

## CHAPTER III

### THEORY

#### Principle of the Plating Process

Electroplating of plastics requires that the substrate surface be made sufficiently conductive to allow electrochemical deposition of metals and the surface should be prepared to allow for good adhesion of the metal plate to the substrate. This is done by chemical processes which deposit a thin film of copper or nickel on the surface. A typical process for plating on plastics uses chemical etches to provide a microroughness on the substrate to ensure good adhesion. After etching, the surface is sensitised and activated by treatment with tin and with palladium salt solutions so that a thin metal layer can be deposited or precipitated on this surface from electroless copper or nickel plating solutions, and further metallisation can be performed by standard electroplating techniques.

#### Mechanical and Chemical Theories of Adhesion Between Plastic and

#### Plated Metal

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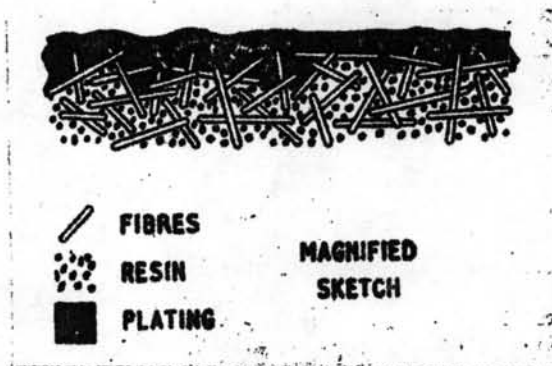
There are two schools of thought as to how the bond strength, or in other words, the ability of the metallic deposit to adhere to the plastic, is acquired. One school considered it to be the result

of chemical bonding, while the other considers it to be a physical keying effect produced by chemical treatments.

Mechanical keying is achieved by chemical etching the polymer surface with chromic-sulphuric acid solutions, which must cause uneven localized dissolution without degradation. From the point of view of plating adhesion, it is important to recognise two types of structure, one of which is exemplified by ABS plastic. ABS contains two polymer phases, a glassy copolymer of styrene and acrylonitrile (SAN) filled with more or less spherical particles of rubbery polybutadiene as shown in Fig. 3-1. Sometimes the polybutadiene phase is chemically bonded to the SAN phase and this is known as a grafted copolymer.

The ability to obtain an adherent electrodeposit on ABS is directly due to the presence of this two components structure and to the effect of etching the surface by chromic-sulphuric acid solution. In the first place the etchant preferentially attacks the butadiene globules producing a network or shallow pits in the surface and fissures extending deeper into the plastic. The subsequent process of activation and chemical plating provide a metal deposit which is anchored in these pits and fissures as shown in Fig. 3-1. This produces an excellent mechanical keying effect (mechanical theory of adhesion).

The second type of structure is known as crystalline structure.



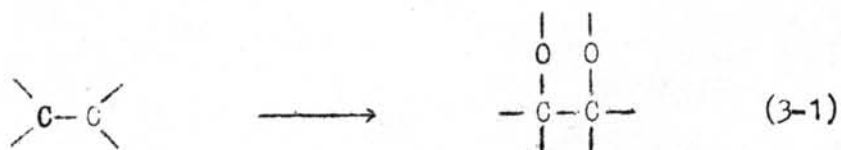
**Fig. 3-1 Penetration of the solution into the surface layer and deposition of metal in the minute cavities between glassy fibres and globules**

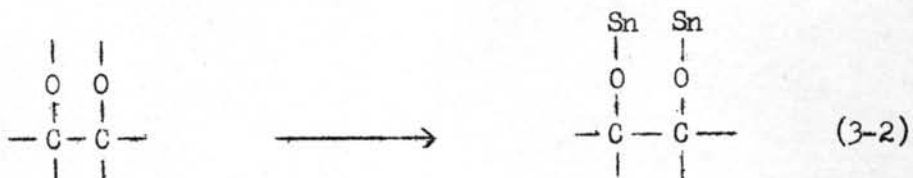
Plastics, of course do not form crystals in the conventional sense since their microstructure consists of chains of molecules carrying substituent groups and cross-linkages. Frequently, however, they contain regions in which the directions and spacings of the chains are less random, exhibiting more or less ordering, that is, more chains may be parallel or at right angles to each other than elsewhere in the structure. This is the special sense in which the term crystallisation is used in plastics technology. Such crystallised areas which may be distributed throughout the plastic and its surface, are more resistance to etchants and solvents than the amorphous areas.

The etchants preferentially attack the amorphous regions producing shallow pits in the surface and fissures deeper into the plastic. Such plastics exhibit basically two-component structure similar to the ABS plastic, an electrodeposit adhesion can be obtained by the same basic pretreatments.

According to this two component structure of plastics, a number of other plastics are being electroplated in production, though with varying degrees of success. A range of polymers has been used which includes polypropylene, polystyrene, polycarbonates, polysulphones and other thermosetting plastics such as urea-formaldehyde, phenol-formaldehyde plastics, and polyesters.

Chemical bonding is achieved by an oxidation process using chromic-sulphuric acid electrolytes, which is thought to oxidise surface double bonds in the polymer to form free single bonds, oxygen in the solution can link with these single bonds to form oxide layers with the plastic surface as shown in Eq.(3-1). Oxygen with free bonds will permit chemical bonding with tin from sensitiser solution. Organo-tin compound layer is formed and bridges between plastic and plated metal as shown in Eq.(3-2).





After sensitising in the stannous solution, plastic surface is activated by treatment with palladium salt solution. Palladium ions are absorbed on the surface of plastics and are reduced by previously deposited stannous ions which remain in the grooves and deep pores of the plastic surface after rinsing. The palladium ions deposited in this way serve to nucleate further deposition from the electroless plating bath. Palladium salt solutions can be replaced by the use of silver salt solutions. Silver can also act as nuclei for copper or nickel to deposit on. Walker and Cambel (1976) found that silver can form larger nuclei than palladium but silver solutions are less stable than palladium solutions.

### Electroless Plating

In any electroless plating solutions, the metal is present in the form of ions. In order to reduce the ions to the pure element metal, a reducing agent must be added. A limited number of metal ions in solution can be reduced to the metallic state by chemical means. According to Goldie (1968), these metals are gold, silver, chromium, iron, nickel, cobalt, copper, antimony, arsenic, and palladium.

Alloys such as nickel-tungsten and arsenic-zinc have also been reported in his literature to have similar property. Although many reducing agents are possible, the two most commonly used are hypophosphites and aldehydes.

Table 3-1 shows a part of the Periodic Table, which Goldie concluded that the metals marked with an asterisk can be reduced by hypophosphite ions at elevated temperatures.

Period	Group							
	V		VI		VII		VIII	
	A	B	A	B	A	B		
	V		Cr *		Mn		Fe * Co * Ni *	
IV		As *		Se		Br		

Table 3-1 A part of the Periodic Table

Metal in group 1B (see Table 3-2) can normally be reduced by aldehyde at room temperatures, although silver and gold may be reduced using the hypophosphite system. Saubestre (1969) found that all three metals in group 1B are capable of being complex with ammonia and reduced by hydrazine, whereas cobalt, nickel, and iron, hydrazine is normally used as a supplementary reducing agent to



hypophosphite.

In the electroless solutions, some salts have to be added to form complex with the metal ions in order to prevent the precipitation of these ions.

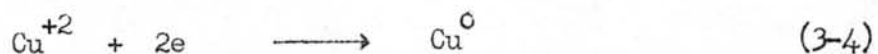
Period	Group	
	A	B
IV	K	Cu*
V	Rb	Ag*
VI	Cs	Au*

Table 3-2 A part of Periodic Table

### Copper Electroless Plating

The chemical or 'electroless' copper plating process is widely used for preparing plastics for electroplating. The copper plating solution normally consists of copper sulphate as the source of the metal together with complexing agent such as Rochelle salt (sodium potassiumtartrate) and a reducing agent such as formaldehyde. Caustic soda is added to the solution to adjust the pH to the working range of 11 - 12.5.

In aqueous solution, copper is present in the form of copper ions ( $\text{Cu}^{+2}$ ). Formaldehyde will reduce these ions to copper metal as shown in Eq.(3-3) and Eq.(3-4). Copper metal will deposit on palladium nuclei to form a thin film of copper on plastic surface. The copper film is to be thick enough to conduct electricity, so that further electrodeposition can be done on this copper layer.

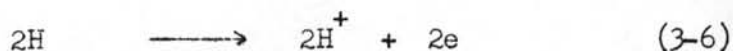


#### Nickel Electroless Plating

Nickel electroless plating bath consists of nickel sulphate or nickel chloride as the source of the metal together with complexing agents such as sodium citrate, sodium acetate, sodium pyrophosphate or sodium succinate with a reducing agent such as sodium hypophosphite. Nickel may be chemically deposited from both acid and alkaline media. Acid electroless nickel solution has been performed at temperatures from  $40 - 60^\circ\text{C}$  and at a pH of 5. The alkaline type is operated at pH 10 and at temperature of 60 to  $70^\circ\text{C}$ .

In aqueous solution, nickel is also present in the form of nickel ions ( $\text{Ni}^{+2}$ ) which are reduced by nascent hydrogen produced by hypophosphite decomposition as shown in Eq.(3-5) to Eq.(3-7).





Nickel metal formed will deposit on palladium nuclei to form a thin film of nickel on plastic surface. This film is to be thick enough to allow further deposition by electroplating technique.

#### Principle of Electroplating

Electrodeposition is the application of metallic coatings to metallic or other conductive surfaces by electrochemical processes. The article to be electroplated is immersed in a solution known as the electrolyte and connected to the negative lead of a low voltage D.C. supply. To complete the electrical circuit, anodes are immersed in the solution and are connected to the positive lead as shown schemetically in Fig. 3-2.

The electrolyte is generally an aqueous solution of a salt of the metal to be deposited or of an inert insoluble conductive material. The current supply is direct current at a voltage usually between 2 and 16 volts depending upon the process. The current is supplied by means of a transformer-rectifier set or a generator.

For very small scale plating, accumulators or dry cells may be used.

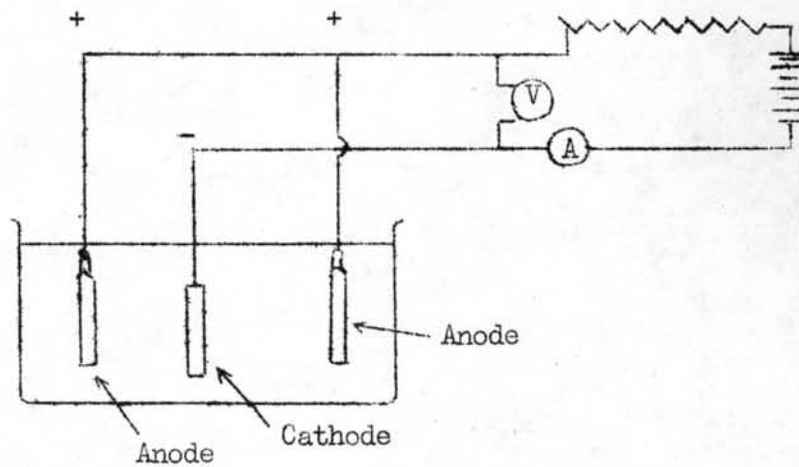


Fig.3-2 Schematic circuit for electroplating