Primer Coating System for Electroless Nickel Plating of Non-Metallic Surfaces

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A sprayable primer coating is described for the purpose of preparing non-metallic composite surfaces for adherent electroless Ni plating. The primer consists of a mixture of filamented Ni powder, suspended in a solution containing a polymer resin, and is coated and cured to the composite to produce a porous Ni-plus-resin surface. Electroless Ni adhesion is derived predominantly from mechanical interlocking within the cured primer's open porosity. Results of a designed experiment evaluating primer composition, application conditions on the primer roughness, and plated electroless Ni adhesion are discussed.

Polymer matrix composite materials are increasingly replacing metals as structural components in weight-sensitive applications.[1] Applications that involve contacting or moving parts, however, routinely continue to be constructed from heavier metallic components because the poor erosion and abrasion resistance of the polymer matrix precludes their use. This limitation can be overcome by plating the composite with a wear-resistant electroless Ni coating, but EN adhesion to the composite surface, even following chemical etchants or mechanical roughening, often has been unreliable from a final composite performance standpoint. Commercial primer systems for preparing polymeric surfaces for electroless plating are generally unacceptable for this application inasmuch as they have been developed for either EMI/RFI shielding or electronic applications, and are, therefore, not conducive either to the application of thick electroless Ni coatings or to high-stress final applications.[2-5] Electroless nickel plated over these systems often develops interfacial blisters during deposition of thicknesses exceeding a few thousandths of an inch (mils) or delaminate during subsequent composite flexure.

It was discovered that a branched Ni powder, such as used in the manufacture of porous Ni battery electrodes,[6,7] could be blended with a polymer resin as a binder, dispersed in an appropriate solvent, and spray-coated and cured onto non-metallic substrates for use as an adherent plating primer. The resin serves both to bind the Ni powder together, thereby providing structural integrity to the primer layer, and to tie the primer to the composite surface. A sketch illustrating an idealized structure for the primer layer is shown in Fig. 1. The porous surface is derived from the unique morphology of the branched Ni powder chains, which may compose the majority of the layer by weight, but is typically less than 25 percent by volume. During EN deposition over this primer, the plated metal penetrates the porous surface of the primer and becomes mechanically interlocked with it, thereby providing a strong degree of mechanical adhesion.

Fig. 1—Sketch illustrating theoretical Ni primer layer structure.

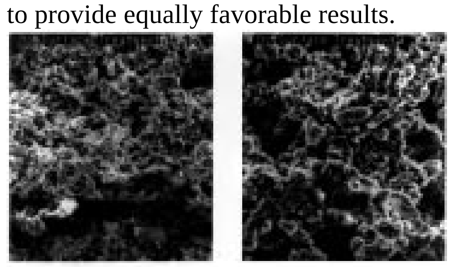
From this illustration, it can be seen that the final EN/composite adhesion will be influenced by conditions that affect the primer layer's structural integrity, including the interfacial attachment of the primer to the composite surface, the primer surface morphology, and effective interlocking of the plating within the primer layer. These are in turn affected by:

- The primer composition (*i.e.,* the Ni powder type, Ni/resin ratio, and resin type) [affects the surface morphology and porosity of the primer layer].

- The primer coating conditions (*i.e.,* substrate temperature and spray conditions) [affects primer integrity, roughness and adhesion to the composite surface].

- The plating process, especially surface preparation and preplating conditions (affects the ease with which the EN deposit penetrates the primer's porous structure).

Results reported here will detail only those using a polyamide-imide resin to prepare the primer layer. Selection of an appropriate resin must take into account the thermal stability of the underlying composite because oxidation of the composite during resin cure results in poor interfacial bonding. Limited work was done using other resin systems, including a low-temperature-cure epoxy to demonstrate the generic nature of this technique. All other factors being equal, changes in the resin yielded only modest differences in metal adhesion arising from changes in the cured primer layer morphology. It is believed, however, that adhesion for any resin could be optimized by changes in solvent selection, resin loading, etc., to provide equally favorable results.



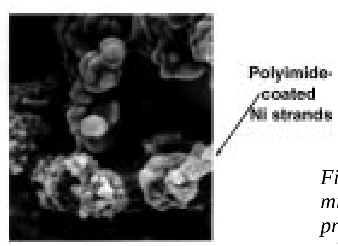


Fig. 2—SEM micrograph of coated Ni primer layer prepared with Ni 255 powder.

Table 1
Electroless Ni Plating Process
for Cured Ni/resin Primer

1. Abrade surface	glass bead or sand to expose Ni strands
2. Surfactant solution	commercial surfactant or soap treatment to yield hydrophilic surface
3. Catalyst treatment	commercial plating catalyst for EN
4. EN Plate	either high- or low-phosphorus EN

Table 2
Peel Adhesion Values as a Function of
Various Surfactant Pretreatments

Sample Preparation	Adhesion
Not sanded	blistered
Sanded	3.8 lb/in.
Sanded + Surfactant	
Micro Cleaner*	8.7 lb/in.
Fluorad# FC135 cationic	8.9 lb/in.
Fluorad# FC95 anionic	9.2 lb/in.
Fluorad# FC170C nonionic	9.8 lb/in.
Coco Soap§	10.8 lb/in.

* Micro® Cleaner, International Products Corp., Burlington, NJ.
# Fluorad® surfactants, 3M Company.
§ Coco Soap®, Share Corp. Milwaukee, WI.

Experimental Procedure

Ni powders of various morphologies were used. Polyamide-imide (PAI) varnish was obtained as 35-percent polyamide-amic acid dissolved in 1-methyl-2-pyrrolidinone (NMP) solvent. The PAI varnish was diluted to a lower resin content for spray application, with a final solvent composition of approximately 50 percent by volume NMP and MEK (methylethylketone). The Ni powder was added and roller-milled without media overnight. The primer was sprayed onto heated substrates, using a HVLP spray gun. Following coating, the resin component of the primer was cured by heating to 500 °F for several hr in a forced-air oven.

Electroless Ni plating onto the cured primer followed the protocol outlined in Table 1. The cured primer surface was lightly abraded, using small glass beads (*i.e.*, BT13) at low pressure (20 psi) or light sanding with <350-grit SiC paper to expose Ni particulates free of resin. The sample was then degreased and made slightly hydrophilic by immersion in a surfactant solution, rinsed, and catalyzed for electroless plating using a commercial Pd catalyst series developed for electroless deposition onto polymeric materials, prior to immersion in the EN bath. Details of the surfactant treatment, which is essential to maximizing penetration of the EN plating within the porous primer, will be covered in the text.

Plated metal adhesion is measured, following EN deposition of less than one mil, by electroplating the metallized surface with ~2 mils of Cu, followed by striping the Cu surface with 1/8-inch-wide strips of tape, back-etching the metal not covered with tape, using HNO_3, and peeling the remaining 1/8-inch-wide metal strips at a rate of 2 in./min, normal to the surface. The force required to separate the metal film from the substrate, measured using a force gauge, is converted to lb/inch width peel adhesion.

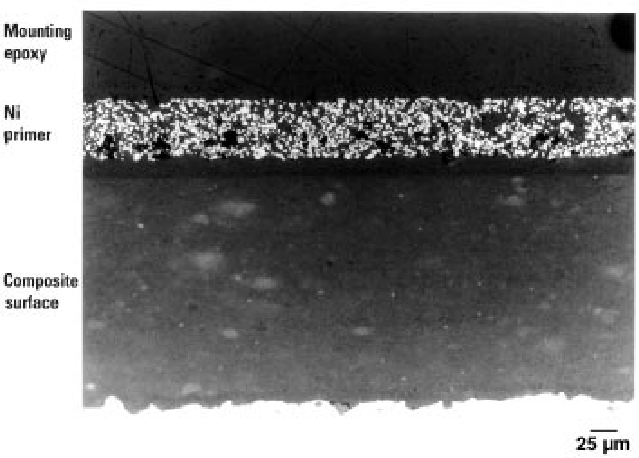


Fig. 3—Polished cross section of primer comprising resin and Ni 255 powder.

Results and Discussion

Figure 2 shows a SEM photograph of the surface of a cured primer layer comprising Ni 255 branched Ni powder and a Ni/resin ratio of 2:1 by weight. The pore morphology seen here is reminiscent of that developed for porous Ni electrodes, using this same Ni powder with the exception that a fraction of the pore volume here is filled with resin. Figure 2 also shows that most of the Ni strands are themselves coated with a thin layer of the polyimide resin, as in the idealized illustration above. Direct EN plating of this structure, following catalysis, but without the surfactant pretreatment noted previously, yields poor metal adhesion as a result of the hydrophobic character of the primer resin, which limits EN penetration of the exposed pores. Penetration is improved somewhat by abrasion to expose some metallic surfaces, however, the exposed Ni is itself limited to the primer surface and therefore does little to promote catalyst and plating penetration within subsurface pores. Table 2 lists typical peel adhesion values obtained for samples that are not abraded or that are sanded, followed by surfactant treatments. The fact that all soaps/surfactants tried had a significant impact on final adhesion confirms that their effect is simply morpho-

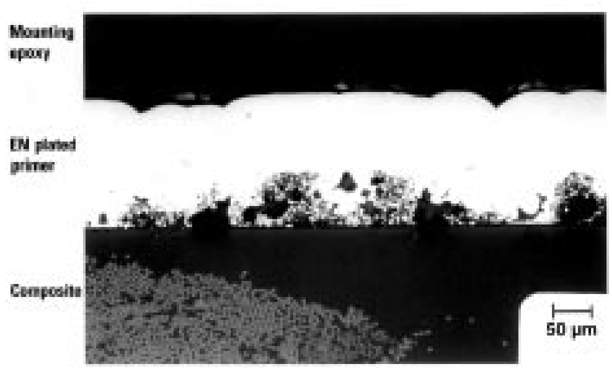


Fig. 4—Polished cross section of electroless Ni-plated primer comprising resin and Ni 255 powder.

Table 3
Types of Ni Powder Used in the Ni-Filled Topcoat Layer

Ni powder type	Ni powder description	Bulk density g/cm^3
Ni 123	spheres	2.2
Ni HCA-1	platelets	1.2
Ni 287	chains	0.9
Ni 255 AC	chains	0.6
Ni 255	chains	0.5

logical in aiding EN penetration, rather than by a modification of the resin chemistry. All adhesion data reported in Table 2 was obtained using a 2-percent aqueous coco soap treatment (10 min, 50 °C) prior to catalysis and EN plating.

Figures 3-5 show polished cross-sections of the plated and unplated final structures obtained, using a primer comprising Ni 255 branched powder and a Ni/resin ratio of 2:1. During epoxy mounting prior to cross sectioning, the pores in the unplated primer layer, Fig. 3, are filled with mounting epoxy, making it difficult to identify the porosity distribution in the original structure. By comparison with the cross section following metallization, in which approximately 5 mils of EN deposit have filled these voids, Fig. 4, the penetration by the metallization into these areas is apparent. Some of the remaining "voids" at the insulator interface following metallization are, on closer inspection, filled with the original resin and are therefore not voids (Fig. 5).

Primer Composition Effects

The morphology of the primer layer and, therefore, the level of final EN adhesion, is affected predominantly by the primer composition and secondarily by the processing conditions. The most important compositional parameters are the microstructure of the Ni powder, as reflected in its bulk density, and the volume fraction of Ni in the final cured coating, reflected by the Ni/resin ratio. Our nickel supplier offers several different types of commercial Ni powders that differ greatly in structure. The ones examined in this study are listed in Table 3, along with the bulk density obtained from the product data sheets. The powder labeled 255 AC is an air-classified version of the 255 powder in which both the fines and some of the larger and more highly branched Ni strands have been removed.

Each of the Ni powders shown in Table 3 was spray-coated and plated with electroless nickel for adhesion measurements under nominally identical conditions. An inverse relationship was found between the bulk density of the selected Ni powder and the resulting electroless Ni adhesion, as illustrated in Fig. 6 for a Ni/resin ratio of 2:1 by weight. EN peel adhesion values varied from around 2 lb/in. for the spherical Ni 123 and platelet-shaped Ni HCA1 prepared layers, to >9 lb/in. for the lowest density branched chain Ni 255 powder. This relationship is consistent with the fact that adhesion is derived predominantly from mechanical interlocking of the EN plating within the cured primer and that the primer porosity is maximized with the Ni powder that possesses the lowest intrinsic packing density. In contrast to the EN adhesion, the higher bulk density powders tended to yield a smoother plated surface; however, this influence was less important than the application conditions to be discussed.

Figure 7, which shows the relationship of the primer Ni:resin ratio to EN adhesion, reveals a broad maximum around 2:1 to 3:1 by weight for the Ni 255 powder. The increase in adhesion with increasing Ni ratio is related to an increasing level of surface porosity. This is illustrated in Fig. 8, which shows cross sections of primer layers from the 1:1 and 4:1 cases. The 1:1 by weight Ni/resin case corresponds to approximately 9.6 percent Ni by volume in the primer. Figure 8a shows that this primer produces a relatively dense layer, with only limited open porosity available for mechanical attachment. On the other hand, Fig. 8b shows the 4:1 by weight Ni-to-resin case, which corresponds to 30 vol. percent

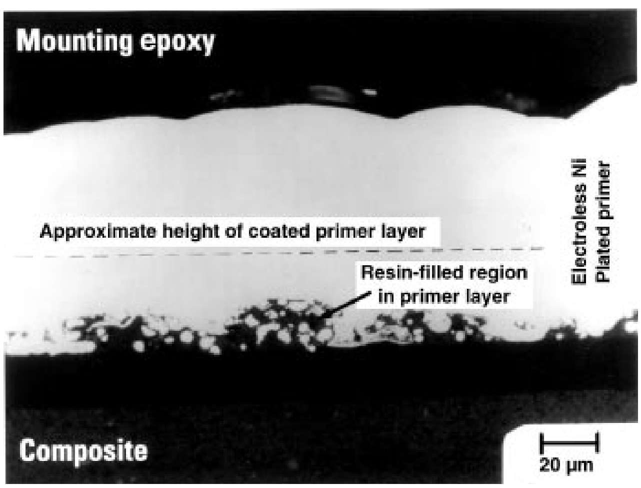


Fig. 5—Polished cross section of electroless Ni-plated primer comprising resin and Ni 255 powder.

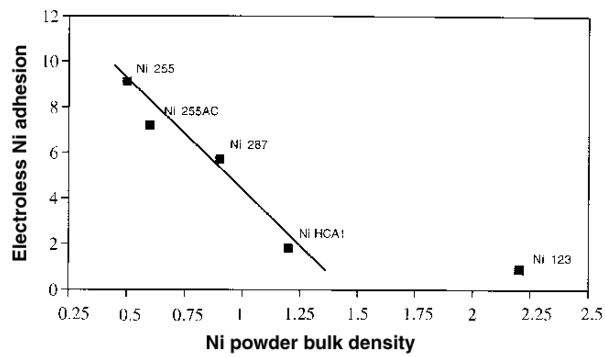


Fig. 6—Electroless Ni adhesion and Ni powder bulk density for various Ni powders.

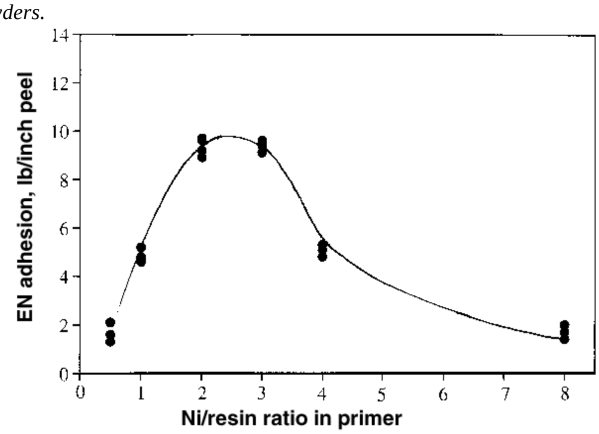


Fig. 7—Electroless Ni adhesion for Ni 255 powder for Ni-to-resin ratios (wt %).

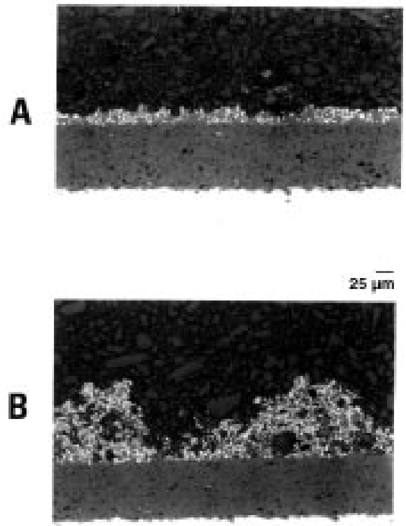
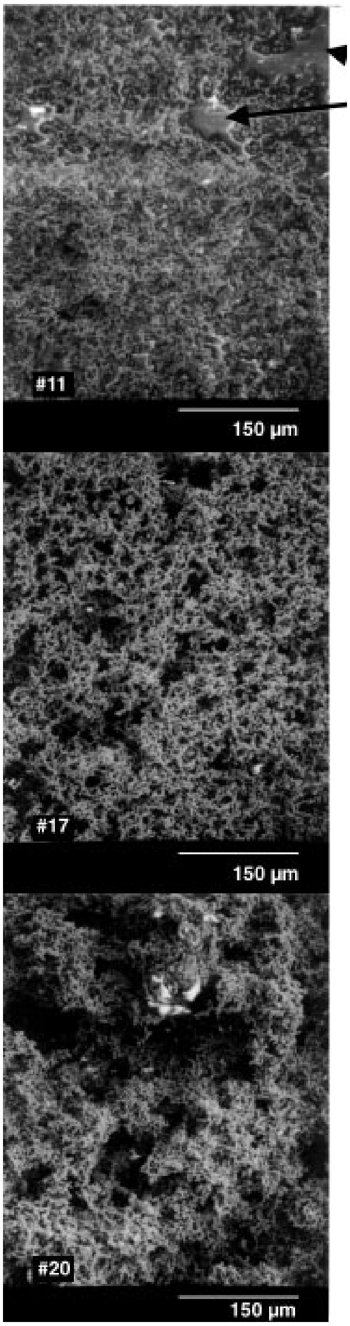


Fig. 8—SEM micrographs for (a) 1:1; and (b) 3:1 Ni/resin ratio primer layers.



150 °F

180 °F

240 °F

Fig. 9—SEM micrographs for a Ni 255 2:1 ratio primer coated onto substrates preheated to 150, 180, and 240 °F.

Ni, to have a much higher porosity, which translates to a significantly greater EN adhesion. The downturn in adhesion at still Ni/resin ratios exceeding 3:1 is likely a result of declining structural integrity for the primer layer itself. In all cases, the point of failure during the peel test is within the primer layer and often near the primer-to-insulator interface. Very high Ni ratios, therefore, potentially do not possess sufficient resin content to bind the individual Ni particles or strands together or to bind the primer layer to the insulator surface. An illustration of this can be noted in the larger interfacial voids seen in Fig. 8b. A similar trend in adhesion vs. Ni/resin ratio is seen for other types of Ni powders, with the maxima for those materials displaced somewhat, because of the optimum development of exposed porosity and layer strength. For example, the optimum ratio for Ni HCA1 is between Ni/resin ratios of 4:1 and 6:1 by weight.

Primer Application Effects

The effect of the application conditions, during the coating process, on the morphology of the final layer is more subtle and somewhat less controllable than the primer composition. The primer layer is spray-coated from a blended solvent system consisting of a high (NMP) and a low (MEK) boiling point solvent. The most desirable situation is to have the lower boiling point solvent rapidly evaporate from the coating as it is being deposited on the insulator surface. This prevents the primer layer from becoming “too wet” on the coated surface, where it can “run” or, if on a flat surface, where the level of open porosity can decrease as the Ni strands settle within the resin. On the other hand, too rapid solvent removal can lead to lower adhesion either by the formation of large voids at the primer-to-insulator interface, or by a decrease in primer integrity. In many respects, variables of this type are the same as those faced in conventional spray painting, where the paint must be applied with uniform consistency to obtain a quality finish.

For this process, non-uniformity is minimized by heating the substrate during coating to promote rapid vaporization of the lower boiling point solvent. This affects both the EN adhesion and the surface roughness. Table 4 lists the adhesion values obtained with a Ni 255 primer layer prepared at a 2:1 Ni/resin ratio and applied to substrates preheated to temperatures from 150 to 280 °F. These temperatures bracket

Table 4
EN Adhesion for Substrates Heated from 150 to 240 °F

Temperature °F	Adhesion lb/in.	Roughness
150	3.7	very smooth
180	7.5	smooth
210	9.7	moderate
220	10.2	moderate
240	9.1	rough
260	8.8	rough
280	2.6	very rough

the MEK boiling point (176 °F) and the results show a broad adhesion maximum, with a significant decline in adhesion at both extremes. The roughness category is a qualitative scale based on visual examination; however, SEM and cross-sectional analyses later supported the general ranking. For example, Fig. 9 shows SEM photographs of the sample surfaces for coatings at 150, 180, and 240 °F, respectively. A noticeable reduction in open surface porosity is evident in the primer coated on the lowest temperature substrate, arising from the fact that the coated surface remains wet after spraying, giving the Ni powder time to settle into the resin. This condition, coupled with the formation of pools of resin that appear to be devoid of Ni powder, accounts for the low adhesion value shown in Table 4. On the other hand, the primer layer coated onto a 240 °F substrate, while possessing excellent adhesion, is excessively rough. Peak-to-valley roughness measurements, via polished cross-sections, exceeded 5 mils for a 3-mil nominal primer thickness for the 240° preheat. This would require deposition of a considerably thick EN deposit for applications in which the final plated surface is to be polished or ground for form fitting. The application temperature operating window appears to be quite wide, however, as there is no decline in adhesion and only a modest increase in coating roughness as the substrate temperature is increased from 180 to 220 °F.

Summary

Spraying a solution of a filamented Ni powder and a polymer resin onto the exterior of a composite provides an easy and versatile primer for the subsequent application of a wear-resistant electroless Ni layer. Ni deposits exceeding 10 mils in thickness have been plated without blistering, while possessing adhesion values exceeding 10 lb/in. peel. The composition of the primer itself, and in particular the morphological characteristics of the Ni powder, play a dominant role in defining the final adhesion level, while the temperature of the substrate prior to application plays a major role in determining the coating roughness. If desired, the surface of the plated composite can be ground or polished to provide for form fitting or, if desired, to yield a metallic appearance.

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