

Surface Modification of an Organic Photoconductor in an Electrophotographic Charging Environment

K. Nauka, Seongsik Chang[^] and Hou T. Ng[^]

Hewlett-Packard Laboratories, Hewlett Packard Company, 1501 Page Mill Road, Palo Alto, California 94304

E-mail: chris.nauka@hp.com

Abstract. Prolonged exposure of a commercial organic photoconductor in a plasma environment corresponding to an industrial electrophotographic process caused the formation of a parasitic surface layer with properties that are different from the original photoconductor. The parasitic film consists of a heavily oxidized surface region and oxygen-free subsurface layer with a chemical composition similar to the original photoconductor but having a significantly different bonding arrangement. The formation of this film has been correlated with damage induced by the energetic particles and UV photons originating from the electrophotographic plasma discharge. An in-depth understanding of the formation and the properties of this parasitic layer could provide an effective means to overcome its detrimental impact on printing cost and quality. © 2010 Society for Imaging Science and Technology.
[DOI: 10.2352/J.ImagingSci.Technol.2010.54.5.050304]

INTRODUCTION

The electrophotographic process relies on the formation of a high fidelity electrostatic image on a photoconductive surface that is subsequently used to transfer solid toner particles or liquid electrophotographic ink onto the paper's surface. Traditionally, a corona discharge has been used to generate the electrical charges deposited on the surface of inorganic photoconductors. More recently, advances in the commercial electrophotographic printing yielded the development of more complex organic photoconductors frequently used in conjunction with the charge roller.^{1,2} However, the employment of these components in the applications requiring prolonged printing runs and high speed printing demonstrated potential problems related to not well defined, so-called photoconductor's "wear-out," manifesting itself in form of undesirable changes of the physical and chemical properties of the photoconductor and the corresponding print quality degradation.^{3,4}

This work was aimed at elucidating more detailed information concerning the nature of the structural and compositional changes occurring within the surface region of a commercial organic photoconductor during a prolonged usage within an environment imitating the electrophotographic process. A charge roller was used as the primary charging tool, though some experiments involved the appli-

cation of a scorotron. Since the experiments were conducted using a generic electrophotographic setup built exclusively from commercial components and the printing parameters were similar to the ones routinely used in commercial printing, the results are expected to provide useful guidelines to development of electrophotographic commercial applications involving an organic photoconductor.

EXPERIMENTAL

The experimental setup similar to a common electrophotographic print engine was used in the experiments.⁵ It consisted of an organic photoconductor covering the surface of a large diameter drum and a small diameter charge roller in contact with the photoconductor. In several cases the charge roller was replaced by a scorotron. A bank of light emitting diodes in the vicinity of the photoconductor was used to neutralize the electrical charges on the surface of the photoconductor. All components of the experimental setup are commercially available. The commercial organic photoconductor consisted of a polycarbonate layer deposited on the metalized Mylar™ substrate. The bottom part of the polycarbonate film was doped with organic molecules providing holes when illuminated, while the top part contained a small amount of the molecules, enabling hole transport (arylamine-substituted hydrazone-based species).

Following the common electrophotographic process, the negative charging of the photoconductor's surface was achieved by applying a negative bias between the charge roller and the metalized base of the polycarbonate layer of the photoconductor under room ambient conditions.^{1,2} The charging of the photoconductor's surface occurred when the bias exceeded the threshold of Paschen discharge. It took place only in the region in direct vicinity of the charge roller (approximately 1/250 of the total photoconductor' surface). In order to reproduce the effect of the prolonged plasma exposure on the photoconductor's surface, the photoconductor was rotated with charge roller in contact and bias applied. This process corresponded to printing multiple pages, thus, during the subsequent analyses of the photoconductor, its modification was measured either in terms of the plasma exposure time or as a function of the equivalent printed pages.⁵

Light emission related to Paschen discharge was detected with an optical fiber (UV transparent at wavelengths above 270 nm) pointed at the center of the plasma cloud

[^]IS&T Member.

Received Jan. 29, 2010; accepted for publication Jul. 3, 2010; published online Aug. 16, 2010.

1062-3701/2010/54(5)/050304/5/\$20.00.

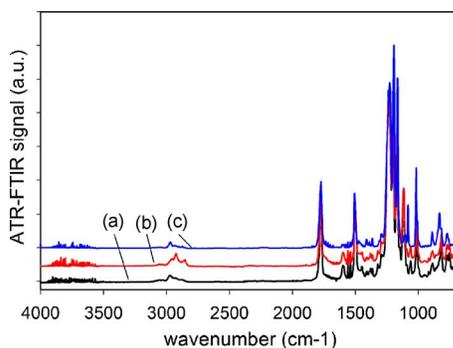


Figure 1. ATR-FTIR spectra of: (a) new photoconductor, (b) photoconductor after an extensive use (approximately 100 K equivalent printed pages), (c) reference commercial polycarbonate. Spectra have been staggered for clarity.

and analyzed with the help of spectrometer equipped with a photomultiplier detector having a resolution of about 0.25 nm which was calibrated with an external reference spectrum. This resolution could not resolve all the fine details of the emitted light but allowed for the identification of the major emission features.

The current flowing between the charge roller and the photoconductor as a function of the applied bias was monitored throughout the entire experiment. Simultaneously, the surface potential of the photoconductor was monitored with a noncontact electrostatic probe placed in the vicinity of the photoconductor. In addition, charges introduced within the photoconductor were measured using a high-sensitivity Kelvin probe over a time period after the charging was completed and the photoconductor was removed from the experimental setup.⁶ The original photoconductor surface topography was measured with a high resolution surface profiler (Dektak 150) capable of resolving surface undulations less than 10 nm and mapping an extended surface area. These measurements were repeated after an extended charging/discharging operation.

The x-ray photoelectron spectroscopy (XPS) and the attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) were used to evaluate chemical modifications introduced by prolonged plasma exposure of the photoconductor corresponding to continuous printing of multiple pages. XPS measures the chemical composition of the photoconductor's surface, while ATR-FTIR can provide information about the nature of chemical bonding within a thin region below the surface. Both techniques can provide information regarding the nature of chemical bonds present within the photoconductor. ATR-FTIR can detect specific molecular vibrations, while chemical shifts of the XPS elemental signal can provide insight into the nature of chemical bonding formed by the selected element.⁷

RESULTS AND DISCUSSION

Figure 1 compares the ATR-FTIR absorption spectra of (a) an unused photoconductor, (b) extensively used photoconductor, and (c) a reference undoped polycarbonate. Absorption spectrum of an unused photoconductor is virtu-

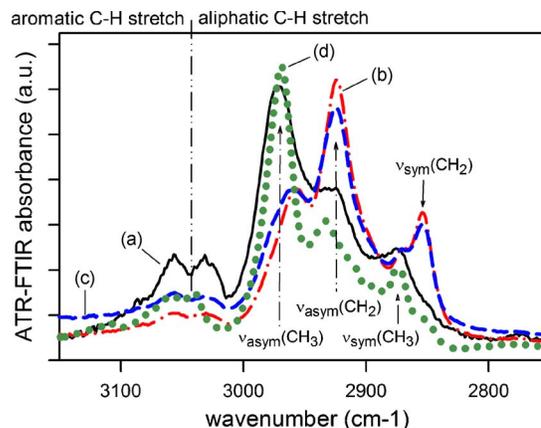


Figure 2. C-H stretching IR absorption region (ATR-FTIR). (a) new photoconductor, (b) used photoconductor (charge roller—after approximately 6 h of continuous use), (c) used photoconductor (scorotron—after approximately 10 h of continuous use), (d) reference polycarbonate. Individual aliphatic stretching vibrations have been identified.

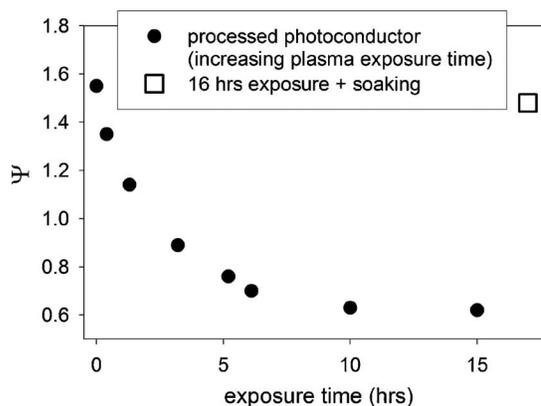


Figure 3. Parameter Ψ (symmetric vibrations CH_3/CH_2 peak height ratio) as a function of processing time (charge roller has been used). Soaking in isopropyl alcohol returns Ψ largely to its original value.

ally identical to that of a reference polycarbonate. Most of the features found in the spectrum of a photoconductor can be associated with the corresponding components of a monomer (Bisphenol A) used to synthesize the polycarbonate.⁸ IR spectra of unused and extensively used photoconductors are very similar except for changes in the wave-number region of 2800–3100 cm^{-1} . Figure 2 illustrates details of these changes, namely, the increase of aliphatic methylene (CH_2) stretching vibrations, decrease of aliphatic methyl (CH_3) stretching vibrations, and decrease of the aromatic C-H stretching.⁹ These changes have been found so reproducible that the aliphatic CH_3/CH_2 absorption peak height ratio (parameter Ψ , Figure 3) has been proposed as a parameter used for a routine evaluation of the photoconductor's wear-out.⁵

It has been shown⁵ that wiping the processed photoconductor with a solvent-wet cloth or short time soaking in selected solvents can return the Ψ close to its original value (Fig. 3). The soaking method is preferred to wiping because of the possibility of accidentally scratching the

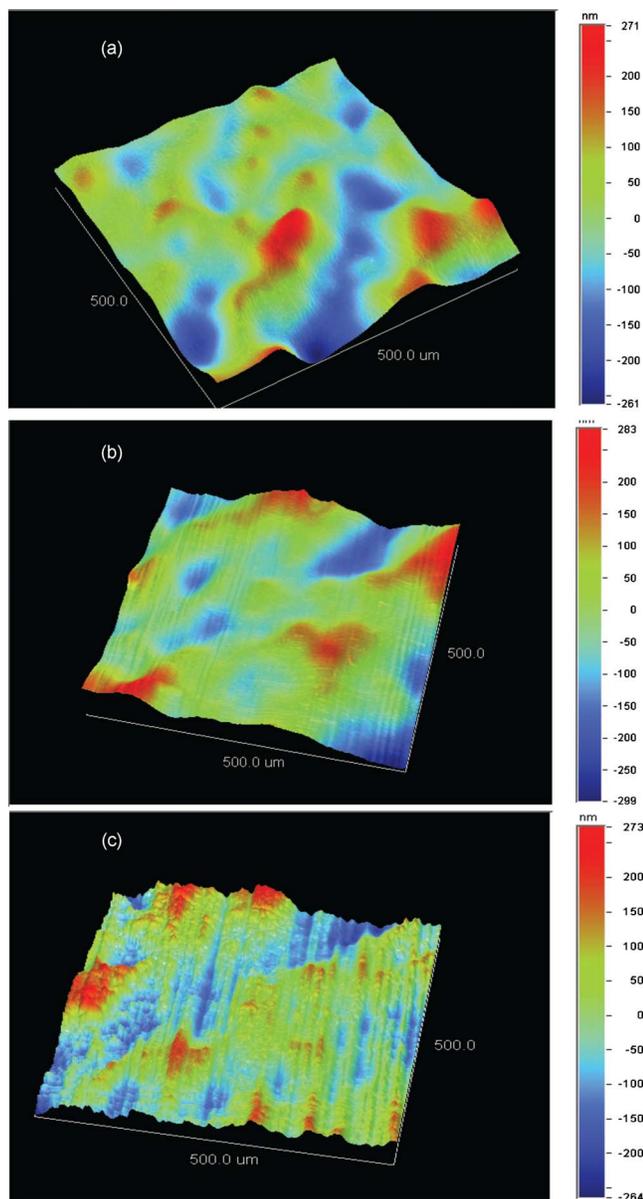


Figure 4. Photoconductor surface topography: (a) new photoconductor, (b) used photoconductor (100 K equivalent printed pages), (c) photoconductor used (as in B) and then soaked in an isopropyl alcohol.

photoconductor. This process removed a 150–200 nm thick top layer of extensively used photoconductor (determined by exposing a small area of the photoconductor to a solvent followed by washing the solvent out and measuring the resulting step height). The same process removed only negligible amount of material (less than 20 nm) when applied to a new, unused photoconductor. In both cases, doubling the soaking time did not significantly change the thickness of removed layer suggesting that the surface layer modified by extended exposure to plasma has a finite thickness of several hundred nm.

Figure 4 shows surface topography maps (Dektak 150). A new, unused photoconductor shows gentle surface undulation with period of several hundred microns representing typical surface roughness observed for all the investigated organic photoconductors [Fig. 4(a)]. Similar topography was

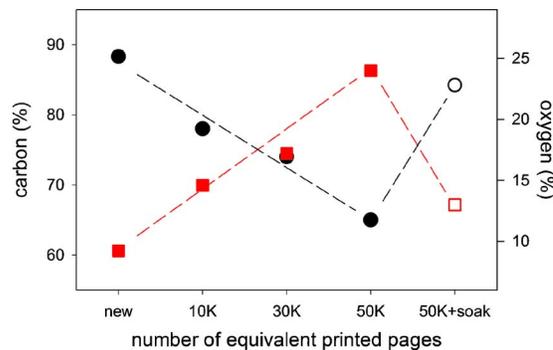


Figure 5. Carbon and oxygen concentration after a prolonged processing (5×10^4 equivalent printed pages; charge roller used).

found after a prolonged processing, as shown in Fig. 4(b). However, a completely different surface topography was observed when the plasma exposed photoconductor was soaked in the aforementioned solvent [Fig. 4(c)]. This surface exhibited linear and sharply defined topographic features superimposed on the top of the original surface undulations. The period of linear roughness is on the order of tens of microns with its depth in the several hundred nanometer range. This pattern was probably created by filamentary discharges from the charge roller following the photoconductor's movement direction.¹⁰ Fig. 4 suggests that extended exposure to electrophotographic plasma damages the photoconductor surface. However, the resulting thin parasitic film covering the surface follows the contour of an original photoconductor and hides the newly created surface damage.

Although both surface topography and wet etching data suggest that the chemically modified top region is on the order of several hundred nanometers, XPS data suggested yet another shorter range modification of the surface region. Carbon and oxygen are the major elemental components of the photoconductor as measured by the XPS (neglecting hydrogen). The prolonged exposure caused gradual changes of their ratio, as shown in Figure 5. These changes were associated with the corresponding modification of the molecular structures within the photoconductor's surface region (Figure 6). However, the low energy *in situ* ion beam sputtering combined with the XPS measurements showed that the observed modification of the photoconductor's surface region was limited to the top 50–60 nm (Figure 7).

These results suggest the presence of complex processes resulting from the interactions between the organic photoconductor and the plasma present within the electrophotographic environment. According to previous reports, plasma modifications of the photoconductor are primarily due to energetic particles, such as electrons and radicals, impinging upon the photoconductor and to UV photons. Charged particles have a limited penetration depth of the order of tens of nanometers and they are primarily responsible for the structural damage and shallow implantation of oxygen detected with the XPS. UV photons can penetrate several hundred nanometers causing chemical bond breakage and the reformation of molecular arrangement within

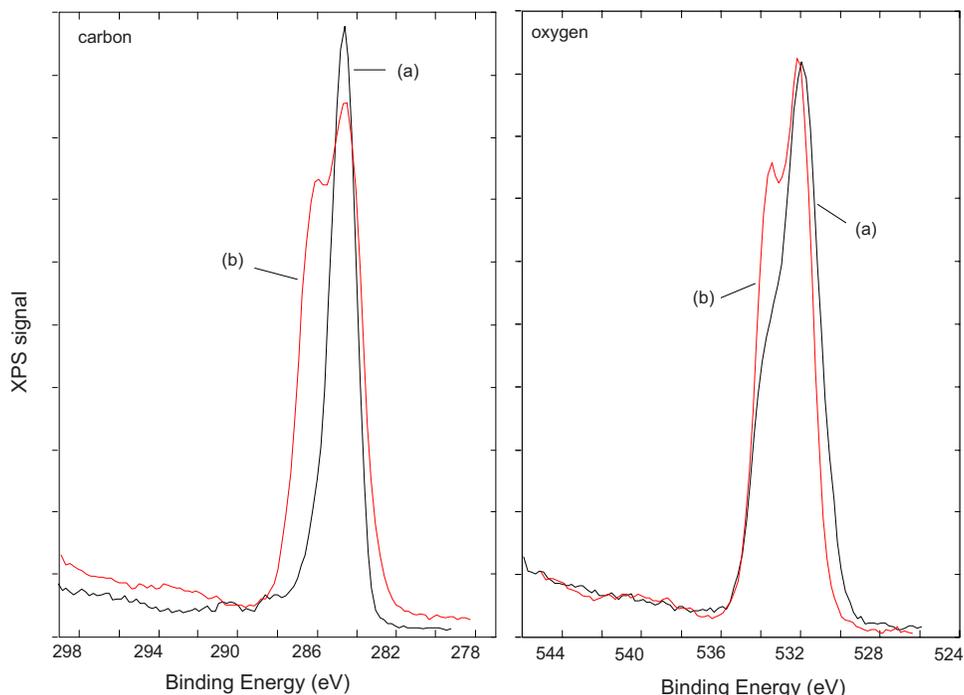


Figure 6. Changes in the molecular composition of a photoconductor as demonstrated by the chemical shifts of the carbon (C1s) and oxygen (O1s) XPS signals. (a) New photoconductor, (b) photoconductor after 50 K equivalent printed pages (charge roller used).

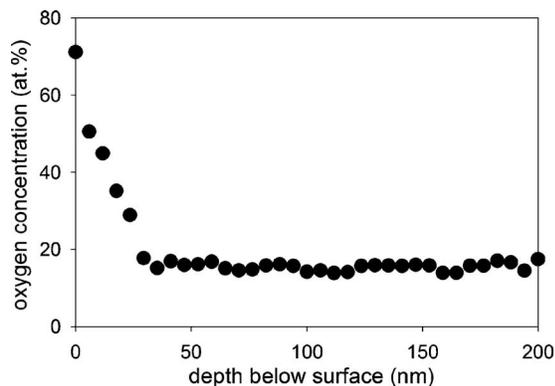


Figure 7. Oxygen depth profile after 6 h processing. XPS data were obtained by *in situ* low-energy beam ion sputtering followed by XPS measurement of freshly sputtered surface.

the top 300–400 nm region while retaining the original elemental composition. They may cause a variety of intramolecular reactions resulting in decrease of the aromatic C-H ATR-FTIR signal and the corresponding changes of the Ψ parameter (CH_2 content increases while CH_3 concentration remains relatively constant).^{11–13} The further analysis of the photochemical processes occurring when photoconductor is exposed to the UV radiation of an air Paschen discharge is beyond scope of the present results. It needs to be noted that after a prolonged processing the Ψ value reaches a steady state and that the aromatic C-H signal is still present meaning that not all benzene rings have been eliminated and transformed into species bearing aliphatic methylene groups. This effect is likely due to previously reported observation suggesting that continuous bombardment of the

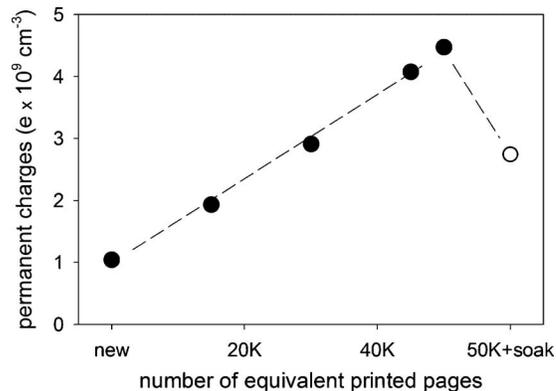


Figure 8. Permanent charges introduced by prolonged processing (Kelvin probe measurement).

photoconductor causes its gradual erosion and surface material removal, thus the interface between the modified surface region and unmodified bulk of the photoconductor gradually moves inward.⁵

A Kelvin probe measurement showed that extended processing caused a gradual increase of charge density within the photoconductor. Figure 8 presents photoconductor charge measurement approximately one week after the processing. Exposure of a photoconductor to an electrophotographic environment usually introduces a large surface charge buildup. The surface charges are then quickly dissipated and after several hours only permanent charges present within the photoconductor remain. These charges are likely due to molecular modifications introduced by plasma exposure. The aforementioned solvent soaking can

reduce their number (most likely charges associated with the top, soluble parasitic film). However, the majority of charges located further from the surface remain unchanged. The presence of these charges may have deleterious effect on a successful ink transfer within the electrophotographic process.

Although the present work was primarily focused on the charge-roller based electrophotographic systems, preliminary evaluation has also been made for the case when a scorotron was used. Although the scorotron plasma generation mechanism is quite different from the charge roller, a similar photoconductor damage phenomenon was observed (the same behavior of Ψ parameter), except that the damage was less severe for the same exposure time (the same equivalent number of printed pages). It appears that even though the energy and density of scorotron generated particles impinging upon the photoconductor may be lower than in the case of a charge roller, a scorotron likely produces copious amounts of the UV photons degrading the surface region of an organic photoconductor.

CONCLUSIONS

The goal of this work was to elucidate the degradation mechanism of a commercial organic photoconductor within a modern electrophotographic environment aimed at the high-speed, high-throughput applications. It was observed that the prolonged exposure of the photoconductor to energetic particles and UV photons originating from the discharge region caused significant structural and compositional changes within the region up to several hundred nanometers below the surface of the photoconductor, corresponding to the UV penetration depth. UV-driven photochemical processes involving dearomatization and cracking of the benzene rings appear to be the major mechanism driving these changes. They result in reduction of the aromatic C-H bonds and corresponding increase of the aliphatic CH_2 species within the bulk of the modified region, while the surface reactions with oxygen radicals result in formation of multiple C-O bonds near the surface. Similar degradation mechanism occurs regardless of whether charge

roller or scorotron are used for charging of the photoconductor.

ACKNOWLEDGMENTS

The authors acknowledge collaboration and fruitful discussion with Eric Hanson, Xia Sheng, Omer Gila, Michael Lee, William F. Stickle, Nir Mosenson, and Dafna Shunary of the Hewlett Packard Co. The technical assistance of Paul Matheson and Quang Lam (Hewlett-Packard) is also acknowledged.

REFERENCES

- ¹L. B. Schein, "Benjamin Franklin and electrophotography", *J. Vac. Sci. Technol. A* **25**, 1256 (2007).
- ²C. B. Duke, J. Noolandi, and T. Thieret, "The surface science of xerography", *Surf. Sci.* **500**, 1005 (2002).
- ³Y. Kanemitsu and H. Funada, "Reversible light-induced fatigue of two-layer organic photoconductors studied by time-of-flight photoconductivity measurements", *J. Phys. D* **24**, 1409 (1991).
- ⁴C. K. H. Wong, Y. C. Chang, J. Pflieger, Y. V. Lam, K. M. Leung, and D. S. Chiu, "Fatigue in hydrazone-based xerographic photoreceptor—Effect of ultraviolet irradiation", *J. Mater. Res.* **12**, 106 (1997).
- ⁵K. Nauka, S. Chang, and H. T. Ng, "Interactions between organic photoconductor and plasma discharge within an electrophotographic environment", *J. Vac. Sci. Technol. A* **27**, 566 (2009).
- ⁶C. Cismaru, J. L. Shohet, K. Nauka, and J. B. Friendmann, "Relationship between the charging damage of test structures and the deposited charge on unpatterned wafers exposed to an electron cyclotron resonance plasma", *Appl. Phys. Lett.* **72**, 1143 (1998).
- ⁷J. M. Hollas, *Modern Spectroscopy*, 4th ed. (Wiley, New York, 2004), p. 289.
- ⁸N. M. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed. (Academic Press, New York, 2000), p. 215.
- ⁹Absorption due to vibrations of aliphatic methylene groups (CH_2), though not present in the case of Bisphenol-A molecules, is likely due to methylene side or end groups of the polycarbonate macromolecules.
- ¹⁰U. Kogelschatz, "Filamentary, patterned, and diffuse barrier discharges", *IEEE Trans. Plasma Sci.* **30**, 1400 (2002).
- ¹¹A. Larsson and H. Derand, "Stability of polycarbonate and polystyrene surfaces after hydrophilization with high intensity oxygen RF plasma", *J. Colloid Interface Sci.* **246**, 214 (2002).
- ¹²G. Kaupp, "Photochemical rearrangements and fragmentations of benzene derivatives and annelated arenes", *Angew. Chem., Int. Ed. Engl.* **19**, 243 (1980).
- ¹³M. Charbonnier, M. Romand, E. Harry, and M. Alami, "Surface plasma functionalization of polycarbonate: Application to electroless nickel and copper", *J. Appl. Electrochem.* **31**, 57 (2001).