Palladium-free Direct Plate Technology for Plating on Plastics without Electroless Chemistries

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Plating on plastics has traditionally been accomplished by use of tin/palladium colloidal-type activation systems with electroless chemistries. Although well understood, these processes can be costly and require extended process lines with high water consumption.

A method to electroplate directly onto non-conductive plastics has been developed. This revolutionary technology does not use precious metals to activate or electroless chemistries to produce the first conductive metallic layer. Instead, this process allows electrolytic nickel to plate directly onto the plastic substrate. This direct plate technology decreases the number of process steps, significantly reduces water consumption, eliminates chelates, and improves productivity.

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A new direct metallization process eliminates the need to use electroless chemistries and shortens the pre-treatment time by reducing the number of processing steps. This new direct plate technology employs a mild etching process that ensures a high degree of adhesion. It has been used in production in several pilot plants since 2001.

The increasingly stringent environmental conditions as well as substantial cost reductions called for by the automobile industry have forced the electroplating industry to look for new techniques such as new direct metallization processes.

To reap the benefits of direct plate systems certain processing considerations must be well understood. The etching process is an important factor and is responsible for the degree of adhesion on both ABS and ABS/PC resins. The etching process is also responsible for the actual ability to metallize such plastics. The best possible degree of adhesion and 'metallization' for the new direct-plate process is achieved by using a mild etch.

Mild Etch

Figure 1 shows an ABS surface that has been etched in a conventional colloidal ABS process chromic-sulfuric acid etch. The rough, heavily attacked surface required by the classic type of colloidal activation processes is depicted here. This aggressive etch is necessary for proper adhesion in a colloidal process. As a result of such strong roughening the plastic compound may destroy the surface of the molded part. The result could impact adhesion and will degrade the surface quality.

Figure 2 shows a surface that has been etched under mild conditions in the direct plate process. This slightly roughened plastic surface with individual cavities is well suited for the 'buttonhole' adhesion mechanism between the surface of the substrate and the metal deposit. This is very important as it provides a high degree of adhesion while maintaining the 'Class A' as-molded surface of the parts.

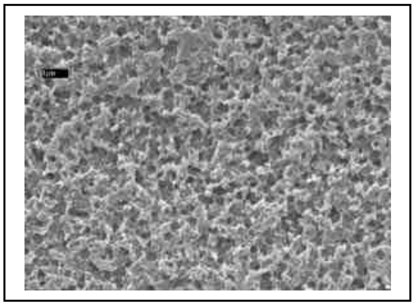

Figure 1: The ABS surface after colloidal etching is very rough.

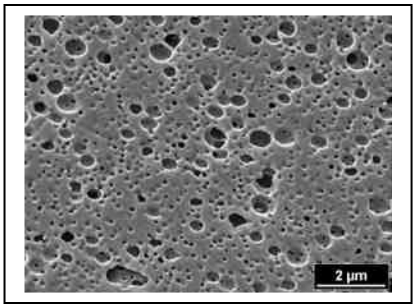

Figure2: The surface that was mildly etched by the direct plate process is only slightly roughened with individual cavities.

The etching parameters have a direct influence on the chemistry of the surfaces. The mild etch enhances the formation of polar functional groups (-OH, -C=O, -COOH) on the plastic surface, where the percentage of hydroxyl groups (-OH) are found to be particularly high. These make a chemical link with the positively charged activator molecules possible. In the following conducting solution the active metal is ‘wetted’ to the plastic substrate via a bridge of sulfur as a result of a kind of vulcanization.

These two reactions achieve an additional chemical adhesion. Bayer in Leverkusen investigated the adhesion on ABS and ABS blends. The results reached the range specified (Figure 3).

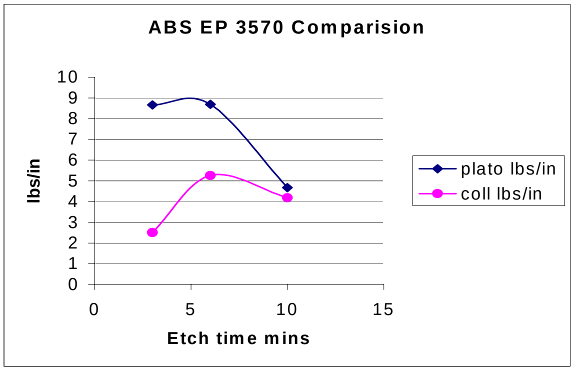

Figure 3

Wide Scope of Application

Tests have clearly shown that the possibility of being able to metallize a particular surface was decisively dependent upon the applicable etching conditions. The metal activation on the ABS surface increases in line with the etch time (Figure 4), and the etch temperature (Figure 5). Thus, by raising the etching parameters we get a corresponding increase in micro-structuring, the result is an increase in the area size. ABS/PC surfaces do not undergo such a critical change.

From experience, the deposit coverage will be achieved more quickly by increasing the amount of surface metallic activation. This property can also be seen with the use of direct metallization based palladium activators. Consequently, the metallization speed on ABS should increase with higher etching parameters but on ABS/PC this is less significant. As opposed to expectations, the metallization speed on both types of material will become slower when the etching parameters are increased. At certain etching times and temperatures complete inhibition may occur (Figures 6 and 7).

Under increased etching conditions the effective plastic area per area unit will increase. A reduction in area growth is, therefore, understandable. Complete metallization inhibition cannot however, be so explained. It is quite possible that the etching parameters will have an affect on the percentage and composition of the functional groups on the plastic surface. The presence of hydroxyl groups (-OH) with mild etches is far higher than after strong etching. However, the activator contains both “active” and “inactive” metallic compounds, that are deposited on the plastic surface. Therefore, it would appear that hydroxyl groups enhance the deposition of “active” molecules on plastic surfaces. Based on this theory, a catalyst was used which further reduced the attack by etching, but also simultaneously enhanced the formation of increased hydroxyl groups on the plastic surface. It was then seen that by adding this etch catalyst the number of “active” molecules was indeed increased and at the same time the metallization speed was also increased (Figure 7 and 8). This step considerably widens the scope of application for the new direct-plate process.

Reduction of Process Steps

Activation is carried out following a mild etch and subsequent rinsing in a complex metal amine solution. With the new direct plate process there is no need for chrome reduction. The quality of the activator, i.e. its operational life and its “activity” depends on the conditions applicable during production. Drag-out and work volume reduces the quality of the activator, but this can be easily managed by replenishment. Temperatures higher than 30° C can have a negative impact on the activator. The immersion time in the activator will have no effect on the metallization process. One must only ensure that the components are completely ‘wetted’ and is accomplished after four minutes.

After activation the parts are given an alkaline rinse. Hydrolysis washes off loosely adherent complex metals as metallic hydroxides from the rack insulation. Immersion in the conditioner should be less than two minutes since complex metals would be chemically removed from the surface of the production parts as a result of hydrolysis. The final sulfide conducting solution produces a grey, firmly adhering film that consists of metal and polysulfides. During the reaction that occurs between the complex metal and the sulphurous solution, further reactions take place on the highly active plastic surface. Here again the immersion time has no effect on the metallization; one minute is quite sufficient.

For the first electroplating bath, only electrolytes with potential lower than the reduction potential of the sulfide activator deposit may be used. Typically nickel is used as the potential from acid copper electrolytes is too electropositive. Tests have shown that the sulphamate-nickel has excellent metallizing characteristics. The voltage must start at 2-3 volts and be increased step-by-step. The prescribed voltage should have been reached after about 4 minutes. In this manner burning will be avoided and a constantly high area growth of about 0.5 to 1.0 dm^2/min. will be ensured. The immersion time will depend on the size of the parts, the capacity of the rectifier and the number of contact points. The nickel plating time should be 5-12 minutes depending on the size and complexity of the parts. Further metal deposits may then be applied as required. The advantages of the new direct plate process in comparison to conventional processes (Table 1) for plating on plastics quite clearly outweigh the disadvantages. The reduction of the number of processing steps and rinsing baths shortens the pre-treatment time from 50 down to 20 minutes.

Practical Results

Since 2001 name signs and emblems made of ABS/PC used in the automobile industry are being treated in a plant with a tank volume of about 600 litters. The plant is being operated one shift per day. The cycle time is 7.5 minutes and the electroplated plastic area per goods carrier is 1.2 m²

At the end of January 2002 the throughput was about 4000 m². The metallization test of large area automobile interior articles made of ABS/PC T85 was also conducted without any problems.

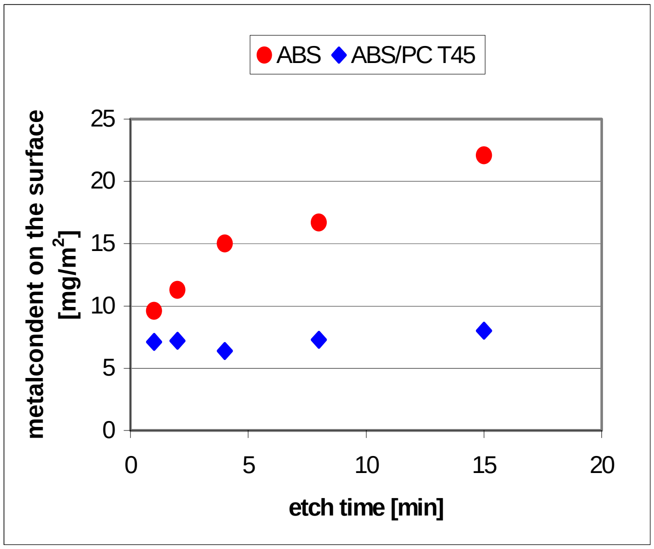

Figure 4:
Activator metal coating vs.
etching time

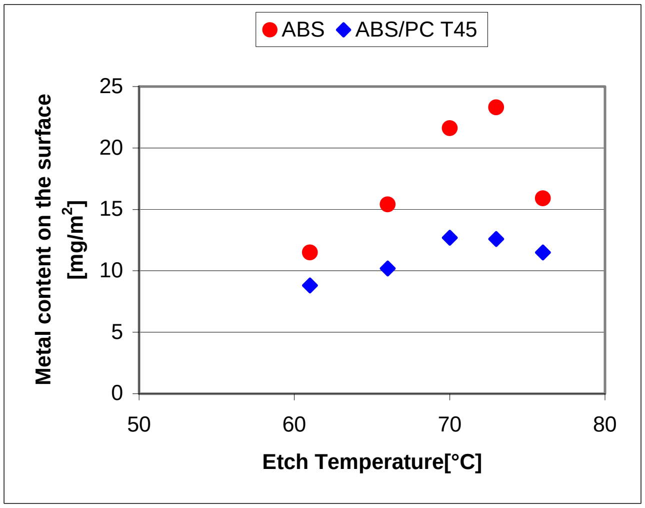

Figure 5: Activator metal coating vs. etching temperature

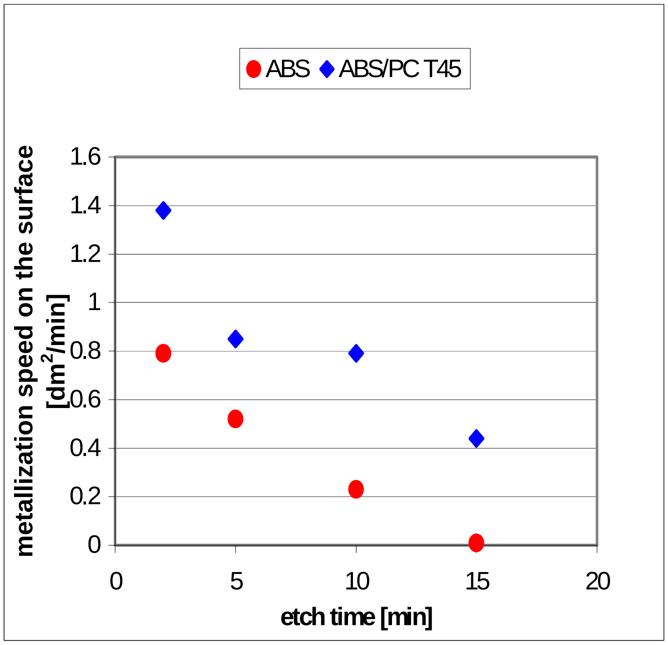

Figure 6: Area growth in sulfamate nickel at
2 volts for 1 min., with a pointed contact, depending
on etching time.

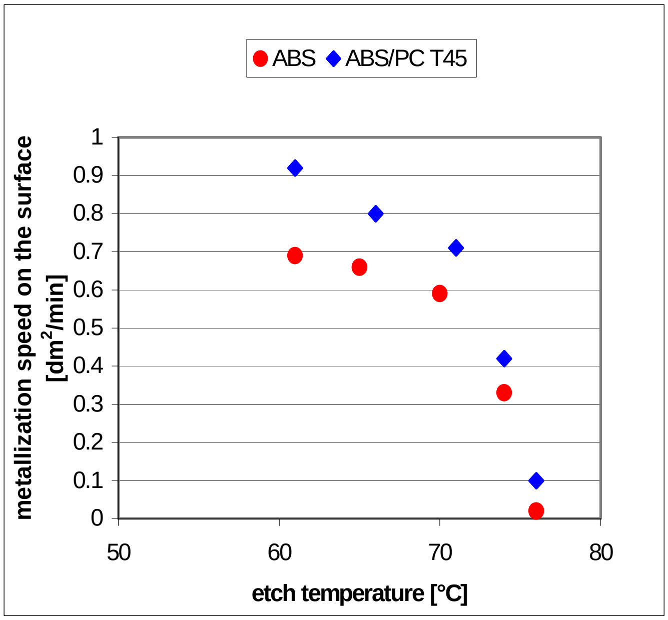

Figure 7: Area growth in sulfamte nickel
at 2 volts for 1 min., with a pointed contact, depending on
etching temperature.

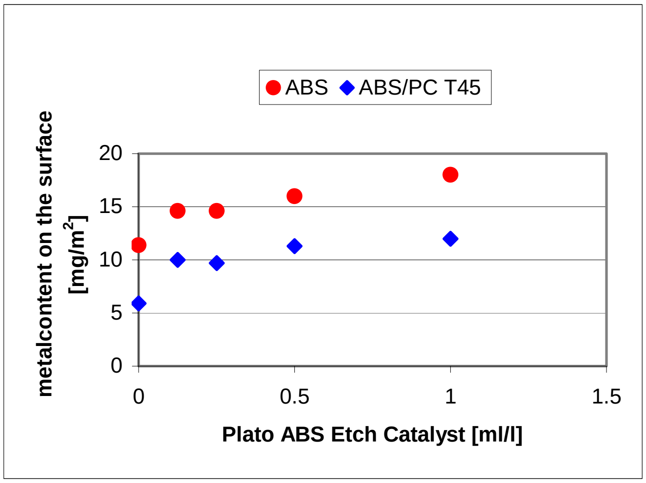

Figure 8: Activator metal coating vs. concentration of etch catalyst

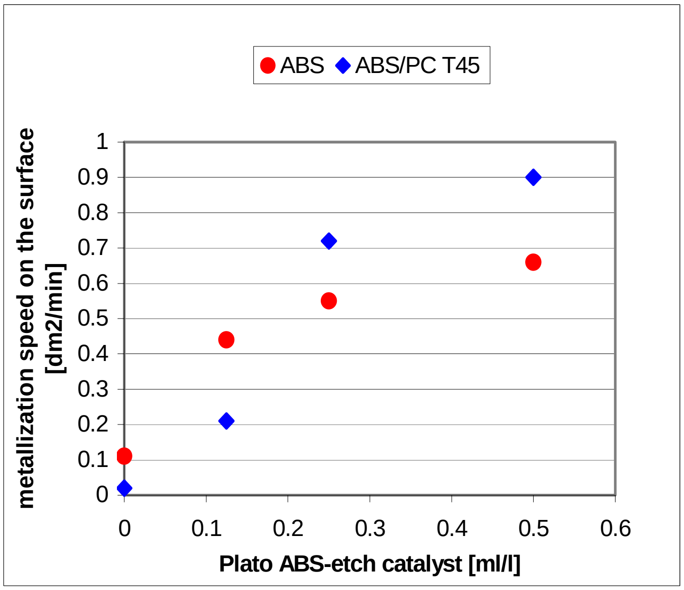

Figure 9: Area growth in sulphamate nickel
at 2 volts, 1 min. with a pointed contact, depending on the
concentration of the etch catalyst, on ABS and
ABS/PC sample panels.

Colloidal	**New Direct Plate Process**	**Economical and Ecological Advantages and *Disadvantages***
Etch 12 minutes, 68°C 400 g/l H_2SO_4 400 g/l CrO_3 without catalyst	**Etch** 5 minutes, 63°C 400 g/l H_2SO_4 320 g/l CrO_3	• Reduced treatment time • Less production of Cr^{3+} • Less Cr drag-out • *Catalyst cost*
4 Rinses	**4 Rinses**	• Reduced waste water costs due to lower drag-out
Reduction 2 minutess, 30-50°C	None	• No cost, no space required
3 Rinses	None	• No cost, no space required
Pre-Immersion Dip in HCl	None	• No cost of chemicals, no effluent costs
Pd – Activator **4-5 mins, 30°C**	Activator **4 minutes, 18-22°C**	• Complexed metal, Ammonium, • Palladium-free • *Possible need for cooling in summer,*
3 Rinses	Conditioner **0.5 minutes**	• Less effluent
Accelerator 2-3 minutes, 50°C	**Conducting Solution** 1 min, room temperature	• Less energy and effluent costs • No complexing or reducing agents! • Unlimited operational life
3 Rinses	3 Rinses	• No complex treatment of effluent
Electroless Nickel 10 minutes, 30°C	None	• No HNO_3, no tank stripping • Reduced energy costs • No complexing agents • No expensive reduction agents • No new make-ups due to high salt concentrations
3 Rinses	None	• No waste water • Less space
∑ 24 positions	**∑ 11 positions**	• Less space needed
∑ 48 minutes	**∑ 18 minutes**	• Improved efficiency
Electrolytic Nickel and Electrolytic metal build up	**Electrolytic Nickel and Electrolytic metal build up**	• Electroplate to specification, no other line changes

Table 1

- As a direct plate process, the equipment requirements are much shorter and there are fewer process steps.
    - Significantly shorter than colloidal
        - Lower cost equipment
        - Greater throughput

- Because the new direct plate process does not use electroless chemistry, there are fewer waste treatment issues to deal with.
    - No formaldehyde
    - No chelates
    - No unstable electroless baths to ‘plate-out’

- The new direct-plate process is a non-palladium activator system.
    - No wild palladium price swings
    - No precious metal surcharges

- Following pretreatment with new direct-plate process and electroplating in sulphamate nickel, the parts can be electroplated in any conventional sequence to achieve the final finish.
    - Cu - NI - CR for decorative
    - Multilayer NI for automotive CASS requirements
    - ‘All Nickel’ process for recycleability

- The new direct-plate process has been shown to be an effective pretreatment process for ABS and ABS/PC blends.
    - ABS and ABS/PC represent 90% of the market
    - Other resins can be plated