2007 SURFIN Technical
Section Plating on Plastics:

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

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

Abstract

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 plastic pretreatment process.[1] Many of the alternatives have met one or another requirement but suffered with limitations when compared to conventional chrome 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 (Daicel Co.) 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]

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[1] US Government OSHA PEL Standard Chromium(VI)1910.1026, 2006
[2] W.A.Waters, Mechanisms of Oxidation of Organic Compounds, London, 1964
[3] WO 00/29646, Enthone
[4] US Patent 6,610,365, Shipley
[5] McCaskie and Tsiamis, Plating and Surface Finishing , 69,July 1982
[6] Forster and Springer, Metalloberflache, 40(10) 417-421, 1986.
[7] US 4,315,045A1 and US 4,309,462A1, Crown City
[8] US Patent 5,591,394, JP Labs.
[9] US Patent 5,316,867, General Electric
[10] Addiposit PA process, Rohm Haas Electronic Materials
[11] Delrin™ Etch TDS 610030-E, Rohm and Haas Electronic Materials
[12] T. Nagao, et.al., Chromic Acid Etching –free Plating Process Using ABS Alloy Resin, Surfin 2006

In general, all of the previous non-hex chrome etch systems had limitations such as higher cost of chemicals, with even higher cost if process solution is not capable of regeneration. In addition, adhesion may be too low for commercial requirements or the process was limited to specific non-ABS plastics. Also some processes would 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 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 5 lb/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 Chrome top coat
(Heat Soak 70°C, 1hr before TC testing)
cycle time and temperatures for this sequence are in line with current practice

The etch itself consists of dilute nitric acid and 2 oxidants which synergistically treat the polymer surface to enhance adhesion of subsequently applied metal films.

The conventional etch formulation used to pre-treat ABS and ABS/PC is 3.4 M $CrO_3.H_2O$ and 3.4M H_2SO_4.

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

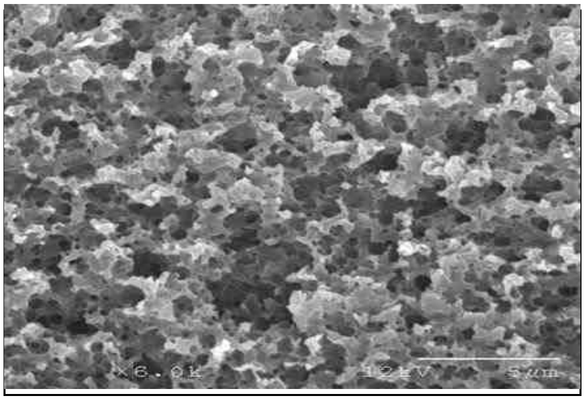

Figure 1. Cycolac MG37 EP ABS exposed to 3.4 M H2SO4 and 3.4 M CrO3 160F, 8 min.

Peel strength of copper foils (40 micron thickness using ASTM B533-85 test conditions) were 9-10 lb/in width with either electroless copper or electroless nickel as the first layer. These measurements were made after annealing test panels (1 hr, 70C).

By contrast the Cr free etch systems produces a different surface morphology and should be designated a milder etched surface when compared with chrome/sulfuric.

In Figure 2 and 3 we show 2 different ABS substrate after exposure to the Cr etch solution.

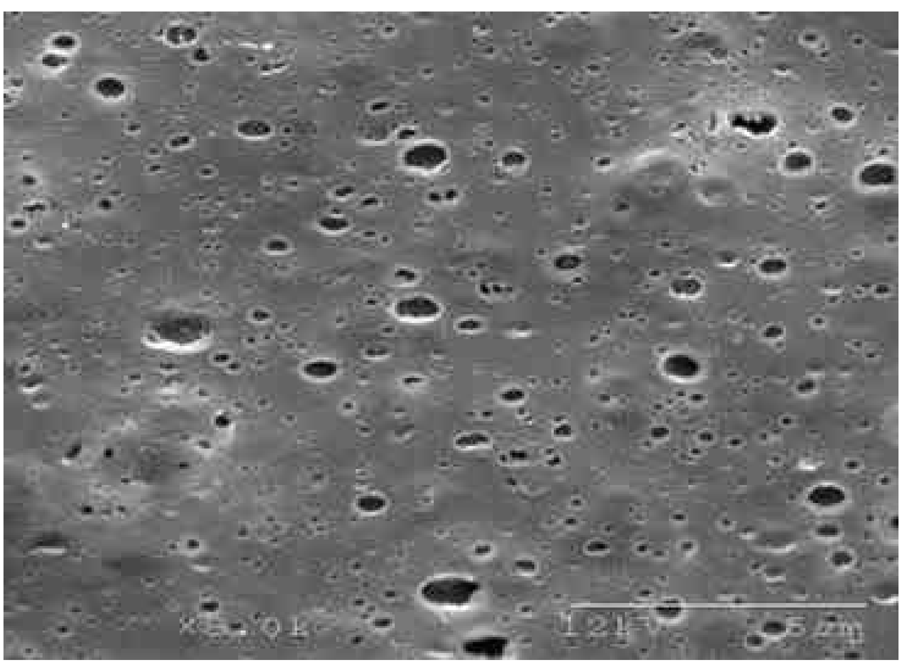

Figure 2, Cycolac MG37 EP, exposed to etchant 30 min., 160 F

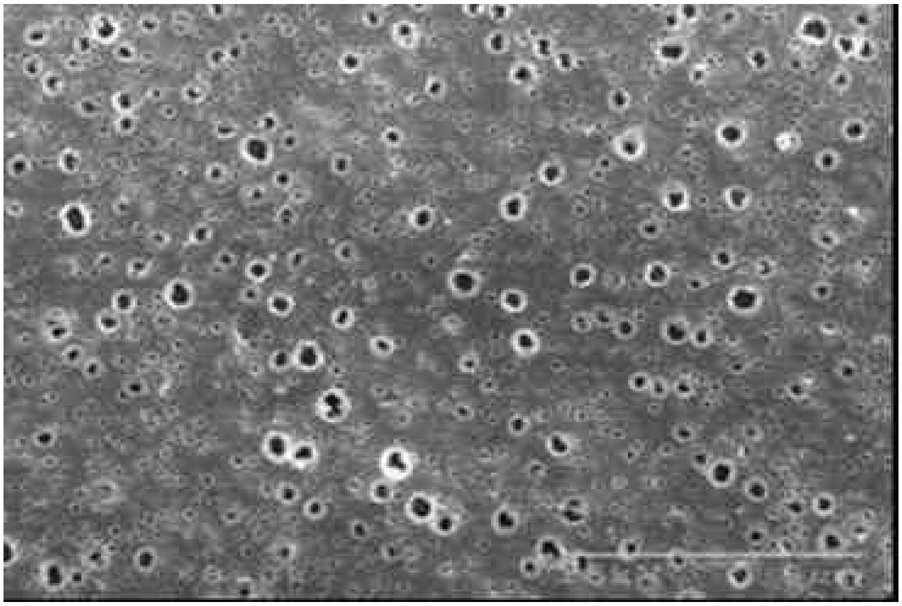

Figure 3 ABS Novodur P2MC after etch 15 min , 160F

The depth and size of the microporosity is different than the surface produced in Chrome/sulfuric and also different from one ABS grade to another depending upon the size and distribution of what appear to be butadiene islands in the acrylonitrile/styrene matrix.

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

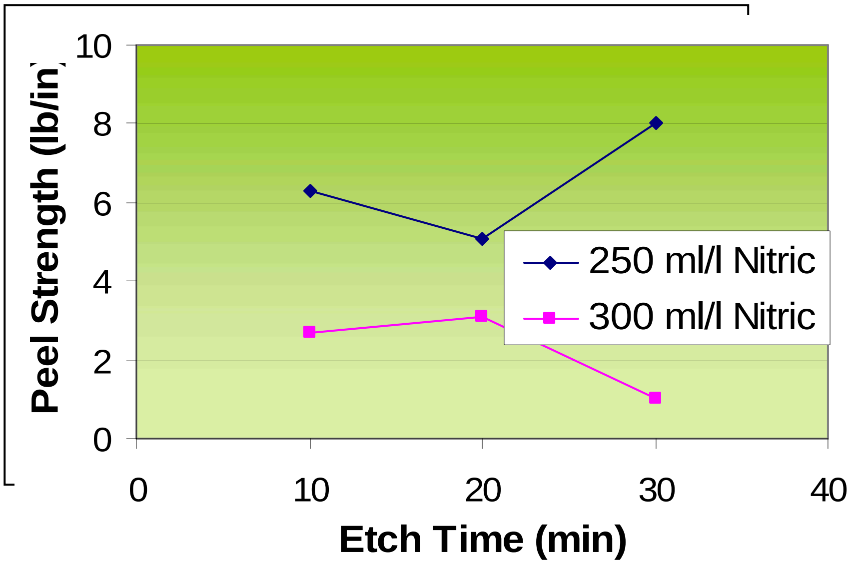

Figure 4.
Adhesion of Copper foil to Cycolac ABS exposed to Cr free etch at different acid content and time

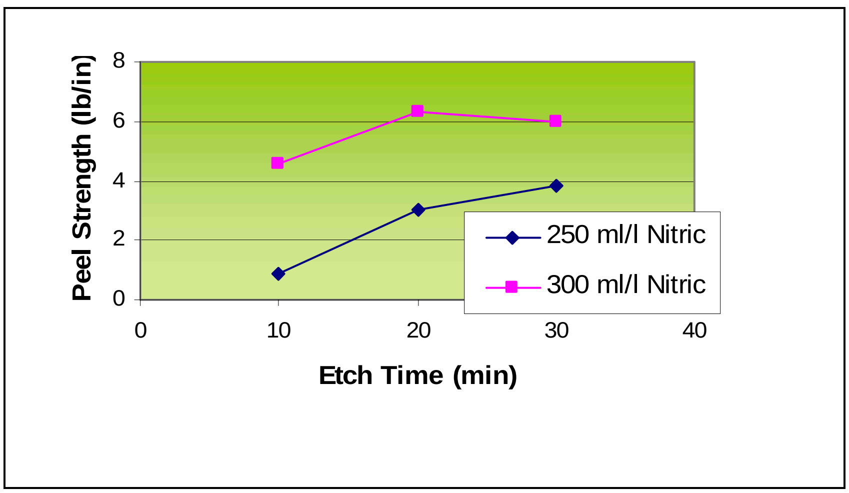

Figure 5. Adhesion of Copper Foil to Novodur ABS exposed to Cr free etch at different acid content and time

In Figure 6 we show a TEM of 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 and different grades can have a skin effect in which there is less BD particles at the surface of the mold and other grades in which there is no skin effect and BD is uniformly distributed at surface and bulk. Figure 7 shows a diagram of this. Figure 8 shows a skin effect in a Lanxess ABS product PG 298.

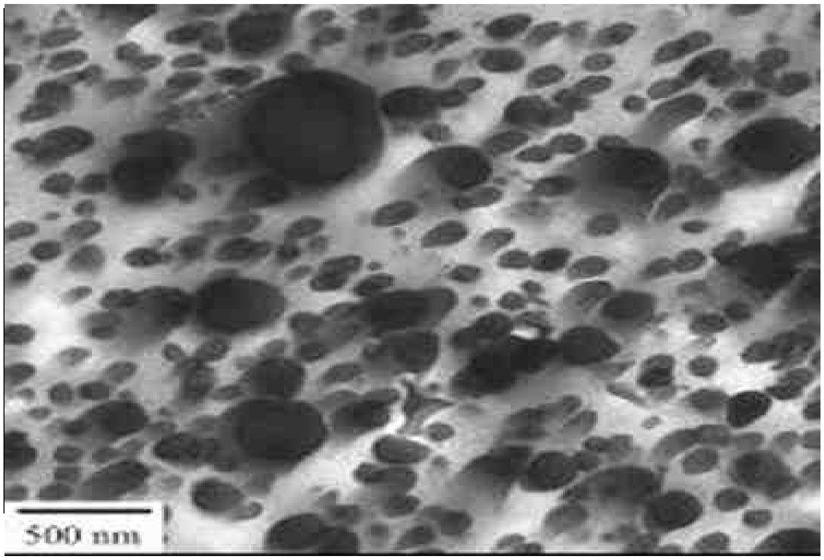

Figure 6. TEM of BD particles by OsO_4 in Cycolac EPBM3570

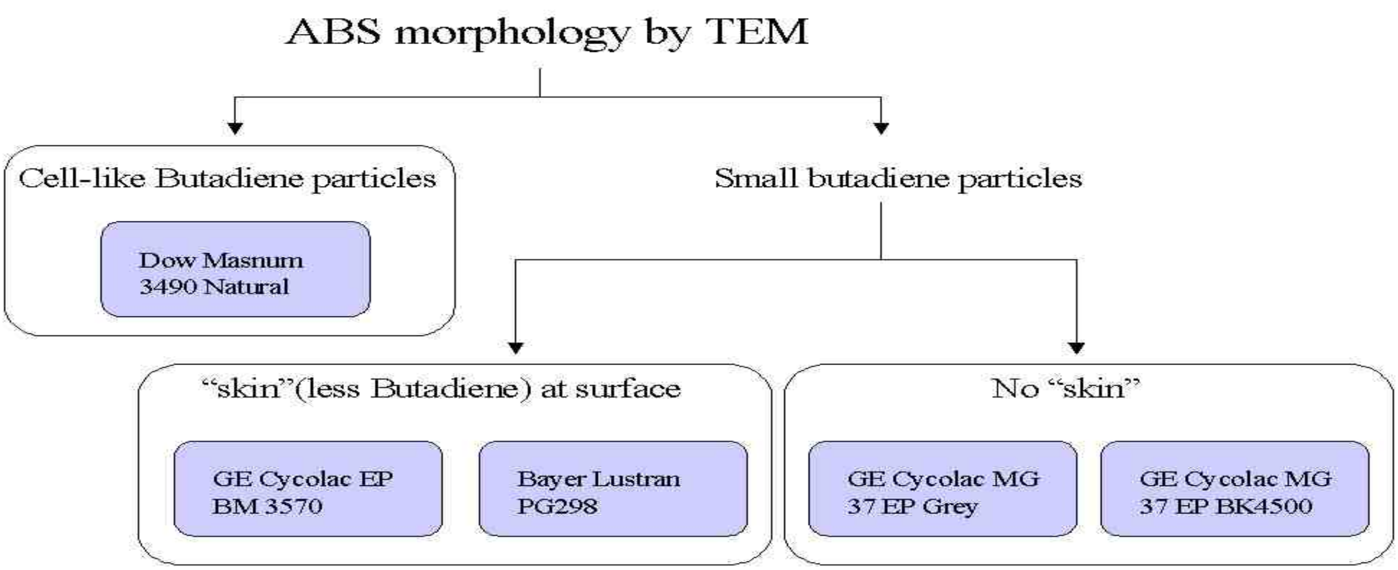

Figure 7. ABS Morpholgy of BD particles from different ABS grades and sources

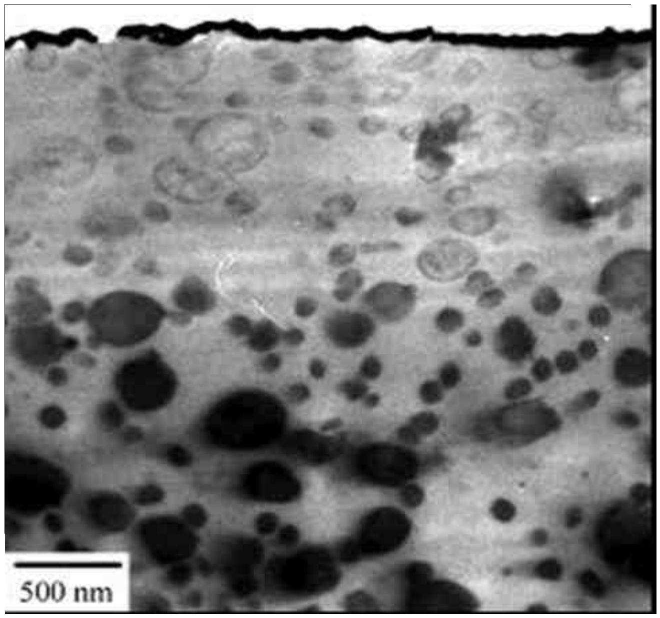

Figure 8. Lustran PG 298 TEM after OsO4 stain showing surface skin effect of BD particles near surface

The adhesion values obtained by pull test of copper foil with Cr free etch and Novodur P2MC ABS substrate showed little variation with varying exposure time or acid concentration. The adhesion range was 6.4 to 9.7 +/- 1 lb/in. There was a slight tendency toward lower values when acid was 35% vs 30% concentration. The concentration of oxidant 1 in this series was 2x the value used in series of Figure 5.

Molded parts processed on racks through the Cr free etch and Electroless nickel were then electroplated with copper strike, copper plate , semi bright nickel, bright nickel and bright trivalent chrome or dark trivalent chrome to automotive thickness specifications. Subsequently these parts were tested for adhesion by thermal cycling 3 repeats through the following time and temperature sequences :
-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 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 0.8-1.12 N/mm(4.6-6.4lbf/in.) compared to 1.3-1.44 N/mm(7.4-8.2 lbf/in) for Cr 6 etch controls.
Parts passed the required 5 cycles of thermal cycles 80°C, 80% Rel. Humidity 4 hrs followed by -40°C 4 hr. The rock chip impact test carried out on parts gave equivalent results to Cr etched control parts.

Chrome free etched molded parts with automotive specification thickness and trivalent Chrome 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, after which the test was discontinued.

Semi-bright nickel: 15 - 17 microns
Bright nickel: 10 - 12 microns
Trivalent chrome: 0.3 - 0.5 microns

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 of the chrome layer.	

SURFACE CHEMISTRY

In terms of surface chemistry and mechanism of adhesion, Table 1 shows XPS analysis of the surface before and after Cycolac MG37 EP ABS materials were exposed to the etch solution.

Table 1 XPS of ABS before and after exposure to etch

				Average Surface Composition (Wt %) XPS					
	N-C	N O3	C	O	Cl	S ulfate	S ulfide	Si	M1
ABS Cycolac MG 37 EP	4.34	nd	88.58	5.19	nd	0.09	0.06	1.75	
ABS Cycolac MG 37 EP 15 min etch	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. f	3.1	0.6	75.2	10.9	1.18	0.21	nd	0.82	5.5
ABS Cycolac MG 37 EP etched 10 lb/in. p	3.6	0.3	79.3	6.4	1.11	0.13	nd	0.42	8.1
Averages and standard deviations were calculated using 5 (800umx800um) analysis areas									
The surface compositions are calculated neglecting H, which is not detectable by XPS									

The XPS data shows significant oxidation has occurred in and on the surface by the rise in O% and 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.

ABS/PC

More frequently, auto trim parts are being specified with ABS/PC resin blends with varying concentrations of PC 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 3.6 to 6.4 lb/in. Values greater than 5 lb/in were more consistently achieved when acid was low, time was low and oxidant was low.
For some ABS-PC blends with higher PC content such as Cycolloy CP 8320 a conditioner was inserted in the line prior to the etch to achieve 4 lb/in foil peel adhesion. In both alloys, 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.

