A Direct Plate Process for ABS and ABS/PC without use of Pd Catalyst or High Chrome Etch

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This paper outlines the process sequence and performance tests for decorative plated plastics, which have been plated using a new process containing no palladium and very low concentration of Cr VI salts. The function and influence of each process step on the final performance requirements of adhesion and appearance of the plated parts will be discussed. Surface analytical and morphological changes in the surface will also be examined as function of process conditions in an attempt to better understand the mechanism of surface reaction and adhesion with the new process. The benefits of such a process are significant for cost, environmental, and productivity reasons in decorative plating of ABS and ABS/PC blends.

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Introduction

In the last fifteen years, commercial processes for plating on plastics and printed circuit board metallization have been developed, which directly electroplate the modified surface without the use of intermediate electroless copper or electroless nickel deposition. The purpose of these shortened process cycles has been to improve productivity, reduce costs, reduce hazardous materials in workplace, and reduce metal bearing sludge requiring disposal. For example, elimination of electroless Ni can eliminate the use of ammonia and elimination of electroless Cu eliminates use of formaldehyde inside the plant and complexants in the waste stream. These direct plate processes generally have the following basic steps:

- surface preparation
- activation
- reduction or exchange
- nickel or copper electroplate

A non-comprehensive list of commercial direct plate processes includes the following: Conductron DP™, Ronapop DP, Crimson 1™, and Ecoposit™[1], Futuron® and Neopact [2], Envision DPS™ and Plato[3]. A direct plate process, in terms of total steps, is considerably shorter in time and number of steps than the conventional pre-plate (see Table 1). For example, some processes claim as much as 65% increase in productivity.

Table 1. Comparison of Various Process Schemes for Plating ABS

Colloidal Pd/Sn	Ionic Pd	Direct Plate Pd	Direct Plate 2[4]	Direct Plate 3[5]
Cr03/H2SO4 Rinse Neutralize Rinse pre-activator	Cr03/H2SO4 Rinse	Cr03/H2SO4 Rinse Neutralize Rinse Pre-activator	Cr03/H2SO4(3.2/4.0M) Rinse	CrO3/H2SO4(0.1/14.8M) Rinse
Activator Pd/Sn Rinse	Pd+2 Activator Rinse	Activator Pd/Sn Rinse	Activator non Pd	Activator non Pd
Accelerator Rinse Electroless Ni/Cu Rinse Electrolytic Cu or Ni	Reduction Electroless Ni Rinse Electrolytic Cu or Ni	Exchange Step Rinse Electrolytic Cu or Ni	Rack cleaning Conductor solution Rinse Electrolytic Ni	Conductor solution Rinse Electrolytic Ni

Applications using direct plate in printed circuit board manufacture have included process schemes for copper clad epoxy glass laminate, as well as more exotic dielectric substrates.[6] For plating on plastics, the processes were developed to directly plate ABS and ABS/PC substrates for sanitary, hardware, and auto-parts applications. In conventional plating processes using

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[1] Processes available from Rohm and Haas Electronic Materials

[2] Processes available from Atotech

[3] Processes available from Cookson Electronics

[4] A. Koenigshofen, P. Pies and A. Moebius, *Proc. 24th Ulmer Gespraech*, p.38-43 (May 2002).

[5] Ecoposit™, Rohm and Haas Electronic Materials

electroless coating, 85 to 90% of all plated plastics substrates for a wide range of industrial applications are formed from ABS polymer (acrylonitrile Butadiene styrene) and its alloys with polycarbonate. In the last 25 years, ABS polymer usage has grown almost fivefold to reach 150MM MT (300MM lbs) of resin or 90-150 MM m^2 (900MM- 1,500MM ft^2) of plated surface area. The material is plated in all major industrial regions of Asia, Europe, and North America for markets in auto parts (60% for exterior and 15% interior), plumbing (10%), appliance (10%), and for other uses (5%). Other materials which are being electroplated are polypropylene, approximately 10% and mineral filled nylons 5%.

Historically, plated plastic was prepared by first mechanically roughening the part surface in bulk operations followed by a precious metal catalyst and an electroless metal coating. Parts were then transferred to another barrel for electroplating in bulk. Later, to increase throughput and improve economics, large scale, straight through processing of piece parts mounted on insulated rack fixtures were processed through a chemical etch solution, a colloidal palladium tin catalyst and electroless step followed by electroplate.

Experimentation

A Kratos Axis-Ultra X-ray photoelectron spectrometer was used to collect XPS data with a monochromatic Al Kα (1486eV) x-ray source. This source was operated at 300W (25mA). High resolution data was collected using a pass energy of 40eV and 0.05eV steps. Data was collected from at least 5 (1mm diameter) analysis areas per sample. Elemental compositions were calculated and curve fitting routines were performed with CasaXPS software.

Surface Modification

This first step in plating non-conductive materials is commonly called the etch step and for most polymers of commercial interest in POP, the etch composition consists of an oxidizing acid that chemically and mechanically changes the surface of the plastic. Over the years, various formulations have been used, including high and low concentration of chromium trioxide in sulfuric acid and water and also sometimes containing phosphoric acid.[6] Literature also cites persulfate/sulfuric and iodate/sulfuric mixtures for oxidizing the plastic surface.[7] All etchants produce reactions on the surface which provide both chemical and mechanical binding cites for exchange and absorption of catalytic ions and species, which promote electroless or direct plating coverage in subsequent process steps. For some plastics, notably ABS/PC, especially with PC content >35%, wider process window is achieved when the blend is exposed to an aqueous organic swellant/conditioner before the etch step. This conditioner softens and swells the surface to some extent and allows for a deeper and more uniform etch of these blend materials.[8]

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[6] R. Weiner, ed., *Electroplating of Plastics*, Finishing Publications (1977).
[7] Shipley Co. (now Rohm and Haas Electronic Materials) US Patent 6,610,365 B2
[8] DE 2623716 Crown City Plating

Since the plastic parts are most commonly processed on racks that go through sequential immersion in all pre-plate and electrolytic steps during the metallization process, the rack coating insulation, commonly made from vinyl compounds, is designed to adsorb less catalyst, which might promote rack plating in the electroless step. In direct plate processes, this difference between reactivity of rack surface and part surface must be preserved in order to provide economic and quality advantages to justify the adoption of these new processes.

In the Direct Plate 3 process above, the etch is a very low Cr, high sulfuric acid aqueous mixture which produces acceptable adhesion (>20N/25mm, 4.0 lb/in) and good part finishes. Thermal cycle requirements for auto parts and water immersion cycles for sanitary applications have been met by this process. ASTM peel adhesion test values for various commercial grades of ABS and ABS/PC[9] are listed in Table 2.

Table 2. Copper Foil Adhesion Peel Test Results for Various ABS and ABS/PC Substrates after ECOPOSIT™ Process

Substrate Grade	Adhesion N/25mm
Magnum 3490 Natural	20+/-2
Magnum 3490 Grey	27+/-2
Cycolac MG37EP Grey	29+/-2
Lustran PG 298	20+/-2
Novodur P2MC	38+/-3
Cycolac EPBM 3570	30+/-3
Cycoloy 1300 45%PC	10+/-1

Some of the variation in adhesion levels may be due to differences in size and distribution of Butadiene rubber particles in the ABS matrix of different commercial grades. Manufacturers of ABS use different polymerization systems to make the material. The rubber particles are more easily oxidized than the styrene acrylonitrile part of the resin. For example, melt flow ratio, impact strength, elongation at break, and tensile modulus variations for Lustran PG 298 (1), Cycolac MG37 EP (2) and Magnum 3490 (3) indicates less rubber (1), more rubber (2) and larger rubber particles with less rubber (3) respectively.

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[9] ASTM B-533

Several of these samples were examined by TEM after OsO4 staining to characterize size and distribution of the rubber particles in various ABS grades. The key differences are outlined in Figures 1-4 below.

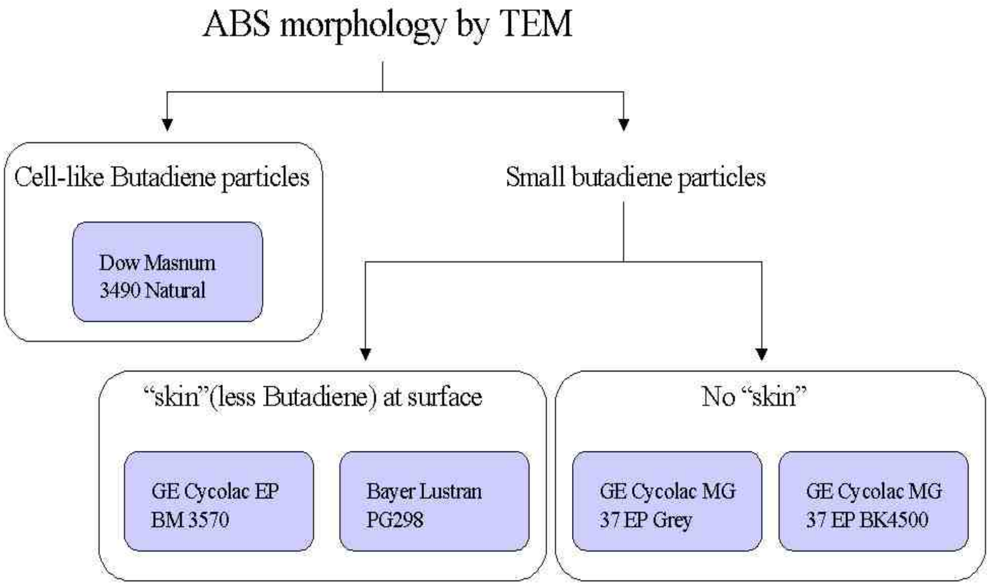

Figure 1. Type and distribution of Butadiene rubber particles in commercial ABS samples (Note: "Skin" is defined as a layer of about 100 micron thick that contains significantly less rubber particles.)

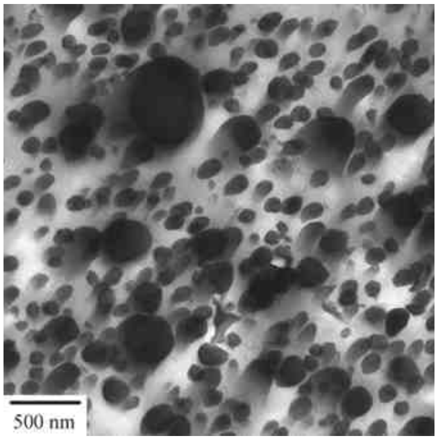

Figure 2. TEM of Cycolac EPBM 3570 after OsO4 staining

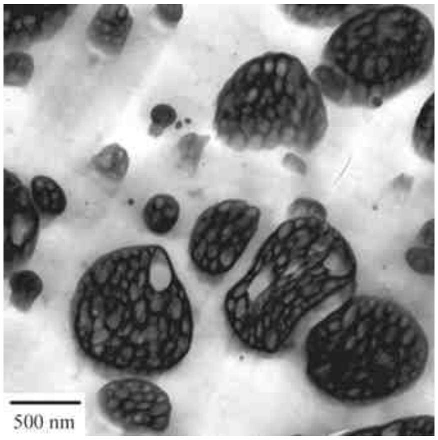

Figure 3. TEM of Magnum 3490 Natural after OsO4 staining

OsO4 selectively reacts with carbon-carbon double bonds in unsaturated rubber particles and enhances the contrast with increased electron scattering.

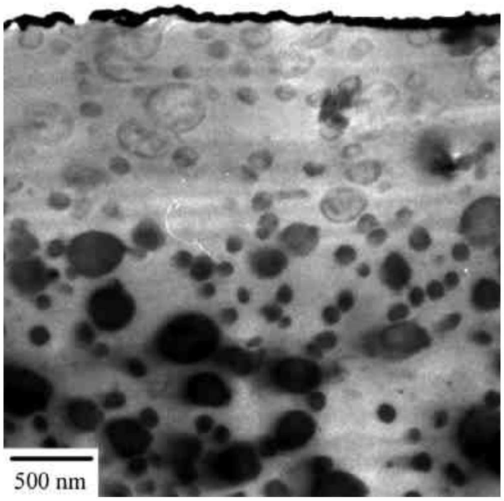

Figure 4. TEM of Lustran 298 after OsO4 staining (Note: "Skin" region at top.)

SEM picture (Figure 5) of an ABS surface exposed to 0.1M CrO3/14M H2SO4 appears less attacked compared to the same material exposed to 3.75M CrO3 /3.8 M H2SO4, which is commonly used in conventional etch systems for straight through processing of plated ABS plastic today (Figure 6).

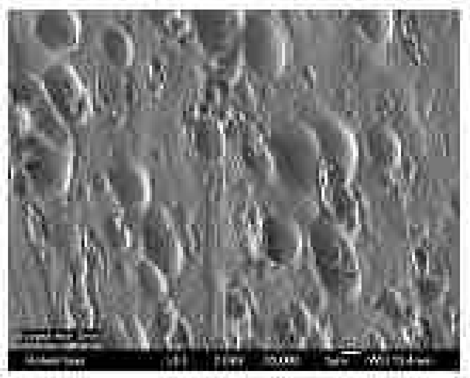

Figure 5. Magnum 3490 etched in 0.1M CrO3/14M H2SO4 x 500

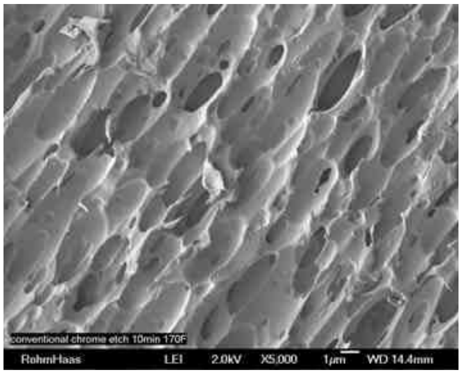

Figure 6. Magnum 3490 etched in 3.7M CrO3/3.8M sulfuric acid

Table 3 shows results of examination by XPS of the interface, backside of copper foil, and mating face of ABS base, on peel test specimens, which had been processed through Direct Plate 3 and copper plated.

Cohesion separation occurred within the ABS or the sulfonated ABS layer. No Cr or Cu was detected on either side of the interface. There appears to be a trend in that the interfaces with peel strengths below 30N/25mm have very low sulfur concentrations with slightly more sulfur on the foil side of the interface. This would suggest the cohesion separation in the polymer is occurring at or slightly below the sulfonation layer.

The two Cycolac MG37EP samples that yielded the peel strengths over 30N/25mm have the highest sulfur concentrations at the exposed interface. The sulfur concentrations are very similar, which suggest cohesive failure in the sulfonation layer. There is also evidence of a small amount of Mx and reduced S at these interfaces, as well.

Table 3. XPS of Interfaces of Copper Plated ABS Peel Test Specimens

	Average Interfacial Composition (weight percent)						Adhesion N/25mm
	C	O	N	S Ox	S=	Mx	
MAGNUM 3490 ABS side	92.6	3.9	3.3	0.1	nd	nd	21
MAGNUM 3490 Foil side	92.5	3.9	3.5	0.1	nd	nd	21
CYLOLAC EPBM 3570 ABS side	93.4	1.3	5.2	0.1	0.0	nd	26
CYLOLAC EPBM 3570 Foil side	92.1	2.9	4.7	0.3	0.0	nd	26
CYLOLAC MG37EP GRY ABS side	84.3	8.3	4.9	2.4	0.1	0.0	30.5
CYLOLAC MG37EP GRY Foil side	84.6	7.8	5.4	2.1	0.1	0.1	30.5
CYLOLAC MG37EP BLK ABS side	88.8	3.5	6.4	1.1	0.1	0.1	35
CYLOLAC MG37EP BLK Foil side	88.8	3.7	6.4	1.0	0.0	0.0	35

The XPS surface analysis of the etched and un-etched plastic surface is shown in Table 4. C, O, S, N, and Cr are measured and normalized to 100 weight percent. This data indicates the reaction with the etch chemicals produces oxygenated species, especially as -SO3H acid groups at the surface are detected as a function of exposure time to etch and rinse step. These groups are responsible for ion exchange reaction with subsequent metals used to make the surface conductive.

Table 4. XPS Data on Surface Analysis of ABS Etched in 0.1M CrO_3/ 14M H_2SO_4, 3min, 50C

Average Surface Composition in Weight% by ESCA Analysis					
	C	O	N	S Ox	Cr
ABS as received	86.9	6.2	5.3	nd	nd
ABS etched	64.2	24.6	4	5	1.8

By comparison with the data in Table 4 for ABS treated in very low Cr VI/ high sulfuric acid, the SOx level is much lower in Table 4a. This could mean that ion exchange when it occurs on this surface is more likely at sites with carboxylic acid or alcohol functional groups, which are weaker cation exchange groups than –SO3 group. If the Cr species detected is Cr+3 its relative weight is similar to the percentage on the surface of ABS in Table 4.

Table 4a. XPS Data on Surface Analysis of ABS Etched in 3.8M CrO_3/ 4.0M H_2SO_4, 10min, 76C

Average Surface Composition in Weight% by ESCA Analysis					
	C	O	N	SOx	Cr
ABS as received	86.9	6.2	5.3	nd	nd
ABS etched	62.9	22.4	4.8	0.28	6.1

In Table 5, WXDRF spectra of the etched and rinsed sample of ABS shows increase in S % as function of etch time and some loss of this layer at extended rinse time. The Cr is most likely Cr+3 ion, which is probably associated with ion exchange at sulfonation sites formed in the etch step.

Table 5. WXDRF Data of ECOPOSIT Etched and Rinsed ABS

Sample ID: GE MG37EP	Wt% S	50% intensity from	Wt% Cr	50 % intensity from
etch = 1 min; rinse = 45 sec	0.307	21u	0.0026	300 u
etch = 1 min; rinse = 5 min	0.232	20u	0.0018	287 u
etch = 3 min; rinse 45 sec	0.478	21 u	0.0030	296 u
etch = 3 min; rinse = 5 min	0.337	19 u	0.0020	281 u

Cr LOD = ~5 ppm based on software calculations

Roubal[10] and McCaskie[11] showed that polymers exposed to SO_3 dry gas, followed by wet ammonia neutralization, formed sulfonation sites on the surface and underwent ion exchange reactions with catalytic metals. Depending upon the subsequent treatment used after exposure to SO_3 gas, the treated plastics could be electroless coated or plated directly. Adhesion of the copper foils from these processes were similar to the current Direct Plate 3 results, 30-50 N/25mm, depending upon the substrate material and grade. Seita, et.al. also exposed PWB substrates to sulfuric mixtures and achieved ion exchange sites for subsequent catalysis and metallization.[6]

In addition to ABS and ABS/PC resins other plastic types may also be functionalized by this etch, such as polystyrene, polypropylene, some epoxies, phenolics, and polyimides.[8] After exposure of the resin surface to the etch solution the parts are rinsed by immersion in water for an optimum time. It has not been necessary to neutralize the acid or chromium ions on the surface with hydroxide or reducing agents.

Catalytic and Reduction or Acceleration Steps

The catalyst exposure step is necessary to obtain subsequent metallization whether electroless or direct plate. For example, in ionic catalyzation, Pd+2 ion can be complexed at the surface and later reduced to Pd^0. Other ions can also be used and once reduced can initiate electroless deposition. Alternatively, and most widely practiced for straight through processing, colloidal Pd/Sn catalyst is adsorbed on the etched surface and subsequently stripped of the protecting Sn shell in an accelerator.[12] This palladium metal can initiate electroless deposition.

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[10] J.Roubal, *Metallization of Plastics by the SAN Process*", Galvanotechnik, 75/7, p.845-851, (1984).

[11] J.E.McCaskie and C.Tsiamis, *A Gaseous Acid Etch System to Prepare Plastics for Plating*, Plating and Surface.Finishing, p.50-54, (July 1982).

[12] DE 1197720, Shipley Co.

In direct plate processes, the metal catalyst is adsorbed and complexed on the etched part surface. By reaction of catalyst with a subsequent step(s), the surface becomes sufficiently conductive to allow direct electrodeposition to occur in an electroplating bath. The type, activity and concentration of the catalyst and the subsequent reduced or exchanged form of this catalyst must be sufficiently conductive to allow direct current to pass through this film and build a metal layer across the surface.

In Direct Plate 3 process, for example, following the rinse after etch, the part is exposed to an Activator, a Group VA metal ion in water solution, which ion exchanges with protons on the sulfonic acid groups on plastic surface. Following this exchange, the part is exposed to sulfide reduction with the complexed metal. A very generalized scheme of the surface reactions may be written as:

R-SO3H + Mx → R-SO3-Mx → Reduction or Sulfide treatment →R~~ Mx-Sy film

Electroplating Step

Following the reduction to metal sulfide film on the part surface, the part is capable of being electroplated after further reduction to metal film in the plating step. If the film were intrinsically conductive as the sulfide, it would seem possible to plate many metals directly on this surface film at reasonable deposition rates, which is not the case. Indeed, if copper ion is greater than 20 ppm as a contaminant in the Watts nickel plating bath, no deposition occurs on the part.

Koenighofen, Pies and Moebius theorize that the metals capable of being deposited on the MxSy layer must have a deposition potential more negative than the slightly positive reduction potential of the metal sulfide to metal.[4] Nickel fits this criterion but acid copper does not, since it has a deposition potential higher than the reduction potential of metal sulfide. At the contact, the most electropositive metal, copper in acid solution, would preferentially deposit but the resistance of the metal sulfide film would not allow propagation along the surface of the plastic. The model for the process describes a step wise reduction from MxSy to M^0 building out from the contact and spreading across the plastic surface. Almost simultaneously, the conductivity of the metal film formed from the sulfide is able to support sufficient current at a given minimum voltage to electrodeposit Ni ions on the surface and build an adherent layer of metal over the part. The exact voltage ramp for optimum coverage and adhesion in production is found by a screening experiment within known limits.

The rate of growth of the nickel film across the surface of the conductive plastic has been measured at 5-8 cm/min. Coverage of parts carried on racks made for conventional electroless processing has not been a problem in production. For example, 30cm long shower fixtures with 3 contacts have covered completely in the nickel process within 10 minutes.

Figure 8. Production parts through Direct Plate 3 process after acid copper plating

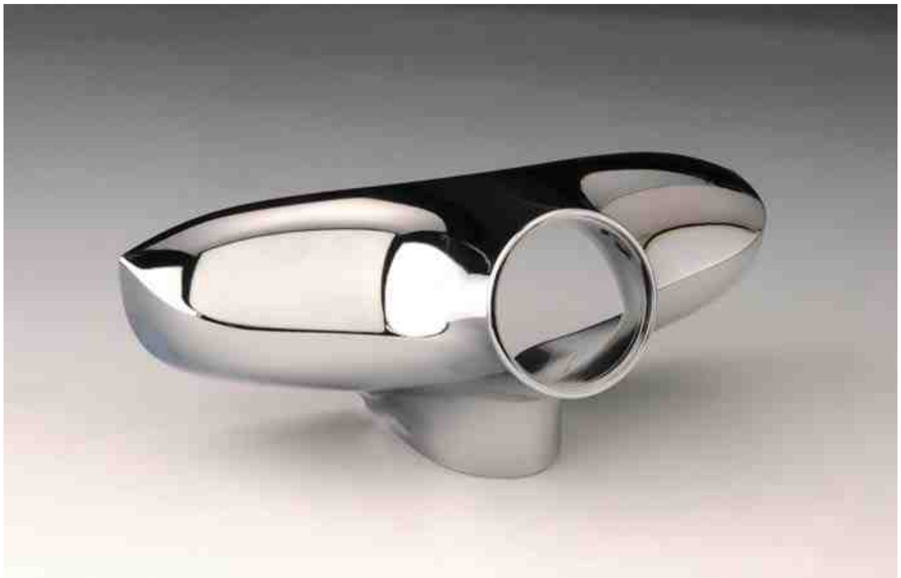

Figure 9. Photo of ABS production part of sanitary ware industry processed in ECOPOSIT^{TM} and copper/nickel chrome

In summary, this new process which uses a very low Cr VI containing etch solution and a metal from Group VA of the periodic table for catalyst has successfully plated ABS and ABS/PC parts on racks in a straight through process sequence. It represents an economical and environmentally friendly method to process various plastics for decorative and functional applications.

Acknowledgment
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