New Hexavalent Cr Free Etch for ABS and ABS/PC Electroplated Plastics

*Walter Sommer, Kai Wang, Neil Brown & Jack McCaskie**
Rohm and Haas Electronic Materials, Freeport, NY

With the increasing concern for both personal and environmental safety in plating operations handling hexavalent chromium, a new process which prepares plastics without this hazardous material would be advantageous. This paper outlines new advances in pretreatment, chemical metal deposition and electrolytic metal deposition of commercial grade resins of interest to decorative plastic platers. The requirements and results of adhesion testing, thermal cycle performance and appearance of part finish will be discussed and demonstrated. Coupled with various trivalent chromium final finishes, a decorative process line which is completely free of hexavalent chromium is possible.

Introduction

Over many years, and more recently with greater urgency, because of environmental health and safety concerns associated with the use of hexavalent chromium containing materials, the industry for electroplated plastics has explored alternatives for hexavalent chromium in the plastic pretreatment process.[1] Many of the alternatives have met one or another requirement but suffered with limitations when compared to conventional chromic acid-sulfuric acid etch systems. Previously published studies of alternatives have included acidic or alkaline permanganate,[2] phosphoric acid with persulfate,[3] sulfuric acid with peroxide,[3] sulfuric acid with periodate,[4] sulfur trioxide gas,[5] ozone gas,[6] trichloroacetic acid,[7] nitrosyl sulfuric[8] and cerium ion in nitric acid.[9] These oxidants have been tested for treatment of ABS resins. Non-hexavalent systems exist for specific resins other than ABS. For example, nylon can be effectively prepared for plating in hydrochloric acid-based etchants with no hexavalent chromium.[10] Delrin™ (polyoxymethlyene) can be treated with a mixture of mineral acids prior to plating.[11] Recently a 50/50 blend of nylon and ABS has been pretreated and plated with a mineral acid-based system, which primarily attacks the PA phase of the material and renders the part platable.[12]

In general, all of the previous non-hexavalent chromium etch systems had limitations, such as higher cost of chemicals, with even higher costs if the process solution is not capable of regeneration. In addition, adhesion may be too low for commercial requirements or the process may be limited to specific non-ABS plastics. Also some processes may require major changes in the conventional process flow or present engineering challenges for economic implementation into existing process lines. Lastly some of the above alternatives have significant safety challenges in their handling and use.

The new process we describe here has the goal of effective pretreatment of commercial ABS and ABS/PC resin materials with a minimum Jacquet foil peel test of 0.88 N/mm (5 lbf/in.) width and no compromise in aesthetic quality of the surface or in the process sequence commonly employed in the industry.

The process sequence

- Conditioner (optional for some ABS/PC grades)
- Cr-free etch
- Activator predip
- Activator (Pd/Sn conventional concentrations)
- Accelerator
- Electroless nickel (or copper)
- Copper strike
- Copper plate
- Nickel (single, duplex or triplex layers)
- Trivalent chromium top coat

(Heat Soak 70°C, 1 hr before TC testing)

The cycle time and temperatures for this sequence are in line with current practice.

The etch itself consists of dilute nitric acid and a combination of oxidants which synergistically treat the polymer surface to enhance adhesion of subsequently applied metal films.

The conventional etch formulation used to pretreat ABS and ABS/PC is 3.4 M $CrO_3 \cdot H_2O$ and 3.4M H_2SO_4.

The surface of this ABS (Cycolac MG 37EP) looks micro-roughened as shown in the SEM photo in Fig. 1.

The peel strength of copper foils (40 μm thickness using ASTM B533-85 test conditions) was found to range from 1.58 to 1.75 N/mm (9 to 10 lbf/in.) width with either electroless copper or electroless nickel as the first layer. These measurements were made after annealing test panels (1 hr, 70°C).

By contrast the Cr-free etch systems produced a different surface morphology and should be designated as a milder etched surface when compared with the morphology obtained with chromic acid-sulfuric acid etchants. In Figs. 2 and 3, we show two different ABS substrates after exposure to the Cr-free etch solution.

*Corresponding Author:
Jack McCaskie
Rohm & Haas Electronic Materials
Freeport, NY

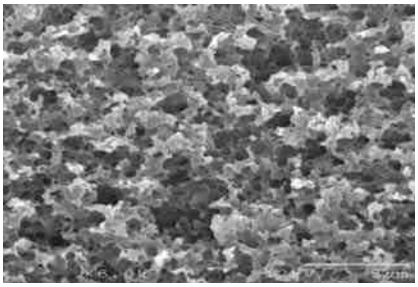


Figure 1—Cycolac MG37 EP ABS exposed to 3.4M H_2SO_4 and 3.4 M CrO_3, 8 min at 71°C.

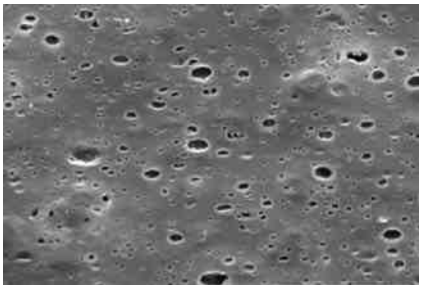


Figure 2—Cycolac MG37 EP ABS exposed to etchant for 30 min, at 71°C.

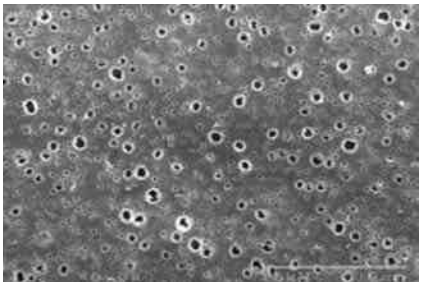


Figure 3—ABS Novodur P2MC after etch for 15 min, at 71°C.

The depth and size of the microporosity is different from the surface produced in a chromic acid-sulfuric acid etchant. Also, it differs from one ABS grade to another, depending on the size and distribution of what appear to be butadiene islands in the acrylonitrile/styrene matrix.

In Figs. 4 and 5, we see that when only the nitric acid concentration and dwell time in the etch are varied, adhesion levels of the copper film also vary. The variations are probably due to differential rates of attack of these vulnerable butadiene sites and the size and density of the butadiene sites contribute to the overall adhesion, which in turn is a function of acid content.

In Fig. 6 we show a TEM of an OsO_4 stained section of Cycolac EPB 3570 ABS showing the shape and distribution of butadiene nodules in the matrix. Characteristically, this material has small particles. Different grades can have a skin effect in which there are fewer butadiene particles at the surface of the mold. There are other grades in which there is no skin effect and butadiene is uniformly distributed through the surface and bulk. Figure 7 shows a diagram of these variations. Figure 8 shows the skin effect in a Lanxess ABS product PG 298.

The adhesion values obtained by pull test of copper foil with a Cr-free etch on a Novodur P2MC ABS substrate showed little variation with varying exposure time or acid concentration. The adhesion range was 1.12 to 1.70 ± 0.18 N/mm (6.4 to 9.7 ± 1 lbf/in.). There was a slight tendency toward lower values when the acid concentration was 35% versus 30%. The concentration of oxidant in this series was twice the value used in series of Fig. 5.

Molded parts processed on racks through the Cr-free etch and electroless nickel were then electroplated with a copper strike, copper plate, semi-bright nickel, bright nickel and bright trivalent chromium or dark trivalent chromium to automotive thickness specifications. Subsequently these parts were tested for adhesion by thermal cycling three repeats through the following time and temperature sequence: -40°C for 2 hr; RT for 1 hr; 85°C for 2 hr.

Parts were examined for any blistering, cracking or other defects and none were observed. Additionally the parts were scribed with a cross hatch blade through the metal layers and showed no sign of lifting when tape tested. External testing at a molder/plater measured the peel strength of Cr-free etched panels of 0.8 to 1.12 N/mm (4.6 to 6.4 lbf/in.) compared to 1.3 to 1.44 N/mm (7.4 to 8.2 lbf/in.) for a conventional hexavalent chromium etch used as a control.

Parts passed the required five thermal cycles of 80°C, 80% RH, for 4 hr followed by -40°C for 4 hr. The rock chip impact test carried out on parts gave equivalent results to those for conventional Cr etched control parts.

Chromium-free etched molded parts with automotive specification thickness and trivalent chromium top coats were subjected to CASS corrosion testing at an end user site. The durability of the finish on these parts showed acceptable appearance after CASS up to 96 hr, at which point the test was discontinued. The plated finish used in these tests was:

Semi-bright nickel:	15 - 17 μm
Bright nickel:	10 - 12 μm
Trivalent chromium:	0.3 - 0.5 μm

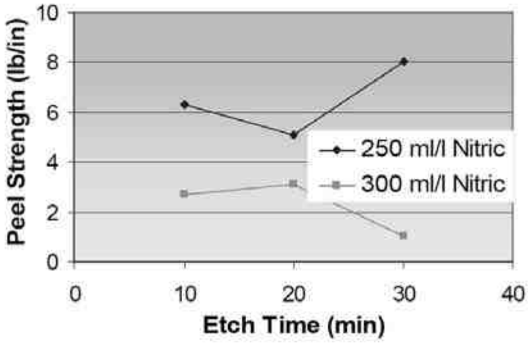


Figure 4—Adhesion of copper foil to Cycolac ABS exposed to a Cr-free etch at different acid contents and times.

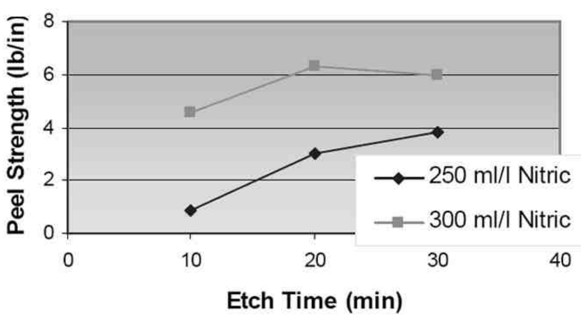


Figure 5—Adhesion of copper Foil to Novodur ABS exposed to a Cr-free etch at different acid contents and times.

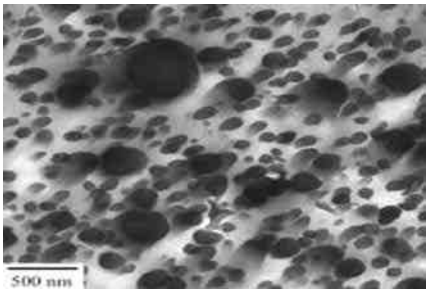


Figure 6—TEM of butadiene particles after OsO_4 stain in Cycolac EPBM3570.

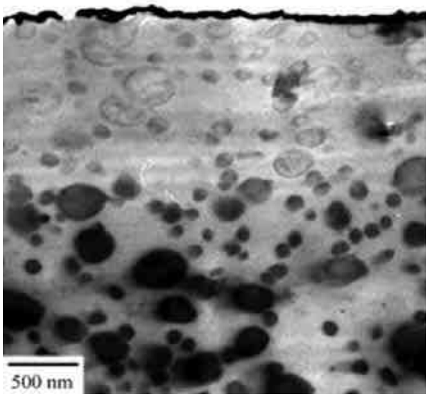


Figure 8—TEM of Lustran PG 298 after OsO_4 stain, showing surface skin effect of butadiene particles near the surface.

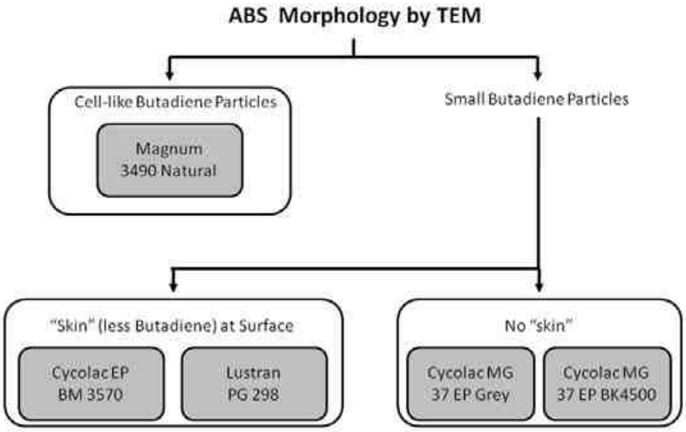


Figure 7—ABS morphology of butadiene particles from different ABS grades and sources.

The results of the CASS testing were as follows:

	Appearance	Corrosion
After 72 hours:	10/10	10/10
After 96 hours	8/10	10/10

Note: Slight pitting in the chromium layer.

Surface chemistry

In terms of surface chemistry and mechanism of adhesion, Table 1 shows the XPS analysis of the surface before and after Cycolac MG37 EP ABS materials were exposed to the etch solution. The XPS data shows that significant oxidation occurred in and on the surface by the rise in %O and the decrease in %C. In addition, there is some concentration of the metal oxidant from the etch solution at the interface of the peel adhesion. Also some nitration of organic groups is observed as well as some minor attack and reduction of acrylonitrile sites in the polymer.

Table 1
XPS of ABS before and after exposure to etch

	Average Surface Composition (XPS), Wt%								
	N-C	NO_3^-	C	O	Cl	$SO_4^=$	$S^=$	Si	M1
ABS Cycolac MG 37 EP untreated	4.34	nd	88.58	5.19	nd	0.09	0.06	1.75	
ABS Cycolac MG 37 EP (15 min etch) + 1 min pre-swell)	2.85	1.88	49.29	13.95	2.10	0.16	0.48	nd	23.18
ABS Cycolac MG 37 EP etched 10 lb/in - foil back	3.10	0.60	75.20	10.90	1.18	0.21	nd	0.82	5.50
ABS Cycolac MG 37 EP etched 10 lb/in - plastic side	3.60	0.30	79.30	6.40	1.11	0.13	nd	0.42	8.10
Averages and standard deviations were calculated using five 800×800 μm analysis areas.									
The surface compositions are calculated neglecting H, which is not detectable by XPS.									

ABS/PC

More frequently, auto trim parts are being specified with ABS/PC resin blends with varying concentrations of polycarbonate in the matrix to increase the maximum deflection temperature, impact strength and improve durability for exterior parts compared with pure ABS resin grades.

The new Cr-free etch was tested with several grades of commercial ABS/PC blends to assess adhesion performance and cosmetics. In the case of Bayblend T45 alloy, varying exposure times, metal oxidant concentrations and nitric acid contents resulted in a range of adhesion from 0.65 to 1.12 N/mm (3.6 to 6.4 lbf/in.). Values greater than 0.88 N/mm (5 lbf/in.) were more consistently achieved when the acid concentration was low, the immersion time was low and the oxidant concentration was low. For some ABS/PC blends with higher PC contents such as Cycolloy CP 8320, a conditioner was inserted in the line prior to the etch to achieve 0.70 N/mm (4 lbf/in.) foil peel adhesion. In both alloys, the cosmetic appearance of the parts after plating was excellent.

Summary

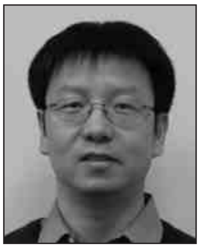
A new non-Cr^{+6} etchant for ABS and ABS/PC has been developed to meet the requirements for metal adhesion to commercial resin grades and meet the end use requirements of the auto, cosmetics/plumbing and consumer electronic users of electroplated plastic.

References

1. U.S. Government OSHA PEL Standard for Chromium(VI) 1910.1026, 2006.
2. W.A. Waters, *Mechanisms of Oxidation of Organic Compounds* (*Methuen's monographs on chemical subjects*), London, UK, 1964.
3. L. Naruskevicius, *et al*. (Enthone), International patent WO 00/29646, 2000.
4. M. Baranauskas (Shipley), U.S. Patent 6,610,365, 2003.
5. J.E. McCaskie & C. Tsiamis, *Plating & Surface Finishing*, **69** (7), 50 (1982).
6. F. Forster & J. Springer, *Metalloberflache*, **40** (10) 417 (1986).
7. D.A. Dillard, *et al*. (Crown City), U.S. Patent 4,315,045, 1982 and U.S. Patent 4,309,462, 1982.
8. G.N. Patel, *et.al*. (JP Labs), U.S. Patent 5,591,354, JP Labs, 1997.
9. H.S. Chao, *et al*. (GE), U.S. Patent 5,316,867, 1994.
10. Addiposit PA process, Rohm and Haas Electronic Materials, Freeport, NY.
11. Delrin™ Etch IDS 610030-E, Rohm and Haas Electronic Materials, Freeport, NY
12. T. Nagao, *et al*., "Chromic Acid Etching-free Plating Process Using ABS Alloy Resin," *Proc. NASF SUR/FIN 2006*, NASF, Washington, DC, 2006.

About the Authors

Walter Sommer has worked as a Senior Research Chemist for Rohm and Haas Electronic Materials for the past 22 years. He holds a Master of Science degree in Chemistry from Adelphi University and a Bachelor of Arts degree from Queen's College of the City University of New York. Walter's areas of expertise include electroless metallization chemistries and copper electroplating processes.



Kai Wang is currently a Research Chemist in Packaging and Finishing Technologies Division, Rohm and Haas Electronic Materials. He has a Ph.D. from the Dept. of Materials Science and Engineering, Pennsylvania State University (2002). His research interests are in the area of plating on plastics and metal finishing.

Neil Brown is Research Manager at Rohm and Haas Electronic Materials, Packaging and Finishing Technologies Division in Freeport, NY. He is responsible for the development of finishing processes for connector, semiconductor packaging and industrial finishing applications. Neil received his B.S. degree in Chemical Engineering from Rensselaer Polytechnic Institute. During his 22 years at Rohm and Haas, he has held various positions within the R&D group and holds a number of patents in the area of electroplating and surface finishing.

Dr. Jack McCaskie is currently Sr. Business Manager, Finishing Technology, Rohm Haas Electronic Materials, in Freeport, New York. He earned his Ph.D. from the University of California - Los Angeles (UCLA). He has held senior positions in R&D with Lea Ronal, M&T Chemicals, M&T Harshaw, Atotech and Atofina over last 35 years. In that time, he has authored numerous patents and publications in chemistry, material science and surface finishing.