Is There Relevance of Deposit Brightness in Electroless Nickel Processes?

Nicole J. Micyus, Carl P. Steinecker, MacDermid, Inc., New Hudson, Mich., USA

The degree of brightness of decorative and functional applications for electroless nickel (EN) deposits is sometimes hard to distinguish with the naked eye. Gloss and distinctness of image (DOI) measurements quantify the level of light reflection and image sharpness, respectively. With current legislative and regulatory limitations on the use of cadmium (Cd) and lead (Pb), gloss and DOI measurements statistically help evaluate non-regulated organic and inorganic brighteners. The quantification aids with the development and continuing brightness improvement of EN systems used for decorative applications. Ultimately, these measurements provide a benchmark for appraising the brightness of End of Life Vehicle (ELV) formulations relative to bright deposits obtained from conventional electroless nickel solutions containing Cd and Pb.

For more information, contact:
Nicole J. Micyus
MacDermid, Inc.
29111 Milford, Rd.
New Hudson, MI 48165
Phone- (248) 437-8161
Fax- (248) 437-1560
E-mail: nmicyus@macdermid.com

Introduction

With current regulatory limitations on conventional electroless nickel (EN) brighteners such as cadmium and lead, new organic and non-organic brighteners/additives are being tested and implemented. However, the effectiveness of these new brighteners is still being compared to the brightness levels obtained with traditional EN systems. It can be difficult to judge whether the Restriction of Hazardous Substances (RoHS), End of Life Vehicle (ELV) and Waste Electrical and Electronic Equipment (WEEE) Directive- compliant deposit is bright enough for a particular application or substrate. How does this new deposit compare to conventional EN deposits obtained from baths containing cadmium and lead? When is an EN deposit, bright enough?

The relative brightness of electroless nickel deposits is sometimes difficult to ascertain with the naked eye. The brightness can depend on obvious variables such as the substrate, direction of the substrate grain, surface roughness and the deposit thickness. However, it can also depend on more subtle environmental parameters, for instance the type, amount and relative angle of light shining on a deposit. Gloss, distinctness-of-image (DOI), and haze measurements provide numerical results for the relative brightness or visual impression of a deposit and/or substrate.

Gloss, DOI and haze each evaluate a different visual characteristic of a surface and impart a numerical rating. The American Society for Testing and Materials (ASTM) defines gloss as “the angular selectivity of reflectance, involving surface-reflected light, responsible for the degree to which reflected highlights or images of objects may be seen as superimposed on a surface”.[1] Basically, gloss is the measure of light intensity reflected by the surface of a material at a particular specular angle. ASTM defines distinctness-of-image gloss as “the sharpness with which object outlines are reflected by a surface”.[2] DOI measures the reflective clarity of an object’s reflection. Haze measures the cloudiness of a specimen caused by scattering light.[3] On surfaces with reflection haze, a halo is observed around the reflected image. Gloss, DOI, and reflection haze can help quantify surface brightness on a variety of substrates: plastics, metallic, ceramic, paint and paper finish.

Gloss meters direct light onto a specimen at a specific angle (depending on the material) relative to normal and then detects the light reflected at the same angle on the other side of the normal.[4] The specular light or component (R_s) is the light that is reflected from an object at an angle equal to but opposite the incident light as shown in Figure 1.[5] Most gloss meters measure at specular angles of 20, 60, or 85°.[4] Gloss readings are calculated according to equation 1.[6]

$$(1)\ R_s = (R_{s\ sample} / R_{s\ standard})*100$$

$R_{s\ sample}$ is the light reflected at the specular angle for the specimen and $R_{s\ standard}$ is the R_s value for the gloss standard. A black glass standard is used when measuring

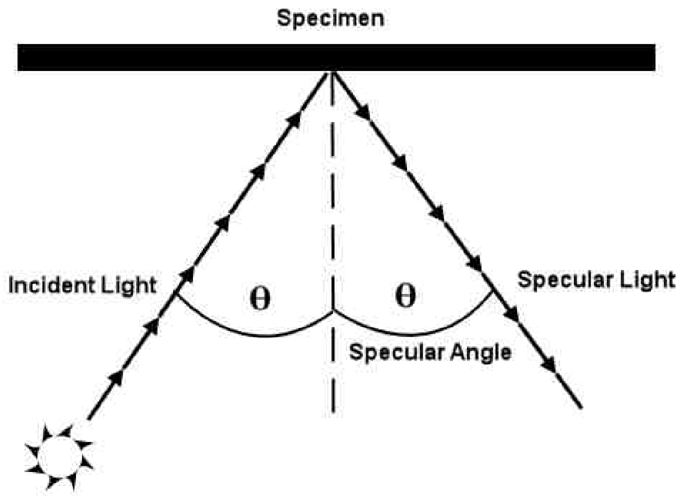

Figure 1. Gloss Measurement

nonmetals and a mirror when measuring metals. Gloss is reported as gloss units (GU).

There are several different geometric angles for measuring gloss. A 20º angle (0-2000 GU) is used to measure highly reflective materials, such as high-gloss EN deposits and other brightened metals. An angle of 45º is used for semi-gloss materials such as ceramics and films. A 60º angle (0-1000 GU) is used for most semi-gloss materials such as plastics and related products. A 75º angle is used for low-gloss products such as paper and vinyl. An angle of 85º is used for matte materials, which exhibit low gloss (0-160 GU). This measurement is also called sheen.[4]

Distinctness-of-image and gloss tests measure surface quality in a similar manner, by projecting light onto a surface at a particular angle, however their methods of detecting the reflected light differ. DOI goes one step further than gloss (specular reflection) by indicating how light is distributed around the specular angle.[6] Figure 2 illustrates the configuration for distinctness-of-image measurements.[5] A light spread of 0.3° from the specular is responsible for DOI gloss. DOI is calculated according to equation 2.[6]

$$(2)\ DOI = [(R_s - R_{0.3}) / R_s] * 100$$

Measurements are made 0.3° ($R_{0.3}$) from the narrow specular band to determine how much the specular reflection is spread. A larger value of DOI corresponds to a more distinct image. Distinctness-of-image measurements range from 0 to 100 and like gloss depends on substrate and surface roughness.[6]

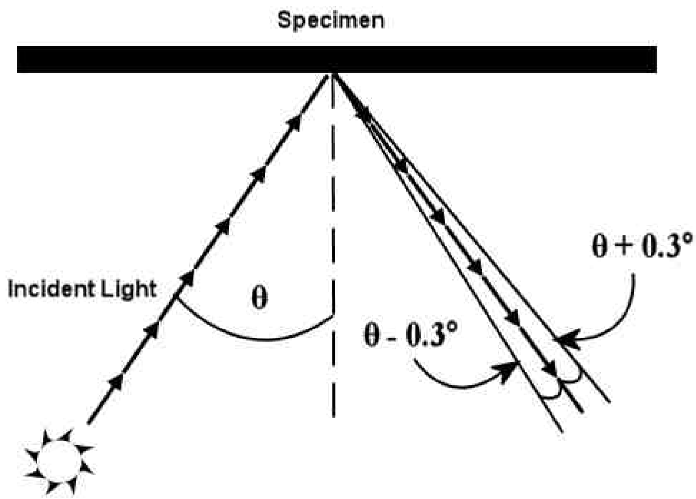

Figure 2. Distinctness-of-Image Measurement

Reflectance haze, like DOI, indicates how light is spread around the specular angle. The light spread 2, 5 and 15° from specular is responsible for narrow-angle reflection haze, wide-angle reflection haze, and diffuseness, respectively.[7] Equation 3 is the calculation for haze, where $R_{x°}$ is the reflectance at x degrees from the specular angle.[7]

$$(3)\ x° \text{ haze} = (R_{x°} / R_s) * 100$$

Since haze measurements are so similar to DOI, most distinctness of image instruments also measure haze at various angles.

Many standardized tests exist for gloss and DOI measurements of surfaces. Table 1 lists some gloss and DOI related standardized methods.

Table 1. Standards for Gloss and Distinctness-of-Image

Gloss	Distinctness-of-Image (DOI)
ASTM D523-89	ASTM E430-05
ISO 7668: 1986	ASTM D5767-95
ASTM D2457-97	ASTM D4039
JIS Z 8741-2002	
ISO 2813:1994	

Gloss standards include a variety of tests for various substrates and angle measurements. ASTM D523-89 “Standard Test Method for Specular Gloss” covers the measurement of the specular gloss of nonmetallic specimens for gloss meter geometries of 60, 20 and 85º.[1] Most commercially available gloss meters conform to ASTM D523. ISO standard 7668 deals with specular gloss of brightened aluminum. JIS Z 8741-2002 is the Japanese counterpart to ASTM D523-89. ASTM D2457-97 is basically equivalent to test D523, but for plastics and ISO 2813 determines the specular gloss of non-metallic paint films.

Most commercially available DOI instruments cover ASTM E430-05 and/or D5767-95. The DOI measurements presented in this work are covered by ASTM E430-05, the "standard test method for measurement of gloss of high-gloss surfaces by abridged goniophotometry".[2] A goniophotometer measures reflected light as a function of angle of detection. ASTM D5767-95 (2004) covers instrumental measurements of DOI gloss of coating surfaces.

A related measurement to DOI is reflection haze. ASTM D4039 is a test method for reflection haze of high-gloss surfaces.[3] The higher the haze value the more surface cloudiness the deposit exhibits. Reflected haze is typically used to measure clear coatings and brushed metals. Most commercial DOI instruments can measure haze at 2, 10 and 15º. Gloss-haze gloss meters are now commercially available as well, capable of haze measurements at 2°.

Gloss and DOI measurements were used to determine brightness variations. First, deposit thickness and substrate influences were investigated, so suitable testing conditions could be established. ELV EN bath temperature and pH were tested to optimize deposit brightness. The measurements were also used to compare conventional EN deposit brightness to ELV deposits and evaluate ELV deposit brightness over bath life to 6 metal turnovers (MTO). Haze measurements were performed to compare the relative cloudiness of mid-phos (7-9%) EN systems, both conventional and ELV. Most importantly, gloss and DOI testing was used to helped evaluate new organic and inorganic brighteners for ELV EN systems to improve brightness.

Test Methods

A BYK-Gardner haze-gloss gloss meter was used for gloss measurements at a specular angle of 20°. A HunterLab Dorigon® II series DOI instrument was used for DOI measurements. Testing for gloss and DOI measurements were performed by South Florida Test Services, a division of Atlas Material Testing Technology LLC (Miami, Fla.). A Tricor Systems, Inc. Model 807A DOI/Haze Meter was used to perform all haze measurements (Elgin, Ill.). Tricor Systems, Inc. performed all haze measurements at a 2° angle.

Deposit parameters were kept constant throughout the study to maximize gloss and DOI reproducibility. All deposits were plated using best practice bath parameters (i.e., pH and temperature) unless otherwise noted. Also deposit thickness for all panels were 0.5 ± 0.05 mil (500 μin) unless otherwise noted. Gloss, DOI and haze measurements were taken in the same direction as the grain of the substrate, which led to higher values. All gloss, DOI and haze measurements are reported as an average of twelve readings (6 on each panel side) unless otherwise specified. The average of the two sides was necessary due to slight variations in substrate lots. Twelve readings per panel resulted in an average gloss percent difference of 1.3% for identical panels.

Initially, several tests were completed to determine adequate parameters for reproducible surface quality measurements. Five panels were plated with an ELV low/mid-phos (3-5%) system to determine how gloss would be affected by deposit thickness. Deposit thicknesses between 0.20 and 0.90 mil were plated on steel panels at a bath life of 0 MTO. Deposit thicknesses were determined using x-ray fluorescence, XRF (Oxford Instruments, Whitney, U.K.).

In addition, gloss testing was accomplished to ascertain the effect different substrates had on gloss measurements for identical EN deposits. The four substrates used for testing were: 3” x 6” steel GMC 42E panels, 3” x 6” cold rolled steel (CRS) panels, 3” x 3” 3105-H24 aluminum panels (ACT, Inc., Hillsdale, Mich.), and 2.75” x 3.88” 267-mL size zinc-coated Hull cell panels (Larry King Corp., Rosedale, N.Y.). Steel panels were prepared by the following cleaning cycle: 50% HCl, rinse, anodic cleaning, rinse, acid activation, rinse, and plate. Aluminum panels were cleaned by soak clean, rinse, deoxide clean, rinse, zincate (1 min), rinse, zincate strip (50% HNO_3), rinse, zincate (30 sec), rinse, and plate.

The gloss and DOI results for several EN system deposits were compared on steel panels to determine whether one test or both tests are needed to evaluate differences between ELV bath variations. All deposits were plated on steel panels at 0 MTO. Both gloss and distinctness-of-image were run on the same panel.

Also, various EN deposits on Hull cell panels were evaluated for reflectance haze to determine whether the haze measurements are crucial for evaluating surface quality. Reflectance haze measurements, at a 2° angle, were performed to compare the cloudiness of a traditional ultra-bright EN deposit containing Cd and Pb and an ELV mid-phos system. Haze measurements both in the direction of the substrate grain and across the grain were evaluated.

An electroless nickel system was evaluated for gloss and optimal bath parameters were established to produce the brightest deposit. A mid-phos ELV system at various bath pH and temperature levels was compared to the gloss results at normal operating specifications. The EN deposits were plated on steel panels at 0 MTO.

A variety of brighteners were evaluated in a mid-phos ELV EN system. Gloss numbers were used to compare organic and non-organic brighteners’ efficacy based on gloss units obtained. All deposits were plated on steel panels at 0 MTO. Several EN brighteners for an ELV mid-phos system were also evaluated for their extended brightening power. Deposits were plated on steel panels and evaluated at 0, 1, and 6 MTO.

Results

Gloss values are influenced by the thickness of the nickel phosphorus (NiP) deposit. Figure 3 shows a relationship between gloss and thickness for an ELV low/mid-phos EN system plated on steel panels. As the thickness increases,

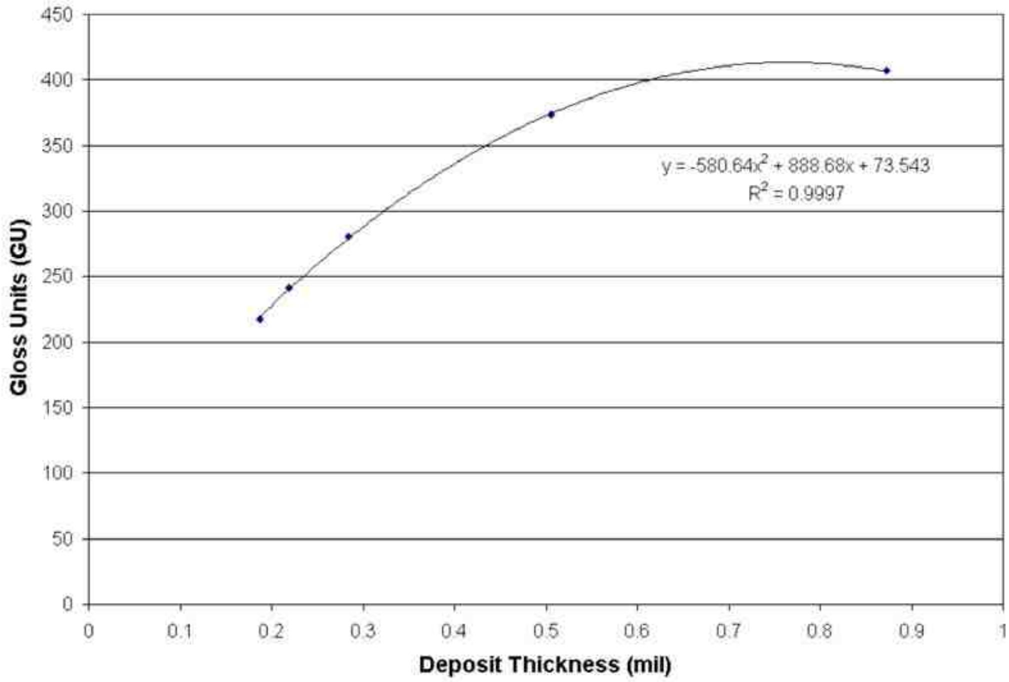

Figure 3. Deposit Thickness Influence on Gloss Results for EN ELV Low/mid-phos System

the gloss units also increase. Each EN system can be represented as a graphical line (either linear, logarithmic or polynomial) depending on substrate and thickness ranges chosen. Different EN systems will yield a singular relationship between gloss and thickness. It is important when comparing gloss numbers obtained from different panels to make sure the thickness is within 5 to 10% of one another. The graphical representation of gloss versus deposit thickness can be a useful tool for visualizing at what rate the gloss values climb when a thicker deposit is plated and at what point the gloss does not increase with increasing thickness.

Gloss results are substrate dependent. Four different substrates were used to determine the differences in gloss for various EN systems. The differences in gloss between the conventional mid-phos containing Cd and Pb and the ELV EN systems is easily detected in Figure 4 for the steel GMC 42E, CRS and aluminum substrates. For example, the differences between the ELV mid-phos and the ELV mid-phos with brightener B4 on either the steel GMC, CRS, 3105 aluminum or Hull cell is a 30, 43, 44 and 3% increase in brightness, respectively. The substrate selection has a large impact on the gloss readings and consequently the gloss differences obtained between EN systems. Substrates with high gloss background values absent any deposit or coating make it more difficult to judge gloss differences or improvements.

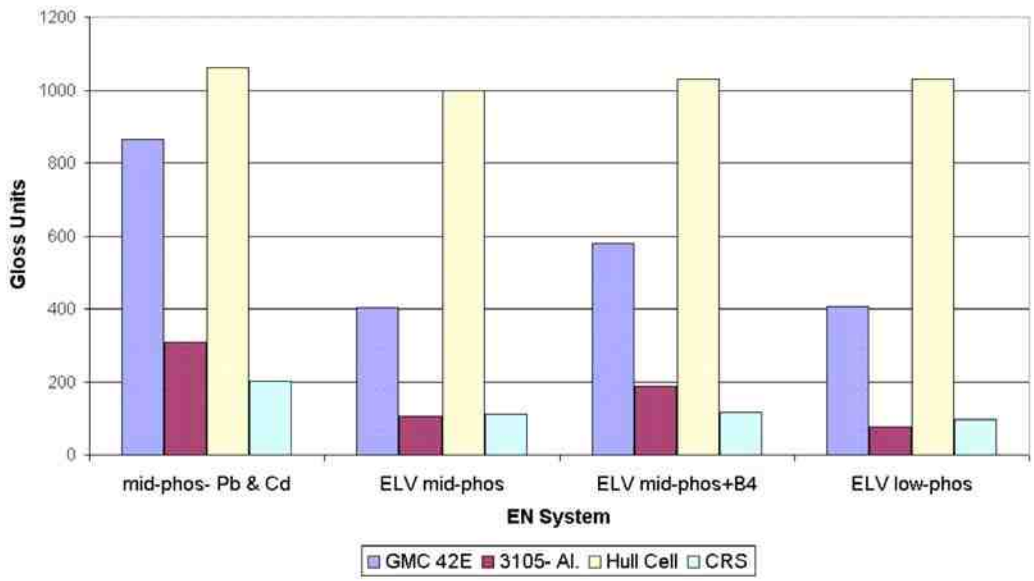

Figure 4. Gloss Results Dependence on Substrate

Surface roughness also has an effect on the gloss readings. The order of increasing surface roughness for the panels is Hull cell, GMC 42E steel, 3105 aluminum (with zincate) and CRS. The cold rolled steel and aluminum panels have the lowest gloss results in Figure 4 and have the highest surface roughness of the four types of panels. Provided that subsequent substrate lots are similar in surface roughness, gloss results can be easily compared regardless of the level of roughness.

Figure 5 is a graph of the gloss and DOI values obtained from several ELV EN systems. The EN systems evaluated are an ELV mid-phos and ELV low/mid-phos bath at 0 MTO. Also, two brighteners added to the ELV mid-phos bath are assessed. Note that the gloss numbers increase steadily for the ELV mid-phos system with brighteners B2 and B3 added. The gloss value rises from 401.5 to 581.5 GU, a 31% increase from the original ELV mid-phos system to the one with brightener B3 added. Alternatively, the DOI values increase from 82 to 88, a 7% increase. The gloss test demonstrates a greater deviation with respect to modifications in the deposit, than DOI exhibits. To judge changes in brightness by DOI alone would be difficult. While DOI offers a numerical value for the visual clarity of a deposit, which can enhance the overall quality of a decorative coating,

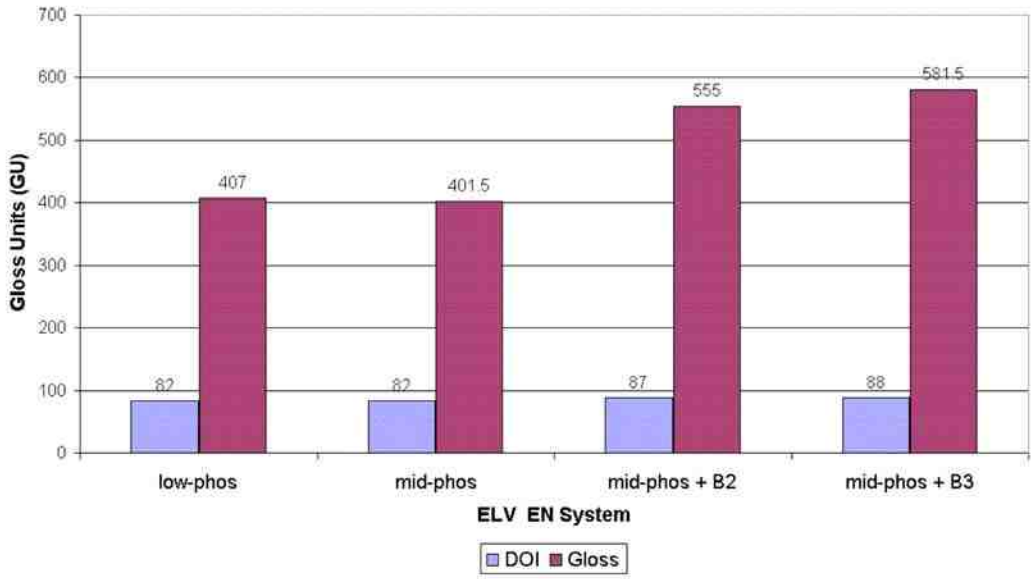

Figure 5. Comparing Gloss and DOI of Various EN Deposits Plated on Steel

it shows little or no variation for different deposits and so it makes evaluation more cumbersome.

A conventional mid-phos and a mid-phos ELV EN system were evaluated for haze to determine the relative cloudiness of the deposits. The with-grain measurements for the non-ELV and ELV mid-phos deposits were 0.08 and 0.14, respectively. The cross-grain haze measurements for the mid-phos with Cd and Pb and the ELV mid-phos EN system were 0.09 and 0.45, respectively. The ELV system has slightly more cloudiness in the deposit. The greatest difference between deposit haze measurements was with the cross-grain view. Haze measurements can aid in quantifying the overall surface quality of a deposit. However, for daily results of deposit differences and quick comparisons between possible brighteners, gloss measurements are more easily taken and show a larger degree of variance.

Gloss results helped optimize EN bath operating parameters such as pH and temperature in order to produce the brightest deposit. An ELV mid-phos EN deposit was plated at various pH values and temperatures on a steel panel at 0 MTO. The results are shown in Figure 6. At a pH of 4.9 the ELV deposit was the brightest. At the lower and higher pH values the gloss results were lower. In this case, the normal operating pH is the optimal pH evaluated by gloss testing. The normal operating temperature of the ELV mid-phos bath is 190°F. The results in Figure 6 shows that the brightest deposit can be obtained at 180°F when compared to 190° and 195°F. While the brightest deposit might be obtained at 180°F, undoubtedly the rate will be lower which is a disadvantage over the current operating parameters. The gloss results can help evaluate bath parameters

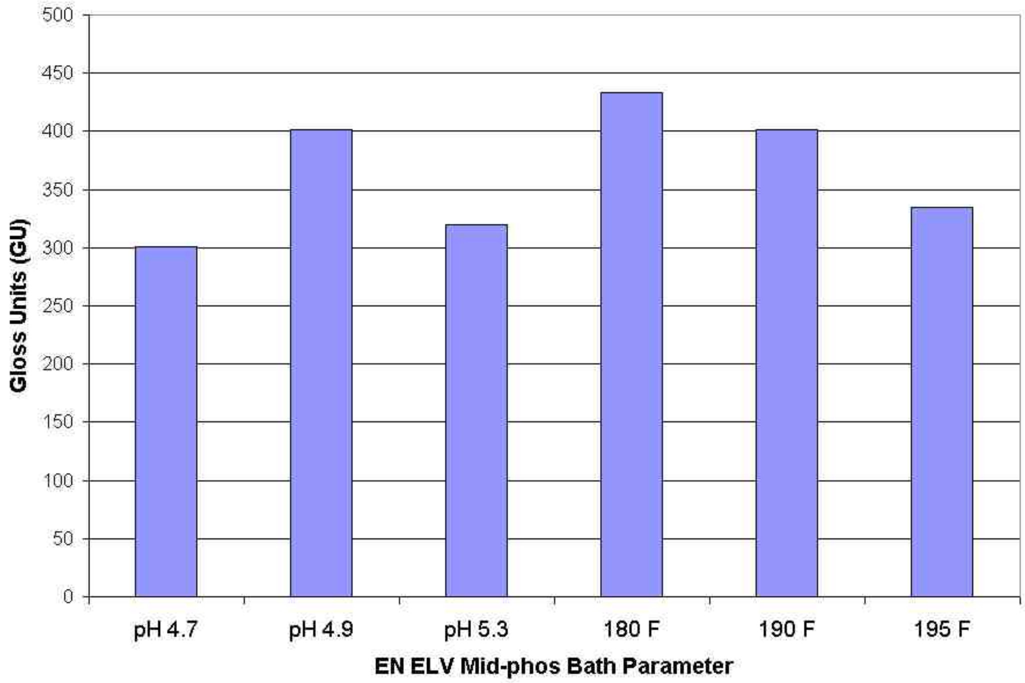

Figure 6. Mid-phos ELV EN Gloss Results with Various pH and Temperatures

to yield the brightest deposit, whether or not those changes can be implemented depends on the EN process specifications.

Organic and inorganic brighteners added to ELV systems can be evaluated easily by gloss testing. It can be visually difficult to compare panels for brightness. Figure 7 shows the gloss results of an ELV mid-phos system with various brighteners added to the plating bath. Note that the brightness of the original ELV mid-phos EN can be increased 33% by adding brightener B5. Gloss values can measure the relative brightness of a deposit based on additives or changes to the original formula to enhance brightness. While other testing will have to be completed to evaluate other properties associated with the modifications such as stress, hardness and plating rate, the assessment of new ELV-compliant brighteners is easily conducted with gloss testing. Comparisons are easy when the brightness of conventional EN deposits containing cadmium and lead are used as a benchmark.

Gloss results can also assess the brightness of panels over the life of the working bath. A brightener's efficacy cannot be judged simply by the initial brightness it obtains, but also based on the brightness it sustains over the working bath life. Figure 8 shows the gloss values for the ELV mid-phos and ELV mid-phos with brightener B3 and B4 added at 0, 1 and 6 MTO. The initial gloss results are higher with the addition of brightener B3. When the bath was run out to 6 MTO, it was established that the deposits with brightener B3 would have higher

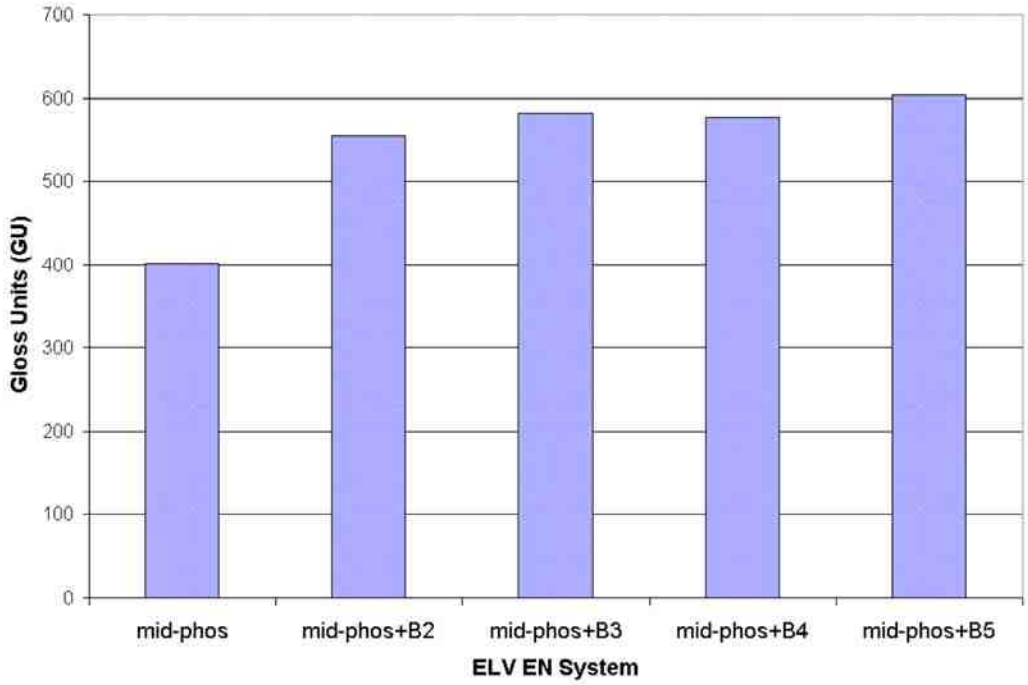

Figure 7. Evaluation of Brighteners for Mid-phos ELV Electroless Nickel Deposits

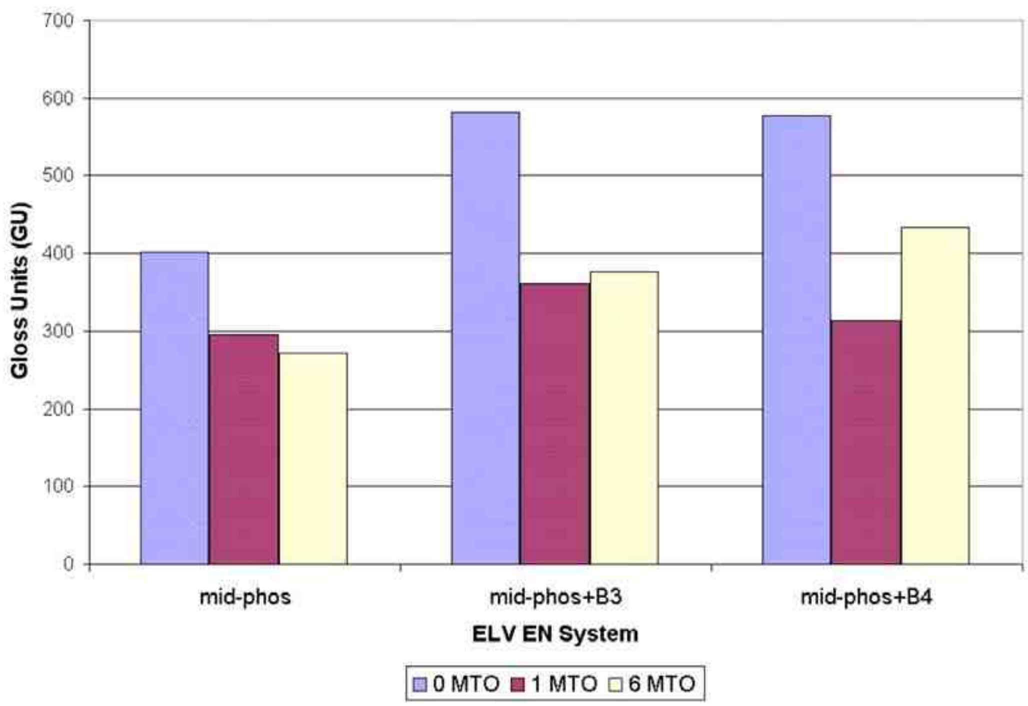

Figure 8. Evaluation of Gloss Over Bath Working Life

gloss values than the original mid-phos. The initial gloss values obtained with brightener B4 are similar to those obtained with brightener B3. However, at 6 MTO the brightness with brightener B4 is greater. The gloss results can be utilized to decide on future improvements that can be made, i.e., to increase the gloss from 0 MTO to 6 MTO.

Conclusion

Gloss, distinctness-of-image, and reflectance haze tests are used to evaluate different visual impressions of a deposit. Gloss testing can be a useful tool for evaluating the “brightness” of a nickel phosphorus deposit used in a decorative application. Careful consideration must be taken to get bath temperature, pH and deposit thickness consistent from panel to panel in order for the results to be comparable. But once accomplished, gloss results can be directly compared and used to help assess brighteners and other additives. DOI is another valuable test for evaluating the “mirror-like” quality or visual clarity of a deposit although it does not have a wide numerical range when testing metallic coatings and therefore does not show deposit differences as readily. Reflectance haze is a third test component for comparing coatings. Haze or cloudiness in the deposit can impede the total visual quality of a deposit. However, if the deposit cloudiness is small, then the main goal for the deposit again becomes the overall brightness. With each of these tests, the results help measure improvements to EN ELV systems that must be achieved in order to have a deposit similar or better than conventional Pb/Cd-based EN systems traditionally held as a benchmark for acceptable brightness.

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