaction of a nickel salt and a reducing agent. Typical EN baths also include one or more complexing agents, buffers, brighteners when desirable, and various stabilizers to regulate the speed of metal deposition and avoid decomposition of the solution which is inherently unstable. Diligent control of the solution's stabilizer content, pH, temperature, tank maintenance, loading, and freedom from contamination are essential to its reliable operation. EN solutions are highly surface area dependent. Surface areas are introduced to the solution by the tank itself, in-tank equipment, immersed substrates, and by contaminants. Continuous filtration, often sub-micron, of the solution at a rate of at least ten turnovers per hour is always recommended to avoid particle contamination which could lead to solution decomposition or imperfections in the plated layer. [1]

Composite electroless nickel: Composite EN is intriguing; therefore, as it intentionally introduces insoluble particulate matter into the solution for subsequent codeposition into the coating. The stability ramifications to the plating bath are significant. One gram of 1.0 micron sized diamond particles, for instance, contains 310,000,000,000 particles. [2] This creates a surface area loading near 100,000 cm2/L, approximately 800 times the preferred loading of a conventional EN bath. [3] Early work on composite electroless coatings was attempted in 1966 by W. Metzger et al. [4]

This natural incompatibility between an inherently unstable, surface area dependent plating bath and an extraordinary loading of insoluble particles has been overcome by the precise addition of particulate matter stabilizers or PMSs as taught in U.S. Patents 4,997,686, 5,145,517, 5,300,330, and 5,863,616. The methods disclosed therein have made composite EN plating reliable and commercially viable by modifying the Zeta potential of particles in a plating system. Zeta potential is an effect of electrostatic charge. [5]
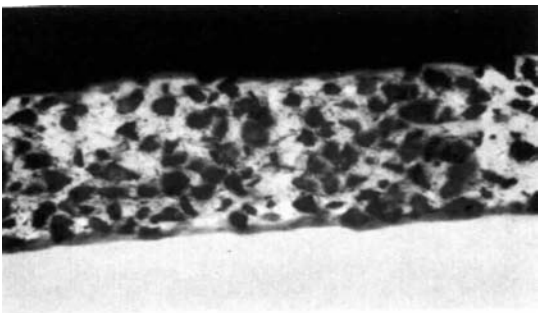

Photo 1 -- A cross sectional photomicrograph at 1000x displays a dispersion of diamond within EN

Composite EN coatings are regenerative, meaning that their properties are maintained even as portions of the coating are removed during use. This feature results from the uniform manner with which the particles are dispersed throughout the entire plated layer, as observable in cross sectional photograph 1. Photograph 2 displays the surface of a composite coating of diamond EN. Particle matter suitable for composite EN incorporation can be up to approximately 10 microns in size. There is essentially no lower limit to the size of particles that can be incorporated. For example, beneficial work with nanometer sized diamond particles has even been achieved in applications requiring wear resistance without surface roughness due to contact with sensitive materials. Narrow particle size distributions are specified for the various categories of composite EN coatings, as discussed below. Certain performance benefits have been discovered (U.S. Patents 4,547,407 and

4,906,532) when a composite coating is generated simultaneously utilizing two distinct particle sizes. It is theorized that the smaller particles fill the spaces between the larger particles.
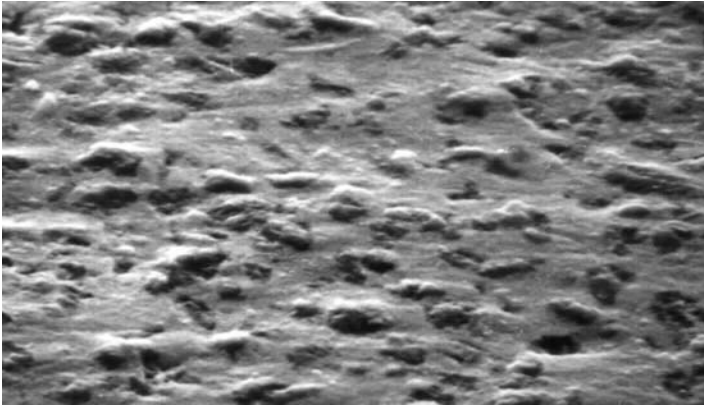

Photo 2 – The surface at 1200X of a composite EN – diamond coating

Depending on the particle sizes and certain plating conditions, coatings can be produced with a particle density of up to 40% by volume. Particle densities of 20 to 30% are optimal for most commercial wear applications. Lesser densities may not provide the maximum benefit available from the particulate matter, and significantly higher densities risk premature wear of the coating since there may not be enough of the metal "glue" to prevent the particles from being removed. This observation indicates that the typical wear mechanism of composite EN coatings is not wear to the particles themselves, but rather wear to the surrounding metal matrix which eventually allows the particles to be removed. It is for this reason that proper selection of particle size, shape, and density is useful to optimize each application.

Composite EN coatings naturally deposit uniformly in thickness regardless of geometry, including non-line of sight areas such as internal diameters. Composite EN coatings with consistent particle distribution have been applied to the internal diameters of metal tubing as small as 0.020" in various medical devices. This inherent feature of uniform coating thickness provides numerous savings of time, material, and costs compared to hard chrome plating and other processes that require the over-application of coatings to then be ground or polished back into tolerance.

Coating thickness specifications are typically set on a value between 10 and 25 microns (0.0005" to 0.001") are typical for most applications. Very tight specifications of coating thicknesses can be established for particular applications and routinely reproduced within a few microns by the plating service provider. As with conventional EN, composite EN coatings can be heat treated after plating to enhance their hardness and their adhesion to the substrate. Most composite EN coatings can operate at continuous temperatures of 400°C (750°F). They have a shear strength of 20,000 to 45,000 psi (138-310 MPa) on aluminum substrates, and 30,000 to 60,000 psi (207-414 MPa) on steel substrates.[6]

A wide variety of particulate matter is capable of codeposition in EN coatings. In each instance, the plating bath must be modified to accept the specific particles and produce an optimal coating. The three general categories of composite EN coatings that have been developed and commercialized are for wear resistance, lubricity and indication. This paper focuses on how composite EN coatings with wear resistant and lubricating particles surpass chromium. This paper also provides a brief description of composite EN coatings for indication purposes as well as certain advanced combinations of composites and deposition techniques have recently been developed.

Wear resistance: Coatings designed for increased wear resistance have proven to date to be the most widely utilized composite EN coatings. Within this category, an extensive array of suitable particles can be used including diamond, silicon carbide, aluminum oxide, tungsten carbide, boron carbide, and chromium carbide. These materials differ not only in hardness and wear resistance, but also in their shape. Any of these factors can affect surface and performance characteristics. These particles are typically used in nominal size ranges of 1 to 4 microns with a few applications benefiting from 6 micron sized particles. Such coatings generally have particle densities of 20-30% by volume, and coating thicknesses of 20 to 25 microns (0.0008" to 0.001"), although 50 microns (0.002") coatings have proven advantageous in certain extremely high wear applications.

Proper selection of the optimal particulate material specifications including size, shape, density, and material for specific wear resistance applications depends on many factors including the specific wear mechanism involved. For this reason, standardized wear testing methods are instructive, but cannot substitute for controlled testing of various composites under the actual intended use conditions.

Various test methods have been employed to evaluate wear resistance of different materials and coatings. The results of one of these tests is depicted in Chart 1 [6] below. The results in Chart 1 are from a yarnline test where a yarn of textile material is drawn across the surface of coated test pieces according to a constant speed and contact pressure. Wear rates are in mil^3/hr. It provides an indication of the wear resistance of various materials in textile applications. The performance advantage of the composite EN – diamond coating over hard chromium is dramatic.
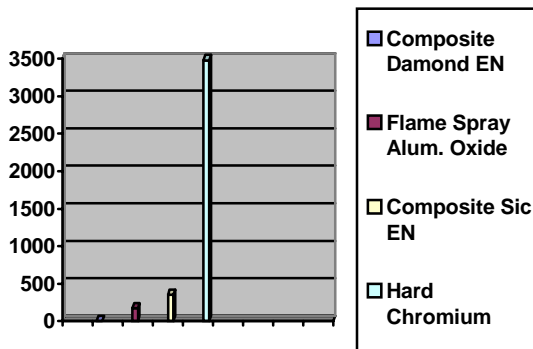
Chart 1 – Yarnline Abrasive Wear Test

Table 1 [6] below further demonstrates the wear resistance of a composite EN - diamond coating versus other surface treatments including chromium plating and a common tool steel by the Taber test method. This Method evaluates the resistance of surfaces to abrasive rubbing produced by the sliding rotation of two unlubricated, abrading wheels against a rotating sample. This test measures the worn weight or volume in 10^4 mil^3. As Table 1 indicates, hard chromium plating wears at a rate four times as fast as the composite EN – diamond coating in this wear method.

Table 1 -- Taber Wear Test Data

Coating or Material	Wear Rate per 1000 cycles	vs. diamond
Composite diamond-EN	1.159	1.00
Cemented tungsten carbide Grace C-9 (88WC, 12 Co)	2.746	2.37
Electroplated hard chromium	4.699	4.05
Tool steel, hardened R_c 62	12.815	13.25

In a recent study on the wear resistance of various materials codeposited into EN, extensive attention was given to produce samples with particle material being the only variable. Coating thickness, nickel-phosphorous alloy, particle density, particle size range and, post plating heat treatment were all tightly controlled on 2.0 inch^2 steel panels. Seven such panels were tested with one bare steel panel and one electroless nickel plated (particle free) panel as controls against five composite plated panels incorporating aluminum oxide, boron carbide, diamond, silicon carbide and tungsten carbide particles. All panels were wear tested by an alumina slurry of 5 micron powder contacting the panel surface under a constant load. The wear data was converted to a new constant equating the volume of material lost (microns^3) per unit force (Newton) for unit length (mm). The results are contained in Table 2 below.

Table 2--Abrasive Slurry Wear Resistance of Composite EN Coatings

Coating	Wear Constant	Wear vs. Steel	Wear vs. EN
None	28	—	1.75
EN	16	0.57	—
Al$_2$O$_3$-EN	10	0.36	0.63
BC-EN	7	0.25	0.44
Diamond-EN	7	0.25	0.44
SiC-EN	12	0.42	0.75
WC-EN	9	0.32	0.56

Lubricity: Certain particles can be incorporated into EN to produce a coating with all the properties of EN as well as a low coefficient of friction[7]. Although these composite coatings also provide wear resistance benefits, they are in a separate category based on the unique characteristics they embody including dry lubrication, improved release properties, repellency of contaminants such as water and oil. Coatings in this category of composite EN have also proven advantageous in replacing and surpassing the performance of chromium plating.

Applications employing composite coatings with lubricating particles typically utilize coating thicknesses of 6-25 microns (0.00025" to 0.001"). Since these thicknesses are less than those typical of the wear resistant composite coatings discussed above, an underlayer of conventional (often high phosphorous) EN is applied to insure maximum corrosion resistance when required.

Most commercial interest in composite lubricating coatings has focused on the incorporation of PTFE into EN deposits. The properties of PTFE are widely recognized. Composite PTFE-EN is commonly available in two density ranges: 10-15% and 25-30% by volume. The desired density depends on the specific usage conditions of the individual application. PTFE particles in such composite coatings are 1 typically micron or smaller.

There are a variety of other particles with self lubricating properties when codeposited into EN. Materials other than PTFE have become an area of increasing interest in the plating field, especially those materials that are inorganic. PTFE is organic and decomposes at temperatures above 300°C. This distinction results in significant performance differences. Many inorganic lubricating materials are harder than PTFE and withstand higher temperatures than PTFE. As PTFE is a very soft material, its inclusion in EN makes the composite coating comparatively softer, especially as the percentage of PTFE increases.[8] Higher temperature resistance permits higher post-plating heat treatment temperatures yielding greater hardness of the EN matrix. These factors make the composite inorganic lubricant coatings harder and more wear resistant than PTFE-EN in many conditions.

Table 4 -- Friction Coefficients for Various Composites and Materials

Load	Friction		Load	Friction		Load	Friction

Coating	kg/cm^2	Coefficient	Coating	kg/cm^2	Coefficient	Coating	kg/cm^2	Coefficient
EN-PTFE	0.1	0.12	EN-BN	0.3	0.09	EN-BN	0.5	0.08
EN-BN	0.1	0.13	EN-PTFE	0.3	0.13	EN-PTFE	0.5	0.13
EN (No particles)	0.1	0.18	EN (No particles)	0.3	0.16	EN (No particles)	0.5	0.15
Chrome	0.1	0.25	Chrome	0.3	0.40	Chrome	0.5	150.00

Table 4 [9] documents the coefficients of friction for a variety of coatings under different load conditions. Boron nitride (BN) is one such inorganic material with lubricating properties. It has the ability to withstand temperatures up to 3000°C depending on the atmosphere; and, as demonstrated in Table 4, composite EN with boron nitride has a lower coefficient of friction than composite EN-PTFE under higher load conditions, <u>and a lower coefficient of friction than chromium plating under all load conditions tested.</u>

Additional testing results included in Table 5 [10] demonstrate another feature of composite EN with lubricating particles compared to chromium plating and plasma coatings. In a Falex apparatus, coated blocks were tested against uncoated steel rings. The volume losses of the rings are listed in Table 5 which show a dramatic improvement in wear resistance for all three composite EN coatings with lubricating particles over chrome and plasma coatings for this type of wear mechanism.

Table 5—Falex Testing Results

Block Coating	Steel Ring Volume Loss in 3^{10-6}
EN-BN	0.43
EN-PTFE	3.44
NiSLIP 25 TC*	7.31
Chrome	16.35
Plasma	45.60
Plasma	122.18

*NiSLIP 25 TC is a proprietary composite EN with inorganic lubricating particles of Surface Technology, Inc., Trenton, NJ.

Indication: This category of composite EN coatings is a more recent and novel development in the field. These coatings have all the inherent features of EN, and appear normal under typical lighting; but when these phosphorescent coatings are viewed under an ultraviolet (UV) light, they emit a distinct, brightly colored light. Particles of a number of different materials, each generating different colored light emissions, have been successfully codeposited in EN. Photograph 3 shows three aluminum shapes under UV light each coated with a composite EN coating containing a different material which emit red, blue, and white colored light respectively. This unique property has been developed for two main uses, as taught in U.S. Patents 5,514,479 and 5,516,591.

Photo 3 – Aluminum shapes coated with composite EN with three colors of light emitting particles photographed under UV light

First, the light can serve as an indicator layer, warning when the coating has worn off and replacement, or recoating, is necessary. In this case, it is the disappearance of the light that signals wear. This feature permits the avoidance of wear into the part itself which may cause irreparable damage to a potentially costly part, or the production of inconsistent product by a worn part such as a mold, die, presses, etc. Such an indicator layer can even be applied prior to, or under, another functional coating to signal when the functional coating has worn

through to expose the indicator layer. In this case, it is the appearance of light that signals wear. As with any other EN coating, these composite coatings can be chemically stripped, leaving the substrate ready for recoating.

Second, the presence of a colored light emission from the coating can be valuable in authenticating parts from a distinct source. This is especially promising for the identification of genuine OEM parts which otherwise can be routinely counterfeited.   Its value also extends to the identification of specific manufacturing lots where conventional methods of marking are not sufficient or durable. For these purposes, the indicator layer needs only to be 6 to 12 microns (0.00025" to 0.0005") thick, with a density dependent on the particles used.

Hand-held, battery operated UV lights are readily available, and make inspection for the indicator layer at the operating site fast and convenient.

Advanced Composite Variations: *Combination Composites*: For certain applications, hybrid combination composite coatings have been developed to satisfy unique requirements. These coatings incorporate particles of two or more materials into the same plated layer. When significant wear resistance and a low coefficient of friction are necessary, for instance, wear resistant particles can be combined with lubricating particles in the EN bath to produce a coating with both characteristics. Light emitting particles can also be combined with particles of the other categories to create a more wear resistant or lubricious coating that also emits light to identify the origin of the part or to indicate when the layer is worn from use. Thicknesses, materials, particle sizes, and densities for these combination composites all depend on the specific application.

Overcoating: Overcoating is a procedure often utilized for composite wear resistant coatings. Composites containing particles (as discussed above) are smooth to the touch, and sufficient as is for most applications. There may be, however, some particles on the surface of the coating that are only partially entrapped in the coating as seen in photograph 2. When the coating is intended to contact certain delicate materials such as textile and paper products, these protruding particles may be deleterious or require a break-in period of use to smooth the surface. Instead of employing mechanical means to smooth the surface, and instead of operating a coated part for a less productive "break-in" period; an overcoat can be applied. For a composite EN coating, a conventional EN overcoat layer of only about 5 microns is sufficient to cover the composite surface and provide a new surface which will be smoother and more easily leveled by use. U.S. Patents 4,358,922 and 4,358,923, which disclose this method, teach that the smoothness provided by the overcoat layer persists even after it has worn and the composite layer is contacted.

Composite Gradients: A new method to accomplish the physical benefits of an overcoated composite coating without requiring immersion of a substrate in two separate plating baths has recently been developed. The new method involves plating a substrate in a composite plating bath for a period of time sufficient to deposit the desired thickness of a composite layer, then altering certain parameters of the plating conditions to continue depositing the metal, but with less or no particles being codeposited. This, in effect, replicates the dual layer overcoat structure.

Selective Codeposition: In a subsequent refinement to the composite gradient development described above, another novel method has recently been developed. Instead of generating a gradient in particle density across the thickness of a composite layer (from substrate to top surface), the invention disclosed in U.S. Patent 5,674,631. provides for different particle densities in different areas of the plated article. This invention is useful for an article where only a certain area(s) needs the beneficial properties of a codeposited particulate material; and if the particles are costly, if codeposited particles would be problematic in certain areas, or if conventional methods of masking are impractical.

Conclusion: Incorporating particles within electroless nickel allows the creation of coatings embodying all of the inherent features of EN as well as the characteristics of the particulate material. Many of the varieties of

composite EN which are already available on a reliable industrial scale can not only replace chromium plating, but also surpass the performance of chromium plating. As this paper has demonstrated, this is especially true for wear resistance and lubricity properties. These properties consequently offer economic benefits to the use of composite EN coatings. In addition, the uniformity of EN coating thickness across complex geometries provides economic benefits in the production of the coatings themselves. This is especially evident when compared to electroplated coatings such as chromium which often must be plated in thicknesses above specification in some areas of workpieces (to achieve the proper thicknesses in other areas) and then mechanically brought back into tolerance. As evident by the variety of composite EN coatings and new methods of deposition presented in this paper, these coatings can be tailored and optimized according to the requirements of specific applications.

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Biography:

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Michael D. Feldstein is President of Surface Technology, Inc.; a world recognized leader in metal finishing founded in 1973. In this position, Mr. Feldstein directs the overall activities of the Company from the production in its state-of-the-art facility to the marketing of its innovative products and services. He has been with Surface Technology, Inc. since 1989. Mr. Feldstein's education includes a B.A. from Tulane University and a M.A. George Washington University. Mr. Feldstein has authored and presented numerous publications internationally, and is the inventor of one U.S. Patent. Mr. Feldstein is a member of the AESF, ASTM, and other organizations. In 2000, Mr. Feldstein founded CoatingDepot.com, an Internet website for sourcing of products and services in all fields of the coating industry.