

High Quality Copper-Nickel-Chromium Plating on Plastics: A Continuous Process & its Challenges

by J.R. Arnold*

In today's global market, the ever-increasing need for high quality decorative chromium plating on plastics is an on-going challenge. Suppliers today must provide quality to satisfy a wide variety of markets and customers. This can only be accomplished with proper equipment and process control. Characteristics such as visual appearance, part performance standards, part design, material selection, processing parameters, equipment limitations and cost, all are critical to the customer's expectation and ultimate satisfaction. Can a supplier today meet these stringent requirements and still be profitable?

History

The electroplating process has been in existence for many centuries and can be dated as far back as the ancient Egyptians. Crude electrical batteries have been recovered from artifacts dating back to the Pharaohs. It is believed that the ancient society utilized this technique¹ to cover less precious metal with gold.

In contrast, the process of electroplating a non-conductor, such as plastic, is a relatively new science. Decorative plating on plastics has only been used in large scale manufacturing for the past thirty years. Prior to this large-scale use of plastics, electroplating similar part designs was done on various metal substrates. The process by which these substrates are fabricated limits the possibilities of some designs. Metal stamping and die-casting are the chief modes of fabrication. Die-casting has limitations as to part design geometry as well as surface finish. In general, die-casting can result in a porous substrate with various imperfections. Stamping on the other hand is limited to designs that will not exhibit a "die lock" condition. This condition would result in a part that is unable to be separated from its fabricating tool.

Both die-casting and metal stamping yield parts that have considerable mass. With the large-scale push to reduce weight in automobiles, in an effort to minimize fuel

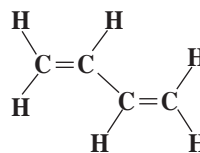
consumption, weight reduction has become a major focus. Plastics offer the opportunity to maintain styling and functionality while reducing weight.

Quality is a major focus for chromium plating suppliers. Not only have performance requirements been toughened, but visual acceptance criteria have also been tightened. Today's customers are requiring chromium plated plastic parts that not only look more pristine than those ten years ago, but last longer in service. These improvements can only be accomplished through design, fabrication and processing improvements. Technological improvements have aided in the evolution of this ancient process and will continue to bring new understanding to an old art.

Material Selection

The process of selecting a material is mainly dependent on the product's end application. Physical, mechanical and chemical properties of specific polymers need to be evaluated when deciding on polymer selection as well as a potential supply base capable of plating those polymers.

The most widely used plastic substrate for decorative electroplating throughout the world is ABS. ABS is an acronym for the amorphous terpolymer polyacrylonitrile-polybutadiene-polystyrene. The key to this polymer is the butadiene molecule, 1, 3-butadiene, which becomes polymerized and chemically bonded.

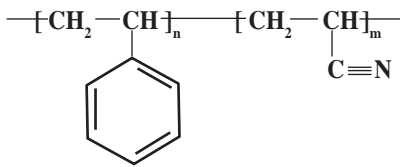


Once a butadiene molecule is polymerized, this "polybutadiene" molecule is the foundation for the plastic plating process because of its chemical and physical properties. The systematic polymerization of the three monomers produces a terpolymer, which has two phases: (1) a continuous phase of styrene-acrylonitrile (SAN)

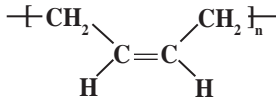
Nuts & Bolts: What This Paper Means to You

In today's global market, the ever-increasing need for high quality decorative chromium plating on plastics is an on-going challenge. There have been many improvements in this technology, in visual appearance, part performance standards, part design, material selection, processing parameters, equipment limitations and cost. This paper reviews all of these facets of plating-on-plastics today.

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and (2) a dispersed phase of polybutadiene rubber.



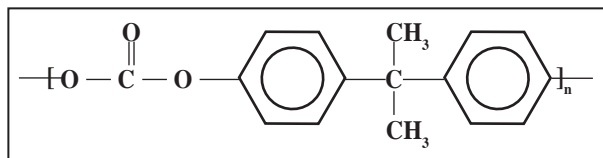
The properties of ABS are affected by the ratios of the monomers and the molecular structure of the two phases. This allows a good deal of flexibility in product design and consequently, there are several grades available in the market. Commercially available grades offer different characteristics such as medium to high impact, low to high surface gloss, high heat distortion as well as plating grade.²

Plated ABS is used for the following applications within industries such as automotive, plumbing and hardware:

- Car and truck grilles
- Body side moldings
- License plate trim
- Mirror housings and trim
- Nameplates and badges
- Interior trim (such as gear shift knobs and shift lever bezels)
- Headlamp bezels
- Household faucets
- Shower heads
- Toilet mechanisms
- Drawer pulls

Other polymers used in decorative plating on plastics are ABS+PC (ABS + polycarbonate), MRN (mineral-reinforced nylon), PPO (polyphenylene oxide), PS (polysulfone) and PC (polycarbonate).

ABS+PC is an alloy of the terpolymer ABS and another polymer, polycarbonate. The amorphous polycarbonate material is blended and not chemically bonded to the ABS.



ABS+PC is typically utilized in high heat applications where ABS is unable to function without deformation. A good example application for ABS+PC would be for chromium plated wheel covers. Other applications for ABS+PC include large trim parts, as well as door handles that are exposed to severe vibration, impact and strain. This substrate is more resistant to cracking under stress and strain than ABS.

MRN, mineral-reinforced nylon, is a crystalline polymer used in high strain applications such as door handles. This material is superior to ABS as well as ABS+PC. However, it tends to generate surface appearance issues that may be less than desirable to the customer. Typical imperfections would be classified as very fine surface “grain” or “star dusting”. This material is very seldom used for the previously stated reason.

PPO (polyphenylene oxide), PS (polysulfone) and PC (polycar-

bonate) are specialty polymers used for very specific applications.

In summary, ABS is by far the highest volume plated plastic in the world today, owing to its physical as well as its chemical properties.

Part Design

The customer more often than not dictates part design. However, in today’s dynamic manufacturing environment, the supplier is becoming more and more responsible for much of the part design. This is especially the case with the automotive supply base. For example, the customer may supply a “surface scan” of the part to its supply base and request that the design details be developed by those suppliers once the job has been awarded. Here, we discuss some basic design techniques employed to improve quality of the finished part while being transparent to the customer.

Material selection can influence the part design as well as the construction of the injection-molding tool. For example, if a relatively large part, 500 to 800 mm (~20 to 32 in.), is to be injection molded for electroplating, the cross sectional thickness may depend on the plastic material used. Some plastics do not flow through the mold cavity as easily as others. It would then be necessary to increase the cross sectional thickness for those types of materials. Other considerations taken into account when dealing with these types of materials is the number and location of the “gates.” Gates are fill points at which the molten plastic enters the mold cavity.

Listed below are a few of the design items to be considered when trying to achieve a high quality part for decorative electroplating. These items as well as others are published in various references³ relating to part design:

- Consistent wall stock thickness
- Nominal wall stock thickness
- Rib and boss design
- Radii and sharp edges
- Parting line location
- Surface texture and crown
- Part rigidity
- Racking location
- Depth of throw aspect ratio
- Auxiliary anodes on plating racks
- Selective plating
- Top coat painting
- Assembly

When discussing consistent wall stock thickness, the real intent is to ensure the cross sectional area of the part remains even throughout its length and width. The main reason for this is to ensure a constant melt flow velocity during the injection process. If a particular part design has “thick-to-thin” and “thin-to-thick” transitions, the melt flow velocity will go from slow to fast and fast to slow. These abrupt changes in flow velocity will create surface stress as well as visual defects on the part face after chromium plating. In severe cases, this variation can cause a product to lose vital mechanical bonding properties that could possibly result in a field failure. Therefore, it is of utmost importance to design a part with consistent wall thickness, as in Fig. 1.

Nominal wall stock thickness is a function of the design intent as well as the performance criteria. For thermoplastics such as ABS and ABS+PC, it is important not to have too large a cross sectional thickness. When a designer is looking at a part application, the goal is to ensure structural stability to endure severe conditions. However, this can have the opposite effect when dealing with a chromium plated part design. The coefficient of linear thermal

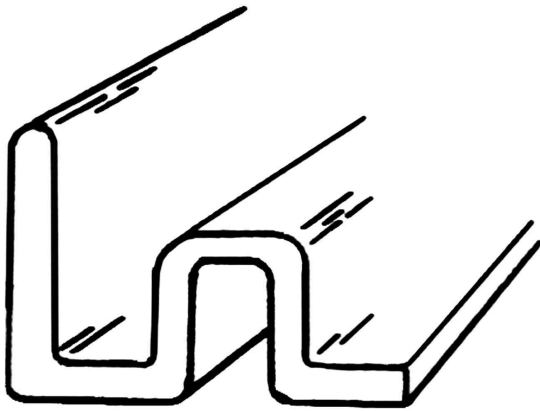


Fig. 1—Nominal thickness should be maintained throughout the part.³

expansion (CLTE) of many of the polymers plated today are in the neighborhood of ten times that of the electrodeposited metal. This means that, as the plated part is exposed to hot and cold temperature fluctuations, the underlying plastic substrate will expand and contract on an order of tenfold when compared to the metal coatings. If the wall stock thickness is too high, cracking will occur in the plated deposit. From a crack, the plated layers could begin to separate and potentially scratch or injure the end customer. Typical designs that might employ a thick wall stock could be door handles, body side moldings and gearshift knobs. The way to remedy this is to remove as much mass as possible from the thick areas and replace them with an alternate design. Such alternatives are ribs and gussets that would give structural stability while reducing wall thickness and part weight.

Ribs and bosses are typical part features that are used to add functionality as well as a means of attachment. The most important aspect of design is to minimize wall thickness of the rib or boss in relation to the intersecting wall. In other words, the rib and boss walls should be sized to approach but not exceed 50 to 60% of the supported wall thickness³ (Fig. 2). This is done to minimize the surface defect seen on the opposite side of the rib or boss commonly referred to as a “sink.”

Radii and sharp edges are another important design consideration. Due to the nature of the electroplating process as well as mold material flow, the incorporation of radii into corners and around support features can greatly minimize surface defects. Radii can also strengthen a part as well as improve the plate-to-plastic adhesion. Sharp edges will tend to develop a greater metal thickness during the electroplating process. Sharp edges and points should be avoided whenever possible. The result of these sharp edges is a defect called “treeing” (Fig. 3).

The “parting line” is the area where the two halves of the steel injection mold come together. At this point on the finish injection molded part, there is a line of demarcation referred to as a parting line. Parting lines can be rough and have a tendency to protrude from the part surface. These parting lines are sharp edges and will tend to build up excess plating. This can cause problems such as interference in subsequent assembly operations or the potential for cutting an operator handling the part after plating. When designing a part, it is best to locate the parting line in an area that is less visible to the end customer whenever possible.

When we discuss the visual quality of a chromium plated plastic part, judging a part to be of high quality versus lesser quality is in the eye of the beholder. Therefore, it is important to design around this interpretation problem whenever possible. A very simple rule to remember is to minimize flat reflective areas and add three-dimensional details to the part surface. Any surface morphology that can scatter an image will draw attention away from minor sur-

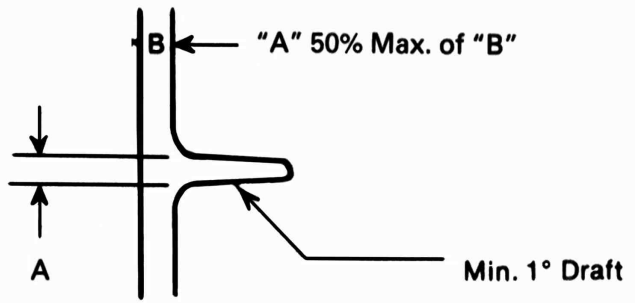


Fig. 2—Rib design criteria.

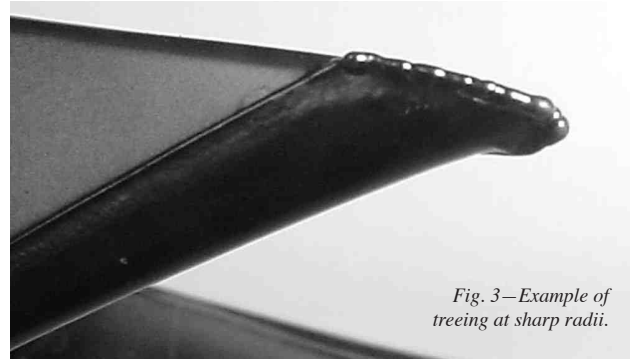


Fig. 3—Example of treeing at sharp radii.

face imperfections.³ In other words, surface imperfections as small as 0.1 to 0.2 mm (~4 to 8 mils) can be easily seen on a flat reflective surface after chromium plating but are much more difficult to detect on a contoured surface (Fig. 4).

Part rigidity is a very important factor when designing a plastic part for chromium plating. When the plastic part first enters the plating process, forces such as temperature, hydraulic pressure and metallic stresses will tend to deform it. Once a part is deformed, it will retain this deformed shape as it is laminated with several separate metal layers. Therefore, it is very important to design rigidity into an injection-molded part for successful chromium plating.

Racking location, *i.e.*, affixing the part to the plating rack, is another very important factor in obtaining high quality plating. Two aspects of racking to consider are contact stain and part deformation. Whenever a rack contact is affixed to an injection molding part and used to carry current to the part during electroplating, a discoloration will develop in a localized area around the contact point. Along with this discoloration will be obvious scratching and indentations. Therefore, it is important to locate these racking areas where they cannot be seen. Another consideration is the tendency of a particular rack fixture to warp the part. As the part is exposed to hydraulic pressures generated in the plating liquids as well as the effects of elevated temperatures, it will expand and twist under the slightest pressure. An improperly designed plating rack can result in failure of a well-designed part.

When considering the surface area to be electroplated and the subsequent design related issues, one must also take into consid-

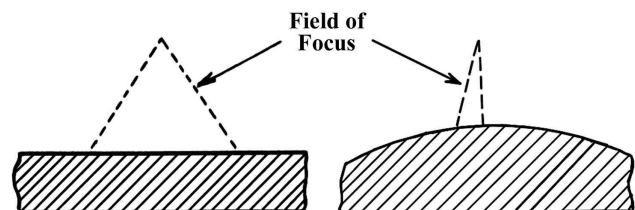


Fig. 4—Recommended crown.

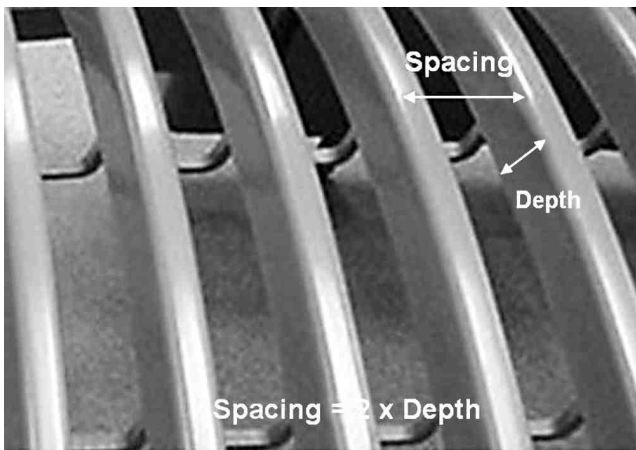


Fig. 5—Spacing criteria.

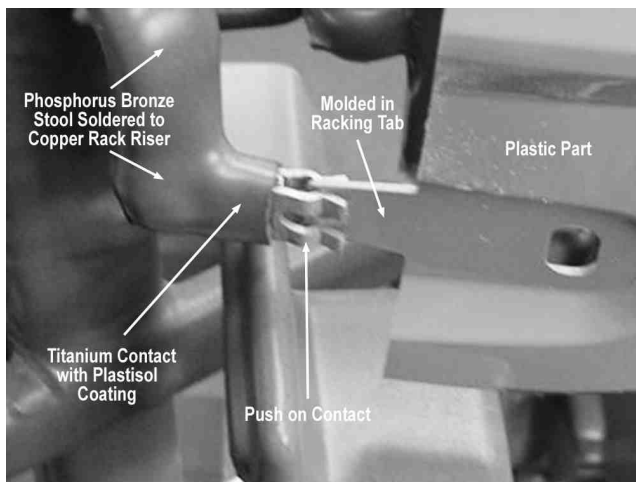


Fig. 6—Plating rack and tip design features.

eration the three-dimensional aspects of the part as it relates to “depth of throw.” The depth of throw is the length or depth that the plated layers must penetrate into the geometry of the part in relation to the part face (assuming it is oriented parallel with the anode surface). In other words, if the part to be plated is a bowl that is 2 in. (5.1 cm) deep, it can be said that the depth of throw is 2 in. When designing a part for electroplating it is important to remember that two parallel side walls that require plating should have minimum spacing between them to allow for maximum depth of throw. A general rule of thumb is to have the parallel walls spaced based on a 2-to-1 aspect ratio for spacing to depth of throw (Fig. 5). This is only a guideline and in this case, more is always better.

In the case of very deep throw or other part design related issues, the need to selectively plate an area frequently arises. This is accomplished by a few different means, the most common of which is resist painting. Resist painting involves painting those areas of the part where no metal is to be deposited. When selective plating is required, it is always best to design around the application to improve the quality. This is accomplished by the addition of a small groove or step around the area to be painted. This will in turn allow the painting mask to seat on the part without allowing overspray. This is also a good technique when applying topcoat paint after the plating process. It is always best to allow the topcoat paint to overlap the resist paint by approximately 3 mm (0.12 in.) in order to assure a “seal” from any corrosive environment.

Another means of achieving deep throw would be to use auxiliary anodes on the plating rack. This brings the anode field much closer to the specific area of concern and can improve the deposit

distribution. Auxiliary anodes are used extensively as alternatives to resist paint in an effort to increase part density on the plating rack. With the use of these auxiliary anodes, parts can be effectively racked closer to each other thus increasing the number of parts per rack.

Post-plating assembly is another important consideration in the design of an injection-molded part. As discussed earlier, there are many factors which influence the part and its ultimate shape after plating. Along these same lines, it must be remembered that the part will “grow” in size because of the additional plating thickness. This typically is 40 μm (1.6 mils) but thicknesses can range from 20 to 100 μm (0.8 to 4.0 mils) based on size and geometry. Therefore, assembly can be influenced by excessive plate build-up resulting in slower throughput as well as reduced yields.

Injection Molding

The injection molding process has many variables, which cannot be discussed in their entirety. Therefore, we will focus on the following topics since they most influence the quality of the chromium plated injection molding:

- Mold temperature
- Melt temperature
- Injection speed

Mold temperature is important because it directly influences the adhesion of the plating to the plastic substrate.⁴ The plastic material supplier will establish processing parameters for each of the specific materials. These parameters are generally expressed in terms of ranges. For example, the mold temperature range for a prominent supplier of ABS is 49 to 82°C (120 to 180°F). In most cases it is best to run towards the higher value.

Melt temperature is important because it also directly influences the adhesion of the plating to the plastic substrate.⁴ Running towards the high end of the recommended temperature range will improve the boundary layer in the part as well as minimize surface stress.

Injection speed has the most pronounced effect on the visual appearance of a chromium-plated part.⁴ Fast injection speeds will tend to develop irregular surface patterns that are visible after chromium plating. These types of patterns are generally called “gate blush” and “jetting.” Other defects that can arise from excessive injection speeds are “splay” and “burning.” All four of these types of defects greatly affect the part quality and will have an impact on yield. The best way to minimize these defects is to reduce the injection speed as much as possible while still being able to achieve a completely filled part.

In summary, the injection molding parameters that are ideal for chromium plating will tend to slow down the molding cycle as well as reduce the pieces per hour produced. When injection molding for chromium plating, one must take into account the reduction in normal process output and factor that cost into the price of supplying parts for plating purposes.

Part Handling & Packaging

Part handling and packaging is key to a high quality chromium plated part. Once the time and money has been spent in the injection molding of the part, it is important to be able to transfer and store the raw part without damaging it. When the part exits the mold, it has not completely cooled. The part surface is still quite warm and very susceptible to scratching or scuffing. The injection-molding operator must wear clean cotton gloves when handling the newly formed parts to ensure that no damage occurs. It is also recommended that employees remove all jewelry that could scratch the parts.



Fig. 7—Plastisol dipping of plating rack⁵.

Packaging design should take three factors into account:

- Part support and presentation
- Environmental protection
- Ease of operator access

When developing a user friendly protective package for plastic injection molded parts it is important to orient them in a way that protects the visible surfaces. It is never advisable to lay a part on its visible surface as it would be vulnerable to scratching. Typically the best way to package a part is to place it in a securely in a form fitted stationary location with the visible surface facing upwards.

The packaging should also provide a degree of protection from the environment. Plastic injection molded parts typically have a high static charge. This charge will tend to pick up dirt and debris from the surrounding environment. Techniques such as plastic enclosures and plastic bags have been used successfully to reduce surface scratching. In any case, a protective environment will lead to higher quality.

When considering the previous two items, it equally important to consider the ease at which an operator is able to place and remove the parts. If an operator has difficulty placing or removing a part from a package, it is likely to be damaged and result in lower quality.

In short, all three aspects of packaging must be considered to ensure quality to the customer. There are two types of packaging that require this consideration and they are work in process (WIP) and finished goods (FG). In some many cases WIP and FG packaging is one and the same. In other cases there are two separate types of packaging. When dealing with automotive customers, suppliers are often required to ship finished goods in returnable packaging. Often these returnable packs are not conducive to use as WIP packaging and alternatives must be used.

Proper Plating Rack Design & Construction

The plating rack or fixture is one of the most important tools in the plating process.⁵ An improperly designed or under-designed plating rack can only lead to poor quality and failure. When working with plastic parts, as opposed to metal, it is very important not to place undue stress on the plastic part. This challenge along with proper construction and the need to secure the part through the plating solutions to withstand the hydrodynamic forces, must all be considered in the design.

Unlike metal parts, the plastic part is very light and susceptible to externally applied forces. Sufficient contact points must



Fig. 8—Curing of plastisol in oven.⁵

be employed to allow for even metal distribution. However, too many contact points can lead to part warpage. When the plastic part enters the plating process it is exposed to high temperature solutions causing the part to expand. If the plating rack does not allow the part to freely expand, a bowing will be noted between two contacts to compensate for expansion. This bow can cause fit and function problems and poor quality later on.

A common cause of poor quality can be directly related to contact “burn-off.” The most common cause for burn-off is poor contact design and connections. If the contact is not properly attached to the plastic part to allow for good current flow, it will generate heat and eventually burn through the thin metal deposits. Frequent adjustments of the rack contacts are necessary to ensure good connections. Once burn-off has occurred, however, the contact will act as a “robber” and draw metal away from the localized area since the plastic substrate is non-conductive. Other variables such as proper electroless metal thickness, contact spacing and solution chemistry can also affect the degree of burn-off experienced.

Plating rack construction begins with a good understanding of current flow and amperage requirements. When designing a plating rack for plating plastics, the first factor to consider is the amount of plating area per part. Other factors such as rectifier size, tank depth, distance, direction of travel and part geometry all play equally important roles in the design and construction of plating racks for plastic parts. Once all of the factors have been taken into consideration as well as a few others, rack construction can begin. The basic steps of rack construction are:

- Contact or tip design and fabrication
- Hook or carrier design and fabrication
- Copper framework sizing and fabrication
- Metal preparation and assembly
- Rack coating
- Trimming and cleaning
- Adjustments

For plastic plating, rack contacts can be constructed from a good grade of stainless steel or preferably titanium (Fig. 6). If titanium is used, one must take into account that the current carrying capacity of titanium is much less than that of stainless steel. Therefore, it will most likely require additional contacts constructed of titanium to carry the current as compared to stainless steel. With that being said, most plastic plating lines use hydrochloric acid for their neutralization and activation processes. Hydrochloric acid will attack stainless steel over time and potentially cause premature rack failure. There are several different contact designs to work from and

they are dependent on the particular part and its available contact points. The rack supplier has the expertise to assist with these design considerations.

The plating rack hook or carrier attaches the copper rack to the flight bar or carrier. Their designs are usually specific to each individual machine and are usually fabricated from a cast bronze or solid copper bar. The most important feature of the hooks are a smooth flat surface to maximize contact between the flight bar, carrier and plating rack. Poor contact will result in heat build-up and low metal thickness.

The copper framework is sized according to the part surface area to be placed on the plating rack. That area is limited by part geometry, rectifier size, tank size and the number of contact points. Sufficient copper should be used to carry the current required in the highest amperage plating bath. This is almost always the chromium-plating bath. Since each plating line differs with respect to these variables, it is important for every manufacturer to develop a rack standard for distribution to their suppliers. If insufficient current carrying capacity is designed into a plating rack, excess heat will build up and the plastisol coating will swell and become brittle over time. This will greatly reduce the useful life of the plating rack and result in premature poor quality.

Once the rack has been properly sized and is ready for assembly to the contacts, care must be taken to ensure good electrical connections throughout the lattice. This is done by sand blasting the copper rails and soldering all joints that will be carrying electrical current. The contacts must also be soldered to the phosphorus bronze stools or copper rails. For proper soldering of stainless steel and titanium, they must first be copper plated. Only after all joints have been soldered and the rack assembled, can it be sent to the coating operation.

The coating operation consists of two primary steps, primer and plastisol coating. The primer ensures good adhesion of the plastisol coating to the metal and the plastisol coating protects the metal from the harsh chemical solutions. Prior to the primer coat, the assembled rack is lightly sandblasted for better adhesion as well as removal of dirt and debris. The primer coating can be sprayed or dipped. After application, the primer must be cured at an elevated temperature for a period of time. Once the primer is cured, the contacts are protected and the rack is heated and dipped into the plastisol tank (Fig. 7). The rack is again heated and cured to allow for cross-linking of the plastisol coating (Fig. 8). Improperly cured plastisol will not withstand the chemical attack in the plating line and will result in overall poor coating characteristics. Poor coatings can shorten the rack life as well as cause plating defects.

Once the plating rack has been coated and the plastisol has been properly cured, the contacts must be re-exposed in order to carry current to the plastic part during the plating process. This is typically done with small metal brush wheels and other cutting utensils. It is important not to expose any of the copper or phosphorus bronze underneath the rack coating since chemical attack will very rapidly dissolve both of these materials.

When the rack has been prepared, one final step remains, the gauging or adjusting of each contact for optimal fit. This is best accomplished by utilizing a raw plastic part for which the rack was designed. Rack gages and templates are often fabricated and delivered with the new plating racks for future adjustments.

Plating Process

Preplating sequence

The preplate is a series of chemical process steps to deposit a thin coating of metal over the plastic surface. The purpose of this layer is to make the plastic part conductive so that it may be electroplated in subsequent plating process steps. The preplate steps are:

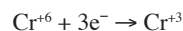
- Etching
- Neutralization
- Catalysis or activation
- Acceleration
- Electroless metal deposition

Etching. The etch is a solution of chromic acid and sulfuric acid operated at elevated temperature. Typical concentrations range from 300 to 500 g/L (40 to 67 oz/gal) of chromic acid and 300 to 500 g/L (40 to 67 oz/gal) of sulfuric acid plus small amounts of wetting agents to allow the viscous solution to enter small grooves and depressions on the parts. The operating temperature ranges from 65 to 75°C (149 to 167°F). This range is broad and normally more tightly defined, depending on the specific plating line and its cycle time. The purpose of the etch is to create a roughened surface on the plastic part to promote good mechanical bonding. The etch roughens the surface and also modifies the chemical structure of the polymer, making it receptive to the catalyst treatment encountered later.

The etch transforms the plastic from a smooth hydrophobic surface to a porous hydrophilic surface. The chemical reaction is a redox (reduction/oxidation) reaction between butadiene and hexavalent chromium. The hexavalent chromium attacks the double-bonded carbon atoms in the butadiene molecule and splits them into much smaller units, causing a cavity or void in the styrene-acrylonitrile (SAN) resin matrix. These cavities or voids are the major means by which subsequent metal deposits will adhere to the plastic surface. The by-products produced from the reaction are carbon dioxide, pigments used to color the resin and trivalent chromium. The build-up of pigment residues such as titanium and silicon dioxide must be filtered from the solution to avoid star dusting and surface roughness. Trivalent chromium, Cr⁺³, has a major impact on the ability of the etchant to oxidize the butadiene. As Cr⁺³ builds up, the speed and efficiency at which the polybutadiene is oxidized is reduced exponentially. The concentration of Cr⁺³ should be held between 20 and 60 g/L (2.7 and 8.0 oz/gal) depending on the resin to be etched. The temperatures and acid concentrations of the bath can be increased to compensate for the buildup of this contaminant. If the trivalent chromium is not removed or controlled within the etchant, poor quality and potential field failures are inevitable. The proper etching of the plastic surface requires tight analytical and physical controls. Chemical concentrations and temperatures must be monitored continuously. Good process filtration and subsequent rinsing are essential for high quality plating.

Neutralization. The neutralization step follows a series of water rinses just after the etching process. The removal of excess etchant solution is mandatory. Hexavalent chromium in particular is a contaminant and is detrimental to the subsequent plating steps. Although several rinses are employed after the etch step, some hexavalent chromium still clings to the etched plastic surface and is trapped in screw bosses and splits in the plastisol coating of the plating racks. It must be completely removed, or neutralized.

The neutralizer consists of a reducing agent and a mineral acid. The reducing agent supplies a ready source of electrons for reduction. The reaction is:



The neutralizer is typically operated at temperatures above ambient to allow better penetration and quicker reaction times. Since this process step produces byproducts and potential contaminants, filtration through a ten-micron particle filter is recommended. A good solution turnover rate would be two times per hour.

Catalysis or activation. The catalyst or activator solution usually contains a colloidal suspension of palladium metal and

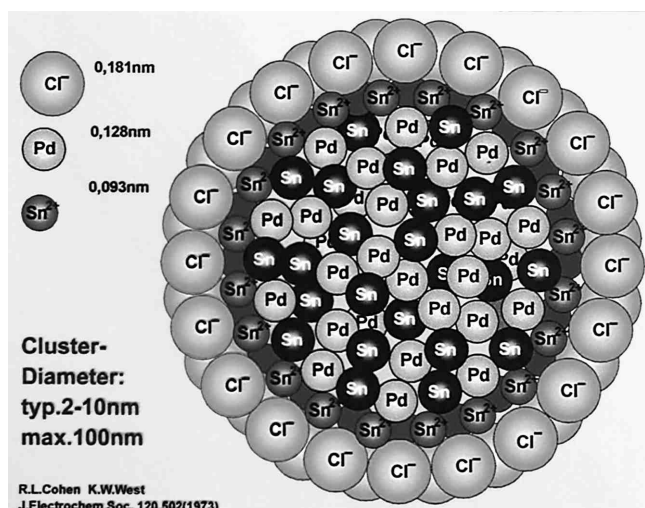


Fig. 9—Structure of tin-palladium cluster.

tin ions.⁶ The function of this bath is to deposit the colloidal palladium, in the form of a tin-palladium cluster (Fig. 9), into the surface porosity of the part to be plated, causing the subsequent catalyzed reduction of copper or nickel (or electroless plating) to form a continuous conductive layer. This deposition is aided by the dissimilar charges of the plastic and catalyst. The plastic becomes positively charged during the oxidation of the surface molecules. The activator solution consists of hydrochloric acid, palladium, stannous chloride and sodium chloride. The palladium metal is very similar in function to the platinum that would be found in the catalytic converter of an automobile. Palladium, like platinum, causes a chemical reaction to occur with no additional input of energy. The activator must be present on every area to be plated. If for any reason the catalyst is not present on the surface of the part, a plating void, referred to as “skip plate,” will result. Skip plate can result from poor catalyst absorption or catalyst removal from the surface. As mentioned earlier, hexavalent chromium is detrimental to the process and considered a poison. Therefore, if any hexavalent chromium comes into contact with the catalyzed surface, the palladium becomes oxidized and skip plate will result. The major source of hexavalent chromium is through bleeding from the plastisol coating on the plating racks. This is another reason why proper rack construction is so important. The catalyst is a very expensive chemical bath and requires continuous filtration to ensure sufficient quality. It is recommended that a ten-micron filter be used to properly clean the bath. A solution turnover rate of one or two per hour is sufficient.

Acceleration. The accelerator is typically composed of an organic acid such as formic, oxalic or citric in a mineral acid solution. The function of this bath is to remove tin ions from the palladium metal that was deposited in the activator to promote a faster initiation of the following electroless plating step. Since this bath is typically operated at temperatures above ambient, small amounts of reducing agents, such as those found in the neutralizer, are often added to keep any hexavalent chromium contamination from poisoning the palladium and causing skip plate. The mineral acids used are typically sulfuric and hydrochloric with the latter being most common. This process step is also vulnerable to contaminant build up. It is recommended that this bath be filtered at a turnover rate of one to two per hour using a five to ten micron filter. Once this step is complete, the plastic substrate is ready for the catalytic deposition of metal from the electroless bath.

Electroless metal deposition. The next process step in the pre-plate cycle is electroless deposition. The palladium catalyst on the plastic surface initiates the electroless deposition reaction of either

copper or nickel. These two metals are the most common for decorative plating on plastics. The overall reaction taking place⁷ within the electroless copper bath is:



And for electroless nickel, the reaction is:



The metal ions receive electrons from the reducing agents changing the ions to metal atoms. The palladium metal islands catalyze this reaction. Once reduced to the metallic state, the deposited metal itself acts as a catalyst and functions like the palladium. As previously noted, the palladium catalyst is discontinuous on the substrate and appears as a network of microscopic islands. As the reduction of copper begins at the islands, they grow and spread. As the islands become larger, they merge with other islands. As the reaction proceeds and merging continues, thickness begins to build and a continuous conductive metal layer is established on a once non-conductive plastic. The rate of deposition and thickness of deposit are governed by temperature, time and concentration. Since this process is “auto-catalytic,” *i.e.*, the depositing metal is self-catalyzing, it requires continuous filtration to remove accumulated contaminants.

Electroplating sequence

Now that the formerly non-conductive substrate has an adherent, conductive layer on its surface, the parts are ready for final electroplating. The electroplating sequence is a series of steps that will deposit several separate layers of metal onto the conductive part, depending on the application. A typical process flow is:

- Copper strike
- Bright acid copper
- Semi-bright nickel (Optional for exterior applications)
- High sulfur/high activity nickel (Optional for exterior applications)
- Bright nickel
- Microporous nickel (Optional for exterior applications)
- Chromium (Typically hexavalent solutions for exterior applications)

The two typical specifications often required for decorative chromium plating on plastics are for interior and exterior applications. The number and thickness of specific metal layers distinguish them.

All electrolytic plating baths generate and collect contaminants that must be filtered to achieve high quality plating. Those contaminants are best removed using continuous filtration. Turn over rates for the electroplating baths should be four to six turnovers per hour for best results. In the past, manufacturers could rely on turnover rates as low as once per hour to maintain quality. However, today's markets are becoming more and more stringent when it comes to surface imperfections. Therefore, it is very important to always keep the solutions as clean as possible.

Copper strike. The copper strike is the first in a series of electroplating baths used in decorative plating on plastics. The copper strike has a relatively high concentration of sulfuric acid in water with copper sulfate, chloride ion and organic brighteners. The purpose of this bath is to deposit copper using only small amounts of current and voltage. Because the electroless deposit is very thin, its ability to carry current is limited. If too much current or voltage is applied, the electroless deposit will “burn off” in similar fashion

to a blown fuse when too much current passes through it. The end result is the loss of electrical continuity and the ability to electroplate. Thus, the purpose of the strike is to build metal thickness slowly for subsequent metal deposition in the following processes that require greater current and voltage.

Bright acid copper. Bright acid copper has two main functions in the plating on plastic line, ductility/elasticity and leveling. The leveling aspect of the bath is less important than the other. The most significant function of the bright acid copper deposit, as it relates to plating on plastics, is its ability to expand and contract without cracking. When plastic is exposed to hot and cold temperatures, it expands and contracts. The severity depends on the temperatures to which the plastic is exposed and the coefficient of linear thermal expansion (CLTE) of the plastic. Typical values expressed in in./in./°F are listed below for various materials:⁸

| | |
|---------------|-------------------------------|
| ABS | 3.6 to 4.5 × 10 ⁻⁵ |
| ABS + PC | 4.0 to 6.2 × 10 ⁻⁵ |
| Nylon | 2.5 to 3.0 × 10 ⁻⁵ |
| Polysulfone | 2.0 to 2.5 × 10 ⁻⁵ |
| Polypropylene | 6.0 to 9.0 × 10 ⁻⁵ |

ABS is on the lower end of the CLTE scale as compared to polypropylene, which expands and contracts many more times through the same temperature range. Since copper is a ductile metal, it can move with the plastic substrate to some extent as it is exposed to temperature fluctuations. The ability of the copper to move with the plastic depends largely on the mechanical bonding to the substrate and the thickness of the deposit prior to the subsequent nickel and chromium-plated layers. If adequate bonding to the substrate is not achieved, delamination of the copper and plastic can occur when exposed to temperature extremes. If the bonding is adequate and the thickness is low, cracking can occur under temperature extremes. The bright acid copper functions as a buffer between the plastic substrate and the brittle nickel-chromium deposits. A general rule of thumb is, the thicker the plastic cross section, the more copper thickness necessary to overcome the thermal expansion and contraction without delamination or cracking.

Semi-bright nickel. Semi-bright nickel is the first nickel deposited in a multi-layer nickel system designed for exterior and/or severe exposure applications. The name "semi-bright" is descriptive of the deposit appearance. The deposit resembles a matte finished stainless steel with little or no reflectivity. It plays two major roles in the plating of exterior plastics. The first function of the deposit is similar to that of the bright acid copper in that its ductility is superior to subsequent nickel and chromium deposits. Since exterior and severe applications are exposed to large temperature fluctuations, the use of a ductile semi-bright nickel layer adds one more zone of protection. The second function of this deposit is to establish a barrier between the copper layers and the corrosive environment. As corrosion takes place and penetrates the chromium and bright nickel layers, the semi-bright nickel protects the copper deposits and prevents blistering of the plating. The nature of the deposit, as determined by the bath chemistry, gives the semi-bright nickel a natural resistance to corrosion. The nickel deposited in this step has very little sulfur compared to the other subsequent nickel layers. This lack of sulfur renders the deposit noble or resistant to attack.

High sulfur/high activity nickel. High sulfur nickel is highly sacrificial because of the levels of sulfur present. Originally used in plating metal substrates to give added protection to the basis metal, its purpose is to extend or improve the corrosion resistance of a nickel-chromium plated part. Over the past few years, however, the high sulfur nickel has allowed the decorative plating on plastics industry to extend the corrosion resistance of a typical part by as

much as two times. This process step is relatively inexpensive and can be incorporated into existing systems with minimal cost.

Bright nickel. Bright nickel is the only nickel layer used for interior or less severe applications. As its name implies, this is a bright reflective deposit, which ultimately determines the luster of the finished chromium plate. It can be applied directly over the copper layer or it can be incorporated into a multilayer nickel deposit. For interior applications, this single layer of bright nickel followed by chromium plating gives a durable surface finish that will withstand years of normal wear and tear. For exterior applications, another nickel layer follows the bright nickel layer, which is porous and more noble than the bright nickel. After that subsequent layer, chromium is plated. A typical rule of thumb applies: "If the bright nickel layer is not bright, then the finished chromium plated part will not be bright".

Microporous nickel. Microporous nickel is used to develop porosity in the final chromium layer of 10,000 to 20,000 pores/cm² (65,000 to 130,000 pores/in.²). This technology was developed to hide the corrosion from view as the chromium plated part aged. It is used for exterior or severe exposure applications. The chemistry of this solution is very similar to that of bright nickel. However, the concentrations of the organic additives are typically less than those in the bright nickel bath. The purpose of the lower organic additive content is to achieve a more noble metal deposit compared to the bright nickel. Another additive used in this bath consists of finely dispersed powders, which are comprised of materials such as talc, silicon dioxide or aluminum oxide. The purpose of these insoluble particles is to develop pores in the nickel layer during plating. As the particles come in contact with the part surface, they adhere and nickel plating takes place around them. This, in turn, develops a pore through the porous nickel layer to the surface of the bright nickel. These particulates are typically in the 0.5 to 1.0-micron size range, generating similar pore sizes. It is desirable not to electroplate thick deposits of porous nickel because the pores would plate over, resulting in no direct channels to the bright nickel layer. However, a thickness sufficient to bridge the corrosion that takes place under the microporous layer is necessary so that a collapse will not occur. It is very important to maintain a clean porous nickel bath in order to achieve a nobler layer than the bright nickel. Because the bath contains particulates, continuous filtration cannot be used. Therefore, frequent bath purification must be done as prescribed by the proprietary chemical supplier.

Microporous nickel is the most significant of all the nickel layers in maximizing corrosion resistance. It can also have the most profound visual effects depending upon its efficient operation.

Chromium. The chromium deposit serves two major functions, abrasion and corrosion resistance. In decorative plating the deposit thickness is much lower than in functional or hard chromium plating. Typical thicknesses range from 0.1 to 0.5 μm (3.9 to 19.7 μ-in.). This thickness is adequate to protect the underlying nickel and copper layers without adding undue stress, which would be produced with much thicker deposits. When corrosion begins, it begins at an exposed nickel site. In the process described above, corrosion begins at the site of a pore. Corrosion, as with most natural processes, will seek the path of least resistance. In the case of microporous chromium, the intent is to let corrosion begin at the pore sites and take the path of least resistance through the porous nickel and down to the bright nickel layer. It is very important to understand that this will only occur if the porous nickel layer is nobler, *i.e.*, less sacrificial, than the bright nickel layer. Ideally, the corrosion would take place under the porous nickel layer, in the bright and high sulfur deposits, keeping it out of view of the observer.

There are hundreds of variables within the plating process.

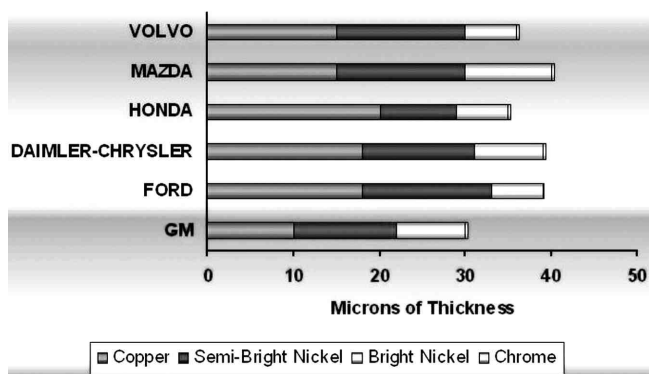


Fig. 10—Variation in customer thickness requirements.

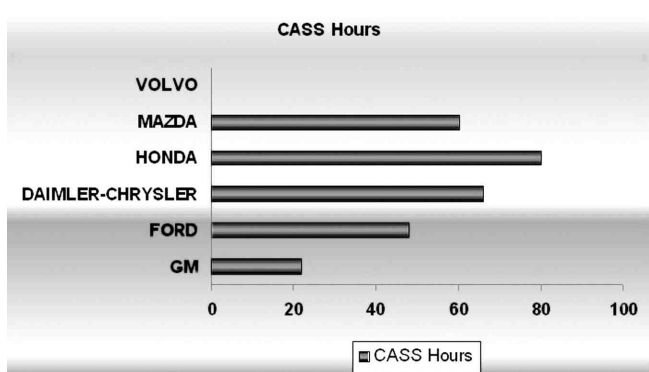


Fig. 11—Variation in customer corrosion performance requirements.

Many of these variables have interactions with one another. With that being said, it is obvious that process control is a major factor when plating a quality part. Analytical process control, achieved by sophisticated chemical and physical analysis, frequent processing checks, continuous replenishment of additives, high filtration rates for all processing and rinse tanks, good housekeeping and trained personnel are only a few of the items necessary for successful chromium plating on plastics. Equipment plays another important role but cannot be completely relied upon to compensate for those items previously listed. Systems must be established as well as checks and balances to ensure that the systems procedures are being properly followed. Documentation and good record keeping will also help with continuous improvement. The plating on plastic industry continues to evolve to meet the increasingly demanding customer expectations.

Customer Specifications

In today's plastic plating industry, the supplier is asked to furnish a quality part built to exacting specifications. Each customer will generally supply a specification relating to the chromium plating process for plastic as well as a series of performance tests to conduct for verification. The process specification generally is incorporated with the performance specification. The process specification will dictate metal thickness, types of chromium deposits, physical properties of those deposits and even chemistry suppliers. The plastic plating line today must be flexible enough to fulfill these different requirements without sacrificing costs on other products. Figure 10 compares just a few of the many different thickness specifications called out by various customers.

Most specifications require metal thicknesses to fall within prescribed values.⁹ These values will ensure the performance of the finished part during its intended use. Metal thickness determinations can be done in several ways. The use of cross sectional microscopic examination, ASTM B487, is the most accurate analysis. However, the use of a coulometric measurement, ASTM B504,

and non-destructive techniques such as ASTM B567 and B568 can be used in some instances instead of the microscopic measurement. Since the final chromium layer is very thin, it must be checked using the coulometric measurement or a spot test method, ASTM B556. The microscopic cross sectional analysis is a destructive test whereby a section of the plated part is cut perpendicular to the plated layers, polished and examined under a microscope. It is important that the cut and polish of the plating to be measured is perfectly perpendicular or the readings will be excessive.

Coulometric measurement is also destructive. It is performed on an instrument that makes the specimen the anode and strips the plating using an acidic solution with small electrical current. The thickness is related proportionally to the time and current required to strip the metal off the substrate.

The Copper Accelerated Acetic Acid Salt Spray, or CASS Test (ASTM B368) is an accelerated weathering method used to evaluate the corrosion resistance of decorative plated parts. A plated part is cleaned and placed in a test chamber operated at specified parameters. The chamber is heated and fogged with a solution of sodium chloride (salt) and copper chloride in water at a pH of 3.0. This low pH makes the solution acidic, which accelerates the corrosion process. Within a few hours of continuous fogging, samples will begin to exhibit fine pitting or crazing. Whether a test part is considered acceptable or unacceptable depends upon the size, quantity and depth of the pits. Specifications differ among customers on parameters such as exposure time, pit size and density. Once a cycle is complete, the test specimen is removed from the chamber, washed and dried for evaluation. A general rule of thumb is to expect that the smaller the pitting after a corrosion cycle, the better a part will perform in the field.

As a comparison to the thickness specifications shown in Fig. 10, Fig. 11 exhibits the differences between the CASS (Copper Accelerated Acetic Acid Salt Spray) testing requirements by various customers. Volvo does not specify CASS testing but rather employs a neutral salt spray test.

The dynamic thermal cycle test (ASEPTP-201)¹⁰ determines if a specific part will withstand extreme temperature variations without experiencing loss of adhesion between metal-to-plastic, plastic-to-plastic and metal-to-metal. The procedure typically begins with exposure to high temperature in an air-circulated oven. The temperature is typically regulated to a value of 10 F° (5.6 C°) less than the heat deflection temperature under a stress level of 1.82 MPa (264 lb/in.²) for the particular plastic substrate being evaluated, as determined by ASTM D648. Once the heat cycle has reached its term, the part is removed from the oven and left at room temperature for a period of time prior to being placed in the freezer. The freezer temperature is set at -40°C (-40°F) and maintained at that temperature throughout the test. This hot/cold sequence constitutes one thermal cycle. Once the prescribed number of cycles is run, the parts are closely evaluated for lifting, peeling and cracking of the metal layers. Proper part design and molding parameters will help insure a capable part.

The simultaneous thickness and electrochemical potential determination, or STEP test, is described in ASTM B764. This destructive test, specified for exterior or corrosive environments, is run on multilayer nickels to determine the potential of the coating system to resist corrosion. A plated specimen is treated with hydrochloric acid to remove the top chromium layer. The exposed nickel is affixed to an apparatus that holds the specimen while it is being anodically stripped. The nickel layers are removed in reverse order from their original deposition. During the anodic stripping process, a coulometric measurement is taken which reads the potential (in mV) required to electrically dissolve each nickel layer. This millivolt difference between the nickel layers is an excellent measure for correlating the corrosion resistance of the plated part in the

field. This test is an important control in the plating process. It allows an engineer to determine the success rate of the process in a relatively short period of time.

Porosity is a physical condition that is intentionally produced in the final nickel layer to aid in the corrosion resistance of the multilayer nickel process. Porosity is usually used for exterior or corrosive environments. Test method ASTM B456 is used to identify the size, quantity and distribution of the metal porosity. A good even distribution of micropores will ensure a good distribution of corrosion products, making them less visible to the human eye.

In summary, the plating supplier has to be very flexible in order to supply a variety of customers. The process specifications can be a challenge to meet while remaining cost competitive. The nature of the automotive industry is directed towards the supplier being totally responsible for the longevity of the parts supplied. In other words, if a part is out in the field and still under manufacturer's warranty, the plating company is liable for all defects in workmanship related to the production and durability of their product. This is another example of how quality continues to be the focus of plastic plating suppliers worldwide.

Visual Inspection

Visual inspection is more often than not the last line of defense that keeps suspect product from our customer's shelves. As it has often been stated, visual inspection is only 85% accurate. This means that if a plating line is having quality problems, there is the possibility that 15% of the product shipped could be suspect. In today's competitive industry, this equates to 150,000 parts per million, which is clearly unacceptable. Customers today want to see quality ratings from their supply base in the single digits. What can the plating company today implement to ensure that quality reaches its customers? The answer is not a simple one. As discussed here, many factors influence the quality of a chromium plated plastic part. Good communication with the customer and proper understanding of the customer's expectations can limit quality concerns.

Without a doubt, the most difficult detail to quantify in decorative electroplating is a visual acceptance standard. No matter what precautions or measures are taken, defects will occur and a decision must be made whether to use, rework or scrap the product. When working with a potential customer, it is imperative for the chromium plating supplier to understand the customer's expectations and for the customer to understand the plating supplier's capabilities. This can only be achieved with open lines of communication.

The most common defect found in the plating process is "dirt." Dirt will settle on the parts in various stages of the process, causing a rough or dusty appearance. Since gravity plays a large role, part orientation is very important. Critical visible surfaces should be placed in the down position, reducing the chances of dirt settling on those surfaces. When dealing with dirt, the question always arises as to how much is too much. The best way to quantify acceptance criteria is by using a grid with specific particle size and number limitations. These criteria should be agreed upon up front with the customer since it can have a large impact on scrap and overall part cost.

Other defects such as scratches, injection molding imperfections and chromium plating process faults must be identified by root cause analysis and systematically eliminated. Without a continuous improvement philosophy, the supplier will not survive the challenges of the future.

Conclusion

There is no magic potion or crystal ball that will fix all ills or predict future problems. Challenges faced in today's plating on plastic shop must be dealt with scientifically and proactively. The

use of appropriate resources, human and otherwise, will help with the outcome desired. From the preceding discussion, the following points are most important in achieving the necessary quality of plated plastic products:

1. Choose a material that fits the application and is able to be processed with minimal scrap and performance concerns.
2. Design a part that will perform to the customer's specification while minimizing opportunities for quality rejects.
3. Injection mold the part according to good practice for chromium plating.
4. Handle and package the part with extreme care.
5. Design robust plating racks that are sufficient to ensure dimensional stability while meeting the customer's specifications for metal thickness.
6. Electroplate the part while ensuring that all process parameters are within specification
7. Perform maintenance proactively.
8. Filter all process tanks and rinses to remove dirt.
9. Test parts to customer specifications and adjust the part design, rack, process and inspection to minimize dissatisfaction.
10. Finally, don't stop the continuous improvement process.

Will following these items listed above always produce flawless parts? The answer would be no. However, common sense and adherence to guidelines will greatly increase your chances for success.

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