

# On the Mechanisms of Plating on Plastics

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**This is a general, yet chemically detailed introduction to plating of plastics. The emphasis is on plating of ABS plastics, with explanations for the widespread use of this plastic. Many concepts, from the three-dimensional structure of ABS plastics, to the use of Pourbaix diagrams to explain electroless nickel plating, are integrated. The result is a step-by-step study of the whole process, from pre-etchants to electroless nickel. ESCA characterization and transmission electron microscopy are used to explain the surface chemistry.**

**T**he field of plastics plating is a gray area to many plating chemists. The reasons for this are easy to see. Electroplating is done on practical conductors, almost all of which are inorganic, and the materials deposited are inorganic. In contrast, plastics plating is done on a non-conductive organic substrate. Many plating chemists tend to have an inorganic background and an inorganic outlook. This results in emphasis on the electrolytic steps in plastics plating. Often there is little appreciation of the processes needed to get the initial conductive electroless film.

This has important consequences when an electroplate tries to understand plastics plating. No practical plater would fail to appreciate the differences between plating aluminum and plating steel strip. Most platers are also aware of how alloy composition, grain size, cleanliness and other factors can affect the final properties of the deposit.

When the average chemist is asked to plate plastics, the following thought sequence is likely to occur: "Plastics are non-conductors. If a layer of a conductor is deposited on a non-conductor, then it can be electroplated. Because all plastics are non-conductors, the plastic has no effect on the final coating. Therefore, all plastics are equivalent." This is an example of the "black box" approach.

Practical experience has shown that not all plastics can be plated satisfactorily. The highest volume platable plastic is acrylonitrile-butadiene-styrene polymer, or ABS. Others in-

clude epoxies, phenolics, polyphenylene oxide and smaller amounts of polypropylene, polysulfone, nylon, polyvinylidene chloride, polycarbonate and others.<sup>1</sup> In terms of performance, ABS is by far the easiest plastic to plate, with the best adhesion and thermocycle resistance. This polymer is composed of three different types of molecules—styrene, butadiene, and acrylonitrile. They are not polymerized or attached to each other in random order.

Inorganic chemists typically view a plastic as a homogeneous mass. While some plastics may be like this, ABS is not. ABS is a two-phase system that exhibits some of the properties of metal systems, including grain boundary phenomena, surface layer disorder, and differential volatility.

Figure 1 is a transmission electron microscope (TEM) picture of a slice of plating-grade ABS polymer at 10,000X magnification. The circular cross-sections are mainly polybutadiene particles. The background bulk material is largely polyacrylonitrile-styrene. Other compounds, such as lubricants, pigments, antioxidants, filler, and plasticizers may be present. Also evident is the range of sizes of the polybutadiene spheres, which may or may not indicate the actual particle size distribution. Because this is a slice of bulk material, it shows random cross-sectional slices of the spheres. It can be seen that an ABS polymer is not a simple system. Its properties depend critically on such parameters as the amount of polybutadiene, the ratio of acrylonitrile to styrene, and the sizes and dispersion of the polybutadiene spheres.

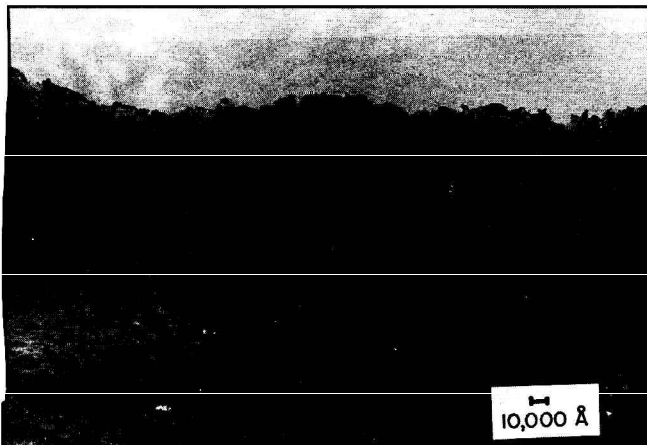


Fig. 1—TEM photograph of ABS polymer cross section. 10000X.

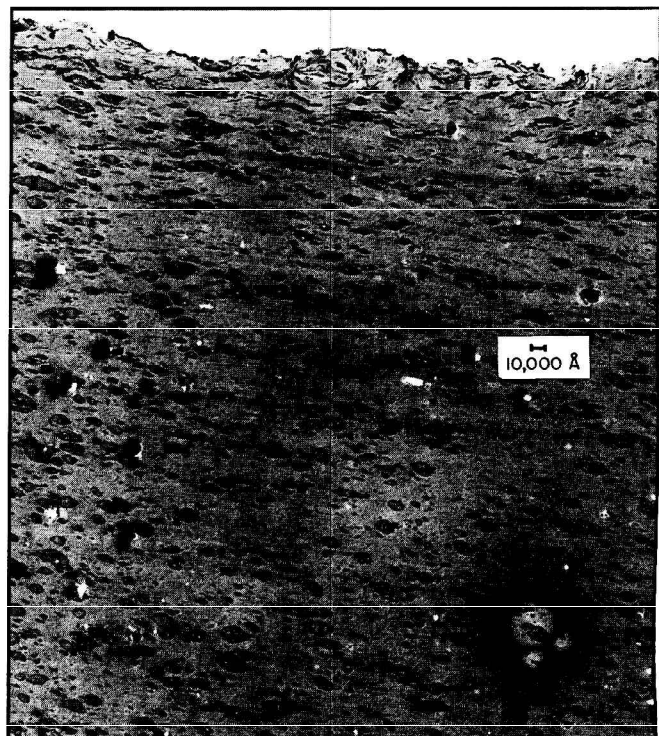


Fig. 2—Structure of surface layer of ABS. 10000X.

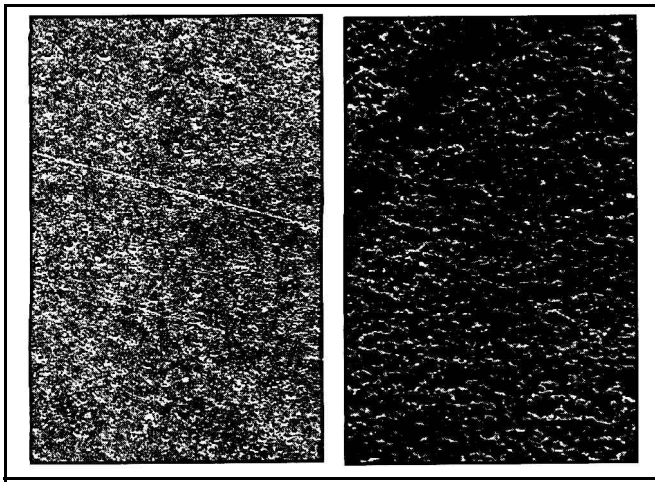


Fig. 3—ABS surface before (left) and after etching (right).

### Adhesion

The two-phase character of ABS seems to be crucial in explaining its plating behavior. Polymers such as polypropylene can have grain boundaries, but they are essentially single-phase systems. Unfilled polypropylene is very difficult to plate. If an inorganic filler, such as glass, is added to polypropylene, it becomes relatively easy to get good metal-to-plastic adhesion.'

There has been a low-key controversy in the literature about the adhesion mechanism itself. One school of thought claims that the plastic surface must be chemically modified so that the metal will be held by the polar or hydrophilic surface groups, such as carbonyls and carboxyls. Another group claims that a lock and key mechanism, the very rough etched surface itself, holds the metal to the plastic.<sup>3,6</sup>

Without elaborating, it may be stated that it is very difficult to give a totally convincing picture for either mode. It is hard to separate these two effects in a practical system. The original plastics plating process used mechanical roughening—sanding—to get a good bond. This involves friction and local heating effects, however, that can chemically modify the surface. On the other hand, some model polymers can be chemically treated to give a hydrophilic surface with minimal topographic changes, and these do show improved adhesion.

The problem is that real systems, such as ABS, are more complex. To overcome this problem, the concept of the pre-etch was introduced a number of years ago.<sup>7,9</sup> This is basically an organic liquid with poor solvency power for ABS. It materially improves adhesion by plasticizing and relieving the surface layer strain of the plastic, especially the polybutadiene spheres, while allowing better etching. Although either or both of these

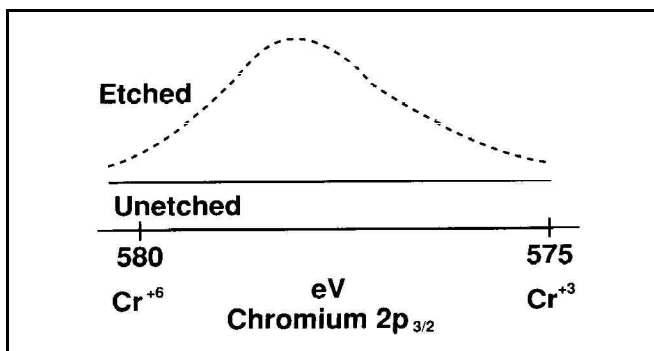


Fig. 5—ESCA characterization of Cr(III) and Cr(VI) before and after etching of ABS.

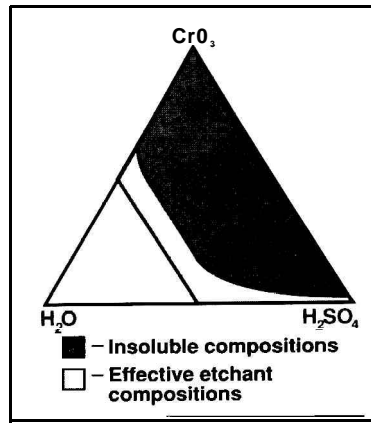


Fig. 4—Effective etching range of  $\text{CrO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  mixture (small, inside triangle).

adhesion theories may be true, they neglect one important phenomenon: As long as there is any metal-plastic adhesion, the point of separation in a peel test is not at the metal-plastic interface. All peel test specimens that we have seen show that the failure takes place within the polymer itself. Molding an ABS part introduces a highly stressed surface having properties much different from the bulk polymer. Significant adhesion

improvement results when this strained layer is removed by etching, or the strain is partially relieved by a pre-etch.<sup>7,10,11</sup>

### Etching

This leads to the importance of the plating process itself. Plating of bulk plastics is distinctly different from plating of printed circuits. Printed circuit plating is functional—the sides of holes and flat boards are the main items plated and the main electrolytic step is to plate a thick layer of copper over the electroless copper.

Plastics plating, whether for a decorative or a functional purpose, necessitates good appearance. The metal must also have good adhesion, thermocycle resistance and, usually, good corrosion resistance.

The major difference is the etching step, essential for good adhesion and thermocycle resistance, and to increase corrosion resistance. A smooth plastic surface allows relatively unhindered mass transfer of reactants between the metal and

board layers. An etched surface gives a long, more or less tortuous path, greatly slowing any diffusion-mediated corrosion. Figure 2 shows the structure of the surface layer of a molded ABS part. The polybutadiene near the surface is no longer spherical, showing that it has a large molded-in strain. This strain results when the moving molten polymer is rapidly cooled against the mold cavity. Only the surface layers of the injection-molded part show bulk polybutadiene deformation. Proper etching of the plastic surface with a hot chromic-sulfuric acid solution removes this strained layer (Fig. 3). Because ABS is a two-phase material, differential oxidation is expected. The acrylonitrile-styrene oxidizes more slowly than the polybutadiene, so the etching roughens the surface.

Current etching solutions are a mixture of water and chromic

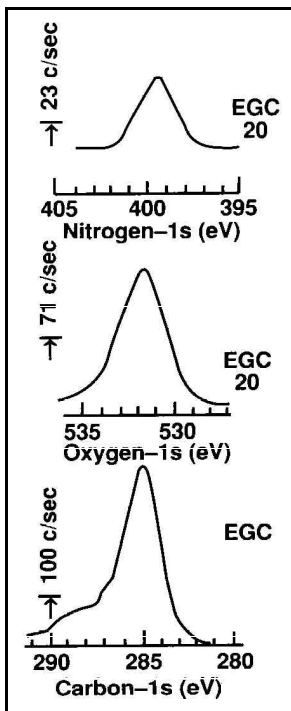


Fig. 6—ESCA characterization of carbon, oxygen and nitrogen for etched and unetched ABS.

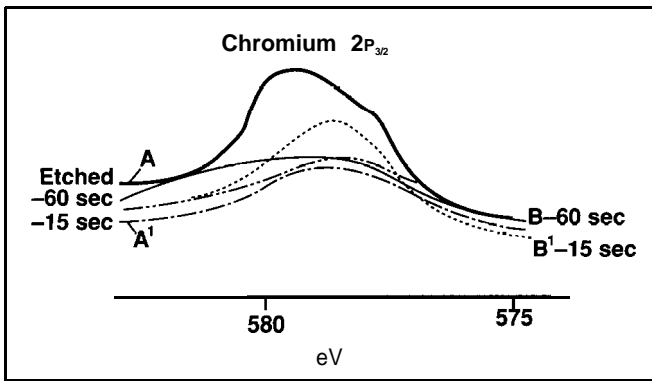
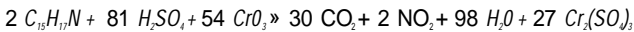


Fig. 7—ESCA characterization of Cr(VI) reduction by (a) inorganic and (b) neutralizers.

acid, or water, chromic acid and sulfuric acid. Not every mixture of these components will work well (Fig. 4). Optimum results are obtained only when the solution is saturated with chromic and sulfuric acids.<sup>12</sup> For this reason, careful bath control is necessary to maintain optimum etching. Etching will selectively, and more slowly, oxidize the acrylonitrile-styrene portion of ABS, then the polybutadiene portion, thereby roughening the surface. The following equation shows the overall reaction for complete oxidation of a 1:1:1 acrylonitrile-butadiene-styrene polymer.



It is obvious that large amounts of acid and  $Cr^{6+}$  are consumed during the oxidation, and much  $Cr^{3+}$  and  $H_2O$  produced. Despite etch control problems, the chromic-sulfuric acid system is the cheapest and most practical available, given the present state of the art. Because of the ecological advantages,  $KMnO_4$ -based etches are also employed.<sup>13</sup>

The etch bath can be used to illustrate another problem peculiar to plastic platers. This is solution absorption by the substrate. Metals are, fortunately, non-porous, so simple rinsing usually removes all excess solution. ABS is actually quite sponge-like. Most platers don't realize this; a molded, unetched part is hydrophobic because of the disordered, highly strained surface skin. Etching removes this skin, greatly roughens the surface, and makes it hydrophilic. Water is rapidly absorbed through the surface of the plastic at elevated temperatures. Palladium, tin, and chromates are also absorbed.

Figure 5 shows an ESCA (Electron Spectroscopy for Surface Analysis) diagram of ABS before and after etching. It is very interesting that the chromium peak is not represented by just the reduced  $Cr^{3+}$  and  $Cr^{6+}$  species. Instead,  $Cr^{4+}$  and  $Cr^{5+}$  seem to be stabilized in the polymer matrix, perhaps as chromium complexes or esters. Their presence is good evi-

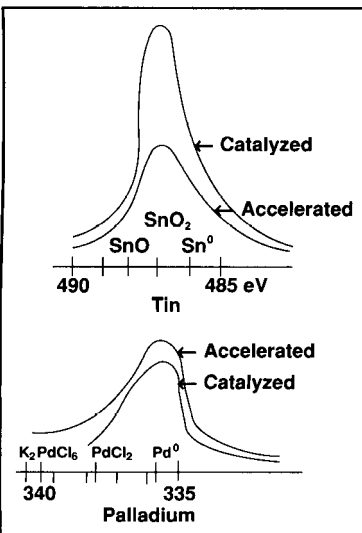
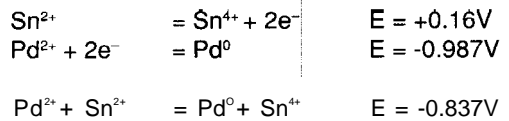


Fig. 9—ESCA characterization of palladium and tin concentrations before and after acceleration.

### Theoretical redox behavior



### Actual kinetic behavior

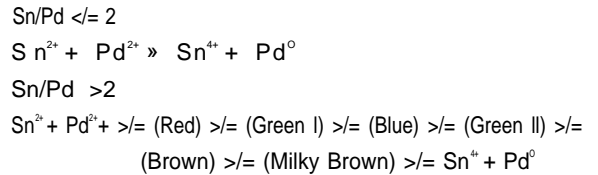


Fig. 8—Palladium-Tin reactions.

dence for chromium absorption into the polymer itself inasmuch as  $Cr^{4+}$  and  $Cr^{5+}$  are normally very unstable.

Figure 6 shows the carbon, oxygen, and nitrogen peaks for etched and unetched ABS. The absence of sharp peaks for carbon, especially, indicates a variety of different forms for this element. Etching strongly crosslinks and toughens the surface, forming a continuous membrane that can be isolated. This membrane is thought to be a good ion exchange surface that may also contribute to some of the effects seen in plating. Other studies have shown the presence of carbonyl, carboxyl, and  $-SO_3H$  groups.<sup>14</sup>

Figure 7 depicts how neutralizers work. An etched, water-rinsed ABS part is quite dark from ad/absorbed chromium. This chromium can be removed only very slowly by running water. Various types of reducing agents will reduce the  $Cr^{6+}$  to  $Cr^{3+}$  at a rapid rate. These data show two different types of neutralizers. Curve A represents an acid inorganic reducing agent, while curve B represents an organic amine. Plating is possible without neutralization because  $Cr^{6+}$  is reduced by the stannous

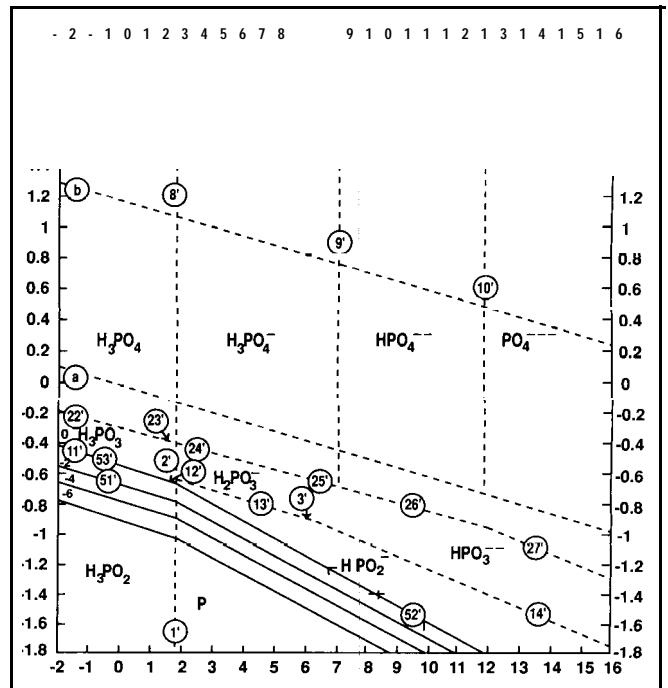


Fig. 10—pH potential equilibrium diagram for phosphorus-water system at 25°C, neglecting hydrides of phosphorus, but considering white phosphorus.

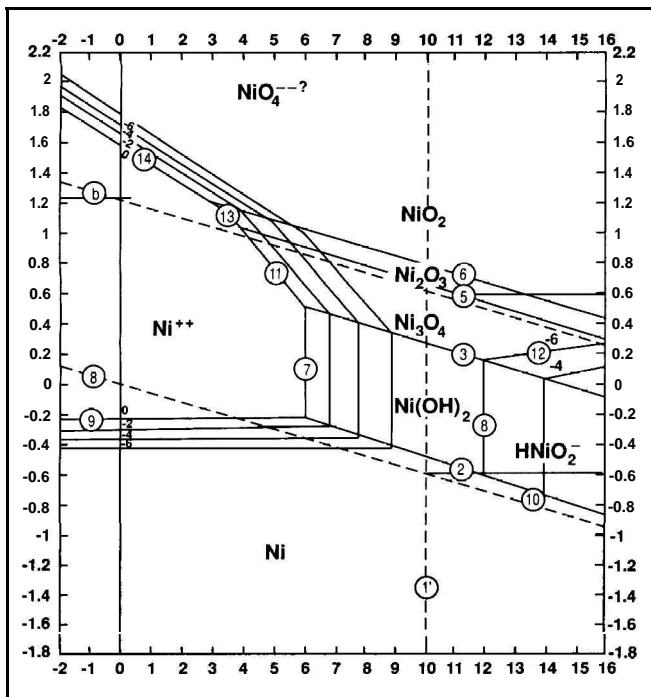


Fig. 11—pH potential equilibrium diagram for nickel-water system at 25 °C.

ions in the catalyst step, but this is expensive because it decreases catalyst life. Traces of  $\text{Cr}^{6+}$ , on the order of 5 to 15 ppm, will also prevent electroless nickel deposition. Both of these neutralizers not only reduce the  $\text{Cr}^{6+}$ , but cause it to desorb from the plastic.

### Catalysts

The most-used catalyst currently is an aqueous  $\text{HCl}/\text{SnCl}_2/\text{PdCl}_2$  solution containing a poorly defined tin-palladium reaction product.<sup>15,25</sup> The etched and neutralized plastic part is immersed in this room-temperature bath for 1 to 5 min, then rinsed, and accelerated. The main fact certain about the catalyst system is that it is easily perturbed. Palladium chloride is theoretically reduced to palladium metal easily and quickly by acidic stannous chloride. The actual reaction, however, depends strongly on the ratio of tin to palladium (Fig. 8).<sup>26,27</sup> At a tin/palladium ratio of 2:1, reduction occurs. As the ratio of tin increases, the palladium reduction becomes hindered and several color phases become evident. The brown color phase represents the material used in commercial catalysts. Because of the extreme lability of the system, no one has ever crystallized or satisfactorily isolated any of these intermediates.

Both art and skill are necessary to make a good catalyst.<sup>27,28</sup> Minor variations in the process can give widely differing activities. Chemical analysis of ABS parts shows that good catalysts give excellent plating coverage with only 1 to 2  $\mu\text{g}$  of palladium/cm<sup>2</sup>.

The catalyzed part is water-rinsed (Fig. 9) and accelerated. The act of rinsing decomposes by oxidation and hydrolysis any catalyst structures that may have been present. ESCA shows  $\text{Pd}^0$  and  $\text{Sn}^{4+}$  at this time, with some  $\text{Sn}^{2+}$ . The acceleration step is immersion in a hot acid, such as  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ .<sup>29</sup> It serves to dissolve excess tin and to allow the tin-palladium redox to go to completion if necessary. The ESCA shows very little change in apparent surface palladium, but a large decrease in the amount of tin. Wet chemical measurements have shown that 25 percent of the tin is typically removed, although this is highly dependent on the accelerator parameters.

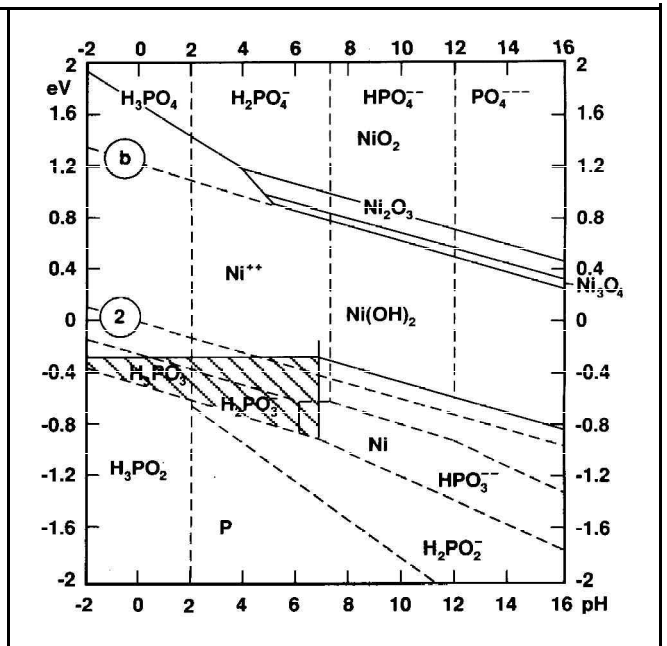


Fig. 12—Theoretical conditions for formation of nickel in acid solution by reduction of  $\text{Ni}^{2+}$  ions by hypophosphite. (0.6 g/L  $\text{Ni}^{2+}$ )

A catalyzed, non-accelerated part will not plate in a room-temperature electroless nickel bath. The actual accelerator can be almost any acidic or basic solution in which the tin is soluble. The electroless redox reaction may be inhibited by the excess tin, inasmuch as tin can be used to stabilize an electroless nickel bath against spontaneous decomposition.

### Electroless Nickel Deposition

Electroless deposition of nickel was rediscovered by Brenner in the early 1940s.<sup>30</sup> His work led to the first commercially useful baths, all of which operated at very high temperatures. It was not until the mid 1960s that the first room-temperature electroless nickels were prepared.<sup>31</sup> Almost all economical baths at present are those using hypophosphite as the reducing agent. The detailed mechanism of the reduction has been thought to involve hydride ions, atomic hydrogen, or other species, because of the odd nature of this reduction.

Figures 10 and 11 show Pourbaix diagrams for phosphorus and nickel. A Pourbaix diagram is a shorthand chart of the electrode potential vs. the pH of all the valence states and solubilities for a given element.<sup>32</sup> It incorporates all available information on the chemical and electrochemical behavior.

The nickel diagram illustrates the conditions necessary to deposit nickel metal electrochemically from an uncompleted nickel salt solution. It can also be seen how critical the constraints are—if the solution is operated at -0.3 volts at pH 6, Ni and  $\text{Ni}(\text{OH})_2$  will be codeposited. Lines a and b are the lines of stability for water—a showing the conditions needed for hydrogen evolution and b for oxygen evolution. The phosphorus diagram shows some of the possible phosphorus species which can exist at each of the potential/pH points.

If the two diagrams are simplified somewhat and superimposed, as in Fig. 12, it can be seen that hypophosphite is the high-energy reducing compound; because it is thermodynamically unstable, it is found only below the water breakdown line. The shaded area is the unstable region between the domains of stability of  $\text{Ni}^{2+}$ , and hypophosphite. If the potential of a solid surface is lowered into this region either by an external source

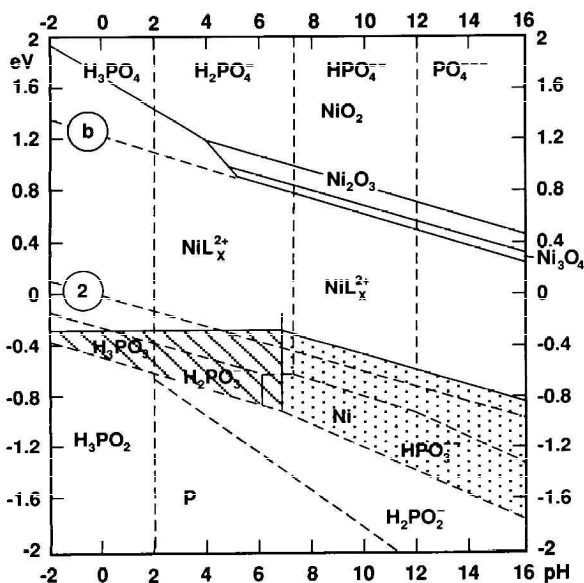


Fig. 13—Theoretical conditions for formation of nickel in alkaline solution by reduction of  $Ni^{2+}$  ions by hypophosphite. (0.6 g/L  $Ni^{2+}$ )

or by a catalyst, the overall redox reaction should occur. The cross-hatched area shows that the widest operating range is from pH 4 to pH 7. Most acid baths operate in the pH 4 to 6 range to eliminate any oxide precipitates.

Alkaline baths have a somewhat different diagram (Fig. 13). Completing agents must be added to keep the nickel in solution, so that the  $Ni(OH)_2$  solid phase is no longer present. Now, the redox range is even larger than in acid solution. Several authors have measured the mixed potentials of this electroless system; all results have fallen within the shaded areas .33

It can be stated that this was simplified, because it doesn't say anything about two important side reactions that also occur—phosphorus deposition and hydrogen evolution (Fig. 10). At the lower left, it can be seen that elemental phosphorus is a constituent of this diagram. Like hypophosphite, it is not stable in the presence of water. Phosphorus is unexpected, both because of this instability and because hypophosphite is being oxidized, not reduced. Hydrogen evolution would be expected because our mixed potential zone is mainly below the hydrogen evolution line.

The actual system gives an alloy of nickel and phosphorus (Fig. 14), where EPN denotes poor etch and EGN denotes good etch. The ESCA shows that elemental phosphorus is present. Depending on conditions, the phosphorus content can range from about 15 percent to less than 1 percent. If atomic hydrogen or hydride ions were included in a Pourbaix diagram, we could probably explain the phosphorus deposition and perhaps see why alkaline solutions usually have less phosphorus.

X-ray studies show that the initial deposit is a solid solution of phosphorus in nickel.<sup>34</sup> After heat treatment, it changes to  $Ni_3P$  or  $Ni_2P$  in a nickel matrix. The nickel phosphorus alloy is much more corrosion resistant than pure nickel. The heat-treated coating can be almost as hard as chromium.<sup>35</sup>

The hydrogen evolution reaction plays a very important role, especially in alkaline baths. No external voltage or current is applied to the part to be plated, so the deposition is driven solely by the catalyzed half-reactions. In the absence of hydrogen evolution, a diffusion-controlled, very slow deposition rate

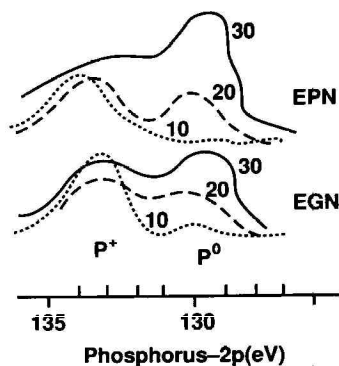


Fig. 14—ESCA characterization of surface phosphorus 2p photoelectron spectra for initial deposition of electroless nickel.

could be expected. Hydrogen gas evolution accounts for 40 percent or more of the hypophosphite usage. This maintains a strongly stirred, turbulent interface with a good plating rate even at room temperature.

The unique feature of electroless plating is the near uniformity of the deposited metal thickness, regardless of part configuration. Electrolytic plating will give differential plating thicknesses on recesses and sharp edges. There are many other interesting aspects of electroless plating, especially regarding the electroless deposition step and the catalyst preparation and characterization. Just a few of the topics include the effect of stabilizers on grain growth, ductility, and corrosion resistance of electroless coppers; the effect of the nickel complexer on the corrosion resistance of the electroless nickel; lamellar deposits of acid and, to a lesser extent, alkaline electroless nickels; inhibition and promotion phenomena; the use of electroless deposition to make nonequilibrium and "impossible" alloys from aqueous solution, such as nickel-molybdenum-phosphorus and nickel-tungsten-phosphorus; the effects of different reducing agents, such as hydrazine and organoboron compounds in place of hypophosphite; the effect of catalyst preparation methods on catalyst activity; and the effects of working bath variables on catalyst absorption by etched and neutralized parts.

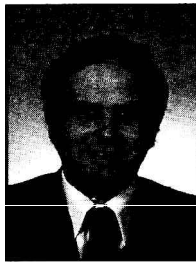
## Summary

Plating on plastics is a complex field still undergoing research. Explanations have been offered for basic theoretical concepts. Surface chemistry of the platable plastics plays an important role in overall reaction mechanisms and it is studied with the help of ESCA characterization. Pourbaix diagrams were presented and examined as a powerful tool for the explanation of the behavior of electroless nickel plating systems.

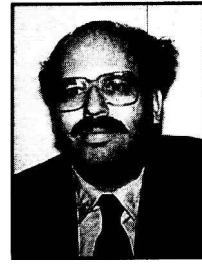
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