Metallizing of Plastics with Virtually Hexavalent Chromium-Free Etch Solutions

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The recent re-classification of chromium trioxide into a higher hazard category has triggered a search for alternatives to the widely used hexavalent chromium etch bath for ABS and its alloys. One alternative is to use highly concentrated sulfuric acid containing a very low concentration of chromium (VI). In place of electroless nickel, used hitherto, electrodeposited nickel was used. This direct electroplating of plastic is made possible using a bismuth-based activation process. The high rate of lateral nickel layer growth over the part surface allows a new approach to selective metallizing. This study describes an industrial scale trial of this new process for plating injection molded sanitary ware parts and compares the results of adhesion, appearance, yield quality, economy and ecology with the conventional electroless processing technique.

Keywords: *Plating on plastics, hexavalent chromium-free etch*

Background

New regulations on chromium trioxide have had, with respect to hazard class incident rules, a wide influence and caused increased costs associated with storage, emergency planning for chromium waste and above all worker protection.[1] The situation calls increasingly into question the handling of hazardous Cr(VI). Moreover, with rising environmental consciousness among customers as well as suppliers, wide activity in search of alternative solutions has been unleashed. Currently, ABS represents 75% of all plastic substrates suitable for plating. The well-known etch mechanism in the standard process which includes oxidative removal of the polybutadiene phase is only achieved within a certain high concentration range of Cr(VI).

Through a combination of a high concentration of sulfuric acid with a very low content of Cr(VI) in conjunction with direct metallization, it is possible to produce decorative chromium-plated plastics using this new process. This paper, with support from the German Environmental Ministry and German Development Bank, is an innovation project to study this new process. The process represents an ecological and economical alternative to former POP processes. During implementing this new process, the limits of the process were found as well as its additional potential, such as selective metallization of a wider range of plastic substrates.

An outline of the new plastic metallization process comprises equipment implementation as well as chemistry changes. The project is understandably a large technical undertaking.

The plating of ABS can be done with different processes.[2] Conventionally, results are achieved using an ionic process (standard process). Palladium ions are attached to cavities in the ABS surface which are generated in the etch solution. The ABS etch contains either chromic / sulfuric or chromic acid. After activation and acceleration, the palladium-catalyzed surface is covered with a nickel coating in the electroless nickel process step. This process is known as ionic ABS metallization and has been used in the plating field for many years.

The newly implemented process, which runs in parallel with the conventional process, differs mainly in the pretreatment section, specifically etch, activation, chemical nickel and nickel strike steps.

The etch solution in the ultra low Cr(VI) process has a Cr(VI) content of 4 - 10 g/L, 50 - 100 times less than Cr(VI) in a standard etching solution. The novelty and innovative part of the project lay in the almost Cr(VI)-free pretreatment in combination with elimination of the chemical nickel step.

Run cycle

The run cycle of the new process has nine steps up to the nickel strike after which both cycles are identical (Table 1). Only the differences in the relevant pretreatment steps will be discussed.

The etch solution in the new process differs from the standard etch in running at 50°C and is continually recycled between a reservoir where it is kept at 45°C in order to avoid overheating during process changeovers. The exposure time of ABS parts in the air agitated new etch is 1.0 - 1.5 min. After half exposure time of 30 - 45 sec., the rack is raised, the parts are sprayed with etch by nozzles from both sides. The rack is turned and re-immersed in

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Table 1
Process scheme of the new POP process

Etch 1.19	Standing rinse 1.20	Flowing rinse 1.21	Predip 1.22
Activator 1.23	Flowing rinse 1.26		
Accelerator 1.29	Flowing rinse 1.30	Spray rinse 1.31	
Nickel strike 1.39	Spray rinse 1.40	Flowing rinse 1.41	

the etch for the remaining time. During the reversal procedure the spray nozzles remain on until the rack is completely re-immersed. This procedure reduces the adsorption of wetting agent breakdown products on the surface. After removal from the etch and during transport, the rack carrier is spray rinsed on both sides and allowed to drain for 20 sec.

In the final immersion rinse, the first 52 sec of rinse time uses air sparging. The rack is then subject to a 20-sec spray rinse, then it is reversed and re-immersed for 20 sec. and finally travels under spray into two cascade high pressure rinses. These rinse steps have reduced defects by lowering the rack and carrier below solution level and making drippage from rack to part impossible. The two closed-loop cascade rinses have a flow rate of 120 - 150 L/hr and the rinse times are 30 sec in each with air agitation.

The activator exposure time is 2.0 min with mechanical agitation. The activator is continually filtered with a turnover rate of two to three times per hour. The following flowing deionized water rinse has a flow rate of 220 L/hr and 60 sec immersion time.

The accelerator has a process time of 1.5 min. The solution is filtered continuously. This step is followed by a 20-sec deionized rinse with a flow rate of 150 L/hr. The following rinse station is a continuous spray rinse for 1.0 min, while the rack carrier is twice reversed.

Finally the parts are placed in the nickel strike at 60°C. Since two baths have a fixed cycle time of 8.2 min including transfer times, a maximum bath immersion time of 15 min is specified, within which time the conductive nickel layer must completely cover the part.

The process cycle and times discussed above and in Table 1 are designed as an example for a hand held shower product. For other articles the current and process times in the nickel strike can change, but the other pretreat steps remain about the same. In contrast to the standard process, for the nickel strike step in the new process, a current ramp is programmed into the controller of (1) 5.0 V for 2.0 min and (2) 7.0 V for the remaining 8.0 min of process time. Mild mechanical agitation and continuous filtration are used during this step. The rack carrier has two-dimensional mechanical movement in the bath. The nickel sulfate solution is filtered five times per hour through a five-micron plate filter. The final rinse steps after the nickel strike are the same as in the standard process.

Process controls

The individual process baths in the new process are under continuous process control and also analytically monitored during operation. Through repeated quality control and maintenance of the analytical parameters, the optimal process window for each process step is maintained. Moreover, this process window maintains a stable running process over days. The parameters followed by Hansgrohe AG for its product spectrum are listed in Table 2.

Table 2
Process parameters for the new POP process**[9]

Etch	**Concentration**
Sulfuric acid, H_2SO_4	1440 - 1460 g/L
Chromic acid, CrO_3	7 - 8 g/L
Trivalent chromium, Cr(III)	< 1.5 g/L
Wetting agent	By analysis and special filtration
Activator	
Bismuth (II), Bi(II)	1.0 - 1.2 g/L
Accelerator	
Sulfide, $S^=$	0.8 - 1.0 g/L
Normality	0.24 - 0.26N
Nickel strike	
Nickel (II), Ni(II)	65 - 70 g/L
Nickel chloride, $NiCl_2$	12 - 16 g/L
Boric acid, H_3BO_3	40 - 45 g/L
Wetting agent	0.2 - 0.3 mL/L

The Cr(VI):Cr(III) concentration ratio range was 1.0 - 2.0.

Mechanism

The mechanism of chemical etching of the ABS polymer is known and described in the literature[2] for the standard process. It involves the roughening of the surface through partial destruction by Cr(VI) of the polybutadiene phase dispersed in the SAN phase in ABS. The TEM in Fig. 1 shows this clearly. In the etched ABS surface, the dark colored polybutadiene phase is removed.

***(Ecoposit™, Rohm and Haas, Subsidiary of the Dow Chemical Co., Philadelphia, PA)*

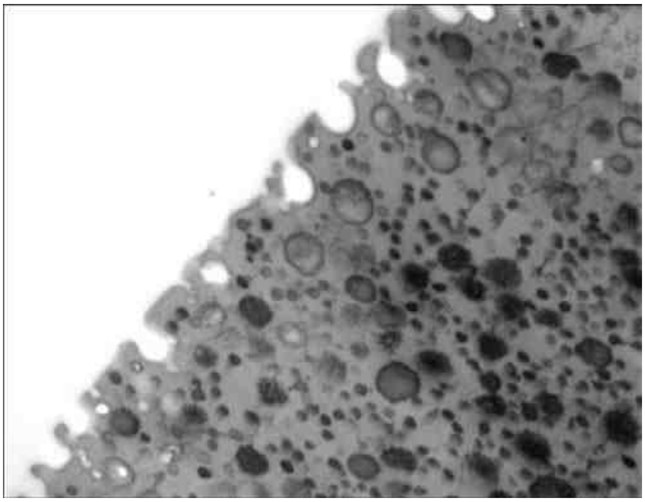


Figure 1—*TEM picture of ABS after etching in chromic/sulfuric acid etch. The polybutadiene phase is stained a dark color with osmium tetroxide.*

The mechanism of the reduced Cr(VI) etch in the new process is entirely different from the conventional etch mechanism. The ABS plastic surface is not destroyed but changed by the chemical reaction of SO_3 with functional groups in the plastic. The surface is made highly polar. The principal reaction is sulfonation but also dehydration and oxidation are possible.[3] Table 3 gives an overview of the reaction products produced from exposure of various functional groups with SO_3 (as concentrated sulfuric acid).

The results of XPS analysis of the surface ABS reacted with SO_3 is shown in Table 4. In the un-etched ABS, only carbon, nitrogen and oxygen atoms are identified. The etched ABS sample from the new process shows a significant increase in sulfur (5%) compared with only 0.3% in the conventional high Cr etched sample.

A comparison of the surface topographies in Fig. 2 clearly shows a difference between the standard etched sample (Fig. 2a) and the ultra low Cr-etched surface (Fig. 2b). The adhesion of the metal coating is obtained by surface micro-roughness in the case of the conventional etch due to the loss of the polybutadiene component. In Fig. 2a, this is seen as black recessed areas in the photo. The sulfuric acid etched surface in Fig. 2b shows a uniform even surface roughness which comes from chemical modification of the surface. The so-called polar layer is generated accompanied by a thickening of the layer and thus the appearance of deglazing.

The question remains whether the small amount of Cr(VI) in the new etch can be eliminated. It has been shown that a certain amount of Cr(VI) is necessary for adhesion of metal to the plastic surface. Cr(VI) acts as a complexor / catalyst to form, within a certain concentration range with H_2SO_4, a complex containing the SO_3 species for the reactions with the surface [$CrO_3 \cdot SO_3$].[4,5]

In the process steps for direct metallization process using the ultra low Cr(VI) etchant, the following reaction sequences take place on the surface:[6,7,8]

1. Etch: $R\text{-}H + SO_3 \rightarrow R\text{-}SO_3H$

2. Activator: $R\text{-}SO_3H + ML\,x \rightarrow R\text{-}SO_3\text{-}MLx\text{-}1$

3. Accelerator: $R\text{-}SO_3\text{-}MLx\text{-}1 + S^{=} \rightarrow R\text{-}SO_3\text{-}MS$

4. Nickel electrodeposition: $R\text{-}SO_3\text{ -}MS + 2e^- + Ni^{+2} \rightarrow$
$R\text{-}SO_3\text{-}M\text{-}S\text{-}Ni_y$

Table 3
Potential reactions of sulfuric acid (high concentration) with ABS components

Functional Group	Reaction	Reaction products
-CH	Dehydration Oxidation Sulfonation	C-C $-C{=}O$; $-CO_2H$; -COH $-CSO_3R$; $-CSO_2C$
Aromatics (Ar)	Aromatic sulfonation	$Ar(SO_3)x$; $ArSO_2Ar$
Nitrile, -C~N	Oxidation	$-C{=}N\text{-}C{=}N\text{-}SO_2\text{-}O\text{-}$ + Hydrolysis products
Alkene, C=C	Oxidation Sulfonation	$>COH\text{-}CSO_3H$ $C{=}CCHSO_3H$ $>C{=}C\text{-}SO_3H$
Arylethylene	Oxidation Sulfonation	$Ar\text{-}C{=}CHSO_3H$ $Ar\text{-}COH\text{-}CSO_3H$

Table 4
XPS analysis of ABS surfaces; elemental concentration mean in wt%; probe depth is approx. 10 nm (N.D. = none detected)

Specimen	Cr	O	N	C	S
ABS, no etch	N.D.	6.16	5.30	86.87	N.D.
ABS, new etch	1.78	24.60	4.00	64.20	5.01
ABS, std. etch	6.10	22.40	4.80	62.90	0.30

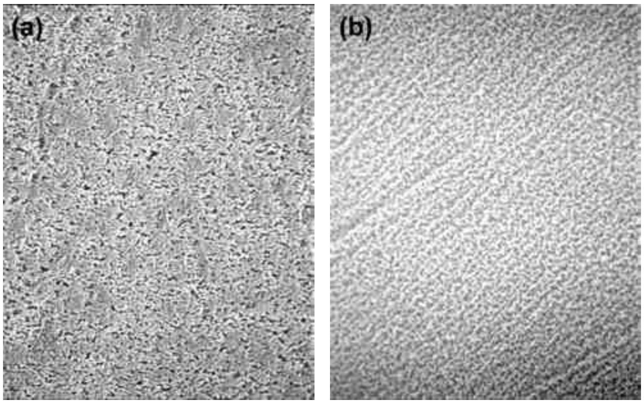


Figure 2—*SEM comparison of the etched ABS surfaces (500×): (a) standard etch 400/400; (b) sulfuric acid/Cr etch 1400/7.*

After the functionalization of the surface through sulfonation (Step 1), dehydration and oxidation produce a highly negative polar surface which, similar to a cation exchange resin, can bind cations. In this case, bismuth ions in the activation process step can be bound to the ABS surface. This chemical bonding is actually different from the adhesion mechanism proposed in the classical mechanical bonding theory after the nodule principle proposed in classical activation with palladium particles.

The bismuth cations in the activator are stabilized with MSA complexant. In the accelerator, sulfide ions displace the MSA ligand because of its higher affinity for bismuth (Step 3). The metal sulfide layer has sufficient conductivity such that a current-induced nickel deposit can be formed on the sulfide layer (Step 4). This is another significant difference from the classical process.

Electrochemical (electroless) nickel metal deposition and direct nickel metal electrodeposition differ in the reduction forces used in the process step and also in the growth mechanism for building the nickel layer over the surface. While the known classical process can be described as field oriented growth of the nickel layer, in the new process the nickel layer grows laterally over the sulfide layer from the contact points until the surface is covered and then further in the direction of the electrical field. The speed of deposition of the field oriented growth is not quite zero until the surface is covered, and then it is overlaid by lateral growth. Growth stops in the new process when the current is broken.

The initial lateral growth of the coating opens the possibility of selective metallization. Through part specific contact and rack design in combination with current parameters and exposure times, one can plate only in desired areas of parts. An example of the unique product application is the metal free interior channel for water flow in a hand held shower fixture without using separate inserts.

Product quality

Surface quality

The surface of a chromium-plated plastic article from the new process is clearly brighter and smoother than the surface processed in the standard process. This means that in decorative applications, the new process has an advantage over the old one. The reason is due to the previously described mechanism. Since the ultra low Cr(VI) etch does not destroy, but rather modifies the surface, it will remain brighter, as seen in the comparison in Figs. 2a and b. Additionally, the levelers in the bright acid copper are more effective in building up the copper layer, since no great micro-cavities must be covered up.

Adhesion

The adhesion level of copper to plastic treated by standard and new processes is not significantly different. In Fig. 3, the peel test results for copper foils from ABS etched with the ultra low Cr(VI) etch were slightly better than conventionally etched ABS test panels.

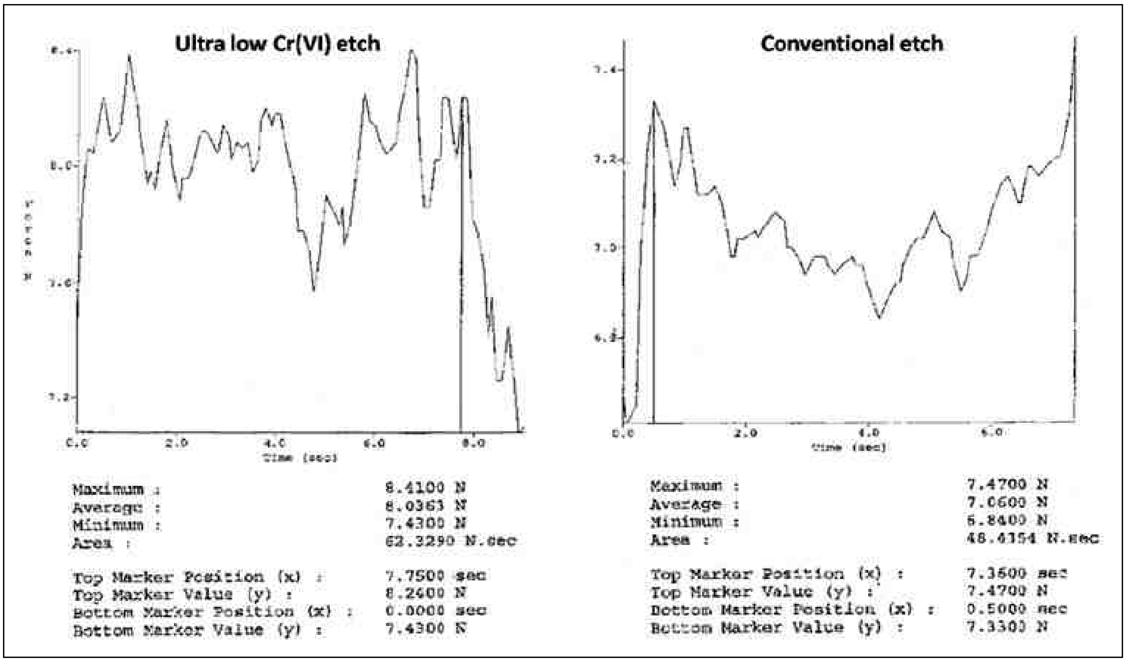
The Jacquet Test (ASTM B533) was carried out to measure the force of peeling a 40-μm thick plated copper layer of defined width from the ABS plastic substrate at a specific constant peel rate. In this example (Fig. 3), the new etch (left graph) showed a 15% higher peel adhesion (8 N/cm) when compared with the conventional etched ABS (right graph) (7 N/cm).

Product requirements are tested by temperature cycling the plated plastic article. As a standard, Hansgrohe AG has a set exposure requirement of 300 cycles from the hot water limit of 80°C for 1.0 min to the cold water limit of 20°C. Both processes meet the 300 cycle requirement. No higher number of cycles was tested since no metal adhesion loss was observed in either case.

Since the peel test specimens must be of defined size for testing they needed to be cut to size with a shear. As seen in Fig. 4, all twenty specimens processed with 400 g/L (Fig. 4a) or 1000 g/L CrO_3 (Fig. 4b) showed rips or tears in the foil vertical to the line of shearing. On the other hand, all test samples run in the ultra low Cr(VI) etch (Fig. 4c) showed no tears in the foil at this interface. It is proposed that the loss of the polybutadiene phase in the plastic layer after conventional etching leaves only the SAN layer behind, making the plastic more brittle. When the shearing force meets this depleted plastic there is no mechanical cushion for the force, which causes the separation and rips in the foil.

Metal-free water channel in interior of plated part

A particular application shed light on one interesting advantage to be realized with the use of this new process. A particular hand shower part was designed with an internal water channel in which metal plated with the conventional process. Using the new process resulted in a metal free water channel.



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Maximum :                         8.4100 N
Average :                         8.0363 N
Minimum :                         7.4300 N
Area :                            62.3290 N.sec

Top Marker Position (x) :         7.7500 sec
Top Marker Value (y) :            8.2400 N
Bottom Marker Position (x) :      0.0000 sec
Bottom Marker Value (y) :         7.4300 N
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Maximum :                         7.4700 N
Average :                         7.0600 N
Minimum :                         6.8400 N
Area :                            48.4154 N.sec

Top Marker Position (x) :         7.3600 sec
Top Marker Value (y) :            7.4700 N
Bottom Marker Position (x) :      0.5000 sec
Bottom Marker Value (y) :         7.3300 N
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Figure 3—*Results of peel testing of metal foil from ABS substrates etched in different pretreatments.*

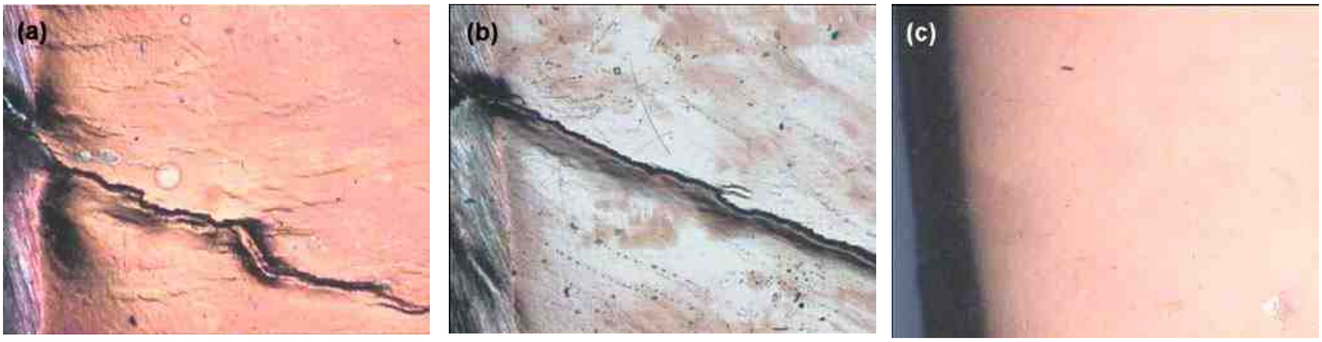

Figure 4—*Plated copper ABS (P2MC) test plaques at the shear cut line (50×): (a) standard 400 g/L Cr(VI); (b) standard 1000 g/L Cr(VI); (c) direct process.*

In the interior of the shower handle shown in the upper part of Fig. 5, many metal layers are visible. Chemical nickel covers the entire inner area. Depending on the throwing power of the following copper, nickel and chromium plating, one can observe different thicknesses and coverage of these layers within the channel. In practical use, these production parts are exposed to water quality and temperature variations which can produce dissolution of the inner metal layers which can affect the proper function of the product. The dissolution mechanism has been previously studied. The new process eliminates metal inside the water channel by selective metallization. Techniques to prevent metal in the channel using the conventional process involve multiple steps and are expensive.

Economic analysis of the project

Investment costs

Investment costs for building a plating line which could handle the new process were avoided since the existing plant was able to accommodate the additional new process steps. Old stations which were unused were available to use in the new process. Expansion of the waste water area, new controls, drip protection on the hoist carrier, tanks, reservoirs, rack conditioning station, etc. involved costs of €900,000 (\$1.20M[***]).

These costs cannot be compared with those for a new plating plant. In this case some costs could be eliminated (*e.g.*, drip protection) while others would be added (*e.g.*, new tanks with plumbing).

The difference in investment for a standard process plant and for a plant using the new process lay in the process steps taking into account the following:

- The new process involves nine steps up to the nickel strike versus twenty steps in the standard process.

- The total process time is two hours (35 steps) versus three hours (47 steps) in the standard process.

- The process time up to the metal plating line is 18 - 23 min versus 63 min for the standard process.

Since the new process has eleven fewer process steps, which have an estimated new cost of €20,000 (\$27,600) per process tank, the total cost saving for the new process plant is about €220,000 (\$292,400).

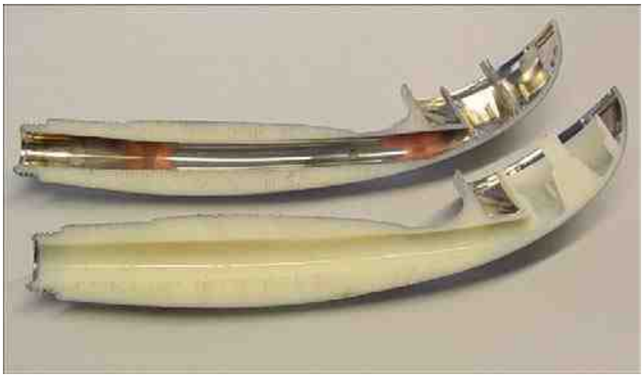

Figure 5—*Lengthwise cross-section of two hand shower parts processed in the standard process (top) and the new direct metallizing process (bottom).*

Operating costs

With respect to operating costs the new process offers potential savings in the areas of chemical costs (lower usage), energy costs and waste water costs. In 2005, the standard process had chemical use costs of €9.07/m^2 (\$1.07/ft^2) for all plating. About 66% of this cost was for electroplating (nickel and copper were at peak price in 2005) and 33% was for preplate costs through electroless nickel (\$0.36/ft^2). The total chemical use cost for the new process was €6.77/m^2 (\$0.80/ft^2). This represents an almost 74% savings in the preplate section (\$0.10/ft^2). This means that a plater who processes 100,000 m^2 (1,000,000 ft^2) plated area per year could save €230,000/year (\$305,700/yr) in chemical costs compared with the standard process.

The energy costs for bath heating with natural gas amounted to €209,500 (\$305,700) in 2005 for the standard process. Since fewer heated baths and lower temperatures are required for the new process, it is calculated that 50% energy cost savings can be achieved with the new process compared to the standard process.

Fewer number of process steps in the pretreatment section (nine instead of 20) generates lower water use for the process and rinsing steps thereby lowering waste water costs by 50% from €152,000 (\$202,700)/year to €75,000 (\$99,700)/year in 2005.

Costs associated with operating, servicing and maintenance of chemical nickel baths, chemical stripping of tanks two times per week, associated waste water treatment of complexors from the baths through UV peroxide are eliminated in the new process resulting in a saving of €20,000 (\$26,600)/year.

[***] *1 Euro = 1.3291 U.S. dollars (04/22/10)*

Part spectrum and reject (scrap) rate

Over 2.5 years, 40 different parts were optimized and plated in the new process. The entire range of parts in the Offenburg plant increased weekly, since new products trialed in small lots in the Schiltach West plant were then transferred to the Offenburg plant. To date the complete part range comprises 100 different products. In Table 5, representative samples of the range of parts are shown with current status of process optimization.

Table 5

Representative samples in the product range and their scrap rates

Article	Name	Scrap rate
	Raindance Large	15.6%
	Raindance 150S	20.1%
	Casetta cover	12.4%
	HS Plus	4.1%
	Axor	3.3%
	Unica D	1.1%

The main criteria to note are:

- Large surface defects (incomplete plated surface)
- Minivoids (pore like defects with 0.1 - 1.0-mm diameter)
- Poor adhesion
- Roughness
- Sharp edges
- Plating in the threaded area
- Build-up at a gate
- Plating in the inner channel of HS Plus shower part

In summary it can be stated that a third of the product produced in the new process meets the requirements and yield of the standard process of less than 5%. A second third is on the way to that goal and the last third, which includes new products, is at the beginning of the development phase. Although new products in the standard process are integrated within a short learning phase (1 - 2 weeks), for new articles to be run successfully in the new process, it required a longer iteration phase. This is because of the still low level of experience with the new process in comparison with many years of production experience with the standard process. Because of current and growing customer demands for assured plated parts delivered in 48 hr, it is still unrealistic to have 100% of production coming from the new process at this time.

Summary

Within the project time frame of two years, with optimization of the process parameters, a very low Cr(VI) plastic plating process was shown to be practical. Commercially saleable products were produced.

The process stability of the new process could be held by maintenance measures and routine analysis. The surface quality of the parts regarding gloss and adhesion has clear advantages over the standard technique.

Articles with smaller visible surfaces for decorative applications are plateable with reject numbers clearly under the limit value of 5%. Also the articles with larger surface area can have their reject rate reduced continually with development effort. Nevertheless, a permanent installation of this process in the plating line is unrealistic at this time for two reasons. First of all, the reject rate for larger parts and new products is still in the second class range and secondly there is a current backlog of orders because the plant is over 100% capacity utilization. That means that every article with greater than a 5% reject rate would require a longer delivery time and pose the danger of losing the customer. During the overcapacity condition at the plant, conditioning of the racks on the weekends is not possible since production is planned for these extra shifts.

The problem of "minivoids," the main defect arising from degraded wetter, was solved by a special filtration technique of the new etch solution along with analysis for wetting agent.

Recommendations

After compiling the results, the transfer of the ultra low Cr(VI) direct metallization process is recommended for other industry segments where the article spectrum is limited. In such a case, a short start up time after implementation is expected. Since the process is suitable for plating not only ABS but ABS/PC, it could even be used in auto parts plating plants. Job platers with a small spectrum for bright chromium plastic parts can profit from the shorter process cycle time. Plastic platers who produce, in addition to bright chromium parts, an amount of matte chromium surfaces, can achieve good yields with even lower risk after a start up time of one to two weeks. The reason is that the defect rate due to minivoids (main defect) is not present with the matte-surface finish. The dimensions of the mini-pores lay within the range of the degree of matteness of the surface and this defect is not recognized.

Acknowledgment

Thanks are extended for generous support from the German Ministry of Environment and the German Development Bank as well as for the technical support from the firm Rohm & Haas.

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