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PLATING OF ABS PLASTIC SUBSTRATE: A REVIEW

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ABSTRACT

ABS stands for Acrylonitrile-Butadiene-Styrene. It is a thermoplastic terpolymermade by polymerizing styrene and acrylonitrile in the presence of polybutadiene. ABS is quite resistant to chemical corrosion and possess good toughness and dimensional stability. It is very easy to machine and has a low melting temperature making it particularly simple to use in injection molding manufacturing processes or 3D printing on an FDM machine. ABS is also relatively inexpensive. Irrespective of all these advantages, ABS has certain short-comings in terms of its mechanical strength, its non-conductivity and property of being easily fretted. Most of these short-comings can be handled by plating ABS with metal. Metal coating on ABS can increase its strength and make it more useful for high temperature applications. ABS is until now the most widely plated plastic because of the ease with which it can be plated. Simple chemical treatment processes are used to coat ABS. This article tries to cover all the aspects related to the plating of ABS including the recent trends and various environment-friendly alternatives to carry out the process.

Keywords: Metallization of plastics, ABS, Electroless plating, Electroplating, Etching, Sensitizing, Activation.

I. INTRODUCTION

The idea of electroplating plastics may seem to be strange because generally we use some sort of plastic coatings over metals to prevent them from corrosion. There are various reasons for choosing plastics as a substrate. One advantage of plastics is that moldings of complex shapes can be produced cheaply, accurately and with good surface finish. Other advantages can be their low density and the fact that they do not corrode. Metal coating on plastic can add various properties to it like electrical conductivity, reflectivity, abrasion resistance etc. Recently metallized plastics have found there usage in various industries like electronic industry, petroleum industry, toys manufacturing industry, automobile industry etc.

The science of plating non-conductors can be roughly divided into two eras – pre-1960 and 1960 to present. Pre-1960, non-chemical methods for plating on non-conductors such as bronzing, graphiting, metallic painting etc. were used. Their characteristics were:

a) Sufficiently thick coating was applied.
b) Adhesion was due to purely mechanical inter-locking.
c) Process involved hand-working.
d) Process permitted plating of any non-conductor.

Post 1960, chemical methods for plating of plastics began to be developed and adopted in the industries. The characteristics of this process are:

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a) Good adhesion was obtained.
b) Adhesion is obtained by the use of chemical conditioning which provide both mechanical and chemical inter-locking.
c) Process can be fully automated.
d) Since chemistry of substrate plays important role, only limited number of plastics can be plated. e.g. ABS and polypropylene.

II. ACRYLONITRILE BUTADIENE STYRENE

ABS plastic began to be used in mid 1940s. Acrylonitrile-styrene co-polymers were in use before but they had certain drawbacks which led to the introduction of third monomer unit i.e. butadiene rubber. The composition of ABS can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene, depending on the usage. ABS is a two phase polymer blend: a continuous phase of styrene-acrylonitrile (SAN) and uniformly distributed fine polybutadiene rubber particles.

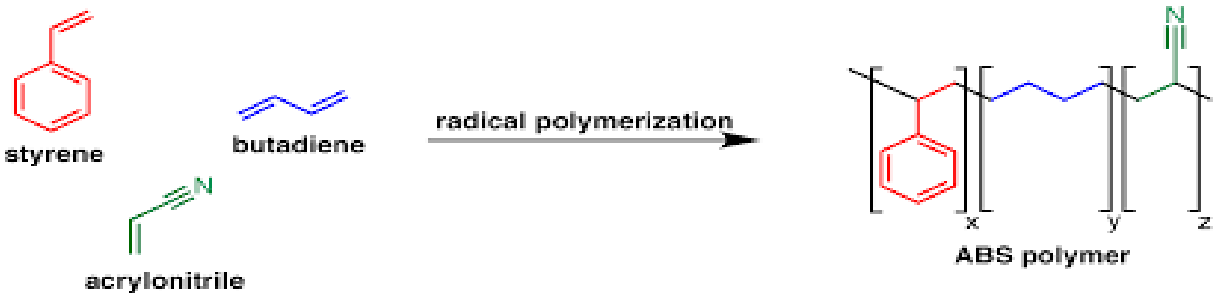

Fig. 1 monomer units and structure of ABS

ABS polymers exhibit a variety of properties that makes it one of the most widely electroplated plastics. It exhibit excellent impact strength with high mechanical strength and rigidity plus long time load carrying capability. In addition, all types of ABS plastics exhibit outstanding dimensional stability, good chemical and heat resistance, surface hardness, and light weight. The properties that are exhibited by ABS can also be engineered according to the requirements. The impact strength can be optimized by carefully controlling the rubber particle size, its distribution and its micro-structure. The toughness can be elevated by increasing the butadiene content and the molecular weight of the SAN phase. Surface gloss values can be controlled by controlling the styrene content. ABS is hydrophobic.

ABS can be easily formed by the various methods of fabricating thermoplastic like injection molding, extrusion, blow molding, vacuum forming, and calendaring. Molded products may be easily machined, riveted, sheared, cemented, laminated, embossed, or painted. Various latest technologies used for the manufacturing of ABS parts are additive manufacturing technologies like Stereolithography Apparatus (SLA), Selective Laser Sintering (SLS), Solid Ground Curing (SGC), Fused Deposition Modelling (FDM) etc.

III. PLATING PROCESS ON ABS PLASTIC

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The molding practices carried out for ABS which will be subsequently plated are quite different from general molding practices. The molding practices have a huge impact on the chemical properties of the ABS at the interface. So, it becomes very important that molding conditions be adjusted to the requirements of the chemical conditioners used subsequently [1-6].E.g.: Moisture control while molding ABS is of utmost importance. Large moisture content while molding causes surface problems which may later form blisters in the electrodeposition. Presence of stress is another parameter which requires attention because they can lead to cracking of the part. To reduce these problems, practices like oven drying of powders, annealing etc. are adopted. Some of the design practices like edges must not be sharp instead it should be made round, blind holes should be avoided, convex surfaces should be preferred than concave ones etc.

ABS surface should be preferably clean before any type of conditioning. However, this is not mandatory. This is because the subsequent conditioners are quite capable of cleaning small amount of contaminations. Sometimes the mold release compounds and routine handling problems like fingerprints etc. require cleaning. Alkaline cleaning solutions can be used for the same. However, it may have to be followed by an acid dip to remove alkaline residues.

Conditioning is the most crucial step in the process of electroplating ABS. It provides inter-locking roughness on the surface and also create sites for chemical bonding of the metals. For ABS the conditioners used are chromic acid and sulphuric acids. The conditioners and other additives are summarized below [7, 8].

1. CrO_3 (75 g/L) and H_2SO_4 (250 ml/L)
2. $K_2Cr_2O_7$ (90 g/L) and H_2SO_4 (600ml/L)
3. CrO_3 (50 g/L), H_2SO_4 (100 ml/L) and HF (100ml/L)

Time may vary from 1 to 5 minutes at about 20°C to 35°C depending upon the desired bonding. These conditioners consist of strongly oxidizing acid mixtures that attack the surface of the plastics in quite controlled manner. These conditioners attack polybutadiene particles preferentially. Various other additives have been suggested in other literatures. Phosphoric acid has been suggested for mild etching [9].Fluorinated surfactants have also been suggested [10]. Permanganates and molybdates can be used as a complete alternative to CrO_3 as oxidants [11, 12].

After Conditioning, the ABS is made catalytic. This builds a thin layer of metal on the plastic surface which catalyzes the chemical plating reaction. It consists of two steps: First is the sensitizing. In this step the ABS surface adsorbs a easily oxidizable sensitizing material. The oxidization of this sensitizer in the subsequent step help in the deposition of the catalytic film on the plastic surface. The composition for this sensitizing solution is

1. $SnCl_2$ (10 g/L)
2. HCl (40 ml/L)

Part is immersed for 1 to 3 minutes at 20°C to 25°C. Periodic addition of HCl is necessary to carry out the reaction. After sensitizing, part must be thoroughly rinsed because excess sensitizer may cause problem in subsequent steps. The aging and the contact angle can effect the efficiency of the sensitizing solution [13, 14].This is followed by nucleation: After thorough rinsing, the part is immersed in nucleating agents which are generally the salts of precious metals such as palladium and gold. When the part is immersed into this solution, the sensitizer previously adsorbed is readily oxidized, reducing the catalytic metal and depositing it in the metallic state at certain locations on the surface. These catalytic locations act as the plating sites in the subsequent electroless plating. The solution used for this nucleation process is

1. $PdCl_2$ (0.25 g/L)
2. HCl (2.50 ml/L)

The duration for immersion is about 1 minute at around 20°C to 40°C. The nature of catalytic sites influence the structure of the subsequently deposited metal [15]. Other approaches for the sensitizing and nucleation process have been formulated in certain literature [16, 17, 18].

Electroless plating is the step where our ABS substrate becomes conductive. Generally, electroless copper and nickel baths are used commercially for plating of plastics. A thin layer varying from 0.1 to 1.5 µm can be developed by this process. The details of the typical copper and nickel baths used for the purpose are given below. Electroless copper bath composition used widely is [19, 20].

a) $CuSO_4.5H_2O$ (15 g/l)
b) $NaHCO_3$ (10 g/l)
c) $NaKC_4H_4O_6.4H_2O$ (30 g/l)
d) HCHO (100 ml/l)

Bath operating temperature is about 15°C to 20°C for 5 to 15 minutes. Here formaldehyde (HCHO) acts as a reducing agent and its reducing power increases with alkalinity, so the pH is generally above 11. Copper salt ($CuSO_4.5H_2O$) is used as a source of copper ions and tartrate ($NaKC_4H_4O_6.4H_2O$) is used as a complexing agent to prevent precipitation of copper hydroxide. Other complexing agents like EDTA[21], amines[22] and glycolic acid[23]can be used.

Electroless nickel baths are preferred over copper baths even after being less catalytic because these baths are more stable than copper baths. The composition used widely is [24]

a) $NiSO_4.6H_2O$ (30 g/l)
b) Sodium citrate (100 g/L)
c) NH_4Cl (50 g/l)
d) $NaH_2PO_2.H_2O$ (10 g/l)
e) NH_4OH (to a pH of 10.5)

Operating time is about 4 to 10 minutes at a temperature less than 40°C. Instead of pure Nickel, the deposition contains about 2% to 5% of phosphorous which may lead to some brittleness. Here hypophosphite acts as the reducing agent. Sodium citrate acts both as buffer and mild complexing agent to prevent precipitation of Nickel hydroxide. The pH of the solution is maintained by ammonium hydroxide.

After electroless plating, conventional acid copper plating is done to build up the thickness of coating and provide it with better bright conductive surface. This is followed by electrolytic nickel plating in order to inculcate corrosion and abrasion requirements.

Various literatures propose different theories for the formation of metal coating on ABS substrate. Among all these theories 'anchor effect theory' provides the most satisfactory explanation [30]. According to this theory, the holes i.e. the anchor points are formed during the surface conditioning step. These holes act as the filling sites in the subsequent metallizing step. Another theory suggests the presence of chemical forces like Van der Waal's forces or valence bond of metals and the charged plastic surface due to the etching process [31].

IV. RECENT DEVELOPMENT IN THE FIELD OF PLATING ABS

The presence of Cr^{6+} in chromic acid is hazardous to human and is considered carcinogenic and is supposed to be the cause of various other problems like causing damage to stomach, respiratory organs, intestines etc. So researchers have been fascinated towards developing more eco-friendly ways to carryout plating of ABS plastics [32, 33].

One strategy employed the use of strong acids as a replacement to the chromium. One literature showed the effect of different combinations of sulfuric acid along with hydrogen peroxide and/or nitric acid [34]. The results obtained were quite satisfactory but were not that intense as achieved by the conventional methods. Another literature discuss the use of a bio-polymer film of Chitosan [35]. This film was used to fix the palladium on the ABS substrate. This process led to the enhancement in the adhesion. Later this method was used to eliminate the use of precious materials like palladium in the metallization process [36]. This Chitosan layer was used to immobilize nickel particles. One of the literature investigated the use of H_2SO_4-MnO_2 colloidal solution as a replacement to the chromium based etching system. One literature showed that the use of precious metal could be avoided. In this the etching was carried out using H_2SO_4-MnO_2 mixture and the particles of copper from the copper sulfate solution were deposited [37]. This eliminated the precious metal activation process. The reduction of the particles was carried out by the use of dimethyamineborane, a reducing agent.

Another strategy developed was the direct metal electrodeposition [38]. This became the popular choice because via this process the complex and costly chemical metallization process could be omitted. The direct metal electrodeposition could be achieved by two steps. First was the chemical deposition of polypyrrole to make the surface conductive and the carrying out the conventional acid copper plating. Another approach in direct metal electrodeposition was to coat aluminum-carbon black containing enamel pastes on the substrate and then the conventional electrolytic coating. However, the samples passed the standard adhesion test at longer deposition time only.

Certain literatures also discussed the use of photocatalytic surface activation as an alternative to the complex chemical surface treatments and the use of precious metals [39]. During the photocatalytic process, the original carbon rings of the ABS are broken and it reacts to the oxygen very quickly. The C=O and C-O groups that gets activated leads the the close contact between the substrate and electroless copper. The adhesion strength was found to increase with the increase of UV power and also with the increase in irradiation time.

VI. CONCLUSION

The use of plated plastics can not only be used to get good texture but the weight of the product can be considerably reduced and in addition to this various properties like appearance, mechanical strength etc can be considerably improved. To achieve this outcome, we have to appropriately choose the path of metallization of plastics. There has been various other literatures that cover the plating of plastics apart from ABS like polypropylene, nylon, polystyrene, polycarbonate etc but still ABS is still the most widely used plated plastic all over the world in various industries like electronics, defense, toys manufacturing, automotive etc.

REFERENCES

Journals:

[1] Weibusch, K., Paper in Proc. Rotofinish Symposium, Oxford (1966); Proc. 7th International Metal Finishing Conference, Hanover. 147 (1968).

[2] Slater, J.R. and Paton, W. Chapter – 16 in Design Engineering Product Finishing Handbook, Ed. Philpott. B.A., Product Journals Ltd., West Wickham (1968).

[3] Rempel, D., Ebneth, H., Christoph, J. and Hoyer, W., Paper in Proc. Of Symposium on Plating in Seventies, Cambridge (1970).

[4] K.A. Klinger, J.J. Randall and J.M. Sakach, U.S. Patent 3,479,160 (1969).

[5] E.B. Saubestre and J.L. Morica, U.S. Patent 3,471,320 (1969).

[6] H. Maekawa, U.S. Patent 3,619,245 (1971).

[7] H. Narcus, Metallizing of plastic, Reinhold, New York, 1960.

[8] F. Pearlstein, Met. Finish., 53 (8), 59 (1955).

[9] E.B. Saubestre and W.M. Emons, U.S. Patent 3,471,313 (1969).

[10] Hepfer, I.V., U.S. Patent 3,515,649 (2.6.70)

[11] W.H. Young, B.Csuthy, and J. Guidess U.S. Patent 3,565,770 (1971).

[12] W.R. Doty and B.D. Knight, U.S. Patent 3,598,140 (1972).

[13] N. Feldstein and J.A. Weiner, Plating, 59, 140 (1972).

[14] N. Feldstein, J.A. Weiner and G.L. Schnable, J. Electrochem. Soc. 1972.

[15] R. Sard, J. Electrochem. Soc., 117,864 (1970).

[16] C.R. Shipley, U.S. Patent 3,011,920 (1961).

[17] E.D. D'Ottavio, U.S. Patent 3,532,518 (1970).

[18] F.W. Schneble, E.J. Leach and J. Polichette, U.S. Patent 3,600,330 (1971).

[19] E.B. Saubestre, Proc. Am. Electroplat. Soc., 46, 264 (1959).

[20] W. Goldie, Plating, 51, 1069 (1964).

[21] O.B. Dutkewych, U.S. Patent 3,475,186 (1969).

[22] O.B. Dutkewych, U.S. Patent 3,383,224 (1968).

[23] L.N. Schoenberg, J. Electrochem. Soc., 118, 1571(1971).

[24] A. Brenner and G.E. Riddell, Proc. Am. Elctroplat. Soc., 33, 23 (1946); 34, 156 (1947); U.S. Patents 2,532,283-4 (1950).

[25] H. Narcus, Metallizing of Platics, Reinhold, New York, 1960.

[26] H.L. Pinkerton, "Preparing Non-conductors for Electroplating", in Modern Electroplating, 2nd ed., F.A. Lowenheim, Ed., Wiley, New York, 1963, p.604

[27] W. Goldie, Metallic coating of plastics, Electrochemical Publications, Hatch End, England, 1968.

[28] Takashi Matsunami, Masahiko Ikeda, Hiroyuki Oka, U.S. Patent 5,908,543 A (1999).

[29] Dapeng Li, Kate Goodwin, Chen-Lu Yand, J. Mater Sci 43, 7121 (2008).

[30] McCaskie JE (2006) Plating on plastics: a survey of mechanisms for adhering metal films to plastic surfaces. Met Finish 104(5):31-39

[31] McCaskie JE, Tsiamis C (1985) Metal plating on plastics. U.S. Patent 4,520,046

ISBN: 978-93-86171-26-9

[32] Wang Z, Li Z, He Y, Wang Z (2011) Study of an environmentally friendly surface etching system of ABS for improving adhesion of electroless Cu film. J ElectrochemSoc 158(11):D664-D670

[33] Li Z, Li N, Yin L, He Y, Wang Z (2009) An environment-friendly surface pretreatment of ABS resin prior to electroless plating. Electrochem Solid-State Lett 12(12):D92-D95

[34] Teixeira LAC, Santini MC (2005) Surface conditioning of ABS for metallization without the use od chromium baths. J Mater Process Technol 170(1):37-41

[35] Tang X, Cao M, Bi C, Yan L, Zhang B (2008) Research on a new surface activation process for electroless plating on ABS plastic. Mater Lett 62(6):1089-1091

[36] Tang X, Bi C, Han C, Zhang B (2009) A new palladium-free surface activation process for Ni electroless plating on ABS plastic. Mater Lett 63(11):840-842

[37] Shu Z, Wang X (2012) Environment-friendly Pd free surface activation technics for ABS surface. Appl Surf Sci 258(14):5358-5331

[38] Bazzaoui M, Martins J, Bazzaoui E, Albournie A, Wang R, Hong P-D (2013) A simple method for ABS metallization. Surf Coat Technol 224:71-76

[39] Zhao W, Ma Q, Li L, Li X, wang Z (2014) Surface modification of ABS by photocatalytic treatment for electroless copper plating. J AdhesSciTechnol 28(5)499-511