Pre-treatment of Exotic Plastics for an Ever-more Technically Demanding Customer

Mariola Brandes, *Atotech Deutschland, Berlin, Germany*

This paper will explore the recent trends from conventional substrates (such as steel and aluminum) toward plastics, focusing on the pre-treatment of polyamide in particular. It will also discuss the implications of the automotive industry and its drive to ever-more exotic materials, as well as the technical demands and changes this imposes on the chemical supplier and his tier 1 and 2 customers.

For more information, contact:
Mariola Brandes (Maja)
Atotech Deutschland
PO Box 21 07 80
Erasmusstr 20-24
Berlin
Germany D-10507
Phone 011-49-3034-985-748
mariola.brandes@atotech.de

Changing substrates and surface finishes

Plating on plastics is becoming a revolution! The need for reducing weight, for example in the automotive industry, means the acceptance of plastics has become progressively easier. The most striking of these changes is the change away from steel. Steel would have formed most of the frame of a car in the 1960's with a large amount of Cu/Ni/Cr plated components. This has fallen by 65% between 1968 and 2002. But this does not necessarily mean a loss of opportunities for electroplating.

On steel, the general decorative requirement was for a Duplex Ni layer followed by chrome. So, although the amount of steel to be plated has fallen, alternative materials such as Aluminium need zincate layers and plastics require electrical sensitization which means more opportunities for the chemistry supplier.

As alternative substrates to steel such as ZBDC, Brass ***(although now virtually non-existent in the design and manufacture of cars, it still has a tremendous use in sanitary applications for example hotel bathrooms where much repeated cleaning is required)*** Aluminium and plastics this has led to different layer combinations. Multi-layer nickels using for example, high-sulphur and microporous sacrificial layers are now well recognised technologies.

Decorative plating of exotic performance plastics

The traditional area in the metal plating of plastics, is the decorative plating of ABS and ABS/PC blend polymers. Initially only pure ABS was used, but with more rigidity and greater thermal requirements, ABS containing Polycarbonate gradually came into use. PC was present in the substrate from as low as 30% through 60% up to 85%. As recently as 10 years ago, 95% of the market involved plating ***only*** ABS polymers. Today, the proportion of plastics using the traditional ABS and ABS/PC blends has fallen to around 85%.

The main limiting factor of plastic is always the tolerance to applied heat. As the melting point of ABS and ABS PC is between 80 and 140C, plastic components can never be used in the hot zone. So the interior decorative application is the main use.

Even though plastic is fairly new in the automobile, the search for higher performance plastics that have improved compatibility with subsequent finishing is continuing. Plastics such **PA**- ***Polyamide***, **Nylon**- ***GTX***, **RRIM**- ***Rigid rapid injection moulding*** and **SMC**- ***Sheet moulding compound*** are being investigated by most global OEM's.

Much different processing routes are needed for such disparate plastic types in providing a nice aesthetically pleasing plated layer with acceptable adhesion. So, the chemical supplier and electroplater have to find a solution.

Of all the new plastics being looked at, PA seems to be the most outstanding candidate to provide a good combination of adhesion and looks.

Polyamide as a Material

Polyamide is inherently stronger and more rigid than ABS or ABS/PC. As a thermoplastic, polyamide can be readily processed from a liquid state.

It has temperature stability from –30°C to around 110°C. In addition to this it has excellent low-friction behaviour and good thermal co-efficiency expansion characteristics with the metals that are later electroplated. Polyamide has high impact strength, a small amount of memory (elasticity), is abrasion resistant and vibration reducing[1].

The low fusion viscosity of polyamides makes them easy to work. Put simply, polyamides have out standing physical properties, combined with low weight and also low manufacturing costs. Some plated Polyamide components are shown below (fig.1).

fig.1.

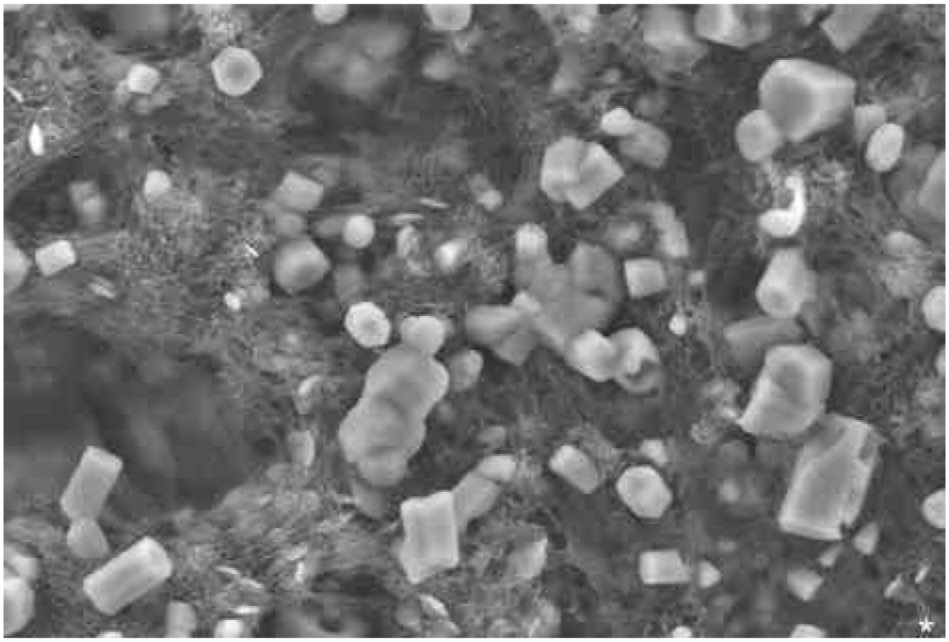
Polyamide types

The various polyamides are identified by the number of polar amide groups (PA 6, 11, 12, 66), This chemical identification distinguishes them from the ABS /ABS-PC blend plastics.

The usual first stage etching process - Chromic acid etching, has some effect on the amides, but produces a surface that does not have a suitable decorative appearance.

A further influential variable is the properties of the "fillers" (generally minerals such as glass fibre), which have to be taken into account in pre-treatment [2/3]. Also, injection conditions, which can vary greatly in polyamide production, is extremely influential and must be closely controlled[4]. A properly prepared polyamide layer is shown below in SEM format below (fig.2).

fig. 2.

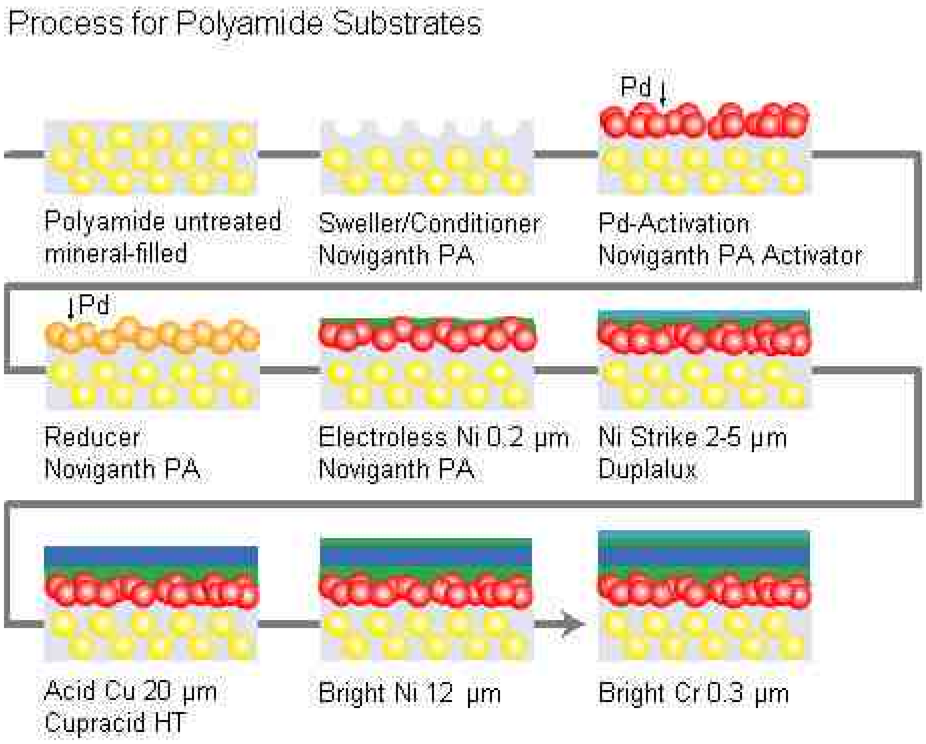


The Pre-treatment of Polyamides

The above description of polyamides makes it clear that there will never be a uniform pre-treatment route. It is very important to carefully match all the pre-treatment steps to the type of PA plastic being processed. The procedure set out in this paper has been designed for the plating of several types of PA (Table1). However, processing modifications will be required for other PA plastics, and these will not be discussed in detail.

PA name
Durethan® BKV 130
Durethan® BM 240
Minlon® 73 M 40

For clarification purposes, figure 3 presents a flowchart of the polyamide coating process.



The etching or swelling stage is of central importance for the visual quality and adhesive strength of the surface coating, because this step ensures the uniform roughening und functional preparation of the surface [5].

Traditional coating of ABS plastics uses a chromic acid etching bath to dissolve the latex (butadiene) constituent of the plastic and provide an adhesive base for the subsequent metal layer. In the PA process, the chromic acid etching process has to be replaced by a swelling system due to the different chemical composition of the polymer. The swelling system involves a solution of organic components, with added substances to ensure uniform removal of the fillers in the PA.

Figures 3a and b are scanning electron microscope photographs of a PA plastic before pretreatment and after the swelling step

figs. 3a and b.

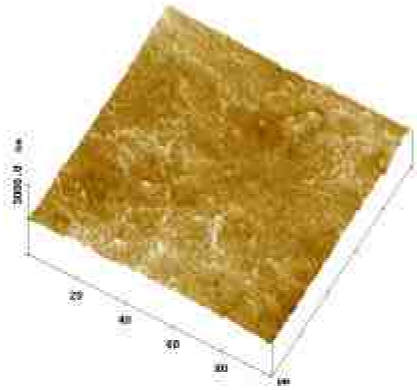


fig.3a: PA before pre-treatment

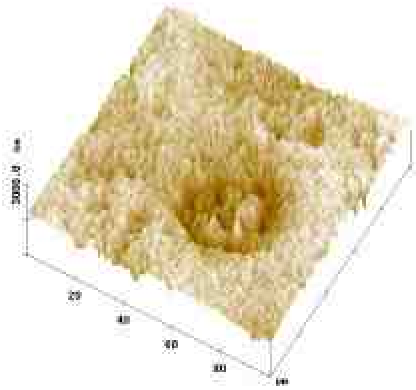


fig.3b: PA after swelling

These pictures clearly show the uniform roughening of the surface, which provides the foundation for the adhesively strong, decorative coatings deposited in the subsequent steps.

Fig. 4 Shows a scanning electron microscope photograph of PA after swelling and conditioning

fig.4.

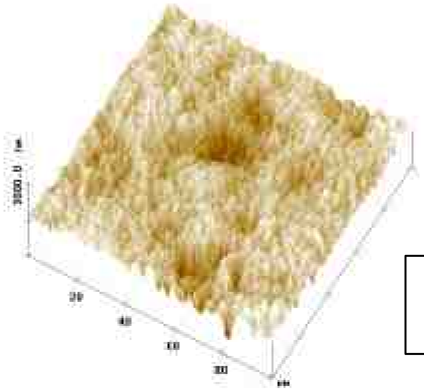


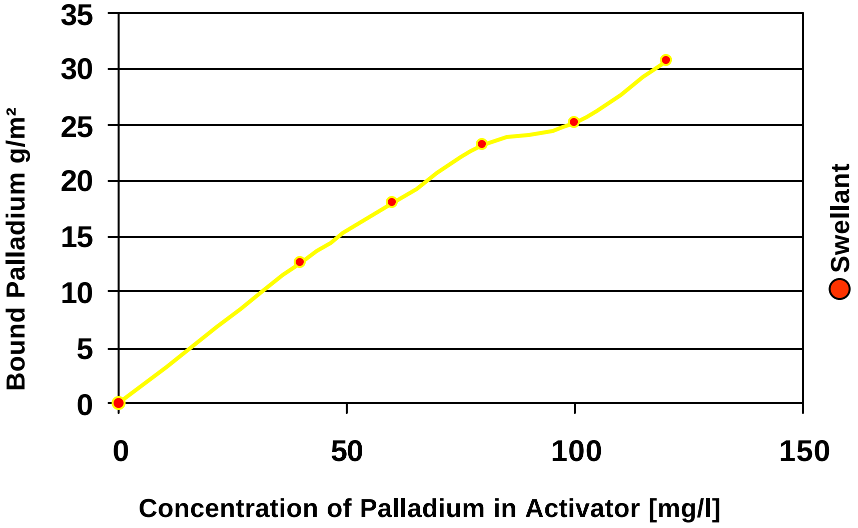
fig.4c: PA after swelling and conditioning

In the standard ABS process, the chromic acid etch is followed by reduction of the remaining CrVI ions in order to protect the activator in the following step from oxidation. In the PA process, this step is replaced by conditioning. The purpose of this is to ensure that the organic solvents are not carried over into the following activator solution, and also to modify the PA surface to better effect adsorption of the palladium ions.

Activating PA Plastics

Following conditioning, the plastic parts move to the activator bath, where palladium ions are bonded by adsorption to the surface of the PA plastic. The reduction of the palladium ions to palladium nuclei then takes place in the reduction solution.

Figure 5 shows how the concentration of the palladium nuclei adsorbed to the surface is dependent on the palladium concentration in the activator solution.



After reduction, there is an almost linear relationship between the palladium concentration in the activator solution and the palladium coating on the substrate surface.

Another advantage of this process compared to the processing of ABS and ABS/PC plastics is the remarkably low level of palladium required to effect good coverage at the following electroless deposition stage. An important further advantage is the fact that the process is free of rack metallisation..

Electroless Nickel Bath Features

Electroless nickel plating of PA requires a specially developed, ammonia-free nickel-phosphorous bath. It should also be tolerant to high bulk loading in the solution and capable of low temperature operation.

Decorative Top Coats

The electroless nickel plating step is followed by the deposition of the decorative plated layer. An optional nickel strike (approx.2-5 µ), is then followed by acid copper plating (approx. 20 µ). This layer ensures the high degree of levelling needed for a good decorative appearance. A bright nickel layer (approx. 12 µ) is then deposited to give improved corrosion protection, combined with the high level of brightness required. The final aesthetically pleasing finish is completed with the deposition of a chrome layer of a thickness around 0.3µ.

Summary

The process described here provides a reliable method for the metal plating of polyamides with an adhesively strong and decorative coating. In addition to extending the scope of production possibilities for the plastics mentioned above, the modified pre-treatment of polyamides gives additional advantages.
The intentional omission of the chromic/sulphuric acid solution used in conventional processes not only produces better coating results, but also brings environmental benefits with regard to concerns about the use of Cr-VI.
The production sequence has been based on the traditional process to ensure that all existing processing equipment can be easily converted to this type of PA process.
The co-ordination of the individual chemical steps also means that there is only a very small tendency to plating of the racks.

References

[1] H. Domininghaus, Die Kunststoffe und ihre Eigenschaften [Plastics and their properties], 5th revised and enlarged edn., Springer (1998)
[2] W.Witt, Kunststoffe 9 (1983), pp. 498-504
[3] F. Fahnler, J. Merten, Kunststoffe 75 (1985), pp. 157-163
[4] Kunststoff-Metallisierung [Metal-plating Plastics, Eugen G. Leuze Verlag, Saulgau Württ.(1991)
[5] U. Tyszka, Galvanotechnik [Electroplating] 2 volumes 80 (1989), pp.

Further references

Article co-authored with Dr. Carl Christian Fels for Metalloberfläche 2002
Paper presented at the ASIA Interfinish conference – Delhi, India, November 2002 by Grant Keers Atotech GmbH