Finishing Technology into the Millenium

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The use of plastic substrates and the application of a metal deposit to the plastic, expands as technology moves to new fields and applications. The markets of opportunity will be investigated. The process of selecting a process for the cleaning and activation of a plastic substrate will be presented. The application and benefits of the specific metal surface will be examined.

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Introduction

Plastics are chiefly synthetic organic polymeric materials (consisting of large organic molecules) that can be molded under heat and pressure into a shape that is retained after the heat and pressures are removed. The large molecules are composed of repeating chemical units (monomers) which make the chain of the plastic (polymer). Examples of monomers to polymers are shown in Table 1.

Table 1

Monomer	**Polymer**
ethylene	polyethylene
propylene	polypropylene
vinyl chloride	polyvinyl chloride (PVC)
esters	polyester
amides	polyamide (nylon)
styrene	polystyrene

Chains of the plastic molecules may be linear, branched, or cross-linked, depending upon the nature of the monomer. Linear and branched plastic molecules will soften when heated, whereas, cross-linked plastic molecules will harden. The different monomers yield plastics providing different properties. These properties include high strength-to density ratios, thermal and electrical insulation properties, and good resistance to acids, alkalis and solvents. These properties have led to the use of engineered plastics to be substituted for metal in numerous applications.

The development of the different polymers of plastic offer competitive advantages over metal; weight reduction, greater design freedom, better corrosion resistance, and lower manufacturing costs. These benefits have been sought out by the automotive, plumbing, appliance, electronic, and decorative accessory industries.

Automotive:

- grills and trim
- door handles, interior and exterior
- interior console and trim
- signal lamp housings
- wheel covers
- headlight bezels
- instrument panels

Plumbing:

- fixtures and handles
- faucets
- piping
- shower heads

Appliance:

- handles and knobs
- trim, interior and exterior
- scale body frames
- electric razor bodies
- blender bases

Electronic:

- knobs and switches
- connectors
- computer frames
- telephone bodies
- radio/CD/cassette player frames

Decorative:

- cosmetic/perfume containers
- costume jewelry
- handles and knobs for furniture
- buttons
- picture frames
- clock trim and fixtures
- plaques and trophies
- lighting fixtures

The practice of commercially plating on plastic began in the 1960's. The majority of plastic substrate plated today is acrylonitrile-butadiene-styrene (ABS). Plastics that also see plating are ABS/polycarbonate, polycarbonate, epoxies, phenolics, polyenylene oxide, polypropylene, polysulfone, nylon, and polyvinylidene chloride. ABS plastic provides excellent adhesion, thermocycle resistance, and ease in plating, over the other choices. The reason is that the surface of the plastic to be plated has significant influence on the adhesion of the metal deposit. In the case with ABS, the chemical pre-treatment preferentially etches the butadiene out of the surface of the plastic. The resultant topography provides numerous bonding sites, promoting the adhesion of the subsequent electroless deposits.

The Freedonia Group reports that ABS will continue to experience the fastest growth for plastic substrates in the coming years. The forecasts for plastic substrates show six percent growth annually to $145 million spent on finishing chemicals in 2003. Plastics will continue to replace metal as new plastics are engineered, yielding higher chemical resistance and temperature tolerance.

Plating on Plastics

An important consideration to keep in mind when preparing a plastic substrate for plating is that there are the different alloys of plastic. There is no universal pretreatment sequence to cover all alloys of plastic. The alloy of the plastic must be known so that the proper sequence of chemically conditioning the surface is selected to achieve optimum results. One can have the purest and optimum plating solutions yet produce reject after reject due to an improper or out of spec pretreatment process sequence. Time and effort must be taken to qualify the composition of the material and the proper chemical sequence.

Decorative Plating on Plastic

Decorative plating on plastic goes through an electroless sequence and then through an electrolytic sequence to obtain the desired final finish. Table 2 represents a typical plating sequence performed for plating automotive trim. The process sequence does not indicate the required rinse cycle between each and every chemical process.

Table 2

Process	**Temperature °C / °F**	**Time**
Conditioner	43.3/110	240 sec
Etch	68.9/156	600 sec
Neutralizer	28/83	120 sec
Activator	28/83	160 sec
Accelerator	57/135	115 sec
Electroless Nickel	34/93	500 sec
Nickel Activator	ambient	45 sec
Copper Immersion	26.6/80	130 sec
Copper Strike	26.6/80	430 sec
Acid Copper	21.5/71	2410 sec
Copper Activator	30/86	105 sec
Semi-bright Nickel	58.9/138	2680 sec
Bright Nickel	55.5/132	840 sec
Duplex Nickel	61/142	145 sec
Chromium	44.4/112	120 sec

In the practice of preparing ABS plastic for plating, the surface of the ABS begins as a hydrophobic (water hating) but after etching, the ABS surface is hydrophilic (water loving). Ineffective rinsing will not remove clinging contaminants. As with any plating sequence, effective rinsing must be practiced and the consequences of inadequate rinsing avoided.

All decorative plating begins with the basic pretreatment sequence to prepare and activate the plastic. Differences begin to appear at the electroless plating step. Some applications substitute electroless copper for the electroless nickel plate. Some may use both. It depends upon the application of the plated part.

Variations of the electrolytic plating processes begin after the electroless process. The cosmetic, plumbing, and decorative markets look for other finishes than chrome. The application of any metal deposit is possible with the most common being precious metals (gold, silver, and rhodium), white bronze, and brass.

Processing the Plastic

This section will provide descriptions of the chemical processes used to prepare ABS plastic for plating.

Conditioner

The conditioner prepares the plastic by chemically modifying the surface of the plastic to allow a uniform etch. The conditioner is usually a solvent such as dimethylformamide or polysulfone. The type of conditioner and/or the operating parameters (concentration of the solvent or temperature) are specific for the alloy being prepared.

Maintaining the proper dwell time, solution temperature, and concentration of the chemistry, controls the activity of the solution on the plastic. Proper conditioning of the plastic surface is critical in obtaining acceptable adhesion of the electroless plating.

Etch

The etch solution prepares the surface of the plastic by removing material, thereby roughing up the surface. It creates topography with microscopic holes, which serve as bonding sites for the electroless deposit. As mentioned earlier, the butadiene is selectively removed in the etch from the Acrylonitrile-Butadiene-Styrene surface. A typical etch used for this purpose is the strong oxidizing solution:

Chromium trioxide	375-450 g/l
Sulfuric acid	335-360 g/l

Again, the alloy of the plastic must be known, for different parameters are needed for different plastics. Some require longer times/higher temperatures and others require less time/lower temperature. Proper etching influences the appearance of the surface, adhesion, and deposit stress.

Neutralizer

The neutralizer is responsible for chemically reducing any residual etch solution to prevent the carry over of chrome to subsequent processes. Sodium bisulfate has been used as an effective neutralizer in an acidic solution.

Maintaining the temperature, neutralizer concentration, and acid concentration controls the activity of the neutralizer. Temperature is the most effective control for increasing the “aggressiveness” of the neutralizer.

Activator

The purpose of the activator is to provide active catalytic sites on the surface of the plastic. This is provided by the absorption of metal on to the surface of the plastic, which will serve to initiate the electroless deposition. The most common solution used is a combination of palladium and tin metal in an acid solution.

Maintaining the catalyst concentrate, temperature, dwell time and agitation control the effectiveness of the activator.

It is important to keep the chromic acid etch material from contaminating the activator solution. The activator solution is an expensive solution and the introduction of chrome will render the activator non-catalytic. Air agitation is not used in this solution for it will oxidize the tin in the solution.

The soaring price of palladium has initiated investigations into new methods of activating plastic substrates. One promising solution is a colloidal copper metal activator working in the same fashion as the more expensive palladium activator.

Accelerator

The presence of tin on the surface of the plastic inhibits the ability of the palladium to act as a catalyst. The purpose of the accelerator is to remove the tin from the plastic, leaving the palladium to initiate the electroless process. The accelerator can be either acidic or alkaline, as long as tin is soluble in the solution.

Maintaining the dwell time, solution temperature, accelerator concentration, and accelerator concentration control the effectiveness of the accelerator.

Electroless Process

Either electroless nickel or electroless copper may be deposited at this step. Again, it depends upon the application. Copper will provide a ductile and conductive base whereas the nickel provides a harder barrier coating. The purpose of the electroless deposit is to supply a metallic base for the subsequent electrolytic plating.

Maintaining the solution chemistry, dwell time, temperature, and pH determine the thickness of the coating. Most electroless operations for plating on plastic utilize automatic controllers to maintain the solution chemistry. The electroless solutions are a delicate balance of a metal source, a reducing agent, organic complexors, stabilizers and buffers

The alkaline electroless nickel solution is usually a low temperature bath (26.6 to 62.8 °C [80 to 145 °F]), operated at a pH of 8.5 to 9.5. Hypophosphite is the typical selection as the reducing agent with ammonium hydroxide as the pH adjuster. The phosphorus content of the alkaline electroless nickel deposit is lower than that found in the acid electroless nickel solutions. The solution, depending on the operating parameters could deliver a thickness of 0.25 to 0.5 micron in ten minutes.

The electroless copper solution is also a low temperature (37.8 to 60°C [100 to 140 °F]), alkaline solution (pH: 12-13). Formaldehyde is the common reducer with sodium hydroxide used as the pH adjuster.

Electrolytic Plating

The electrolytic processes strike solutions immediately after the electroless processes are designed to build the metal on to the electroless deposit. The strike electrolytic deposit is run at current densities that do not “burn” away the electroless deposit at the rack points. The thicker deposit now allows for building heavier thickness deposits produced in plating solutions at higher current densities.

The metallized plastic is now ready for its final decorative, electrolytic finish.

EMI Shielding

EMI shielding refers to electromagnetic interference (EMI) and the action taken to minimize the effect of EMI. The interference is energy waves that are created from a variety of sources. (See Table 3.) The EMI energy waves emitted by rapidly changing voltages can be picked up by the other electronic devices. EMI shielding is the approach taken to provide protection to electronic devices manufactured with plastic. Plastic alone will not stop the EMI energy waves; however, the application of a thin conductive layer will act as a barrier to eliminate or significantly reduce the penetration of the damaging or annoying energy waves.

Table 3

Sources of Electromagnetic Interference
Airplanes
Computers
Electric motors
Ignition systems
Power lines
Radio and television transmitters
Video games
Lightning

EMI waves effect the operation of radio and television receivers, computers, and telephones. The EMI waves can be heard on a car radio as a whine when the motor is accelerated. It is static to the television screen when the blender in the kitchen is operated. It may now be apparent why passengers on airplanes are instructed to keep their electronic devices turned off during lift off and landing. EMI waves could interfere with the ability of the pilot to communicate with the control tower. EMI waves are “noise” to other electronic devices.

The Shield

Metal surfaces reflect EMI energy waves whereas the energy waves have the ability to pass through plastic material. Attenuation is the measurement (measured in decibels, dB) of a coatings’ ability to prevent or reduce the absorption of EMI energy waves. (See table 4.) The most effective method for controlling the EMI energy waves is to coat plastic with materials possessing high conductivity and low permeability.

There are several types of shielding offered today with new applications being investigated. Double sided shielding is the application of the conductive coating over the entire plastic part, providing double protection to the internal electronic hardware. Double sided shielding has the advantages of effective coatings of uniform thickness and of a relatively lower cost through bulk processing

The application of electroless copper with an electroless nickel skin onto the plastic substrate has proven itself as cost effective and an effective shielding deposit. The copper deposit provides the bulk of the effective shielding, as the top layer of electroless nickel provides a corrosion resistant and wear resistant skin to protect the copper.

Testing has proven that a given thickness of electroless copper can provide 25 to 50 dB greater attenuation than that of electroless nickel. The electroless copper provides a soft, conductive, ductile and less expensive coating than electroless nickel. The drawback of the single coating of electroless copper for EMI shielding is the oxidation of the copper surface and the potential damage to the soft copper deposit. The application of a thin top layer of electroless nickel over the copper provides a protective layer which is also a suitable paint base. A typical shielding thickness is is 1.5 to 2 microns of electroless copper with 0.25 to 0.5 microns of electroless nickel.

Table 4

Attentuation	**Shielding Effectiveness**
0 to 10 dB	very little
10 to 30 dB	minimal
30 to 60 dB	average
60 to 90	above average
90 to 120 dB	maximum
120+	state-of-the-art

Selective shielding is the application of a conductive coating to a specific portion of the plastic (usually on the inside of the part). This may be accomplished by the use of a conductive primer or by a conductive paint. The primer acts as a base for subsequent electroless plating whereas the paint acts as a stand-alone shielding finish. The primer or paint can be made conductive by the addition of nickel, copper, or silver. The cost of the material and the effectiveness of shielding are influenced by the choice of metal. The more conductive the metal, the more efficient the shielding. A disadvantage of the primer/paint spray application is the heavier thickness necessary to achieve coverage on limited batch processing and the associated difficulties of hitting all areas of complex parts. (See Table 5.)

Table 5

A Comparison of Shielding Finishes					
	Double sided	Zinc arc-sprayed	copper based	nickel based	silver based
decibels	60-120	60-120	30-70	20-60	
Relative cost	1.0	2.75	2.2	2.75	9.7
Thickness μm	2.5-5	25-50	25-50	25-50	25-50

Producing the Double Sided Shield

The application of a double-sided conductive surface to a plastic substrate requires the similar chemical sequence as with the decorative plating of plastic. The plastic alloy determines the specific conditions of each step.

1. Condition
2. Etch
3. Neutralize
4. Activate
5. Accelerate
6. Electroless plate.

To achieve effective EMI shielding, the sequence is as follows:

6a. Electroless copper
7. Activate
8. Electroless nickel

Electroless Copper

Electroless copper provides a conductive, uniform deposit over the catalyzed plastic surface. The thickness of the copper deposit is determined by the shielding requirement, with higher thickness' yielding greater shielding effectiveness.

The electroless copper solution is a low temperature (37.8 to 60°C [100 to 140 °F]), alkaline solution (pH: 12-13). The solution is more complex in formulation than many of the other solutions on the plating line. The consumption of chemistry is a normal part of the operation, resulting from the autocatalytic reaction of copper deposition, drag out of solution, bail out of solution and chemical side reactions. The solution is made up of copper salts, chelating agents, pH adjuster, reducing agents and chemical modifiers. All of these components must be controlled and maintained for successful operation.

Maintaining the solution chemistry, dwell time, temperature, and specific gravity, control the electroless copper deposition.

Activation

Electroless copper does not initiate electroless nickel deposition and an activation solution is required. The activator contains palladium metal in a different form than in the previous activation solution. The palladium is deposited by a displacement reaction onto the copper surface. As a palladium ion is deposited on to the copper surface, a copper ion comes off and goes into solution.

Maintaining the activator concentration, acid concentration, dwell time, and temperature will control the effectiveness of the solution. Working the solution will result in an increasing copper concentration, which will eventually render the solution ineffective and require a new solution make-up.

Electroless Nickel

Electroless nickel does not oxidize as readily as copper metal, therefore; a thin deposit of nickel is put over the copper to provide a more durable and long lasting finish. Electroless nickel can also brighten the finished part and provide a better surface to paint over.

Electroless nickel is similar to electroless copper in complexity, except no side reactions occur. The solution is made-up of nickel salts, chelating agents, pH adjuster, reducing agents, and chemical modifiers.

The alkaline electroless nickel solution is usually a low temperature bath (26.6to 62.8 °C [80 to 145 °F]), operated at a pH of 8.5 to 9.5. Hypophosphite is the typical selection as the reducing agent with ammonium hydroxide as the pH adjuster.

Maintaining the nickel concentration, hypophosphite concentration, pH, temperature and dwell time control the performance of the solution.

Selective Shielding

Certain applications do not permit the use of double-sided shielding to protect equipment form EMI energy waves. Two methods of selectively processing plastic parts will be examined. The first method is through the use of a conductive paint. The paint material is formulated to contain sufficient metal within the paint to provide sufficient attenuation to the part. Metals, which are commonly used, are copper, nickel, and silver.

The parts to be coated with the conductive paint are positioned or masked to expose the desired area for paint to be applied. The paint can be brushed on or applied with a spray paint gun. The spraying may be performed manually or by paint robotics. (See Table 6.)

Table 6

Conductive Paint Process
mask part
paint
dry

The attenuation of the coating is less than that of the double sided shielding (See Table 5). Providing that the level of attenuation is sufficient for the application, this method of shielding is a single step operation requiring no plating.

The second method of selective shielding is by the use of a conductive primer. The primer material, like the paint, has a conductive metal within. The difference is, the primer is not the final finish, for the primer will then have an electroless copper / electroless nickel topcoat deposited on it. (See Table 7.)

Table 7

Conductive Primer Process
Mask part
primer
dry
rack parts for bulk processing
electroless copper
activate
electroless nickel
dry

The parts for priming would follow a similar processing sequence as the painted parts. Once the primer has been applied, the parts would be positioned on plating racks. The racked parts would then see the same electroless copper / activation / electroless nickel plating tanks as previously described.

The benefit of the primed parts over the painted parts is a greater level of shielding attenuation and a lower cost of materials.

Summary

The use of engineered plastics will continue into the millennium. The desired characteristics of low weight, high strength, corrosion resistance and greater ease to form shapes provide advantages over the use of metal. The process of coating plastic for decorative and functional coatings will also grow.

The growth of the electronics and tele-communications industry has grabbed hold of the use of plastic and the need for providing EMI shielding. The most effective shields for controlling the EMI energy waves are materials with high conductivity and low permeability. The application of electroless copper with an electroless nickel skin onto the plastic substrate has proven itself as cost effective and an effective shielding deposit. The copper deposit provides the bulk of the effective shielding as the top layer of electroless nickel provides a corrosion resistant and wear resistant skin to protect the copper.

The new millennium will also bring new and improved technologies for processing the plastic. The search is out for reducing the costs of the chemical components, substituting costly activators for less costly activators. There are investigations into new environmentally friendly materials to condition and etch the plastic. There are new plastics being developed to provide new challenges to the chemical manufacturer and the plastics plater.

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