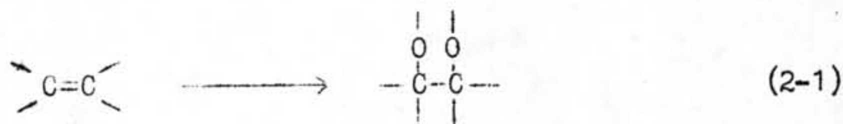
CHAPTER II

# LITERATURE REVIEW

## Pretreatment of the Plastic Surface

Plastics are normally hydrophobic, therefore pretreatment of the material is necessary before any metallising operation can be carried out. Sherwood (1964) found that sulphuric acid reacted with most plastics to introduce sulphonic acid groups on the surface. These groups are very reactive and, since the surface of the material is now hydrophilic, will permit wetting and subsequent copper deposition by electroless means, replacement of the sulphonic acid groups, by metal ions taking place.

Horton and Narcus (1965) reported extensively on the oxidation reaction by sulphuric acid - chromic acid mixtures. They used these mixtures principally as etchants, attention being given to the fact that the surface characteristics of the material were being chemically altered. Oxide layers or oxygen linkages were formed with the plastic surface as shown in Eq.(2-1) and were advantageous for chemical bonding.

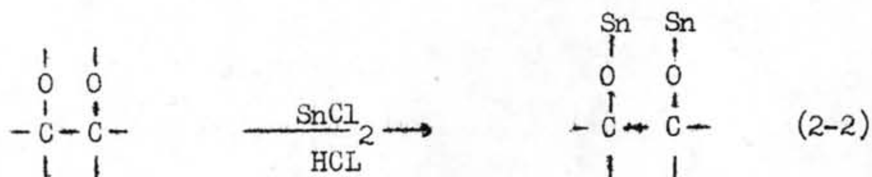


Goldie (1965) also obtained good results using mixtures of potassium dichromate and sulphuric acid to oxidise and roughen the plastic surface.

King (1965), a scientist at the Battelle Institute reported that metal deposition would adhere to a properly oxidised plastic surface, whereas in the past surface roughening was necessary. He claimed that the combination of carbon atoms in plastic and oxygen atoms gives rise to exceptionally good adhesion.

## Sensitisation and Activation of Plastics

Ghorashi (1975) proposed the definition of "sensitisation" as a process in which an easily oxidised species is brought into contact with a polymer substrate that is to be subsequently activated and plated, and "activation" as the next treatment in the electroless plating of nonconductors by using some precious metal solution such as solution of palladium, gold or silver which serves as metal nucleations on the nonconductive surfaces. His sensitiser solution consisted of 40 g of $SnCl_2.2H_2O$ and 40 ml concentrated HCl dissolved in water to form one litre of solution. He found that some stannous ion remained on the surface after rinsing, either trapped in the grooves and deep pores of the surface, or possibly chemically bonded to the oxidised plastic surface as shown in Eq. (2-2).




Ghorashi used electron microscope to characterize the size and distribution of tin - containing particles on the substrates. The results of these studies showed that the tin is in the form of particles about 30 Å dia, and that these particles aggregate to form clumps of 100 to 250 Å dia.

Sard (1975), who studied extensively on activation of plastics, showed that this technique was belived to work because Pd(II) ions from the bath were reduced by previously deposited Sn(II) ions (sensitisation) on the substrate surface. The palladium deposited in this way serves to nucleate deposition from the electroless plating bath. His typical activation bath consisted of 0.7 g of $PdCl_2$ and 20 ml of concentrated HCl in one litre of water.

Rantel and Holtzman (1975) replaced the aforemention two steps by the used of single step mixed $SnCl_2/PdCl_2$ catalyst solutions. A typical formulation consisted of:

| | | |
|---|---|---|
| $PdCl_2$ | 5 | m mole/l |
| $SnCl_2$ | 200 | m mole/l |
| $Na_2Sn(OH)_6$ | 5 | m mole/l |
| HCL | 3 | mole/l |

They concluded that this mixture was essentially noncolloidal and was presumed to be a soluble complex containing Pd(II) and Sn(II) chlorides. The final product of the reaction between stannous chloride and palladium chloride is $SnPd_7Cl_{16}$, possibly an adduct of $SnPdCl_4$ and $Pd_6Cl_{12}$. The reaction proceeds via several intermediates, one of which is founded to be $SnPdCl_4$. The final solution of mixed $SnCl_2/PdCl_2$ will perform as activator for plating on plastic.

Nickel Electroless Plating

Wurtz (1944) published a paper dealing with the reduction of nickel solution to nickel by the hypophosphite ions. Two scientists, Brenner and Riddel (1946) at the National Bereau of Standard, also studied a process for plating the interior of glass tubes with a nickel tungsten alloy using sodium hypophosphite as a reducing agent. They found that the tubes were completely plated with nickel. Their investigations revealed that chemical deposition had taken place on non - conductive material.

The General American Transportation Corporation introduce a commercial version of this process in 1952 following a considerable amount of research and development based on the original work of Brenner and Riddel. This had the effect of increasing interest in electroless deposition techniques in general. As nickel had been successfully exploited on a commercial basis, a great deal of

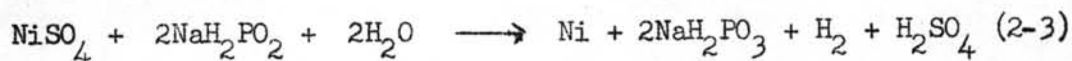
encouragement was derived from this fact, and investigators began to feel that others metals might have a similar future.

According to Swan (1961), nickel may be chemically deposited from both acid and alkaline media and normally employs sodium hypophosphite as the reducing agent.

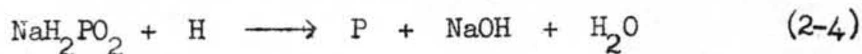
Spencer (1974) suggested that an electroless nickel plating bath contains many of the following :

1. A source of nickel ions, e.g. $NiCl_2$ , $NiSO_4$

2. Hypophosphite anions to give catalytic dehydrogenation active hydrogen atoms which reduce nickel ions and give phosphorous as shown in Eq. (2-3) and Eq. (2-4).



$$NiSO_4 + 2NaH_2PO_2 + 2H_2O \longrightarrow Ni + 2NaH_2PO_3 + H_2 + H_2SO_4 \quad (2-3)$$



$$NaH_2PO_2 + H \longrightarrow P + NaOH + H_2O \quad (2-4)$$

3. Organic chelating agents to complex the nickel ions in order to prevent nickel phosphite precipitation and to serve as a buffer to prevent a rapid rise in the pH due to hydrogen evolution e.g. organic hydrocarboxylic acids such as citric, malic or hydroxyacetic acids are used.

4. "Exaltants" to increase the deposition rate by activating

hypophosphite anions and thus counteracting the slowing effect of chelating agents and stabilisers, e.g. succinic or adipic anions and alkaline fluorides.

Nihei, Osaka, and Asa (1975) studied another reducing agent by using sodium borohydride or various alkyl aminoboranes which gives a nickel-boron alloy deposit. This solution is more expensive than the nickel-phosphorous solution but it does have certain advantages, e.g. the deposit has a higher hardness value.

Dini and Coronada (1966) found that a relatively pure nickel (greater than 99.0 %) can be produced by electroless means using a nickel-hydrazine system. Codeposition of alloys is more common, however, and the most popular are nickel-phosphorous (83 - 97 % nickel) and nickel-boron (88 -99.3 % nickel).

Copper Electroless Plating

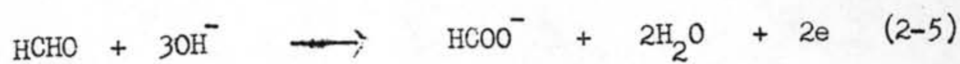
Cahill and Saubestre (1959) found that electroless nickel was not particular suitable in some cases due to its poor solderability and high electrical resistance. Furthermore, the process required relatively high operating temperatures. Since copper is an excellent conductor and has good solderability, Cahill and Saubestre have carried out experiments on copper electroless plating, based primarily on Fehling's solution. Formaldehyde was used as the reducing agent, and copper sulphate as the source of copper ions.

Since 1960, a number of patents have been granted and various articles published in the technical press. Proprietary solutions have also appeared on the market. Goldie (1964) had shown that formaldehyde was a relatively poor reducing agent at lower pH values. Using sodium hydroxide to control the pH, he found that formaldehyde is an effective reducing agent at pH value near 12.

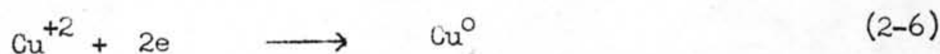
Gutzeit (1965) carried out his work on copper electroless plating of nonconductors and suggested a typical composition for copper electroless solution as follow:

1. A source of copper ions, $CuSO_4 \cdot 5H_2O$

2. Formaldehyde to reduce copper ions in aqueous solution to copper as shown in Eq.(2-5) and Eq.(2-6)



$$HCHO + 3OH^- \longrightarrow HCOO^- + 2H_2O + 2e \qquad (2\text{-}5)$$



$$Cu^{+2} + 2e \longrightarrow Cu^0 \qquad (2\text{-}6)$$

3. Sodium patassium tartrate (Rochelle salt) to complex the copper ions in order to prevent copper ion precipitation.

4. Sodium hydroxide to control pH.

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