

Composite Coatings with Light-Emitting Properties

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Composite electroless nickel (EN) coatings are a developing and promising field in the metal-finishing industry. A wide variety of particulate matter is capable of codeposition in EN coatings. Wear resistance and lubricity are two general categories of composite EN coatings, which have been the most extensively developed and commercialized. This paper presents a more recent category of composite EN coatings: composite light-emitting coatings. These novel coatings are composites of phosphorescent particles dispersed throughout an electroless nickel matrix.

LIGHT-EMITTING COATINGS

This category of composite EN coatings is a 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 coatings are viewed under an ultraviolet (UV) light they emit a distinct, brightly colored light. Particles from a number of different materials, each generating emissions of different colored light, have been successfully codeposited in EN. A large number of particles of naturally occurring metals as well as solid chemical compositions can be used as indicator particles.¹

These are "particles comprised of atoms or molecules that absorb photons of electromagnetic radiation and remit the absorbed energy by the spontaneous emission of photons which, however, are not the same energy as absorbed photons or the same wavelengths. The phenomenon is generally referred to as luminescence, having light-emitting properties. Luminescence is further classified into fluorescence and phosphorescence. If the emitted radiation continues for a noticeable time (generally between 10^{-4} and 100 seconds) after the incident radiation is removed, it is referred to as phosphorescence. If the emission ceases almost immediately (10^{-9} – 10^{-4} seconds) after the incident radiation is removed, the process is referred to as fluorescence."²

Figure 1 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. Figure 2 is a SEM of the surface of a composite EN coating incor-



Figure 1. Composite electroless nickel coatings on aluminum emit red, blue, and white colored light under ultraviolet exposure.

porating phosphorescent particles. This unique property has been developed for two main uses as described in U.S. Patents 5,514,479 and 5,516,591. They are *indication* and *authentication*.

INDICATION

The light-emitting properties can serve as an indicator layer, warning when the coating has worn off and replacement or recoating is necessary. This feature makes possible 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 worn parts such as molds, dies, presses, and others.

When a composite coating with light-emitting

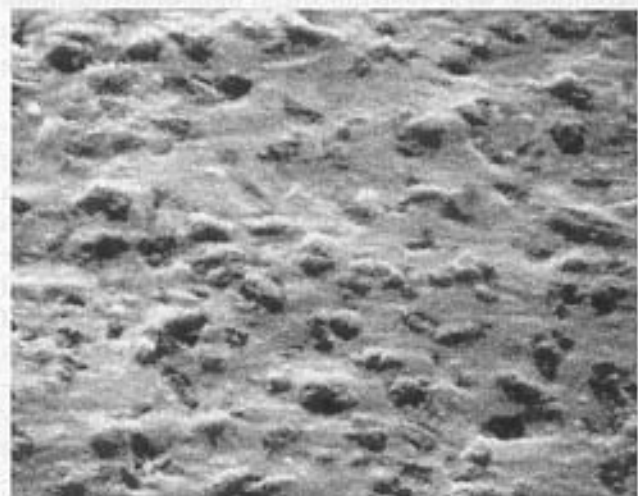


Figure 2. SEM of a composite electroless nickel coating with incorporated phosphorescent particles.

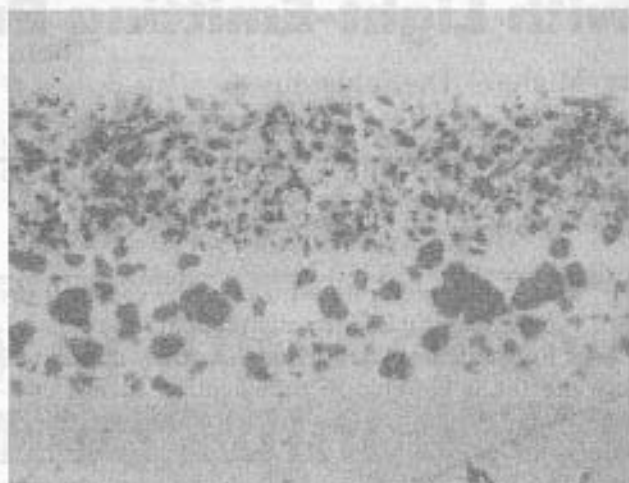
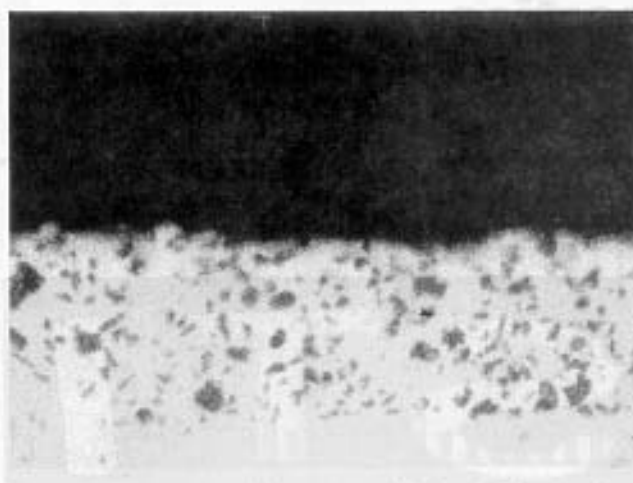


Figure 3. Diamond particles codeposited in addition to phosphorescent particles provide a coating with exceptional wear resistance and light emitting properties.

Figure 4. Cross section of a two-layered coating including a basecoat with light-emitting properties and topcoat of electroless nickel-diamond.

particles is employed alone it is the disappearance of the light that signals wear through the indicator layer. As long as UV inspections of the coated part result in a light emission reaction, the coating's presence is confirmed. While the EN matrix of such an indicator layer will provide a valuable degree of wear resistance, corrosion resistance, hardness, and the other properties inherent to EN, these properties can be further enhanced by the simultaneous codeposition of other particles within the indicator layer. These other particles can be of a wear-resistant nature, such as diamond and silicon carbide, or have self-lubricating properties such as PTFE and boron nitride.

Figure 3 demonstrates one such example where diamond particles are codeposited in addition to phosphorescent particles to create a coating with exceptional wear resistance and light-emitting properties. Such indicator layers can range in thickness from a few microns to a few mils depending on the requirements of an application.

A light-emitting indicator layer can even be applied prior to or under another "functional" coating to signal when the functional coating has worn through, thus exposing the indicator layer. In this case it is the appearance of light that signals wear has occurred through the functional layer to reveal the indicator layer. Figure 4 shows a cross section of a substrate plated with two distinct layers; first, a light-emitting indicator layer, followed by a composite EN-diamond coating. The functional layer may be of any material(s) applied by any method to serve any number of purposes ranging from wear resistance, corrosion resistance, and lubricity, to friction, conductivity, insulation, and the like.

As with all varieties of composite EN, light-emitting 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 observed in cross-sectional Figures 3 and 4. Thus, even if wear has occurred to a portion of the light-emitting coating, any portion of the remaining coating will continue to display the same properties.

As with any other EN coating these composite coatings can be chemically stripped, leaving the substrate ready for recoating. U.S. Patent 5,516,591 describes in detail the procedure to use, regenerate, and reuse coated parts for multiple generations by employing the indicator layer technology.² Specific instruction is provided for parts commonly used in the textile, paper, and tobacco industries, which are critical dimensions, undergo highly abrasive conditions, and are costly to remove, mechanically restore, or replace once wear has occurred to the base materials.

The novel properties of an indicator layer are especially advantageous to parts that:

- defy conventional wear and thickness testing due to complex geometries and/or specific wear patterns,
- are difficult, time consuming, or costly to remove from associated components to test, or
- are expensive and require nondestructive wear testing to avoid wear into the substrate.

AUTHENTICATION

The presence of a colored light emission from a coating can be valuable in authenticating parts from

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a distinct source. This is especially promising for the identification of genuine OEM parts, which otherwise can be routinely counterfeited.

Numerous examples exist in the aircraft industry where counterfeited parts have notoriously found their way onto private and commercial aircraft. Such components may appear identical to the OEM authorized components, but numerous critical material parameters are not visible or readily verifiable to the technician installing the part. If, however, such a technician is able to make an instantaneous visual verification of a component's authenticity under exposure to a UV light, installation of unauthorized components can be avoided. While a machine shop may be able to fabricate a convincing counterfeit part the ability to produce such a part with a light-emitting composite EN coating is substantially diminished by the technology, know-how, and patent rights required.

Similar benefits extend to the automotive industry where the sales of counterfeit and imitation replacement parts were recently estimated to be \$12 billion.³

Further frustrating the capacity of an unauthorized manufacturer is the opportunity for the OEM and the authorized plater to produce authenticating coating(s) to emit a variety of colors. The color of the coating's emission can be changed at specified times or intervals by changing the type of particles codeposited in the plated layer. This potential for color variation further enables manufacturers and customers to perform routine part replacement programs via UV light inspection. This feature is especially viable for the identification of specific manufacturing lots where conventional methods of marking are not sufficient or durable.

This authentication technology is further intended to serve the currency and ticketing industries where counterfeiting is notorious and the practice of incorporating authenticating materials, such as precious metals, is already accepted. A few of the powerful statistics on the magnitude of the problem in these areas include:

- An estimated 120 million in U.S. dollars were counterfeited within the U.S. and another 4 billion were counterfeited abroad in 1994 alone according to the Secret Service.
- 50 million checks are forged in the U.S., costing businesses between \$5 and \$10 billion according to a recent American Bankers' Association survey.
- Losses from counterfeited and fraudulently used credit cards totaled \$1.3 billion in 1995.

- Food stamp fraud equaled \$813 million in 1993 according to the U.S. government.³

For the purpose of authentication the indicator layer needs only to be 5 to 12 microns (0.00025–0.0005 in.) 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.

COATING SPECIFICATIONS

The most developed metal matrix of the composite light-emitting coatings to date is EN (an alloy of 88–99% nickel with the balance of phosphorus, boron, or a few other possible elements). These coatings 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) phosphorus, and electroless nickel-boron with 0.5 to 3% B. Each variety of EN thus provides properties with varying degrees of hardness, corrosion resistance, nonmagnetism, solderability, brightness, internal stress, and lubricity.⁴

Application of composite light-emitting coatings is subject to the same challenges involved in other varieties of composite EN plating since it requires the introduction of insoluble particulate matter into the plating bath for codeposition into the coating. The 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 (PMS) as shown in U.S. Patents 4,997,686, 5,145,517, and 5,300,330. The methods disclosed therein have made composite EN plating reliable and commercially viable by modifying the Zeta potential (or charge) of the particles. For light-emitting particles, specific PMS additions must be made. Coatings containing light-emitting particles in addition to another variety of particles require special PMS additions or combinations.

As with conventional EN, light-emitting composite coatings can be applied to numerous substrates including metals, alloys, and nonconductors with outstanding uniformity of coating thickness to complex geometries. These coatings may further 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.⁵

Light-emitting particles suitable for composite EN incorporation can be up to approximately 10 microns in size. Development to date has focused on particles with narrow size distributions in the range of 1 to 5 microns.

Depending on the particle sizes and certain plating conditions, light-emitting coatings can be produced with a particle density of up to 40% by volume, although densities of 15 to 25% are common for most commercial applications. When composite layers are generated with light-emitting particles in addition to particles of another function, the relative densities of each material depend on the sizes and shapes of the respective particles as well as the requirements of a given application.

SUMMARY

Phosphorescent particles are capable of being incorporated into a variety of coatings to produce light-emitting effects under UV light. This recent and novel development is useful in wear indication and product authentication situations.

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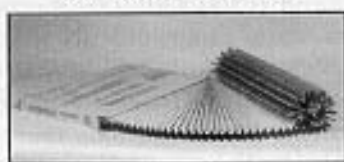
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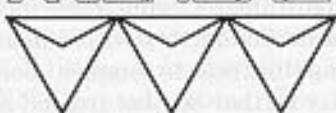
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