ASPECTS OF ADHESION OF METALLISED PLASTICS.

by

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SUMMARY

Electroplating of a range of ABS plastics has been studied with particular reference to aspects of metal to polymer adhesion.

Certain acetylacetonate transition metal complexes have been shown to promote adhesion of copper to ABS, and mechanisms for their action have been postulated.

Alternative methods of plating ABS have been investigated. Some success has been achieved using swelling techniques.

The mechanical properties of metal coated ABS and polypropylene have been studied and it has been shown that reinforcement theory can be applied to certain ductile metal coated composites to predict tensile strength. For low-level adhesion composites it was necessary to modify the theory by including an interaction factor.

The problem of brittleness encountered with copper plated ABS composites has been overcome by careful design in the use of selective area plating, whilst retaining certain other desirable composite properties.

Ion bombardment of ABS by high energy species has been found to prevent subsequent deposition of an adherent electroless copper coating.

PLATING / PLASTICS / ADHESION / SELECTIVE AREA.

CONTENTS

		Page No.
1.	Introduction to plating on plastics.	1
1.1	History of plating on plastics.	1
1.2	Reasons for plating on plastics.	2
1.3	Materials used.	4
1.3.1	ABS	4
1.3.2	Polypropylene.	11
1.4	Plating on plastics.	14
1.5	Nature and role of the organic conditioner.	15
1.6	Nature and role of the chemical etch.	17
1.7	Nature and role of the neutraliser.	21
1.8	Nature and role of the catalyst.	21
1.9	Nature and role of the accelerator.	25
1.10	Nature and role of the electroless metal bath.	26
1.11	Assessment of adhesion.	30
1.11.1	Qualitative tests.	31
1.11.2	Quantitative tests.	31
2.	Metal / Polymer Adhesion Promotion.	35
2.1	Introduction.	35
2.1.1	Nature of adhesion.	35
2.1.2	The Mechanical bond.	35
2.1.3	The chemical bond.	38
2.1.4	Adhesion promotion.	44
2.1.5	Chemical adhesion promoters.	48
2.2	Experimental procedure.	55
2.2.1	Preparation of complexes.	55

		Page No.
2.2.2	Compatibility of above complexes with Shipley solutions.	58
2.2.3	Preparation of test pieces.	58
2.2.4	Peel testing.	59
2.3	Results.	59
2.3.1	Reactivity of complexes with Shipley solutions.	59
2.4	Discussion.	63
2.5	Conclusions.	72
2.6	Suggestions for further work.	72
3.	Methods of plating on plastics.	74
3.1	Introduction.	74
3.1.1	Processes involving metal complex formation.	74
3.1.2	Processes involving U.V. irradiation.	76
3.1.3	Processes involving thermal decomposition.	77
3.1.4	Processes involving hydrolysis.	79
3.1.5	Miscellaneous processes.	79
3.2.1	Experimental scheme.	84
3.2.2	Choice of method.	85
3.2.3	Choice of substrate.	86
3.2.4	Choice of solvent.	87
3.2.5	Choice of metal compound.	87
3.2.6	Method of reduction.	88
3.2.7	Choice of chemical reducing agent.	88
3.2.8	Procedure.	88
3.3	Experimental procedure.	89
3.3.1	Solubility of metal compounds.	89
3.3.2	Effect of reducing agents on selected metal compounds.	90
3.3.3	Effect of reducing agents on ABS.	90

Page No.

3.3.4	Swelling studies.	90
3.3.5	Application of metal salt with binder.	91
3.3.6	Incorporation of metal salt into molten polymer.	92
3.4	Results.	93
3.4.1	Swelling experiments.	96.
3.4.2	Metal salt with binder investigations.	96
3.4.3	Melt mixing investigations.	97
3.5	Discussion.	97
3.5.1	Choice of metal compound.	97
3.5.2	Efficiency of reducing agents.	98
3.5.3	Reduction in situ.	99
3.5.4	Application by means of a binder.	100
3.6	Conclusions.	102
3.7	Suggestions for further work.	103
4.	Mechanical properties of metal / polymer composites.	104
4.1	Introduction.	104
4.1.1	Tensile strength.	104
4.1.2	Ductility.	106
4.1.3	Thermal cycling.	108
4.1.4	Nature of the adhesives.	109
4.2	Experimental procedure.	110
4.3	Results.	113
4.4	Discussion.	120
4.4.1	Effect of metal plate thickness.	120
4.4.1.1	Copper / ABS	120
4.4.1.2	Nickel / ABS	121

Page No.

4.4.3	Correlation of peel test results and interaction factor for plated samples.	123
4.4.4	Effect of varying the level of adhesion in metal / ABS composites.	124
4.4.5	Correlation of peel test results and interaction factors of glued ABS composites.	125
4.4.6	Nature of the failure of glued ABS composites.	126
4.4.7	Nature of the failure of araldited polypropylene composites.	127
4.5	Conclusions.	128
4.6	Suggestions for further work.	129
5.	Selective area plating.	131
5.1	Introduction.	131
5.1.1	Methods of selective area plating.	131
5.1.2	Properties of selective area plated plastics.	136
5.2	Experimental procedure.	138
5.3	Results.	140
5.4	Discussion.	145
5.5	Conclusions.	148
5.6	Suggestions for further work.	149
6.	Ion bombardment.	150
6.1	Introduction.	150
6.2	Experimental procedure.	154
6.3	Results.	154
6.4	Discussion.	157
6.5	Conclusions.	160

Page No.

6.6 Suggestions for further work. 160

7. Overall conclusions. 161

Acknowledgements 165

Appendix 166

References. 170

CHAPTER ONE

Introduction to Plating on Plastics

1.1 History of Plating on Plastics.

Although commercial plating on plastics is a very recent development, deposition of metal onto non-conductors was achieved nearly 150 years ago.

In 1835 Liebig reduced silver salts to a metallic silver mirror with an aldehyde and five years later Robert Murray used graphite to render dieletric materials conductive. As one might expect, the first application of plating non-conductors was in the art world. Wood, glass, flowers and insects were all plated to produce a variety of ornaments. Alexander Jones and Alexander Parkes were both granted patents in 1841 to this end. [1]

At this time adhesion of the metal to the non-conducting substrate was nominal and it was therefore necessary to totally encapsulate the form in metal. This was achieved by roughening the surface of the article to be plated, either mechanically by sand blasting etc. or possibly by chemical means e.g. etching glass with hydrofluoric acid. Next it was necessary to seal a porous substrate with a coating of wax or varnish. A conductive layer had now to be applied. Bronzing, graphiting and metallic painting were common means of achieving this. Chemical metallisation could be affected by spraying the substrate from two adjacent nozzles with a stannous chloride reducing solution and an unstable silver nitrate solution. This redox couple readily deposited a layer of metallic silver. Subsequently a substrate, thus

rendered conducting, could be electroplated.

Around 1960, a series of developments evolved that led to the plating of non-conductors with significant adhesion between metal and substrate. By varying the composition and moulding conditions of acrylonitrile - butadiene - styrene copolymers (ABS) it was found that this material could be furnished with an adherent metal coating. [2,3]

It was also realised around this time that conventional etchants could be used on plateable ABS grades to give good adhesion, without the need for mechanical roughening and complete encapsulation. [4,5]

New electroless copper solutions were produced which did not decompose rapidly, but rather were autocatalytic and could be replenished. [6]

1.2 Reasons for Plating on Plastics.

Modern day applications of plated plastics cover a wide range of both decorative and engineering products, including radio and electronic components, clock and camera parts, automobile accessories, bathroom taps, lighting fixtures etc.

The multiplicity of uses results from the range of properties that this type of composite can offer. The base polymer, usually ABS has the advantages of easy formability, low density and corrosion resistance. The traditional disadvantages of polymers i.e. poor mechanical

properties and heat resistance have been improved to some extent by the production of a wide range of new plastics. However, when plastics are plated these properties are improved even further.

The application of nickel-chrome electrodeposits gives an excellent appearance, good abrasion resistance of the metal, high tensile strength and improved dimensional stability. The metal coating protects the plastic substrate from solvent attack and prevents atmospheric oxidation. It reduces build-up of static charge and the accompanying fire hazard, whilst acting as a heat sink where necessary.

Corrosion of the metal plate is reduced as no galvanic couple can be set up with the substrate.

If a component conventionally produced in metal requires a number of expensive machining operations, it may be made more easily and cheaply by plating a plastic moulding. For a component that is to be produced in large numbers, the initial capital cost of the mould may well be less than the individual machining costs.

Goldie [7] has produced tables indicating the improvements of plastics properties by electroplating, together with examples of cost comparisons of metals and plated plastics. Similar tables have been produced by Müller and Baurand. [8]

1.3 Materials Used.

The most notable plastics which may be electroplated are acrylonitrile - butadiene - styrene two-phase polymers (ABS) and polypropylenes. More recently plateable grades of polysulphones and polyacetals have been introduced. Polysulphones, whilst more expensive than ABS or polypropylene, can be used up to considerably higher temperatures. Exceptional dimensional stability is the chief asset of polyacetal.

1.3.1 ABS

ABS was first produced by U.S. Rubber in the late 1940's from acrylonitrile, styrene and butadiene [9]. Let us now consider each constituent individually.

1. Acrylonitrile

This is a liquid with a boiling point of 77.3°C. It has the molecular formula

$CH_2 = CHCN$ or

$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & C \equiv N \end{array}$$

and polymerises to form chains with the following structure:

$$\left[\begin{array}{cccccc} H & H & H & H & H & H \\ | & | & | & | & | & | \\ -C- & C- & C- & C- & C- & C- \\ | & | & | & | & | & | \\ H & CN & H & CN & H & CN \end{array} \right]_n$$

The regular structure of these chains gives rise to their ability to pack closely and form a highly crystalline material. Because of the electrophilic nature of the

cyano - groups, polyacrylonitrile is a very polar molecule and as such is resistant to hydrocarbon solvents.

2. Butadiene

This monomer is a gas at room temperature (b.p. - 4.4°C) and possesses the chemical formula.

$$CH_2 = CH - CH = CH_2$$

It polymerises to produce polybutadiene with the structure

$$\left[-\underset{H}{\overset{H}{C}}- \overset{H}{C}= \overset{H}{C}- \underset{H}{\overset{H}{C}}- \underset{H}{\overset{H}{C}}- \overset{H}{C}= \overset{H}{C}- \underset{H}{\overset{H}{C}}- \right]_n$$

It is a rubbery polymer at room temperature becoming hard and brittle below -75°C.

Some 1,2 addition may also occur during polymerisation resulting in pendant groups with accessible double bonds.

$$-CH_2-\underset{\underset{CH_2}{\overset{\|}{CH}}}{\overset{}{CH}}-CH_2-CH=CH-CH_2-$$

The residual double bonds may take part in crosslinking reactions in presence of a suitable catalyst. Saubestre [10] and Jarrett [11] have suggested that the double bonds may be capable of forming covalent bonds with metal atoms.

3. Styrene

The third monomer, styrene, is a liquid with a boiling point of 145.2°C.

It has the formula

$$\underset{C_6H_5}{\overset{H}{C}} = \underset{H}{\overset{H}{C}}$$

and polymerises readily to polystyrene :

$$\left[-\underset{H}{\overset{H}{C}}-\underset{C_6H_5}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{C_6H_5}{\overset{H}{C}}- \right] \qquad n = 1{,}000$$

Because of the steric hindrance of the bulky phenyl groups these polymer chains cannot pack closely and this results in polystyrene having a glassy, amorphous structure, with good moulding properties.

In combination these monomers produce a terpolymer with good fabrication characteristics, chemical resistance, surface hardness and toughness, the level of properties being dependent on the relative amounts of each.

ABS polymers are generally manufactured in one of two ways:

(A) By blending SAN copolymer with butadiene - acrylonitrile rubber.

(B) By graft copolymerisation of polybutadiene with styrene and acrylonitrile.

Type A

Production is achieved by either physically blending S/A copolymer with B/A copolymer on a two roll mill or by blending the lattices of these copolymers. In this type of polymer no chemical combination occurs between the S/A and B/A.

In order to achieve improved impact resistance of the physical terpolymer, it is necessary to lightly crosslink the rubber by the use of organic peroxides e.g. benzoyl peroxide.

However, this increase in impact resistance is achieved at the expense of compatibility of the two phases.

Davenport et al [12] have reported that a wide range of polymers can be so produced by varying the ratios of styrene to acrylonitrile and butadiene to acrylonitrile. A typical blend is :

70 parts	(70 : 30)	S : A copolymer
40 parts	(63 : 35)	B : A rubber.

Properties such as processability, toughness, low temperature toughness and heat resistance can be optimised in this way e.g. increasing the amount of butadiene in the B/A rubber improves low temperature toughness.

A further variable affecting the properties of the material is the MW of each of the S/A and B/A copolymers. For high impact resistance the S/A should have a high MW.

Type B.

The second type of terpolymer is produced by adding styrene and acrylonitrile to a polybutadiene latex. The mixture is warmed to absorb the monomers and an aqueous catalyst e.g. potassium persulphate is added to polymerise the styrene and acrylonitrile. Also the catalyst gives rise to grafting of certain of these monomer units onto the polybutadiene chains to produce a chemically bonded copolymer. This grafting process proceeds as follows:

Catalyst ⟶ 2R· Where R. is a free radical

$$\left[CH_2 - CH = CH - CH_2 \right] + \cdot R \rightarrow \left[CH - CH = CH - CH_2 \right]$$

The catalyst radical will abstract an allylic hydrogen atom and give rise to a radical site on the polymer backbone.

$$\left[\dot{C}H - CH = CH - CH_2\right] + H_2C = \underset{CN}{CH}$$

$$\longrightarrow \left[\underset{CH_2 - \underset{CN}{C\cdot}}{CH} - CH = CH - CH_2\right]$$

$$+ \underset{C_6H_5}{CH} = CH_2 \longrightarrow \left[\underset{CH_2 - \underset{CN}{C} - CH_2 - \underset{C_6H_5}{\dot{C}H}}{CH} - CH = CH - CH_2\right]$$

The radical on the polybutadiene chain then reacts with an acrylonitrile molecule to produce a new radical, which reacts with a molecule of styrene. In this way side chains of S/A are grafted onto the rubber.

The final reaction mixture then contains

(i) polybutadiene

(ii) polybutadiene grafted with styrene and acrylonitrile

(iii) styrene and acrylonitrile copolymer.

The graft copolymer gives good compatibility between the rubber and the S/A matrix.

The properties of this second type of material can vary greatly from those of the physically blended ABS. The impact strength is generally greater together with a higher softening point and improved moulded surface appearance.

By varying the relative amounts of each constituent in

the graft polymer a range of mechanical properties can be achieved.

e.g. Tensile strength 17.23 to 62.05 MNm^{-2}

Impact strength 6.29 to 25.17 kJm^{-2}

Heat distortion temp 70 to 110°C

Different levels of properties are suited to different processes. High tensile strength ABS is required for extrusion whilst calendering needs a high impact grade.

Molecular weight again is important in determining the properties of the terpolymer.

During the graft process some crosslinking of the polymer chain occurs.

e.g.

$$\left[\begin{array}{c} H \\ | \\ -C - CH = CH - CH_2- \\ | \end{array} \right]$$

$$CH_2 - \underset{CN}{\underset{|}{CH}} - CH_2 - \underset{C_6H_5}{\underset{|}{CH}} - CH_2 - CH = CH - CH_2 -$$

The degree of crosslinking will further affect the properties of the terpolymer. An optimum amount of crosslinking is required for maximum toughness.

Several transmission electron microscopy studies have been carried out on ABS and they have revealed that the material consists of rubber spheres up to 10Å in diameter, dispersed in a matrix of S/A. The size and distribution of these rubber particles is also important in determining the properties of the material. If they are too large, toughness is reduced, whilst too small a particle size means that the two phases become completely

compatible and no toughening is brought about. An optimum particle size is therefore essential. This becomes particularly important in the case of plateable ABS, as the size and distribution of the polybutadiene spheres affects the anchoring of the metal coating.

A further variable affecting the properties of ABS is the presence of compounding additives e.g. fillers, plasticizers, stabilizers. As well as affecting the mechanical properties of the plastic, they may also change the adhesive bond strength between the ABS and a metal plate, by chemical interactions.

New grades of ABS have been produced by alloying with other polymers e.g. polyurethane, polycarbonate, PVC, to further extend the range of properties. Also fourth monomer units have been incorporated (e.g. α-methylstyrene) which increase the heat distortion temperature.

Any variation in composition and structure etc. that affects the mechanical properties of the ABS will also affect its suitability for plating, since a weak surface layer will fail under stress. Similarly any effect on the chemical reactivity will be important e.g. the etching characteristics of the surface may be influenced and this in turn will control the surface topography. Also the degree of oxidative attack on the polymer will affect the amount of polar interactions with a metal coating.

1.3.2. Polypropylene

Polypropylene is an addition polymer of the propylene monomer.

$$2n \; \begin{matrix} CH_3 & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{matrix} \longrightarrow \left[\begin{matrix} CH_3 & & H & & CH_3 & & H \\ | & & | & & | & & | \\ -C & - & C & - & C & - & C- \\ | & & | & & | & & | \\ H & & H & & H & & H \end{matrix} \right]_n$$

It is prepared by the polymerisation of propylene at 60°C with a catalyst that is the reaction product of $TiCl_3$ and Al $(Et)_3$ or Al $(Bu)_3$ or Al $(Et)_2$ Cl, prepared in naphtha and under nitrogen. These catalysts, developed by Ziegler and Natta in the 1950's, produce so called "stereoregular" polypropylene. Unstructured or atactic polypropylene has a random distribution of methyl groups either side of the carbon backbone.

$$\left[\begin{matrix} CH_3 & & H & & CH_3 & & H & & H & & CH_3 & & H \\ | & & | & & | & & | & & | & & | & & | \\ -C & - & C & - & C & - & C & - & C & - & C & - & C- \\ | & & | & & | & & | & & | & & | & & | \\ H & & H & & H & & H & & CH_3 & & H & & H \end{matrix} \right]$$

As a result it is impossible to get close packing of the polymer chains and this material is soft and rubbery. It does find a use, however, as a primer for isotactic polypropylene since it is slightly more reactive.

Stereoregular polypropylene may possess alternating methyl groups in which case it is described as syndiotactic or it may exhibit isotacticity, that is to say all methyl groups lie on the same side of the carbon backbone.

```
CH3 H   H   H   CH3 H
 |  |   |   |    |  |
-C--C---C---C----C--C-
 |  |   |   |    |  |
 H  H  CH3  H    H  H
```

syndiotactic

```
CH3 H  CH3 H  CH3 H
 |  |   |  |   |  |
-C--C---C--C---C--C-
 |  |   |  |   |  |
 H  H   H  H   H  H
```

isotactic

In actual fact most commercial polypropylenes contain 90-95% isotactic material with some atactic and syndiotactic polymer present in the isotactic chains or as separate molecules.

The regularity of the isotactic polymer chains allows them to pack closely and form crystalline regions. Commercially the amount of crystalline material falls within the range of 65-75%. The relative amounts of crystalline and amorphous polypropylene in part determines the properties of the polymer. The crystallinity increases the tensile strength of the material. Also the crystalline regions are chemically more inert.

The situation is further complicated by the fact that the crystalline regions are composed of spherulites, of which four different types have been observed.(13) The size and type of these spherulites influence the properties obtained. For example, smaller crystals give greater transparency and flexural resistance.

Fitchum et al (14) have proposed that the differing chemical reactivities of the amorphous and crystalline zones are important in the metallising process of polypropylene. These workers suggested that amorphous material is preferentially dissolved from the surface producing microroughness, capable of good adhesion to a metal coating.

A further variable to be considered is the molecular weight of the polymer. Generally an increase in molecular weight produces an increase in melt viscosity and impact strength together with a reduction in yield strength, hardness and softening point. Number average molecular weights vary from 38,000 to 60,000 whilst weight average values are from 220,000 to 700,000. This indicates that the polymer possesses a large molecular weight distribution, which again influences the properties of the material. Boenig [15] has stated that for a small molecular weight distribution, the tensile strength of polypropylene is more dependent on molecular weight.

A wide variety of additives are used in polypropylene to further modify the properties. These include pigments, carbon black, glass fibres, rubbers, antioxidants, nucleating agents. Glass fibres improve the stiffness, tensile strength and creep resistance whilst butyl rubber, blended in, reduces brittleness. Carbon black improves the weathering properties of the polymer by absorbing U.V. radiation.

Unlike the completely nonpolar polyethylene, it is possible for oxidation of the polypropylene molecules to occur in the presence of strong oxidizing agents. The tertiary hydrogen atom is subject to attack and following its abstraction, a peroxy radical will form :

```
   CH3  H   CH3  H
   |    |   |    |
 — C —— C —— C —— C —
   |    |   |    |
   H    H   O    H
             \
              O·
```

The peroxy radical will then abstract a further t-H atom from an adjacent unit to form a hydroperoxide.

```
  CH3  H    CH3  H
  |    |    |    |
— C —— C —— C —— C —
  •    |    |    |
       H    O    H
             \
              OH
```

The new radical will be immediately oxidized.

From this series of reactions a large number of chemically reactive sites may be produced on the polymer surface. The decomposition of the hydroperoxide function, might permit the formation of a covalent bond with a metal atom. At the very least a van der Waal's type interaction should occur between polymer substrate and metal coating.

1.4. Plating on Plastics

Commercially plating on plastics involves the following general steps:

1. Cleaning
2. Etching
3. Neutralising
4. Sensitising
5. Catalysing
6. Accelerating
7. Electroless plating.

The cleaning solution may be a relatively dilute chromic/sulphuric acid mix, formulated to remove dirt and grease from

the polymer surface.

Prior to etching there may be a multipurpose organic conditioner treatment. Etching itself takes place in a strongly oxidising chromic/sulphuric acid solution, and produces a plastics surface capable of good adhesion. In addition to thorough rinsing it is necessary to neutralise chromium residues remaining adsorbed to the polymer.

Catalysation of the surface is generally achieved by producing a uniform distribution of palladium nuclei over the plastics surface. These nuclei must be clearly exposed, by an accelerating solution, to the final electroless metal bath. Copper and nickel are the most commonly used metals for electroless plating.

1.5 Nature and Role of Organic Conditioner

Organic conditioning treatments are typically applied to a number of plastics in preplating systems e.g. ABS, polypropylenes, polyacetals, polyimides, polycarbonates, with or without subsequent chemical etching.

The choice of conditioning solvent depends on the plastic to be treated. Some solvents need to be diluted with an inert liquid if they attack the plastic too severely. Water is used as the diluent where possible. Information on solvents systems is available in the patent literature.[16,17,18]

The solvent may act on the polymer in a number of ways to improve its plateability. Petrow et al [19] have treated ABS with a mixture of 15% $CHCl_3$ and 85% C_2H_5OH.

They concluded that a surface capable of mechanical keying was produced. This resulted from the solvent being adsorbed and diffusing through the two phases at different rates. It was thought that the polybutadiene spheres swelled faster than the SAN matrix and the resultant stresses on the spheres caused them to "pop" out of the surface, leaving a microporous finish.

The organic conditioner is thought to enhance subsequent etching by rendering the surface hydrophilic. In addition the solvent may relieve moulding stresses in a plastic component and by equalising surface stress, permit uniform etching to take place. Kato [20] has obtained electron micrographs of as moulded ABS and ABS treated with acetone. In the former case the polybutadiene regions were elongated in the direction of flow, but after stress relieving the spherical form of these rubber zones was returned. The shape of these rubber particles is important in producing an adherent surface on the ABS, so it is important to obtain the uniformity of shape that stress relieving solvents provide. Dennis and Tipping [21] have shown that best adhesion is achieved with spherical polybutadiene regions and Rempel [22] has observed low peel adhesion at highly stressed areas.

It is also necessary to remove stresses from the matrix, for uniform adhesion. Otherwise thermally induced stress relief may lead to differential shrinkage or expansion and subsequent blistering of the metal plate.

Organic conditioning is generally accomplished by simply immersing the component in a solvent. However it is possible that the surface rehardens to show the same poor qualities. Müller [23] has suggested that this might be overcome by a combination of immersion and annealing.

Shipleys organic conditioner, to be used in the present investigation consists of an aqueous emulsion of organic solvent. GLC investigations indicated this solvent to be CCl_4.

1.6 Nature and Role of the Chemical Etch

The purpose of chemical etching is to provide a good bond between a plastics substrate and a metal plate.

Most thermoplastic etchants contain chromic and sulphuric acids. Saubestre [1] has suggested the following compositions are broadly useful.

1. CrO_3 75 g/l
   H_2SO_4 250 ml/l

2. $K_2Cr_2O_7$ 90 g/l
   H_2SO_4 600 ml/l

The action of such an etchant is hotly disputed. There are two main mechanisms postulated. Firstly a number of workers have suggested that the etchant serves to chemically roughen the plastics surface in order to produce anchoring points for a metal coating. Matsunaga et al [24] believed that in the case of ABS, the etchant

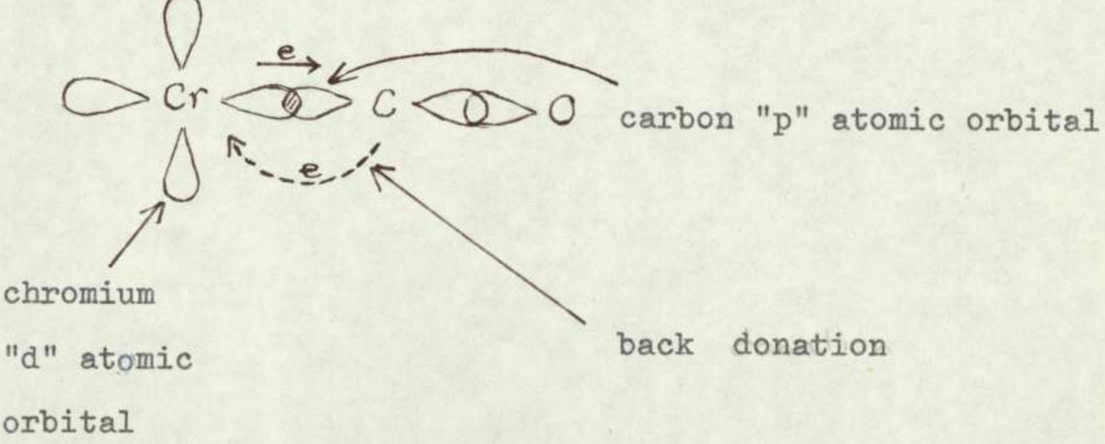
selectively dissolved away the rubber particles at or near the surface leaving "dovetail" cavities which anchored the metal plate. Transmission electron micrographs substantiating this viewpoint have been presented by Kato.[25] However, his method for producing cross-sections of the etched surface has not been reproduced by other workers. Atkinson et al [26] have also suggested that etching of ABS removes polybutadiene globules leaving a microporous surface. They believe that the SAN matrix is also attacked, permitting the rubber particles to be removed to a considerable depth. The rate of attack on the matrix is, however, much slower.

Similarly the etching of polypropylene produced a chemically roughened surface according to Fitchum et al [14]. It was thought by these workers that the amorphous polypropylene surrounding the crystalline regions was selectively attacked, and produced micro-cavities suitable for anchoring the metal.

Armond and Atkinson's [27] original paper contradicted this view. Using 6M chromic acid, their etchant attacked amorphous and crystalline regions uniformly. Nor did I.R. analysis of microtomed sections show any chemical change. However, further work did indicate the formation of some C=O groups and the attack was slightly preferential. [28]

It is believed by other workers that the microroughening role of the etchant giving rise to mechanical keying, is not the only purpose of the etchant. Rather that oxidation of the plastic takes place which results in chemical inter-

actions with the metal coating. Chan and Hawkins [29] have studied the surface oxidation of L.D.P.E. and ABS using internal reflection infra-red spectroscopy. They have demonstrated the development of C=O groups on the ABS surface. It is, however, only a qualitative technique and is difficult to apply to a deeply etched surface, as excellent contact between the radiation reflecting crystal and the polymer is necessary. Atkinson et al [26] have shown by radioactive tracer techniques that chromium remains on the polymer surface after etching and rinsing. They have suggested that it complexes with the -C=O functions, and affects the adhesion to metal. Emission spectroscopy studies by Saubestre and Khera [30] also detected the presence of chromium following etching and rinsing. They too postulated the formation of a chromium carbonyl complex as follows:



Such a complex might be stabilised by back donation electrons into vacant "d" orbitals of the chromium atom. Saubestre and Khera suggested that such a compound may be produced on the polymer surface at the base of crazes and holes and may affect metal deposition and subsequent adhesion

by complexing with tin or palladium catalyst.

On the other hand Logie and Rantell [31] have shown that on polypropylene and TPX, an etched morphology alone will produce only a poor bond between plastic and metal. Beacom and Wedel [32] have demonstrated this with nylon -6 too. The former authors have suggested that good bonding may be achieved if the chromic acid etch chemically modifies the surface to promote atomic interactions. In the case of ABS the etchant roughens the surface and in doing so increases the surface area. More nitrile groups on the polymer surface, are then available for chemical bonding per unit area of metal coating. This observation conflicts with the findings of Rempel [22] who showed that unroughened SAN gave zero peel adhesion unless the etchant increased the surface area available several fold.

Jarrett [11] has suggested that the etchant opens up the conjugated double bonds of the polybutadiene phase and that the metal may then bond to the plastic.

```
                                *
 — CH2 — CH — CH2 — CH ═ CH — CH2 — CH2 — CH —
         |                                |
         CH                               CH
         ‖*                               ‖*
         CH2                              CH2
```

Saubestre [1] agreed with this viewpoint. He also pointed out that the disadvantages of the chemical etch which are that its uniformity of attack depends on the nature of the substrate, pigments, fillers etc. and moulding conditions.

1.7 Nature and Role of Neutraliser

Any chromium residues which remain loosely attached to the polymer surface may subsequently dissolve in the catalyst solution and poison it. It is therefore necessary to remove such residues in a neutralising solution to ensure uniform adsorption of the catalyst.

Shipley's neutraliser solution contains NaOH which will chemically combine with chromium compounds and carry them into solution.

Bauer (33) has patented the use of several compounds capable of complexing with trivalent chromium ions e.g. NH_4OH, $NH_2\ CH_2\ CH_2\ NH_2$, EDTA, glycine.
Phosphates have also been suggested for this purpose.

A 30% hydrochloric acid dip may be used, which would appear to act as a drag out for the Cr (v1) rather than chemically combining with it.

1.8 Nature and Role of the Catalyst

The catalyst is adsorbed onto the chemically roughened plastic surface, where it will induce the electroless deposition of metal on that surface. Adsorption of the catalyst may be achieved in one or two stages. In the two-stage process the first treatment is referred to as sensitisation. This is followed by activation. The basis of the sensitising step is the adsorption of stannous chloride onto the polymer surface. Activation of the surface is then achieved

by immersion in a solution of palladium chloride. When $PdCl_2$ molecules come into contact with adsorbed $SnCl_2$ molecules, the following thermodynamically favourable redox reaction will occur:

$$Sn^{2+} + Pd^{2+} \longrightarrow Sn^{4+} + Pd^{0}$$

Metallic palladium is in this way deposited on the surface of the plastics material. Each solution is generally acidified with hydrochloric acid. Feldstein and Weiner [34] have found that by varying the ratio of $SnCl_2$ to HCl the polymer surface can be made more or less acceptable to the activating solution. A reduction of contact angle from 71° to 24° was achieved, coinciding with more uniform metallisation. However, the chemistry of the situation is not understood.

Feldstein et al [35] have shown that more uniform metallisation of the plastics can be brought about by the addition of aged stannic chloride to the stannous chloride solution. The active ingredient of the aged solution is thought to be a polymer of β-stannic acid. It is believed by these workers to function by providing a mechanism for adsorption of Sn^{2+} ions onto the polymer via the formation of a Sn^{2+} / Sn^{4+} complex.

Radioactive tracer studies have been carried out to determine the amount of Sn^{2+} and Sn^{4+} ions adsorbed. [36] An analysis for Pd metal following activation has shown a surface concentration of 2×10^{-5} to 4.5×10^{-5} μmole mm^{-2} which is only 10% - 25% of the Sn^{2+} concentration. The

Sn^{2+} / Pd^{2+} reaction must therefore be limited by the concentration of available Pd^{2+}.

Sard [37] has carried out an electron microscopy investigation of various catalysed substrates including glass, carbon and polyimide film. On a carbon surface treated with sensitizer, particles of 10Å are resolvable. These agglomerate into clumps of 100-250 Å. Increasing immersion time increases the number of particles. Sard suggested that the densest deposits are the most important sites for further nucleation and growth.

Single step catalyst formulations contain both $SnCl_2$ and $PdCl_2$ in aqueous HCl. An intermetallic complex is thought by Cohen & West [38] to form in this solution, in which each Pd^{2+} ion combines with three Sn^{2+} ions. This complex breaks down on the plastics surface to produce Sn^{4+} ions and a SnPd alloy surrounded by a colloidal layer of Sn^{2+}.

$$(Pd\text{-}Sn)\ \text{complex} \longrightarrow Pd + Sn^{4+} + 2Sn^{2+}$$

$$(Pd\text{-}Sn)\ \text{complex} \longrightarrow (Sn\text{-}Pd)_{\text{alloy}} + 2Sn^{4+}$$

These metallic particles so produced will catalyse the deposition of an electroless metal solution.

Rantell and Holtzman [39] have suggested that the active component of a single step catalyst is the complex Pd_6Cl_{12} $SnPdCl_4$, where Pd_6Cl_{12} is a metal cluster compound. This complex is thought to be adsorbed onto the polymer surface. Rinsing decomposes the complex to yield metallic palladium.

A graphite surface treated with a one step catalyst has been subjected to ion bombardment by Meek [40] in order to determine the number of scattering atoms on the surface. Particle sizes of 10 - 20Å were found, in agreement with West and Cohen's results.

The electroless deposition of Ni-P on $SnCl_2/PdCl_2$ catalysed surface has been studied by Marton and Schlesinger.[41] They have shown that catalytic sites of $<$10Å are produced on various substrates which grow to form hemispherical islands. The density of these sites was found to depend on the hydrophobocity of the substrate, the more hydrophilic substrate having the greater number of nuclei. Rantell [42] found a greater number of catalyst sites were produced on an inert polystyrene surface compared with an aminated surface. However, the nuclei on the more active surface were much larger.

The chemical nature of these one step and two step catalysts has been disputed. Some evidence has been presented indicating that the catalysts are truly solutions whilst other workers believe them to be colloidal in nature. Rantell and Holtzman [39,43] have carried out light scattering experiments and found no colloidal particles. Also these workers found no colloidal particles adsorbed on polymer surface during an electron microscope investigation.[44]

Matijevic et al, [45] however, have presented evidence for the existence of colloidal particles in 16 different

systems. They have separated the particles by ultracentrifuging and found them to be catalytically active. Meek [40] also believes the catalyst system to be colloidal.

1.9 Nature and Role of Accelerator.

Accelerator solutions are usually acidic. Their role is to remove any compounds present on the surface of the catalyst particles, which inhibit their catalytic ability. Ammonium bifluoride is a good general purpose accelerator.

Cohen et al [46] have demonstrated by Mössbauer spectroscopy, a shift from Sn^{4+} ions on the polymer surface, following sensitisation, to Sn^{2+} ions after acceleration. The Sn^{4+} ions are thought to be present as a layer of stannic hydroxide masking the catalyst particles. It is important that the accelerator solution should dissolve this layer completely. Besides lessening the activity of the catalyst excess tin will contaminate the electroless metal bath and codeposit with the metal on later specimens.[40]

The mechanism for the role of accelerator postulated by Rantell and Holtzman [43] is a little different. These workers believed that Sn^{2+} precipitate and adsorbed $PdCl_2$ present after the post-catalyst treatment rinse, redissolve in the accelerator and because they are uncomplexed can now undergo the simple redox

reaction, to deposit palladium. Any insoluble Sn^{4+}/ ammonium bifluoride products which could mask the palladium nuclei are removed in the final rinse.

Rantell and Holtzman have suggested that acidic accelerators may dissolve some of the Pd nuclei with resultant loss of catalytic activity.

Schlesinger et al (49) have carried out X-ray diffraction studies on catalysed and accelerated Formvar surfaces. The originally catalysed surface had an amorphous deposit. After acceleration a F.C.C. deposit was detected with lattice parameters matching Pd_3Sn. This result conflicts with that of Rantell who concluded that metallic palladium is the product following acceleration. However, it should be noted that the above workers used solutions of different composition and differing substrates.

1.10 Nature and Role of the Electroless Metal Bath

The role of the electroless metal solution is to deposit a continuous adherent layer of metal on the plastics surface, of a sufficient thickness to carry current for subsequent electroplating.

For plating on plastics purposes, electroless copper and nickel solutions are most common. Although at first sight the composition of these solutions appears very complex, when the basic chemical reactions are considered the addition of each component can be rationalized.

In the case of electroless copper solutions an obvious starting point is the presence of cupric ions, generally supplied in the form of $CuSO_4 5H_2O$. The cupric ions are generally reduced to metallic copper by formaldehyde in the presence of a high hydroxyl ion concentration. However, at high values of pH, cupric ions will normally precipitate out as cupric hydroxide. To prevent this from occurring it is necessary to add a complexing agent, which will keep the copper ions in solution. Rochelle salt is a useful complexing agent. The reaction will then proceed as follows:-

$$Cu^{2+} \text{ (complex)} + 2HCHO + 4OH^- \rightarrow Cu^0 + H_2 + 2HCOO^- + 2H_2O$$

Formaldehyde has a tendency to react with an excess of hydroxyl ions.

$$2HCHO + OH^- \longrightarrow CH_3OH + HCOO^-$$

This reaction is suppressed by the addition of methanol to the solution.

It is possible for a Fehlings type reaction to occur in the electroless solution, without a catalyst. (50)

$$2Cu^{2+} + HCHO + 5OH^- \longrightarrow Cu_2O + HCOO^- + 3H_2O$$

The cuprous oxide will react reversibly with water.

$$Cu_2O + H_2O \rightleftharpoons Cu^0 + Cu^{2+} + 2OH^-$$

Thus a chain reaction may be set up which results in complete decomposition of the copper bath.

The Fehlings reaction is countered by aeration of the solution, so that any cuprous ions tend to be oxidised to cupric.

Any copper particles should be filtered out and for those which are too small, polyunsaturated alcohols may be added which coat them and prevent them acting as catalytic sites.

Finally the addition of chelating agents to mop up any remaining cuprous ions, prevents the disproportionation reaction e.g. NaI, NaCN.

A typical electroless nickel bath contains nickel chloride as a source of the metal, complexing agents and a strong reducing agent e.g. diethylaminoborane or hypophosphite. The former will reduce the nickel ions as follows:

$$3NiCl_2 + (C_2H_5)_2NH.BH_3 + 3H_2O \rightarrow 3Ni + (C_2H_5)_2NH_2Cl + H_3BO_3 + 5HCl$$

A pH buffer is added to counteract the acid produced in this reaction, otherwise reducing agent would be consumed in the following side reaction:

$$(C_2H_5)_2\ NH\ BH_3 + 3H_2O + HCl \rightarrow (C_2H_5)\ NH_2\ Cl + H_3BO_3 + 3H_2$$

If hypophospite is used as the reducing agent the deposition of nickel occurs by the reaction :

$$Ni^{2+} + (H_2PO_2)^- + H_2O \rightarrow Ni^o + 2H^+ + (H_2PO_3)^-$$

Müller & Baurand [51] list some typical formulations for electroless copper and nickel baths.

The nucleation and growth characteristics of electroless copper and nickel have been widely studied.

Sard [37] has found that electroless copper nucleates only at catalyst nuclei on the polymer surface. Electron micrographs show the rate of growth. After 3 second immersion copper particles of up to 300Å are formed. After 10 seconds they exceed 500Å and are randomly oriented. Fewer aggregates of a larger size are produced with a lower surface concentration. As the 3-dimensionally growing nuclei extend, they converge to form large unstable aggregates which recrystallise. The more recent findings of Wabner et al [52] do not agree with those of Sard, however. These workers have said that nucleation of copper is statistically distributed over the surface of ABS. Using a silver activating solution they carried out an SEM study of electroless copper nucleation. Copper was found to nucleate not only on the active centres, but at a distance from them. This has been explained by currents being set up in the solution in the neighbourhood of the catalyst particles leading to deposition of copper which itself catalyses further reduction.

The deposition of nickel and copper on catalysed PS has been studied. [42] Rantell has suggested that the number of growing islands is not so important but

rather the number of crystallites making up the islands, when considering nucleation and growth characteristics.

Dumesic et al [53] have quantitatively measured the rate of deposition of electroless copper on a silver activated glass surface, by light transmission measurements and atomic absorption spectroscopy. When surface coverage of 0.25 $\mu g\ mm^{-2}$ was achieved the rate of deposition increased rapidly. The initial period probably corresponded to the isotropic growth of the copper nuclei. When the catalyst sites were completely covered and a complete copper film was produced, a faster rate of deposition was achieved, probably corresponding to a different mechanism.

The electrochemical kinetics of electroless deposition were proposed by Paunovic. [54] He stated that at equilibrium the rate of deposition of metal is equal to the rate of oxidation of the reducing agent. Addition agents can affect the rate of deposition by either reducing the "electrode" surface area available for reaction thus increasing actual current density or by introducing a new slow step into the mechanism e.g. transport of reactants across an adsorbed layer.

1.11 Assessment of Adhesion

In order to measure the adhesive force existing between a coating and substrate it is first necessary to define what is meant by this quantity. If it is defined as the force, when acting normally to the coated surface, that will

just separate the upper layer from the substrate, then it is necessary to find a test which will produce separation exactly at the interface. Many so called adhesion tests however, result in the specimen failing at some distance from the interface in either the substrate or the coating. In practise then the results of such tests merely indicate whether or not the interfacial bond is weaker or stronger than the cohesive forces existing in the base material and coating. Such results may well be sufficient for comparative studies or for determining how well a component would perform in service. However certain tests have been developed which may well measure truly interfacial forces, as will be discussed later.

1.11.1 Qualitative Tests

Lowenheim [1] has produced a comprehensive list of such tests ranging from repeatedly bending a sample, filing, and peeling a strip of sellotape from the surface. Some of these tests have the advantage that they can be performed on production components rather than requiring special test pieces, but they rely heavily on visual interpretation and nonstandardised manual application. Also many of the tests are destructive.

1.11.2 Quantitative Tests

The tensile joint strength of metal to adhesive has been measured [55] and it has been claimed to produce results with very low standard deviations compared with the Jacquet peel

test, which will be discussed. A similar test has been developed to determine this quantity for ABS and polypropylene coated with electrolytic copper.[56] For both types of polymer composite failure did not occur exactly at the interface.

A number of peel tests have been described, the most quantitatively rigorous being the so called Jacquet peel test. Saubestre[57] has carried out a mathematical analysis of this test, which involved peeling a metal strip of standard width from a polymer substrate, at a constant rate and measuring the necessary force. The peel force was found to be a function of the mechanical properties of the metal and polymer together with the thickness of the plate and also the thickness of the plastic yielding film. Since failure occurred within the polymer true interfacial adhesion was not determined from this test.

An alternate analysis by Anderson[58] et al has successfully eliminated the mechanical properties of the metal coating from the peel value by considering a debonded region of metal just behind that bent upwards. A debonding force rather than a peel force was determined. However the experimental technique was limited to transparent substrates.

A method of peel testing claimed to be independent of peeling rate and coating thickness has been claimed.[59] This test necessitated peeling a strip of expanding width

from a substrate, under constant force. The width of strip which balanced the applied force was recorded as a measure of peel strength.

Thermal cycling as a means of adhesion testing is well known. Such a test is described in ASTM B 533-71. [60] Separation of coating and substrate due to differential thermal expansion may occur at the actual interface, but thermal degradation of polymeric substrates may be problematic.

Saubestre et al [57] have indicated that there is some correlation between thermal cycling results and Jacquet peel test values for copper plated ABS. However these authors stress that these tests do not in fact measure the same thing since in the case of the Jacquet method failure occurred within the plastic substrate. Thermal cycling on the other hand resulted in separation at the metal polymer interface.

A variety of ingenious test methods have been described. It may be possible for instance, to obtain a quantitative value for interfacial adhesion by the response of the interface to ultrasonic vibrations. Moses and Witt have described such a method. [61]

A further means of determining adhesion based on an increase in temperature has been suggested. When a coating was peeled from a substrate, the work done was assumed to be converted to heat, and the resultant rise in temperature was a direct measure of resistance to peeling. [62]

Such a test however would have suffered from a number of disadvantages e.g. non-uniform release of heat and subsequent formation of hot spots, energy dissipated other than in the form of heat.

Bikerman [63] has suggested that where a polymer of density p_1 coated with a metal of density p_2 is immersed in a liquid of density p_0 so that $p_1 < p_0 < p_2$, gravitation would try to push the metal down and the polymer up. Assuming the force changed direction at the interface, separation of the phases would occur at this place.

CHAPTER TWO

Metal / Polymer Adhesion Promotion

2.1. Introduction

2.1.1. Nature of Adhesion.

There has been much controversy regarding the nature of the bond between metal and plastic. It has been considered to be a purely mechanical bond by some workers whilst others believed it to be chemical. A combination of both seems most likely.

2.1.2. The Mechanical Bond.

Advocates of the "mechanical bond" theory proposed that chemical etchants applied to the plastics surface created a network of shallow pits on the surface. These pits which may have undercut the surface, provided anchoring points for the metallic deposit, the metal being held in position by mechanical keying.

METAL

PLASTICS SUBSTRATE

Pitting of the plastics by the etchant was due to preferential dissolution of certain areas of the surface layer. In the case of ABS it was thought that the discrete spheres of polybutadiene were preferentially attacked by the chromic acid (26) or removed by the organic conditioner to produce the surface pits and undercuts. (19)

Similarly polypropylene has a two phase structure and it was believed that preferential removal of the amorphous polymer, which forms around the crystalline regions, took place.

Much evidence for a mechanical type bond has been presented. Elmore and Davis [64] have demonstrated by electronmicroscopy the capacity for mechanical interlocking on etched polymer surfaces. They found that for a range of plastics, bond strength was similar, and that surface roughness rather than chemical interactions was more important in determining adhesion. However, the plastics under examination did not cover a wide range of polarity to allow for differing chemical interactions and as will be explained later an increase of surface roughness producing better adhesion may also have been argued as evidence for chemical bonding.

Further evidence for the mechanical type bond has been offered by Rempel [22] and others (25, 65).
He observed that when a plastics substrate was overetched, a reduction in peel adhesion occurred. This was thought to be due to the degradation of the plastics material and the resultant loss of mechanical properties. However, it is possible that overetching resulted in a reduction in surface area and hence less opportunity of chemical bonding to take effect.

Optimum etch   Overetch

Similarly the zero peel adhesion of metallised unetched SAN, can be explained by the unetched surface having a comparatively small area. A sufficiently large number of polar - CN groups were therefore not available for chemical bonding with the metal.

Matsunaga et al [24] have examined strips of copper pulled off from a polymer substrate. The metal was covered with a thin film of polymer, through which spots of copper protruded. These workers have suggested that these spots of copper corresponded to metal anchors, mechanically holding the metal to the plastic. Ebneth and Klimaschewski [66] have compared the effects of strong and weak etchants on ABS. They believed that the etchant first produced microcavities on the polymer surface of up to 0.2 µm in diameter by the preferential dissolution of the polybutadiene globules. Further exposure led to dissolution of some SAN and the enlargement of these cavities. These results were in agreement with the observations that the adhesion of electroless copper fell after a short time, whereas less penetrating vaporised copper showed improved adhesion with increased etch time. Again the same argument may be raised against this evidence, that whilst microroughness gives better mechanical keying it also improves the chances for chemical interactions.

In the case of metallised polypropylene Fitchum et al [14] have shown that peel adhesion was related directly to the depth of the crack path. Highest adhesion was obtained corresponding to greatest crack depth. It would seem

therefore that the strength of the surface layer of polymer is important in determining the peel strength of the composite. However, this does not necessarily imply that the bond between the metal and the polypropylene was purely mechanical, as failure will always occur at the weakest point, and this may have still been in the surface layers of the polymer if there were strong chemical bonds at the interface.

Heymann [67] made observations similar to those of Matsunaga et al, [24] and he believed the bond was more likely to be mechanical, as the formation of a covalent bond between metal and polymer was unlikely.

2.1.3. <u>The Chemical Bond</u>

Much evidence has been presented to show that chemical interactions are responsible, at least in part, for the adhesion of plastics to metals. Opinions vary as to the nature of such a bond. Saubestre [4,68] has suggested that a covalent bond may have been formed between the carbon skeleton of the polymer under investigation and a metal atom.

Unsaturation may have been present in polymer chains as a result of processing, or as a functional group in the monomeric units. Any points of unsaturation would have been susceptible to oxidative attack.

−C−C−C=C−C−C−
(arrow from $\bar{O}$ to the C=C bond)

The most likely reaction was the formation of carbonyl groups.

```
   |    |         |    |
 — C —  C —  C —  C —  C —
   |    |    ‖    |    |
             O
```

However, Saubestre has suggested that the attacking oxygen atom may have attached itself to the nucleophilic carbon atom by a single covalent bond, and remained electronically unsatisfied. Such an oxygen atom would have readily bonded to a metal atom.

```
  |    |    |    |       M         |    |    |    |        M = metal atom
 -C —  C —  C —  C-    ——>      -C —  C —  C —  C —
  |    |    |    |                |    |    |    |
       O    O                          O    O
       •    •                          |    |
                                       M    M
```

The viability of this mechanism rests on the stability of the single bonded oxygen function, bearing in mind that in a plating on plastics process, following chemical oxidation, the material is in contact with air and rinse water, prior to immersion in the $SnCl_2/PdCl_2$ solution. Chan and Hawkins [69] have studied surface changes of L.D.P.E. and ABS during ageing, using internal reflection infra red spectroscopy. In both cases they have observed the formation of carbonyl functions. This suggests that the type of intermediate postulated by Saubestre, if it did in fact occur, was likely to produce a carbonyl grouping.

More likely was the later theory of Saubestre and Khera [30]

who postulated the formation of carbonyl functions which themselves reacted to produce chromium complexes. The complex chromium groups may then have been capable of combining with tin or palladium ions.

```
                                     ┌    O    ┐ 2-
  |    δ+   |                        |    |    |
 -C  -  C  -  C  -        +          | O - Cr - O |      ──>
  |     ‖   |                        |    |    |
        O δ-                         └    O    ┘


        O
        |
  O = Cr = O          Sn  2+        -C  -  C  -  C  -
        |                            |     |     |
        O         +   or        ──>        O
  |     |     |       Pd  2+        ┌      |      ┐
 -C  -  C  -  C  -                  | O  - Cr  - O |    Sn (or Pd)
  |     |     |                     └      O      ┘
```

In this way it may have been possible to form a true metal-polymer bond.

The presence of firmly attached chromium, tin and palladium has been determined spectroscopically, which indicated that these elements were chemically bonded to the polymer. However, mechanical entrapment cannot be discounted.

Similarly the presence of chromium has been determined by radioactive tracer techniques. (26)

The experiments of McGregor and Perrins (70) were put forward as further evidence of chemically bonded chromium.

Adhesion resulting from etching plastic in a chromic / sulphuric / phosphoric acid mix, was found to be removable by dipping the plastic in hydrochloric acid. A further exposure to the etchant restored adhesion. A solution of CrO_3 was on the other hand incapable of such restoration. These workers believed that extraction in HCl broke the chemical bonds of the chromium to the polymer. Since chromium ions could have been readsorbed from either the etchant or the CrO_3 adhesion must have been due to the formation of stronger chemical bonds, resulting from the oxidising nature of the etchant. Gorashi (71) has published similar results. Electron micrographs have been presented to show that loss of adhesion by extraction in HCl was not due to over-etching. However, such evidence did not rule out submicroscopic changes having been brought about.

If an actual chemical bond, ionic or covalent did not form between the metal and polymer, at least some form of chemical interaction between the two may have reasonably been expected. Rantell (72) has aminated, hydroxyazotised and diazotised the surface of polystyrene by the following series of reactions.

$$-CH_2-CH(C_6H_5)- \xrightarrow{HNO_3/H_2SO_4} -CH_2-CH(C_6H_4NO_2)-$$

$$-CH_2-CH(C_6H_4NO_2)- \xrightarrow[65^\circ C]{H^+/SnCl_2} -CH_2-CH(C_6H_4NH_2)-$$

$$-CH_2-CH(C_6H_4NH_2)- \xrightarrow[0^\circ C]{\text{nitrous acid}} -CH_2-CH(C_6H_4N_2^+)-$$

$$-CH_2-CH(C_6H_4N_2^+)- \xrightarrow[0^\circ C]{\text{aq. phenol}} -CH_2-CH(C_6H_4-N=N-C_6H_4-OH)-$$

Transmission electron microscopy has revealed no apparent changes in surface roughness during the course of these reactions although submicroscopic alterations may have been affected. However, each reaction resulted in a marked increase in peel adhesion. It seems likely therefore that this increase was due to chemical interactions, e.g. Van der Waals forces between the polar groups produced on the polymer surface, and the metal.

Logie and Rantell [31] have shown that with non-polar polypropylene and TPX an etched morphology is insufficient for producing good adhesion. Rather, the chemical changes which occurred during the etch process were necessary.

In the case of ABS they found good adhesion for all levels of surface roughness under test, and this was attributed

to interactions of the -CN groups of the acrylonitrile, with metal atoms.

Nylon - 6 has been etched in a halogen / halide solution by Beacom and Wedel.[32] Electron micrographs again have shown no visible change in surface roughness during etching but the previously mentioned limitation to this evidence again applies. However, etching improved the peel strength of the metallised polymer significantly. Chemical forces were likely therefore to have been responsible at least in part for adhesion.

The interactions of PTFE and polyimide with various metals have been studied by field ion microscopy.[73] These investigations indicated that the bonds were chemical in nature. The polymer / metal interactions were believed to be via the carbon atoms rather than the fluorine atoms, in the case of PTFE.

Arrowsmith[74] has examined the peel strength of electroformed copper to epoxy laminates. By varying the morphology of the electroformed copper bonding face e.g. producing pyramids and dendrites on the metal surface, it was found that adhesion could be improved. Adhesion was further improved by oxidising the copper foil. Some of the initial improvement may have been due to mechanical interlocking of the dendrites with the polymer. Alternatively, the increased surface area of the dendrites may have permitted more chemical inter-

actions between the polar epoxy and the metal.

Similarly Miksys et al [75] have stated that the prerequisites for good adhesion are a hydrophilic polymer surface which is microroughened by chemical means, rather than mechanical.

Rantell [76] concluded that good peel adhesion resulted from a combination of chemical interactions, surface roughness and substrate toughness.

2.1.4 Adhesion Promotion

Whether or not a metal layer will remain attached to a polymer substrate during service depends on a number of factors. These include the interfacial adhesion, which may be a combination of mechanical keying and chemical bonding, the relative proportions depending on the materials used and their processing, and the mechanical properties of the metal and polymer. Adhesion promotion may be achieved by optimising one or more of the above factors.

Radiation has been used to improve the mechanical properties of the polymer and in so doing, improved peel adhesion. The possibility of producing metal to polymer bonds by the use of radiation has also been suggested.

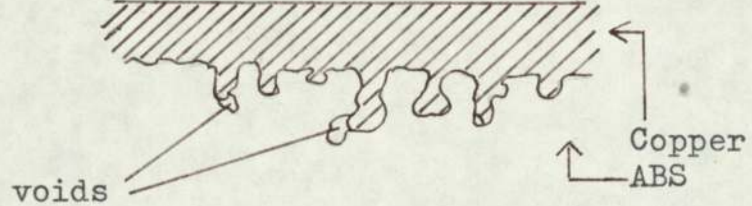
Schonhorn and Hansen [77] have improved adhesion of

metal to low surface energy polymers by irradiating the composites with activated species of inert gases. This led to crosslinking of the surface of the polymer, and resultant higher cohesive strength.

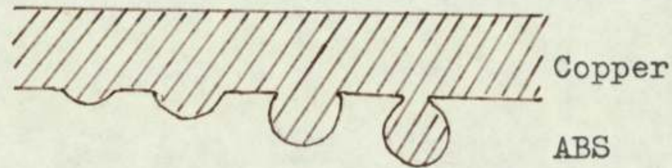
Corona bombardment of fluorocarbons has been described by Goldie.[78] It was suggested that improved adhesion resulted from the production of free radicals capable of forming chemical bonds with metal atoms.

Ion bombardment will be dealt with at length in a later chapter.

Mechanical keying may be improved by varying the etchant, the composition of the plastics substrate and the moulding conditions of the latter.[1] By correct modifications optimum surface morphology may be obtained. Consider an ABS / copper composite with the following cross-section:



In an idealised situation the etch pits of the ABS will be spherical and sunk to different depths in the surface according to the location of the original polybutadiene particles.



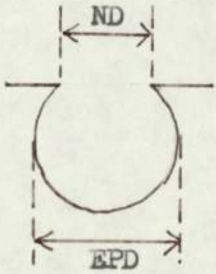
If the copper layer is now peeled from the ABS substrate, failure is likely to occur in one of three ways.

(1) The copper will part cleanly from the ABS, the ABS deforming to an extent sufficient to release the metal.

(2) The copper dovetails will pull out of the ABS hollows and in doing so tear off the etch pit shoulders, which will remain stuck to the metal.

(3) The copper will fracture along the neck of the dovetails, leaving a spherical copper particle embedded in the plastic.

The choice of operating mechanism will depend on the ratio of the etch pit diameter (EPD) to the etch pit neck diameter (ND).



When the ND : EPD is close to one, the first mechanism is most likely. Such a mechanism would result in a low peel strength, as little work is done in deforming the polymer, and the surface area of metal and polymer in

contact allowing chemical interactions, is less than half of the maximum. As the ratio tends to zero the second or third mechanism is more likely. In this instance the copper is much stronger than the polymer, and for this reason the second mechanism will operate, unless the neck diameter is several times smaller than the etch pit diameter. Either mechanism is likely to produce good peel adhesion. In the case of mechanism 2 it will be necessary to expend energy deforming the polymer and overcoming metal to polymer chemical bonds. Mechanism 3 will require fracture of copper dovetails, and this too will have a high energy requirement compared with the first mechanism.

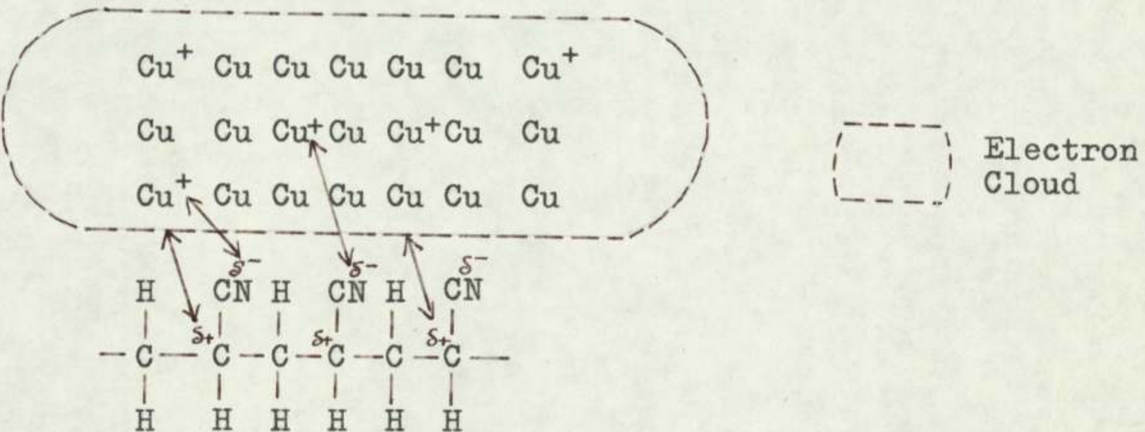
Therefore tailoring the polymer surface morphology, by varying the etch, polymer composition and moulding procedure, to produce etch pits with the maximum amount of dovetailing without severely degrading the shoulders of these etch pits, should lead to improved mechanical keying and better peel strength.

It is also apparent from the above consideration that complete filling of the etch pits by electroless metal is necessary for good adhesion. If the polymer surface is chemically treated to improve its wettability, then this chemical reaction may bring about improved mechanical keying, via more efficient filling of the etch pits.

2.15 Chemical Adhesion Promoters

It is possible to enhance metal to plastics adhesion by increasing chemical interactions between the two.

The metallic coating possesses a cloud of free electrons encompassing a lattice of positive ions, the complete structure being electrically neutral. Because of this electronic arrangement there is plenty of scope for bonding with any polar groups in a polymer substrate. The electron cloud may interact with positive centres, whilst the positive metal ions will be attracted to excess negative charge on the plastics material. Let us consider diagramatically the possible interactions of copper plated polyacrylonitrile for example.



The type and density of these adhesion promoting interactions may be altered by chemically treating the polymer to produce active groups on the chains. This is thought to be the case during chemical etching.

However, there are several other ways of introducing polar functions into the plastics substrate. In the case of polypropylene, it is possible to improve adhesion by incorporating a small percentage of polar monomer during polymerisation e.g. methacrylic acid. The structure of this monomer is highly polar.

```
H         CH3
|         |
C    ==   C
|         |
H         C  =  O
          |
          OH
```

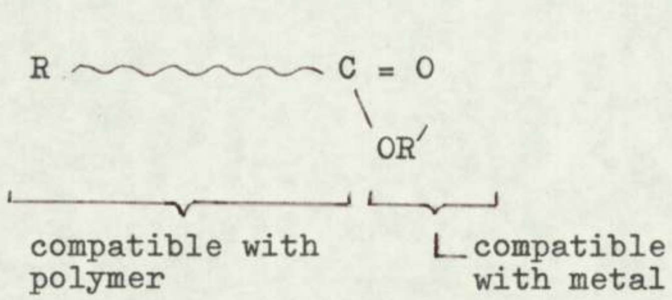
The resultant copolymer is then capable of strong Van der Waals type interactions with a metal coating.

Copolymerising may also improve adhesion in a completely different way. The presence of some polyethylene / polypropylene copolymer in polypropylene reduces the crystallinity of the plastics material, making it more susceptible to chemical oxidation. (79)

A further means of enhancing chemical bonding, is to introduce into the surface of the polymer a highly polar compound. This may be achieved by mixing in the adhesion promoting compound with the other additives when the plastics material is compounded. Alternatively, when the plastics moulding has been produced, the adhesion promoter may be introduced into the surface by swelling it into the surface layers dissolved in a

suitable solvent.

Many compounds have been claimed to promote adhesion, and the common factor of these widely differing molecules is their polarity. A large number of these compounds contain at least one carbonyl function. Takashi et al [80] found that oleic acid and butyl stearate both acted as good adhesion promoters. It is interesting to note that these molecules both consist of a long non-polar hydrocarbon chain with a highly polar carbonyl group at the end. It seems likely that the hydrocarbon section will be very compatible with the polymer substrate whilst the terminal carbonyl groups can interact with the metal plate.



$R' =$ H for oleic acid

$R =$ C_4H_7 for butyl stearat

However, according to Bikerman [81] it is necessary for the oleic acid to be soluble in the plastics substrate, for it to act as an adhesion promoter. This worker found that oleic acid, compounded with polyethylene, diffused to the polymer surface and because it was incompatible with the polymer could not form a link between substrate and metal coating.

The oxyethylates derived from the following have been

patented [82] as adhesion promoters:

Fatty acids ($C_{10} - C_{18}$) + Ethylene oxide

Coconut fatty alcohol + Ethylene oxide.

By using a combination of correctly chosen additives, a synergistic improvement of adhesion may be obtained.

Prior to etching ABS, immersion in a solution containing methyl acetonate and a compound of the following family promotes adhesion. [83]

$$CH_3 - \overset{O}{\overset{\|}{C}} - O - R - O - R'$$

R = Aliphatic $C_1 - C_4$

R' = H, Me, Et, $-C_2H_4 - O - C_2H_5$

The incorporation of 0.7 to 1.5% of isooctyl stearate will promote adhesion according to patent literature. [84] It has been suggested that this molecule actually forms covalent bonds though there is no evidence for this.

Methyl abietate may be blended into or swelled into polypropylene, where it too will promote adhesion. [85] Again the non-polar chain with a highly polar end type structure is found to be effective.

A number of unsaturated fatty acids have been claimed to promote adhesion of metal to polypropylene. These included sorbic acid, linoleic acid, castor oil, and linseed oil.

Solutions of 1,3 diphenyl - 2 - propanone in an organic solvent and 1,5 cyclooctadiene or bicyclo (2,2,1) - heptane - 2 - 5 - diene in aqueous / organic solvents have been patented as adhesion promoters for polypropylene and some of its copolymers. (86) It is believed that the ketone and dienes promote uniform oxidation of the polymer by chromic acid and in so doing, they enhance adhesion.

It has been claimed that adhesion may be promoted by coating the surface of polypropylene with some carbonyl modified polymer. (87) This is produced by heating amorphous polypropylene with an unsaturated mono or dicarboxylic acid in the presence of a free radical generator.

Two further types of adhesion promoting compounds containing oxygen linkages have been described.

The adhesion of metal to PVC, poly (vinylidene chloride) and poly (vinyl dichloride) may be improved by contacting the polymer with an alkali metal alkoxide e.g. $NaOC_2H_5$, $NaOC_3H_7$. (88)

Certain organic peroxides of the types

$$R'-O-O-R^2 \qquad R_1-\underset{\displaystyle OH}{\overset{\displaystyle R_2}{C}}-O-O-X \qquad (R^3CO)_2O_2$$

Where R' = monovalent organic residue

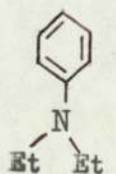
R^2 = H or monovalent organic residue

X = H or R' and R^2

R^3 CO = acyl group

may be used as adhesion promoters.[89] These compounds, e.g. cumylhydroperoxide and diisopropylbenzeneperoxide, are swollen into the surface of polyolefins where they are decomposed by an inorganic acid dip. This results in the evolution of nascent oxygen which activates the surface to the subsequent chromic acid etch.

A number of nitrogen containing compounds have been patented as adhesion promoters. Like oxygen, the nitrogen atom gives the molecule, of which it is a part, some polarity and so there is potential for chemical interactions. Also the nitrogen atom possesses a lone pair of electrons which may be capable of co-ordinating to a metallic lattice and forming a strong chemical bond. Adhesion to polypropylene may be improved by treating the polymer with a solution of a secondary or tertiary amine.[90] The most effective is said to be N,N - diethylaniline



Compounds of the type M - $(L)_x$ - A have been patented[91] where

$M = Ag^{+}, Au^{1+}, Pd^{2+}, Os^{6+}, Ir^{4+}, Rh^{3+}$

L = Nitrogenous ligand e.g. ammonia, sec or tertamine.

A = Organic or inorganic acid anion

e.g. PO_4^{3-}, Cl^-, SO_4^{2-}, CH_3COO^-

X = 2,3,4

Aliphatic amines containing at least one hydroxy, alkoxy or acyl group have been claimed to promote adhesion to polypropylene and some of its copolymers. (92)

e.g. $HO-R_1$, $HO-R_1$ > NR_2 $\quad R_1 = C_2 - C_6$, $R_2 = C_{12} - C_{16}$

The incorporation into ABS of a low molecular weight polymeric material containing a basic nitrogen atom, is claimed to promote adhesion (93) e.g. poly (vinyl pyridine.) Certain pyrrolidones have been patented as adhesion promoters for use with thermosetting resins (94) e.g. 1-butyl - 2 - pyrrolidone.

Both nitrogen and oxygen lie in the first row of the periodic table. Directly below these two elements are phosphorus and sulphur and it is not surprising therefore that certain compounds containing sulphur or phosphorus atoms have been patented as adhesion promoters. The use of a number of phosphorus compounds renders chemical etching of the polymer substrate unnecessary. These phosphorus containing materials will be dealt with in a later section on

alternative methods of plating.

By blending compounds of the type $M^{+} - SO_n - Q$ into polypropylene and certain of its copolymers, adhesion to metal may be improved.[95]

M = alkali metal e.g. Na

Q = aliphatic residue $C_8 - C_{18}$

n = 3 or 4

Similarly a number of sulphur compounds have been patented for use in alternative plating methods.

2.2 Experimental Procedure

2.2.1 Preparation of Complexes

Some transition metal acetyl-acetonato complexes were prepared as follows, and were tested for adhesion promoting activity.

(1) Nickel (11) acetylacetonate

To a solution of 59.4g (0.25 mole) $NiCl_2$ $6H_2O$ in 250ml water was added a solution of 50g of acetylacetone (0.5 mole) in 100ml methanol while stirring. To the resulting mixture was added a solution of 48g (0.5 mole) sodium acetate in 150ml water. The mixture was heated briefly on a hot plate, cooled to room temperature and placed in a refrigerator overnight. The green solid precipitate was filtered off, washed with water and dried in a vacuum desiccator.[96]

$$Ni^{2+} + 2\left[CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\right] \xrightarrow{Na\ COO\ CH_3}$$

$$Ni(O-C(CH_3)=CH-C(CH_3)-O)_2$$

(2) Copper (11) Acetylacetonate

25g ($\frac{1}{8}$ mole) cupric acetate was dissolved in 350ml water, and 25g (0.25 mole) acetylacetone dissolved in 50ml of methanol was added with stirring. The sky blue precipitate was filtered off on a Buchner funnel, washed with water, and dried in a vacuum desiccator. (97)

$$Cu^{2+} + 2\left[CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\right] \rightarrow Cu(O-C(CH_3)=CH-C(CH_3)-O)_2$$

(3) Chromium (111) acetylacetonate

8g $CrCl_3\ 6H_2O$ (0.03 mole) was dissolved in 300ml

water. To the solution was added 60g urea and 18g acetylacetone. The reaction mixture was heated for several hours on a water bath. Deep maroon crystals were filtered off, recrystallized from hot benzene and petroleum ether, and dried in a vacuum desiccator.(98)

Cr^{3+} + 3 [$CH_3COCH_2COCH_3$] → $Cr(C_5H_7O_2)_3$

(4) Iron (111) acetylacetonate

A solution of 33.8g $FeCl_3\ 6H_2O$ ($\frac{1}{8}$ mole) in 125ml of water was prepared. To it was added 37.5g acetylacetone ($\frac{3}{8}$ mole) dissolved in 50ml methylated spirit. Finally 51g sodium acetate ($\frac{3}{8}$ mole) dissolved in 250ml water was added to the reaction mix. A red precipitate formed, which was filtered off and recrystallised from a little methylated spirit. The product was then dried in a vacuum desiccator. (97)

3 [$CH_3COCH_2COCH_3$] + Fe^{3+} → $Fe(C_5H_7O_2)_3$

2.2.2 Compatibility of above complexes with Shipley solutions.

The effect of the Shipley precatalyst, and catalyst solutions on the acetonate complexes was tested. Their solubility in the Shipley organic conditioner was also determined.

2.2.3 Preparation of Test Pieces.

Five 500ml portions of Shipley's Crownplate organic conditioner were made up, and to each portion but one was added a metal acetylacetonate complex up to its saturation point.

Plaques of Z grade ABS as used by Tipping [99] were moulded according to standard procedure [100] and were treated in the modified Shipley Crownplate system, as follows:

1. Alkaline cleaner : 3 mins., 60°C.
   Rinse.
2. Hydrolyser : 3 mins., 64°C
   Rinse.
3. Organic conditioner containing dissolved complex :
   x min., 32°C x = 2,4,6,8 and 10.
   Rinse.
4. Precatalyst acid dip: 3 min., 45°C.
5. Catalyst : 4 min., 45°C.
   Rinse.
6. Accelerator : 3 min., 40°C
   Rinse.

7. Electroless copper : 15 mins., 20°C.

Rinse.

The thickness of the electroless metal deposit was built up to 50 µm by electroplating in a pyro phosphate copper bath.

Plaques were also prepared using conditioner in which no metal complex had been dissolved, for control measurements.

After leaving for one week in a desiccator the plaques were prepared for peel testing by milling two parallel slits 25.4mm apart along the length of each plaque, as described by Tipping.[99]

2.2.4 Peel Testing

Four peel test values were obtained for each treatment using standard peel test procedures.[101] Results are presented in table and histogram form.

2.3 Results

2.3.1 Reactivity of Complexes with Shipley Solutions

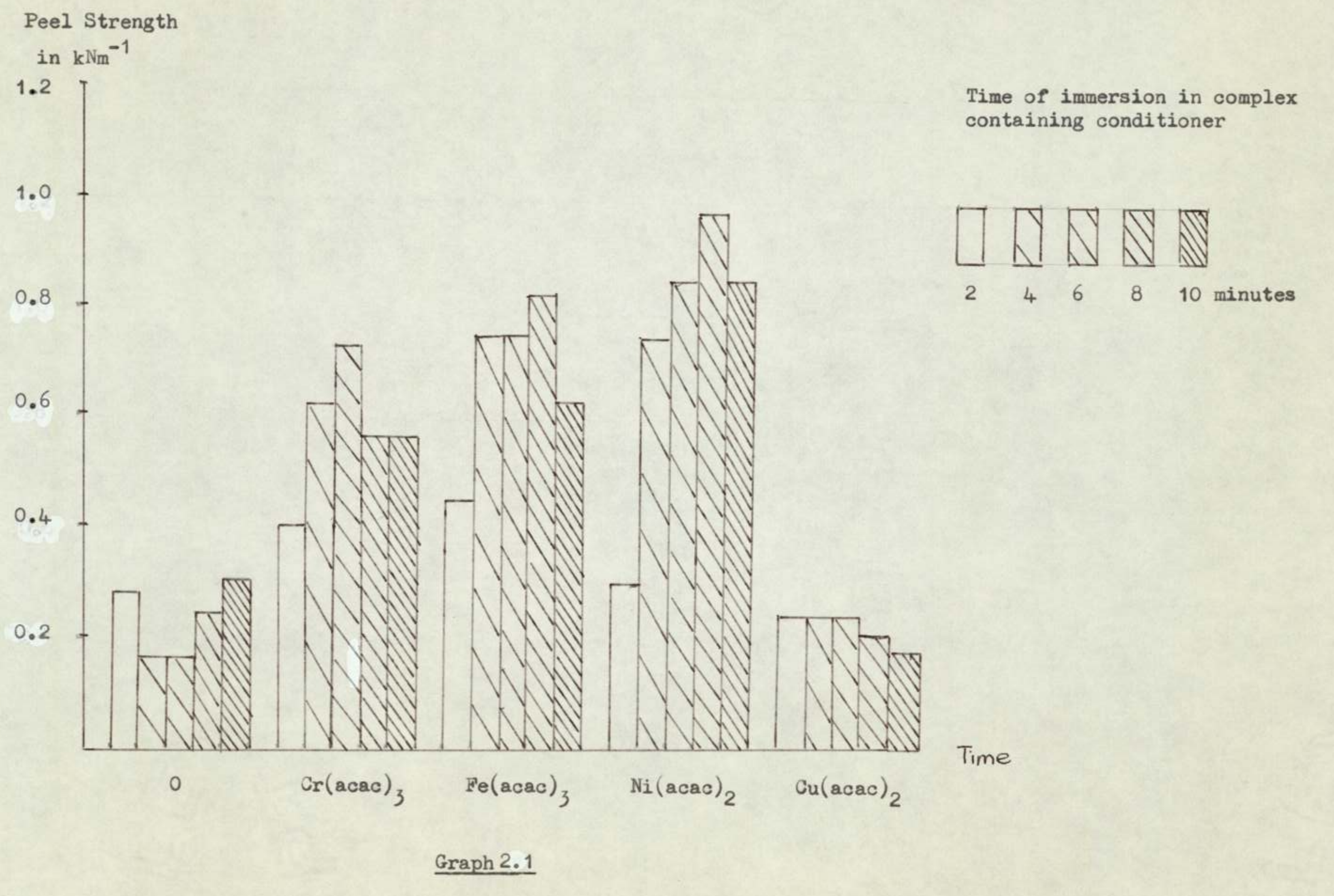
The copper and nickel acetylacetones dissolved rapidly in both precatalyst and catalyst solutions whilst the iron and chromium complexes remained insoluble in both.

Complex	Solubility in Conditioner	
	g/l	Mole / l
$Cr\ (acac)_3$	4.2	0.012
$Fe\ (acac)_3$	2.58	0.007
$Ni\ (acac)_2$	2.81	0.011
$Cu\ (acac)_2$	1.45	0.006

Table 2.1

IMMERSION TIME (MINUTES)	PEEL STRENGTH (kN m^{-1})									
	CONDITIONER ONLY		COND + Cr $(acac)_3$		COND + Fe$(acac)_3$		COND + Ni $(acac)_2$		COND + Cu $(acac)_2$	
	Aver-age	Max	Average	Max	Average	Max	Average	Max	Average	Max
2	0.30	0.30	0.40	0.45	0.45	0.50	0.60	0.60	0.25	0.30
4	0.15	0.20	0.60	0.70	0.75	0.80	0.75	0.80	0.25	0.25
6	0.15	0.15	0.70	0.75	0.75	0.80	0.85	0.90	0.25	0.25
8	0.25	0.30	0.55	0.60	0.80	0.90	0.95	1.05	0.20	0.20
10	0.30	0.40	0.55	0.60	0.60	0.70	0.85	0.90	0.20	0.20

TABLE 2.2

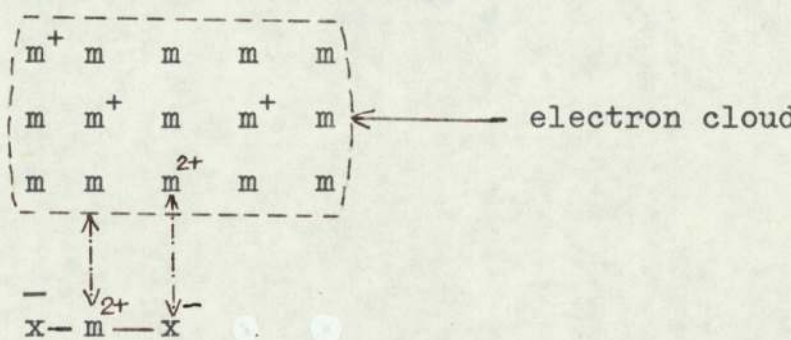


Graph 2.1

2.4 Discussion.

In order to determine the chemical and structural requirements for an adhesion promoting molecule, it was necessary to examine the possible mechanisms for adhesion enhancement.

If the mechanism is of dipolar interactions between the adhesion promoter and the metal coating then polarity in the molecule is important. A negatively charged component would be capable of attracting the positive metal ions in the metallic lattice of the coating, and the electron cloud distributed over this lattice would be attracted by a positively charged component in the adhesion promoter. The incorporation of a simple inorganic salt into the surface of the polymer might fulfil this requirement.



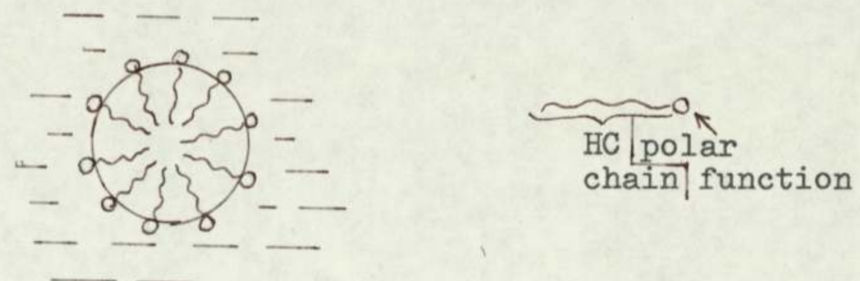
To promote adhesion the salt must reside at the polymer surface and it must also have an affinity for the polymer if it is to form a bridge between the polymer and the metal. Therefore the compatibility of the adhesion promoter with the polymer substrate is also an important consideration. If the molecule is very soluble in the plastics substrate

then it will tend to diffuse into the bulk and be ineffective. On the other hand, if totally insoluble, whilst having an affinity for the metallic coating there would be no bond with the substrate. It would seem therefore that a compound with a fairly low solubility might be most useful, as such a compound would tend to reside at the interface, but some affinity for the polymer would be retained. To achieve the right balance, the nature of the polymer substrate must be taken into consideration. If the substrate has very little polarity e.g. polyethylene or polypropylene, then a suitable compound might well contain a long hydrocarbon chain for compatibility with the polymer coupled with a polar function. Obvious examples are long chain fatty acids and their derivatives. By varying the length of the hydrocarbon chain, the desired degree of compatibility may be found. When the polymer substrate contains polar groupings as in the case of ABS plastics, then the type of compound which is compatible with this family of plastics will be a rather more polar molecule. On this basis it seems reasonable to expect that acetylacetonate metal complexes might be suitable adhesion promoters for ABS.

Assuming that a compound of this type may be found, with the correct affinity for polymer and metal coating in terms of molecular polarity, a number of other factors may still determine its suitability.

The size and shape of the molecule are likely to be

important. It is necessary for the molecule to orientate itself so that the relevant portions can interact with the polymer and metal. For example, in the case of detergent molecules, the hydrocarbon chain can dissolve in the surface layer of an oil droplet, whilst the polar end of the molecule remains in the aqueous matrix.



This type of flexibility would probably be afforded by the fatty acids and their derivatives. However, transition metal acetylacetonates have a much more rigid structure. On the other hand these molecules do have polarity throughout the molecule,

M^{n+} ← $O^{\delta-}$ — $C^{\delta+}$ (CH_3) = CH — $C^{\delta+}$ (CH_3) — $O^{\delta-}$ → M^{n+}

and used with ABS many different interactions should be possible depending on the orientation and situation of the molecule.

The nature of the central atom may further determine the adhesion promoting efficiency of the complex. The

oxidation state of this atom will affect its interactions with other polar species and the number of co-ordinately bound ligands. This in turn will determine the size and shape of the molecule. For example, trivalent iron and chromium will complex with three molecules of acetylacetone whilst copper and nickel, being divalent, can accommodate only two ligands each.

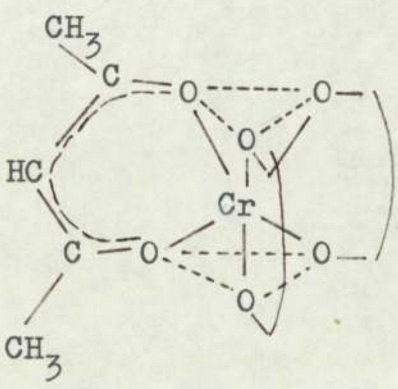
An examination of the experimental peel test results indicated that Cr $(acac)_3$, Fe $(acac)_3$ and Ni $(acac)_2$ promoted adhesion between ABS and copper. However, Cu $(acac)_2$ did not appear to act as an adhesion promoter. For immersion times in the complex solution of 4 - 10 mins, significant improvement in adhesion was achieved with the former. It is difficult therefore to understand why copper acetylacetonate should not have acted in a similar manner. A consideration of the relative solubilities of the complexes in the conditioner does little to explain this observation, since the molarity of the copper complex solution is similar to that of the iron acetylacetonate solution, and the latter has proved to be active as an adhesion promoter.

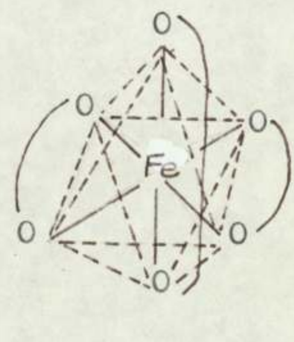
It might be argued that the copper complex is removed from the polymer during subsequent immersion in the precatalyst and Catalyst preparations. However, nickel acetylacetonate which was found to be soluble in these solutions, apparently is not extracted from the polymer surface by them.

Therefore it seems unlikely that the copper analogue should be lost in this way.

The size and shape of the complex molecules might affect their ability to promote adhesion, as these factors will influence their compatibility with the base plastics, concerning the way in which the molecule physically fits between the polymer chains. If the complex molecule is small and flat, this will facilitate diffusion of that molecule through the polymer chains, and may result in the molecule being widely distributed throughout the polymer, rather than remaining at the surface. Also the pattern of ligands around the central atom of the metal complex will affect the availability of that atom for interactions with other species. It is important therefore to examine the structures of the various acetylacetonate complexes under investigation.

Chromium (111) acetylacetonate is thought to have a trigonalbipyramidal arrangement of ligands whilst the iron (111) complex has an octahedral arrangement of chelating oxygen atoms. [102]





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The situation of nickel (11) acetylacetonate is rather more complicated.[103] In the crystalline state this compound exists as the trimer, each nickel atom having an octahedral array of neighbours. However, the presence of water breaks up the oligomer and water molecules occupy the vacant co-ordination sites on the metal, to retain an octahedral arrangement of ligands.

The diketonate of copper has a different type of structure. The copper (11) ion is co-ordinated by four oxygen atoms in a square planar geometry, all the ring carbon atoms lying above or below the CuO_4 framework.[102]

A comparison of these four structures, reveals that the chromium, iron and nickel complexes are similar in that the central metal ion is surrounded by ligands. The copper complex on the other hand appears to have a structure in which the metal ion is not shielded top and bottom.

Also the molecule is more streamlined. In fact the structure of this complex seems admirably suited for interfacial adhesion promotion as the central copper ion is free on one side to interact with the copper coating, whilst the organic ligands are held in the ABS. It may be however, that because of its shape the copper (11) acetylacetonate molecule diffuses more readily into the bulk of the polymer. This would explain its lack of adhesion promoting activity. A determination of the concentration gradient of the complex through the ABS plaque, might show if this is in fact the case.

The electronic configuration of the complexes might also be important in determining the adhesion promoting activity of the molecules. All four are capable of complexing further species through the acetylacetonate oxygen atoms. [104] Silver chlorate adducts of each complex are known, in which the silver ion is co-ordinated through the ligand oxygens, e.g. $Cu(acac)_2\ 2AgClO_4$. If co-ordination through the ligands is required for adhesion promotion then the chromium and iron complexes should be better promoters. However, results indicated that nickel (11) acetylacetonate was slightly better than the two tris complexes.

Incidentally the activity of the $Cu(acac)_2\ 2Ag\ ClO_4$ adduct itself, as an adhesion promoter with its increased molecular hindrance, might be a useful test of the above diffusion theory for the poor performance of $Cu(acac)_2$ as a promoter.

Adhesion promotion resulting from co-ordination to the metal atom is a possible alternative.

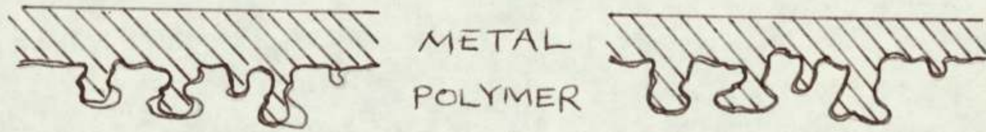
In each case co-ordination to the ion is possible. The reason for the copper diketonates' inactivity cannot therefore be explained simply in terms of electronic arrangement.

Of the three adhesion promoting complexes the nickel compound seemed to be the most effective, followed by the iron complex. However, the strength of adhesion promoting ability of the nickel, iron and chromium complexes was very similar. Each complex has a slightly different arrangement of ligands and therefore identical adhesion improvement would not be expected, but the differences are not sufficiently great to draw any conclusions about precise requirements of size and shape.

In each case there appeared to be an optimum time of immersion in the complex - containing conditioner. For the nickel and iron complexes this time was 8 minutes, whilst the chromium complex achieved maximum adhesion with a 6 minute immersion. As immersion time was increased, the amount of complex carried into the polymer surface was likely to increase. However, longer immersion times would probably lead to the complex being carried well below the polymer surface, where it could not promote adhesion at the interface. Therefore it seems reasonable to expect an optimum immersion time.

The mechanism of adhesion promotion has so far been considered to be a chemical bridging mechanism between polymer and metal, though this is not the only possibility. Saubestre and Khera [30] have suggested that a chromium carbonyl complex is responsible for the deposition of palladium catalyst onto a polymer substrate.

Similarly the acetylacetonate complexes under investigation may function as adhesion promoters by facilitating the deposition of palladium. If the catalyst were to be deposited right inside the surface cavities then better coverage of electroless copper could ensue. This would result in improved mechanical keying and more opportunity for interfacial chemical interactions.



Without adhesion promoter   With adhesion promoter

The ability of the metal diketonate to complex with palladium would be likely to determine its activity as an adhesion promoter. In fact each of the four complexes should be capable of such a reaction as previously indicated, and so in this instance the difference in behaviour of the copper acetylacetonate is unlikely to be due solely to its complexing ability with palladium.

Rather the shape of the molecule and its mobility through the substrate provides a/plausible explanation for the differences observed.

more

2.5. Conclusions

1. Small amounts of the following complexes have been shown to promote adhesion between copper and ABS: Ni $(acac)_2$; Cr $(acac)_3$; Fe $(acac)_3$

2. It was possible to incorporate these complexes into the surface layer of the ABS by dissolving each complex in a mild solvent for this plastics material, namely Shipley's organic conditioner.

3. A similar quantity of $Cu(acac)_2$, incorporated into the ABS in the same manner, apparently did not promote adhesion.

4. The lack of adhesion promoting activity of $Cu(acac)_2$ may have been due to its molecular geometry. The molecules of this β-diketonate, being more streamlined than those of the other complexes under examination, may have diffused into the bulk of the substrate. As a result no significant adhesion enhancement could have taken place.

5. For each adhesion promoting complex it was found that there was an optimum time of immersion in the complex containing solvent which produced the best adhesion enhancement.

2.6. Suggestions for Further Work.

1. Other acetonate complexes might be tested for adhesion

promoting activity. By varying the oxidation state of a given metal and by testing the complexes of a periodic group of metals any electronic effects might be pinpointed.

2. Study of the effect of such complexes on the nucleation characteristics of palladium, by the transmission electron microscopy technique, may show whether or not the acetonate adhesion promoting mechanism is dependent on its effect on palladium nucleation.

3. The preparation and testing of bulky $Cu(acac)_2$ adducts e.g. $Cu\ (acac)_2 \cdot 2AgClO_4$ may elucidate the importance of molecular shape and diffusivity for adhesion promoting activity.

CHAPTER THREE

Methods of Plating on Plastics

3.1. Introduction

Conventional plating on plastics systems, whilst producing a reliable metal coating suffer from the disadvantages of necessitating a large number of stages. A wide variety of alternative methods, some much simpler in concept, have been described or patented.

3.1.1. Processes involving metal complex formation

A number of processes using phosphorus in the elemental form or as a covalent compound have been patented. These processes eliminated the need for an oxidising etchant e.g. the polymer was treated with a solution of phosphine, which swelled into the polymer surface. After drying, the polymer was contacted with a solution of a metal salt e.g. $CuSO_4 \cdot 5H_2O$ which resulted in the formation of a copper phosphorus complex. Electroless deposition onto the activated surface was then possible. The advantage of this method is its applicability to most polymer substrates [105].
A similar method has been patented which involved treating the polymer substrate with a solution of the reaction product of elemental phosphorus and an organometallic e.g. lithium butyl. [106] Next the substrate was contacted with a solution of metal ions to give a metal-phosphorus complex which could be electrolessly plated. A more complicated system has also been patented, using a number of solution additives

e.g. surfactants. [107]

Whilst these processes involved less treatment stages for the polymer, they still necessitated the use of materials that are difficult to handle and dispose of. It seemed possible that the adhesion of metal applied in this fashion resulted directly from the catalyst being produced in the surface layers of the polymer. The subsequent metal coating should have bonded to the catalyst chemically, the latter being well distributed. These methods may have allowed a small amount of mechanical keying, if the swelling solvent, in some way selectively dissolved areas of the polymer surface.

A method for metallising polypropylene and ABS has been patented which involved treating the substrate with a solution of sulphur in perchloroethylene (108). The polymer was then treated with a solution of cuprous chloride followed by a dip in palladium chloride. The surface was then sufficiently conductive to be electroplated. Good peel strengths were claimed and may have resulted from the mechanism proposed above.

A further method involved the swelling of a keto-palladium complex into the surface of ABS, following the conventional chromic acid etch. [109] This complex catalysed the electroless deposition of nickel. Such a method might have been expected to give very good

metal to polymer adhesion, but the levels of adhesion claimed were comparatively low, and only one less treatment stage was required.

3.1.2. Processes involving U.V. irradiation

A means of rendering polyurethane plateable has been patented.[110] The polymer was treated with a solution of 1,3 diphenyl -2- propane and methyl ethyl ketone peroxides. It was then subjected to U.V. light. This was followed by sensitisation in stannous chloride and activation in palladium chloride. The breakdown products of the peroxides were likely to be radical species which may have chemically combined with the tin chloride molecules, and in so doing produced good adhesion.

A patent has been granted for the production of a metal image on a wide range of insulating substrates.[111] The method involved coating the roughened surface of the substrate with a solution of binder and appropriate metal salt e.g. silver, palladium or copper acrylates. On exposure to U.V. light the binder was cured and the salt decomposed to yield metal ions which were reduced to the metal and which diffused into aggregates. Any unexposed metal salt was dissolved away, and electroless copper could then be deposited. Although this method still suffered from the disadvantage of complexity, it did avoid the need to handle potentially dangerous chemicals. Assuming that the binder was compatible with

the underlying polymer, then adhesion would depend on the chemical bonding of the electroless metal deposit to the firmly held catalyst aggregates.

In the field of photography, the reduction of silver halide to metallic silver is well known. [112] It might have then been possible to apply a photographic type emulsion to a plastics surface, mixed with a binder and reduce this to form a conductive metal layer, suitable for electrolytic deposition.

A technique for the production of fully additive printed circuit boards has been described which involved the use of a titanium dioxide filled epoxy base. [113] The base board was dipped in a palladium chloride activator solution, dried and subjected to U.V. light through a negative of the circuitry pattern. Palladium (II) was reduced to metallic palladium by electrons from the titanium oxide liberated by the intense U.V. The palladium then catalysed deposition of electroless copper which built up the circuitry.

3.1.3. Processes involving thermal decomposition

A procedure for the plating of phenolic boards has been patented, [114] which required coating the substrate with a thermosetting resin containing either copper, nickel, cobalt or silver formates. Application of heat cured the resin and decomposed the metal salt.

e.g. $Cu\ (HCOO)_2 \xrightarrow{180^oC} Cu + CO + CO_2 + H_2O$

The reduced metal may then have catalysed electroless deposition, whilst the evolved gases were believed to have produced microporosity in the binder surface and in doing so, enhanced mechanical keying of metal to polymer. This seems to be a very neat method of catalysing the substrate surface for subsequent metallisation. The evolution of gas, however, must have limited the amount of metal salt which could be incorporated and hence a complete conducting film could not be produced. However, this idea will be further developed in a later section.

The application of a thin film of certain thermally unstable complexes of palladium or platinum has been claimed to catalyse electroless deposition onto an inert substrate. [115] Complexes of the form L_mPdX_n or L_mPtX_n,
Where L = ligand e.g. unsaturated organic species

X = halide or alkyl species

m = 1 - 4

n = 0 - 3

when heated to 300°C, decomposed to the metal. In this case, the cost of the complexes prohibited the formation of a complete layer.

The use of gold acetate applied in the same fashion as the copper formate has been patented. [116] Again heat was used to reduce the gold ions to the native metal. However, this method suffered the limitations of both the above procedures.

3.1.4 Processes involving hydrolysis

Lupinski and Jaynson [117] have described a process for rendering a polymeric substrate conductive. The polymer was coated with an elastomeric binder containing either cadmium oxide or zinc oxide. When treated with dilute caustic potash solution the metal ions were reduced. In addition, surface microroughness was produced where oxygen ions (O^{2-}) left the oxide lattice, creating voids, and good adhesion of subsequently deposited metal.

A rather complicated method of metallising roughened polymer surfaces has been developed [118]. A solution of resin containing a hydrolysable metal complex e.g. alkyl ortho titanite was applied to the substrate. When the solvent had evaporated off, the complex was hydrolysed with sodium hydroxide solution. Then the plastics material was dipped into a solution of palladium chloride, and Pd^{2+} ions were adsorbed onto the hydrolysed complex. In the following electroless metal bath the catalyst ions were reduced to metallic palladium then metal deposition ensued. The only advantage of this method seemed to be that mechanical roughening of the substrate was sufficient and that the use of a chromic acid etchant was eliminated.

3.1.5 Miscellaneous processes

A neat method of producing an adherent silver film on phenol-formaldehyde, urea-formaldehyde and melamine resins

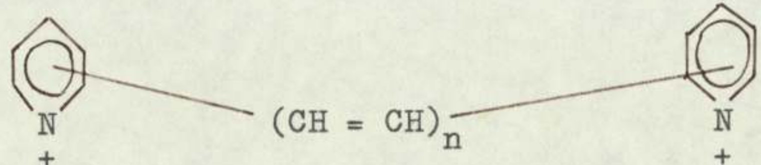
has been described by Stuart.[119] The moulding was simply suspended in a solution of silver nitrate, potassium hydroxide and ammonium hydroxide. The polymer substrate itself reacted with the silver ions to release metallic silver. Adhesion of the silver to the substrate must be as a result of chemical forces.

A metallising procedure for inert substrates was developed, whereby a dispersion of resin binder and zinc powder in an aqueous medium, was applied to the surface.[120] After allowing the polymer to dry it could be electrolessly copper plated. This method was very simple and provided that the adhesion between the zinc and copper was good, it would be economically advantageous. There was one drawback, however, and that was the problem of agglomeration of the zinc powder particles, which would have resulted in a poor distribution of catalytic sites.

A further method requiring the application of a binder has been patented.[121] A solution containing binder and cuprous iodide was applied to the substrate, which was subsequently dipped in an acidic palladium chloride solution. Metallic palladium was thus formed, capable of catalysing electroless copper deposition. Although this method was patented for use with polyethylene terephthalate it may be possible to extend it to other substrates by the correct choice of compatible binders.

Activation of a polymer substrate by impregnation with a

solution of radical cations has been claimed. [122]



Alternatively radical cations could have been cast onto the polymer surface in an aqueous solution of poly (vinyl alcohol). These radical species could then have formed chemical bonds with the deposited metal, and produced good adhesion.

The unusual behaviour of nylon towards water has been exploited in a patented method for plating polyamide. [123] A warm aqueous solution of a catalytic material was swollen into the polymer surface. After treatment with a reducing agent, electroless deposition could be carried out. Again adhesion depended on chemical forces, as the water was unlikely to create microporosity at the nylon surface.

A concise method of plating on polystyrene, isotactic polypropylene and poly (methyl methacrylate) has been patented. [124] A concentrated solution of cuprous trifluoroacetate was swollen into the polymer surface in an appropriate solvent. After drying in an atmosphere of nitrogen the polymer was immersed in a solution of hydrazine in isopropyl alcohol. This resulted in the reduction of the cuprous compound to metallic copper. Electroless copper could then be deposited. This method

claimed to produce very good adhesion. It was likely that diffusion across the initially produced copper and electrolessly deposited copper interface would have occurred. The copper was therefore mechanically bonded in addition to any chemical interactions occurring between metal and polymer.

It is possible to produce polymer chains with metal atoms formally bonded to them. Such atoms have been incorporated into the polymer backbone. [125] Metallation of an existing polymer has been achieved by reacting with lithium butyl for example. [126]

Also, a class of polymers known as ionomers are produced commercially which contain chemically bonded metal ions on side chains. [127] Exploitation of such a product would have required the detachment of bonded metal to form reduced metal aggregates. The Fulmer laboratory has carried out work on detaching metal ions from polymer chains to form aggregates only 100Å in diameter. [128]

Indirect use of attached metal ions has been patented for plating polystyrene. [129] The polymer substrate was first sulphonated to produce $-SO_3H$ groups on the phenyl rings. The ion exchangeable hydrogen was then displaced by a metal ion chosen from gold, silver, palladium or platinum. The metal ions were introduced from solutions of their salts. These ions were then reduced in situ by, for example, hydroquinone. The substrate was then ready for electroplating. Such a method should have produced a

strongly adherent metallic coating since the noble metal layer would have been uniformly nucleated over the entire polymer surface and may even have been embedded within the surface layer .

A general method for plating non-conductors has been patented [130] which involved contacting the substrate to be plated with a hot aqueous solution of a complex of cuprous thiocyanate and thiourea, followed by exposure to hot gaseous ammonia. Metallic copper was thus produced over the entire surface. The degree of adhesion obtained would have probably depended on the strength of adsorption of the cuprous complex which in turn would have been affected by surface roughness and chemical bonding.

Some success has been achieved with directly electroplateable plastics filled with carbon black. [131] A major difficulty with this method was the promotion of lateral growth of the deposit over the entire plastics surface, rather than build up on the first metal deposited, since the conductivity of the plastics substrate was comparatively low. Luch [132] has claimed to have overcome this problem by incorporation of certain additives. However, there are still problems to be surmounted with moulding this material. Also best results are only achieved when using a Watts nickel strike onto plastics material and slowly building up the operating voltage. Luch has claimed that the plated plastic shows good thermal cycling

properties. However levels of peel adhesion are rather low - of the order of 0.5kg / 25.4mm. Since separation apparently occurs at the metal / polymer interface the bonding may well be purely chemical in nature.

It is possible that the additives incorporated in the polymer act by polarising the metal deposition reaction, so that treeing of the initial deposit is inhibited and lateral growth promoted. It may be possible to improve the technique by incorporating polarising molecules into the plating solution itself e.g. an acetylenic compound. This method of plating has the great advantage of drastically reducing the number of stages required for electroplating. Only the cleaning step is required, etching, neutralising, catalysing, accelerating and electroless deposition being done away with.

3.2.1. Experimental Scheme

The problem was to devise a method for metallising any type of polymer, whether of plating grade or not. The metal plate was required to be strongly adherent, and simple to produce. If possible, the use of corrosive chemicals was to be eliminated. Ideally it would have been better to incorporate sufficient metal into the polymer surface to permit electrolytic deposition, without the need to build up an intermediate electroless deposit. However, the practical difficulties of achieving such a situation were very great. Assuming that the minimum thickness of metal required for subsequent electroplating was 1 μm, it was possible to calculate the concentration

of copper ions in the solution or dispersion to be applied.

Consider an area to be plated of $100mm^2$. The necessary volume of metal was therefore $10^{-1}mm^3$.

A typical metal might have been copper, with a density of 8933 kg m^{-3}.

Mass of copper reqd. = 8.93×10^{-1}mg

The concentration of copper ions in the solution

$= (8.93 \times 10^{-4})$ g / $10^{-1}mm^3$.

= 8930 g/l

The concentration of the copper compound would be even greater. This very high figure then limited the use of solutions, to providing sufficient copper nuclei for a catalysing electroless deposition.

3.2.2. Choice of Method

Many of the alternative plating procedures discussed in the literature applied the source of metal in one of two ways:

(1) By swelling the material into the surface layers of the polymer, using an appropriate solvent.

(2) By coating the plastic with a solution or dispersion of the metal source together with a resin binder.

A third possibility would have been to incorporate the metal compound during moulding. The disadvantages of this method are that because the only useful material was that at the surface, most of the compound would have been wasted. Not only was this likely to be costly, but also it may have had a deleterious effect on the properties of the

bulk material. There was also the problem of stability. Moulding of ABS for example was carried out at over 200°C. At such temperatures, thermal decomposition of the metal compound may have occurred.

The most favourable method to pursue seemed to be the first, for the following reasons.

(1) This did not involve the production of an additional polymer to polymer interface at which failure could occur.
(2) The use of a binder may have reduced the solubility of the metal compound in the solvent.
(3) If a dispersion of metal particles were to have been used, it would have been difficult to get a uniform dispersion within the binder. The particles would have tended to settle out.
(4) The additional expense of a binder was avoided.
(5) This did not require the additional selection of a binder.

The first method chosen for investigation, was therefore that using a swelling solvent. The need to select differing solvents for differing polymers in this case was balanced by the need to find binders compatible with the substrate in the second alternative, neither method being universally applicable without modification.

3.2.3. Choice of Substrate

The polymer chosen for investigation was Z grade ABS which was readily available.

3.2.4. Choice of Solvent

The requirements of the solvent, other than cost and safety considerations, were as follows:

(1) It had to be a good solvent for the metal salt.

(2) It had to swell into the surface of the polymer substrate at a controlled rate and carry the salt with it.

(3) The swelling rate should have been such that it reached a depth of 1 - 5 μm below the polymer surface in a few minutes.

(4) It should not have substantially weakened the surface layers of the polymer. Ideally when the solvent evaporated off, the polymer surface should have had the same strength.

(5) The ability to relieve moulding stresses was desirable.

For ABS a perfectly good swelling agent was the Shipley organic conditioner . It seemed sensible therefore to look for a metal salt which was readily soluble in the conditioner.

3.2.5. Choice of Metal Compound

The prerequisites for the metal source were:

(1) High solubility in the conditioner.

(2) Easily capable of being reduced to the metal.

(3) No undesirable by-products were formed during reduction e.g. adhesion inhibitors or large volumes of gas which could completely disrupt the surface.

The selection of the metal compound was also dependent on the proposed method of reduction.

3.2.6. Method of Reduction

The alternatives were:

(1) Chemical reduction.

(2) Thermal decomposition.

(3) U.V. irradiation.

The second and third methods limited greatly the choice of metal salt. Also in the case of thermal decomposition there would have been the problem of heat damage to the plastic. The length of U.V. exposure would have been too short to present a problem of this type. The first alternative seemed to be the most promising, but the other methods were worthy of some investigation. The next step therefore was the selection of a chemical reducing agent.

3.2.7. Choice of Chemical Reducing Agent

The reducing agent had to fulfill the following requirements:

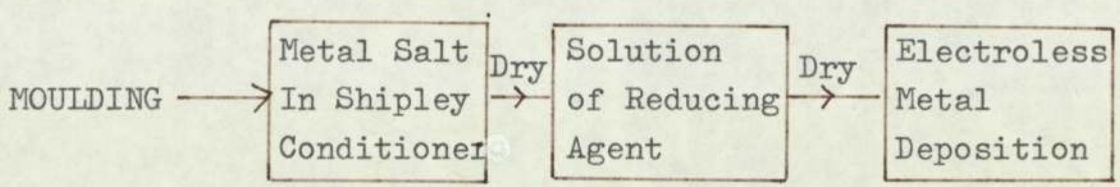
(1) It had to be sufficiently strong to reduce metallic ions to the metallic state e.g. cupric ions to copper, rather than partial reduction to cuprous ions.

(2) It should not have attacked the polymer substrate.

(3) It had to be soluble in a solvent which did not attack the polymer or leach out the metal salt.

3.2.8. Procedure

The procedure to be tested was as follows:



The variables to be investigated were:-

(a) Concentration of metal salt solution.

(b) Time of immersion in same.

(c) Temperature of same.

(d) Conditions of drying.

(e) Concentration of reducing agent solution.

(f) Time of immersion in same.

(g) Temperature of same.

If this method proved unsuccessful then the following alternatives bore investigation.

(1) Incorporation of metal source during moulding.

(2) Application of the metal with binder.

(3) Incorporation of organometallic compounds which could have been decomposed to yield the metal at slightly elevated temperatures.

Impregnation by bombardment with high energy metal ions is dealt with in a separate chapter.

3.3. Experimental Procedure

3.3.1. Solubility of Metal Compounds

The relative solubilities of the following range of copper compounds in Shipley's conditioner at 32°C was determined:

(1) Copper (II) acetylacetonate

(2) Copper (II) chloride dihydrate

(3) Copper (II) bromide

(4) Copper (II) sulphate pentahydrate

(5) Copper (II) nitrate trihydrate

(6) Copper (II) acetate monohydrate

(7) Copper (I) oxide

3.3.2. Effect of Reducing Agents on Selected Metal Compounds.

The reactions of the following reducing agents with $CuCl_2$ $2H_2O$, $CuBr_2$ and Cu $(acac)_2$ were studied.

(i) Formaldehyde, 38% solution by weight.

(ii) Sodium borohydride 5% solution.

(iii) Nascent hydrogen Zn/dil HCl.

(iv) Hydrazine hydrate 5% solution.

(v) Dimethyl aminoborane 5% solution (D.M.A.B.)

Aqueous solutions of these reducing agents were tested at room temperature and at 100°C.

3.3.3. Effect of Reducing Agents on ABS

The effect of the above solutions on Z grade ABS was determined by immersing 10mm square specimens, cut from a moulded plaque, in the heated solutions (100°C) for 10 minutes.

3.3.4 Swelling Studies

To 100ml portions of Shipley's Organic conditioner was added either copper (II) chloride dihydrate or copper (II) acetylacetonate. A low concentration solution containing 500 mg/l was prepared in each case and also a saturated solution. A strip of 10mm wide Z grade ABS, guillotined from a plaque, was immersed in each solution for 2 minutes.

A second set of strips was immersed for 8 minutes. Each solution was heated to 32°C and the experiment was repeated.

The strips of ABS were allowed to dry in the air and were then cut into four. One piece was placed in a boiling 2% aqueous solution of DMAB and another in a 5% solution of the same reducing agent. The specimens were removed after a two minute immersion. The remaining two sections were treated similarly, the time of immersion being extended to 8 minutes.

All specimens were immediately rinsed following treatment by the reducing solution, and introduced to Shipley's electroless copper solution.

Samples treated with copper (II) acetylacetonate solution at 32°C were prepared and immersed in the electroless solution without prior reduction.

3.3.5 Application of Metal Salt with Binder

To 100ml of water was added 5g copper (II) chloride dihydrate and 5g poly(vinyl alcohol). The mixture was warmed to aid dissolution and was left overnight.

Strips of Z grade ABS 10mm wide, were immersed in the solution for 5 seconds. These were removed and allowed to dry in a desiccator for 24 hours.

The samples were then immersed in a hot 5% solution of DMAB in xylene.

After rinsing in cold water the strips were transferred to Shipley's electroless copper solution.

3.3.6. <u>Incorporation of metal salt into molten polymer</u>

To 37.5g of Z grade ABS moulding granules was added 0.35g of Copper (II) acetylacetonate. These ingredients were roughly mixed by hand and were then added to a torque rheometer where the mixture was blended at 180°C for 7 minutes at high speed. Immediately after, it was cooled in water, dried and cut into small pieces, each weighing about 1g. A number of these pieces were placed in a boiling 5% aqueous solution of DMAB for 2 minutes. The samples were then rinsed and immersed in the Shipley electroless copper solution.

3.4 Results

Compound	Solubility in Shipley Conditioner at 32°C
$CuCl_2\ 2H_2O$	Very soluble
$CuBr_2$	Soluble
$Cu\ (acac)_2$	Slightly soluble
$CuSO_4\ 5H_2O$	Slightly soluble
$Cu(NO_3)_2\ 3H_2O$	Slightly soluble
$Cu(COOCH_3)_2 \cdot H_2O$	Almost insoluble
Cu_2O	Insoluble

Table 3.1

EFFECT OF REDUCING AGENTS   Table 3.2

COMPOUND	REDUCING AGENT	TEMP	COPPER FORMATION
$CuCl_2.2H_2O$	38% Soln Formaldehyde	RT	X
		100°C	X
$CuCl_2.2H_2O$	5% Soln Sodium Borohydride	RT	X
		100°C	X
$CuCl_2.2H_2O$	Nascent Hydrogen	RT	✓
		100°C	
$CuCl_2.2H_2O$	5% Soln Hydrazine Hydrate	RT	X
		100°C	✓
$CuCl_2.2H_2O$	5% Soln Dimethyl Aminoborane	RT	X
		100°C	✓
$CuBr_2$	38% Soln Formaldehyde	RT	X
		100°C	X
$CuBr_2$	5% Soln Sod. Borohydride	RT	X
		100°C	X
$CuBr_2$	Nascent Hydrogen	RT	X
		100°C	X
$CuBr_2$	5% Soln Hydrazine Hydrate	RT	✓
		100°C	
$CuBr_2$	5% Soln Dimethyl Aminoborane	RT	X
		100°C	X
$Cu(acac)_2$	38% Soln Formaldehyde	RT	X
		100°C	X
$Cu(acac)_2$	5% Soln Sodium Borohydride	RT	X
		100°C	✓
$Cu(acac)_2$	Nascent Hydrogen	RT	✓
		100°C	
$Cu(acac)_2$	5% Soln Hydrazine Hydrate	RT	X
		100°C	✓
$Cu(acac)_2$	5% Soln Dimethyl Aminoborane	RT	X
		100°C	✓

Reducing Agent	Effect on ABS
Formaldehyde	NONE
5% soln sod. borohydride	WHITENING OF PLASTIC IN PLACES
Nascent H_2 (Zn/HCl)	NONE
Hydrazine hydrate 5% sol.	WHITENING OF PLASTIC
Dimethyl aminoborane 5% soln.	NONE

Table 3.3

3.4.1. Swelling Experiments

Copper (II) chloride dihydrate impregnation

No electroless deposition occurred on samples treated with this compound. The formation of a black precipitate in the reducing solution of DMAB was observed.

Copper (II) acetylacetonate impregnation

Samples immersed for 2 minutes in the diketonate solution did not catalyse electroless deposition. Neither did treatment for 8 minutes in the low concentration solution. However, some deposition did occur as a result of the 8 minute treatment in the saturated solution. The coverage was about 10% for room temperature impregnation and about 20% for impregnation at 32°C. This coverage was developed after 2 minutes in the reducing solution. Prolonging the reducing time did not significantly increase the final coverage.

This deposit showed very poor adhesion. It was easily removed by scraping with the thumbnail.

3.4.2. Metal salt with binder investigations

Electroless deposition of copper onto the polymer surface was achieved. The coverage was about 30% in each case.

During treatment by the reducing agent, some

leaching out of the $CuCl_2.2H_2O$ must have occurred, as the solution took on a pink tinge.

The deposit showed poor adhesion to the substrate.

3.4.3. Melt mixing investigations

Following treatment with the DMAB solution, the ABS containing Cu $(acac)_2$ took on a greyish brown appearance. Immersion in the electroless copper solution resulted in almost complete coverage (90%) of the plastic by the copper deposit. This deposit did not adhere well to the ABS however, being easily removable by scraping with a thumbnail.

3.5. Discussion

3.5.1. Choice of metal compound

Deposition of copper from the Shipley electroless solution is normally catalysed by metallic palladium. However, since the solution is autocatalytic onee the reaction has begun, it seemed that catalysis by copper nuclei might have provided an economic alternative.

Of the materials tested, the two compounds most soluble in the organic conditioner were copper (II) chloride dihydrate and copper (II) bromide. These were therefore selected for further tests. However, the

above compounds are chemically very similar and therefore a third copper salt was chosen for further investigation. This was the organometallic complex, copper (II) acetylacetonate. Although only slightly soluble in the conditioner it was hoped that the different chemical nature might prove useful.

3.5.2. Efficiency of reducing agents

Formaldehyde, the weakest of the reducing agents tested, was found to be ineffective in reducing the cupric ions, to metallic copper.

The most effective reducing agent in the cold was nascent hydrogen, produced by the action of dilute HCl on zinc dust. The use of such a system, however, was very clumsy.

A 5% solution of hydrazine hydrate when heated to boiling, effectively reduced all three copper compounds. Unfortunately, it was also discovered to have a deleterious affect on the ABS substrate, and was therefore rejected.

Reduction of the copper diketonate by a hot 5% solution of sodium borohydride was achieved, but the halides were not reduced to metallic copper. Again the solution had a harmful effect on the base polymer

and was therefore rejected in favour of a solution of dimethyl aminoborane. This solution was capable of reducing $CuCl_2.2H_2O$ and Cu $(acac)_2$. Also it produced no visible ill effects on the ABS substrate.

3.5.3. Reduction in situ

In the case of copper (II) chloride dihydrate impregnation, copper nuclei capable of catalysing electroless deposition were not produced. It is possible that some copper may have been formed but exposure to the atmosphere resulted in passivation due to the creation of a surface oxide film. Certainly there must have been some of the salt at the surface in the first place, as a reaction did occur which produced a black precipitate in the reducing solution, and the chloride had already been shown capable of producing copper when treated with a solution of DMAB. It seems likely therefore that the salt was leached out of the surface, in part at least, and that any copper formed was immediately oxidised to black copper oxide. The solution would have contained the dissolved oxygen, necessary for such a reaction.

Under certain conditions a deposit of copper was obtained as a result of reducing copper (II) acetylacetonate in situ. In fact deposition occurred after treatment in the more concentrated solution for the longer length of time. This was probably due to the increased uptake of the complex. Similarly raising the temperature resulted in better coverage. In this

case the rate at which the swelling agent entered the polymer surface would have been increased and hence the quantity of diketonate carried into the surface layers would have been augmented.

Since Cu $(acac)_2$ is virtually insoluble in water, the problem of leaching out of the surface, did not arise.

There remains, then, the question of why any copper formed did not become coated with oxide, as appeared to be the case with the copper (II) chloride dihydrate. Either the black precipitate formed was something other than copper oxide i.e. an alternative reaction product of the salt and DMAB, and the formation of copper never occurred, or else the copper formed by reducing the acetonate was not exposed to dissolved oxygen. Since the complex did not dissolve in the water it is possible that the copper was not completely oxidised for this reason. One hundred per cent coverage was not achieved and this may have been as a result of oxidation of some copper nuclei.

3.5.4. Application by means of a binder

The binder chosen was poly (vinyl alcohol), the use of which has been patented.[122] It had the advantage of being water soluble. Besides the economies of using water as the solvent, there was the further advantage that water did not attack the ABS substrate. It was necessary therefore to select

a water soluble metal salt, and $CuCl_2 . 2H_2O$ was chosen. Since the binder was soluble in water, a hot aqueous solution of reducing agent could not be used. A solution of DMAB in xylene was found to be effective in reducing the halide, without affecting the binder, for short immersion times.

Since $CuCl_2 . 2H_2O$ is only sparingly soluble in xylene, the problem of leaching out of the copper salt was not expected. However, some leaching out did occur, though this effect was much less than in the case of reduction by an aqueous DMAB solution.

Again the coverage of electroless copper achieved was much less than one hundred per cent. This was probably due in part to the leaching out of the copper salt, and more importantly to the non-uniform distribution of the halide in the binder.

3.6. Conclusions

1. For reducing copper salts incorporated in ABS dimethyl aminoborane was found to be the most convenient reducing agent, having a strong reducing action and no apparent adverse effects on the base polymer.

2. Copper (II) acetylacetonate proved to be the most readily reducible metal compound tested.

3. The most successful means of incorporating the copper (II) acetylacetonate for reduction and subsequent catalysation of electroless metal deposition was to mix it in to the molten plastics material. This gave approximately a 90% electroless metal coverage of the ABS. However this deposit was weakly adherent.

4. Application of copper (II) acetylacetonate with a binder or incorporation by the swelling technique also gave rise to electroless deposits with poor adhesion, but with a much lower coverage.

5. Increasing the immersion time in the copper (II) containing solution and also the metal complex concentration gave better electroless metal coverage, using the swelling technique. The optimum residence time in the reducing solution was found to be 2 minutes.

Longer immersion times did not improve electroless metal coverage.

3.7 Suggestions for Further Work

1. It might be possible to incorporate into or onto the polymer surface, an organometallic compound e.g. phenyl copper which can be converted to metallic copper by the application of heat or by a chemical reaction. This metallic copper may catalyse electroless copper deposition and also give enhanced bonding between coating and substrate. Such a procedure would reduce the number of stages required for plating on plastics.

2. The use of colloidal palladium catalyst to initiate electroless copper deposition is very costly. X-ray probe analysis of accelerated surfaces, may be helpful in determining the presence of any other catalytically active species.

CHAPTER FOUR

Mechanical Properties of Polymer / Metal Composites

4.1. Introduction

4.1.1. Tensile strength

A number of workers have carried out tensile tests on metallised ABS and polypropylene. [133,134,135,136]
Matsunaga and Hagiuda [134] have shown that increasing the thickness of a copper coating on ABS above 21 μm produced an increase in tensile strength of the composite. There was a close linear relationship between metal thickness and composite strength. These workers have suggested that the theory of fibre reinforcement is applicable to ABS composites. The tensile strength of the composite in this case was calculated from the equation:

$$\sigma_c = \frac{\sigma_m t_m}{t_c} + \sigma_p$$

where
σ_c = tensile strength of composite
σ_m = tensile strength of metal
σ_p = tensile strength of plastics
t_m = thickness of metal
t_c = thickness of composite

This equation was derived assuming that the thickness of the polymer was much greater than the metal thickness. The effect of any non-uniform stress distribution due to the level of interfacial adhesion was ignored.

Similarly Roobal et al [135] have applied the theory of combined action to metallised polypropylene. The equation, derived to predict the tensile strength of the

composite, does not make the assumption that

$\frac{t_p}{t_c} = 1$, where t_p = thickness of plastics

and is expressed as follows:

$$\sigma_c = \frac{(\sigma_m A_m) + (E_p \; e_p A_p)}{A_c}$$

where A = cross sectional area

E = modulus

e = strain

Subscripts as above.

Again an interfacial interaction term was not included. These workers noted that the improvement in tensile strength achieved by thickening the metal layer varied with temperature. At room temperature a 25 μm coating of metal gave a 10% increase in strength, whilst the same thickness of metal produced increases up to 53% at 85°C. Therefore if the equation is to be used for design purposes, care must be taken to insert data for the correct temperature.

Tison [136] has extended the same theory to plastics coated with several layers of metal. For each metal

$$\sigma = \frac{E}{1-\mu}(e - e_t)$$

where μ = Poissons ratio

e_t = natural thermal strain

Then $\sigma_{m1} t_{m1} + \sigma_{m2} t_{m2} + \ldots \sigma_{mn} t_{mn} = \sigma_p t_p$

Each of the above applications of reinforcement theory assumed perfect isostrain conditions, i.e. the metal and plastics extend exactly together. If there is perfect adhesion between each layer, then the

isostrain condition will be observed. However, if slip occurs at the interface, due to imperfect adhesion, then the maximum predicted strength of the composite may not be achieved. In this case the modified equation is:

$$\sigma_c = \frac{I\,(\sigma_m\ A_m) + (E_p\ e_p A_p)}{A_c}$$

Where I = interaction factor.

This interaction factor may be loosely described as a measure of the adhesion between polymer and metal. However, as previously discussed, adhesion is itself a rather complex phenomenon encompassing a number of interactions which may be summarised as being either mechanical or chemical in nature. Since, in this chapter, the mechanical properties of metal / polymer composites are under investigation, the mechanical manifestations of the interaction factor will be considered. For values of I approaching unity, the mechanical linkage between the metal and plastics components may be considered to be almost perfect and a theoretical stress distribution will result.

Arithmetically speaking the interaction factor is a measure of the correlation between observed and calculated values of composite tensile strength.

4.1.2. Ductility

Matsunaga and Hagiuda,[134] Tipping and Dennis [133] and Norris [137] have each noted that electroplating of ABS leads to embrittlement. All agreed on the mechanism of

this reduction in ductility. When a tensile load was applied to a composite, the high modulus metal component carried a large portion of the load in spite of its small volume fraction. Because the metal layer was so thin it fractured and the whole load was then suddenly transferred to the plastics substrate, which was effectively impacted. The crack which had traversed the metal, propagated across the metal / polymer interface. Since ABS is very notch sensitive, once the crack had crossed this interface brittle failure of the entire composite occurred. Matsunaga and Hagiuda have observed that the cracks were initiated at the metal surface, which supports the above explanation.

Norris [137] has suggested that a way of preventing crack propagation across the metal / polymer interface and hence producing a ductile composite was to reduce the adhesion between the two layers. The ductility of nickel / chromium plated components has been improved by the use of micro-cracked chromium deposits. [138] When many cracks were present the stress concentration at any particular discontinuity was not so great and therefore there was less tendency for the cracks to propagate.

The failure of nickel plated type units in teleprinters has been investigated. [139] Only the plated ABS units failed by fracture of the metal and substrate. Epoxy, urea-formaldehyde, phenolic and melamine substrates failed by either cracking of the metal (no propagation across the interface) or by peeling off of the metal plate. The latter mode of failure supports Norris' idea that if

adhesion was sufficiently low, which must have been the case for a peeling type failure, propagation across the interface would not have occurred. In those tests when neither peeling nor fracture of the polymer occurred, failure of the crack to propagate may have been due to the notch tolerance of the substrate combined with a slightly higher level of metal to polymer adhesion.

4.1.3. Thermal Cycling

Correlation between the thermal cycling behaviour and the mechanical properties of the electrodeposit for plated components, has been observed.[140] By applying a metal of lower Youngs modulus or lower yield stress, it was thought that thermal stresses were more readily accommodated and blistering was prevented. Increasing the metal thickness reduced the stress on the deposit and a further improvement in thermal cycling performance was achieved. The following mathematical analysis by Hurley and Chart[140] is purely mechanical and does not take into account any thermal cycling resistance due to complex interfacial adhesion.

$$\frac{e_p E_p}{1 - \nu_p} t_p = \sum_{1}^{n} \frac{e_m E_m}{1 - \nu_m} t_m$$

where n = number of metal layers.

$$e_{diff} = e_m + e_p$$

where e_{diff} = strain to be accommodated when the temperature is changed.

$$e_m = e_{diff} - e_p$$

By substitution of the final equation into the first e_p can be determined.

4.1.4. Nature of the Adhesives

A number of adhesives were used in this investigation to vary the level of adhesion between metal and polymer. These adhesives were "Gloy", "Cow Gum" and "Araldite". The former was recommended for use with china, fabrics, leather and wood. Each of these adherents has a relatively rough finish compared with the plastics mouldings, and it was likely therefore that the level of adhesion between "Gloy" and the plastics or metals would be low. The adhesive itself was quite ductile and was weak relative to the polymer substrates.

"Cow Gum" is a rubber solution adhesive. It is weak and rubbery. It is interesting to note that a good bond has been produced between 70/30 brass and rubber.[1] The reason for this good adhesion is that sulphur present in the rubber combined with copper atoms in the brass to produce copper sulphide. The lattice spacing of this compound was very similar to that of the brass resulting in good compatibility. If copper foil were to be plated with 70/30 brass, better adhesion with a rubber adhesive might be achieved.

"Araldite" is an epoxy type adhesive. Much has been reported on the nature of this type of adhesive.[141] Apart from its good mechanical properties, araldite adheres strongly to many inorganic and organic substrates. This is probably due in part to its chemical structure which provides plenty of scope for polar interactions.

$$\overset{O}{H_2C - CH} - CH_2 \left[O - \langle\bigcirc\rangle - \underset{CH_3}{\overset{CH_3}{C}} - \langle\bigcirc\rangle - O - CH_2 - \overset{OH}{CH} \right]_n O$$

4.2. Experimental Procedure

Tensile bars of length 190mm, thickness 3.25mm and width at gauge length 13mm were moulded from S,R,U and Z grade ABS, to ASTM specifications as described by Tipping.[99,100]

Six bars of Z grade ABS were plated with Shipley's electroless copper by the following sequence of treatments:

1. Alkaline cleaner : 3 mins., 60°C.
   Rinse.
2. Hydrolyser : 3 mins., 64°C.
   Rinse.
3. Organic conditioner : 2 mins., 32°C.
   Rinse.
4. Etch : 7 mins., 64°C followed by 2 mins. drain in air.
   Rinse.
5. Neutraliser : 3 mins., 45°C.
   Rinse.
6. Application of Sellotape to stop off the edges of the bar (See Chapter 5 on selective area plating).
7. Pre-catalyst acid dip : 3 mins., 45°C.
8. Catalyst : 4 mins., 45°C.
   Rinse.
9. Accelerator : 3 mins., 40°C.
   Rinse.

10. Electroless copper : 15 mins., 20°C.

The metal thickness was then built up to 50 µm by electrolytic plating in a pyrophosphate copper bath. Further samples were prepared with metal thicknesses of 25 µm, 12.5 µm, 8.3 µm, and 4.2 µm. The current density and plating times used, were those laid out in Cannings handbook.

A similar range of Z grade bars were plated with electrolytic bright nickel.

Six tensile bars of S, R and U grades of ABS were electroplated with pyrophosphate copper to a thickness of 25 µm.

A further six bars of Z grade ABS were plated with 50 µm of electrolytic copper. These samples were immersed in acetone until the polymer substrate had dissolved completely, leaving thin tensile bars of copper. In the same way bars of nickel were produced.

Each specimen was pulled on an Instron tensile testing machine, using wedge grips, at a strain rate of 5mm/min. Unplated bars of each polymer were also tested.

Plaques of each grade of ABS were moulded as described by Tipping.[99] These plaques were metallised with Shipley's electroless copper. A subsequent coating of electrolytic copper was applied to increase the metal thickness to 50 µm. The plaques were prepared for peel testing as previously described. Following a week of storage in a desiccator, the plaques were peel tested. Six tests were carried out on each grade of plastic.

Further plaques were prepared for peel tests on Z grade ABS

substituting 50 μm of bright nickel for the pyrophosphate copper.

Using an ABS tensile bar as a template, a number of tensile shapes were cut from copper foil, 0.0254mm thick. Metal / polymer laminates were produced, Z grade tensile bars being sandwiched by two copper foils. Six bars were prepared, the copper being held loosely in position, by strips of sellotape at the ends. A further six composite bars were produced, the copper being glued in position with "Gloy". Bars were also produced, employing "Cow Gum" and "Araldite". These specimens were tensile tested under the same conditions as the plated samples. Tensile bars of copper foil alone were tested. Also Z bars with a thin layer of each glue were tested. Plaques for peel testing were prepared, 50 μm copper foil being attached by the range of adhesives. These tests were carried out as described above.

Tensile bars of polypropylene were also prepared and copper foil was attached with "Araldite". These were tested. In order to achieve some metal to plastics adhesion in these composites, the polypropylene was sandblasted and primed with a solution of atactic polypropylene.

4.3. Results

Polymer	$\hat{\sigma}_p'$ in MNm^{-2}	Ductility % R in A
R	39.0	31.7
S	38.7	15.4
U	41.1	20.2
Z	38.4	38.1

Table 4.1

Metal Plate	$\hat{\sigma}_m$ in MNm^{-2}	Peel Strength to Grade Z ABS in KNm^{-1}
Copper	688.8	1.20
Nickel	1323.9	0.20

Table 4.2

Metal Foil	$\hat{\sigma}_m$ in MNm^{-2}
Copper	448.8
Nickel	1128.0

Table 4.3

Table 4.4

ABS Substrate	Metal Coating	Metal Thickness in μm/side	Calculated $\hat{\sigma}_c$ in MNm^{-2}	Average measured $\hat{\sigma}_c$ in MNm^{-2}	Interaction Factor.
Z	Copper	50	57.9	53.4	0.70
Z	Copper	25	48.3	47.6	0.85
Z	Copper	12.5	43.4	43.1	0.85
Z	Copper	8.3	41.7	41.3	0.81
Z	Copper	4.2	40.1	39.5	0.61
Z	Nickel	50	77.0	39.2	0.02
Z	Nickel	25	58.0	37.9	-0.02
Z	Nickel	12.5	48.3	37.5	-0.09
Z	Nickel	8.3	45.0	37.4	-0.15
Z	Nickel	4.2	41.7	35.5	-0.83
S	Copper	25	48.6	48.1	0.87
R	Copper	25	48.9	51.4	1.15
U	Copper	25	51.0	52.8	1.09

Table 4.5

Grade of ABS	Metal Plate	Thickness/side in μm	Ductility
Z	Copper	4.2	0%
Z	Copper	8.3	0.25%
Z	Copper	12.5	0.25%
Z	Copper	25	0.0%
Z	Copper	50	0.0%
Z	Nickel	4.2	0.25%
Z	Nickel	8.3	0.0%
Z	Nickel	12.5	0.25%
Z	Nickel	25	0.0%
Z	Nickel	50	0.0%
R	Copper	25	0.0%
S	Copper	25	0.0%
U	Copper	25	0.0%

Foil	Metal Thickness in µm / side	Mode of Attachment to Z grade ABS	Calc. $\hat{\sigma}_c$ in MNm^{-2}	Av. measured $\tilde{\sigma}_c$ in MNm^{-2}	Interaction Factor I	Peel Strength in KNm^{-1}	Ductility % R in A	Mode of Failure
Cu	25	Loose	45.4	38.4	0	0	38.1	Foils snapped and ABS extended at this point.
Cu	25	Gloy	45.4	37.8	-0.09	0.05	36.4	
Cu	25	Cow Gum	45.4	40.2	0.26	0.02	25.7	
Cu	25	Araldite	45.4	44.2	0.83	0.12	21.1	
Ni	25	Loose	56.0	38.4	0	0	38.1	Foils crazed and whole gauge length extended.
Ni	25	Gloy	56.0	41.7	0.19	0.02	35.5	
Ni	25	Cow Gum	56.0	41.8	0.19	0.04	35.6	
Ni	25	Araldite	56.0	42.1	0.21	0.04	35.4	

Table 4.6

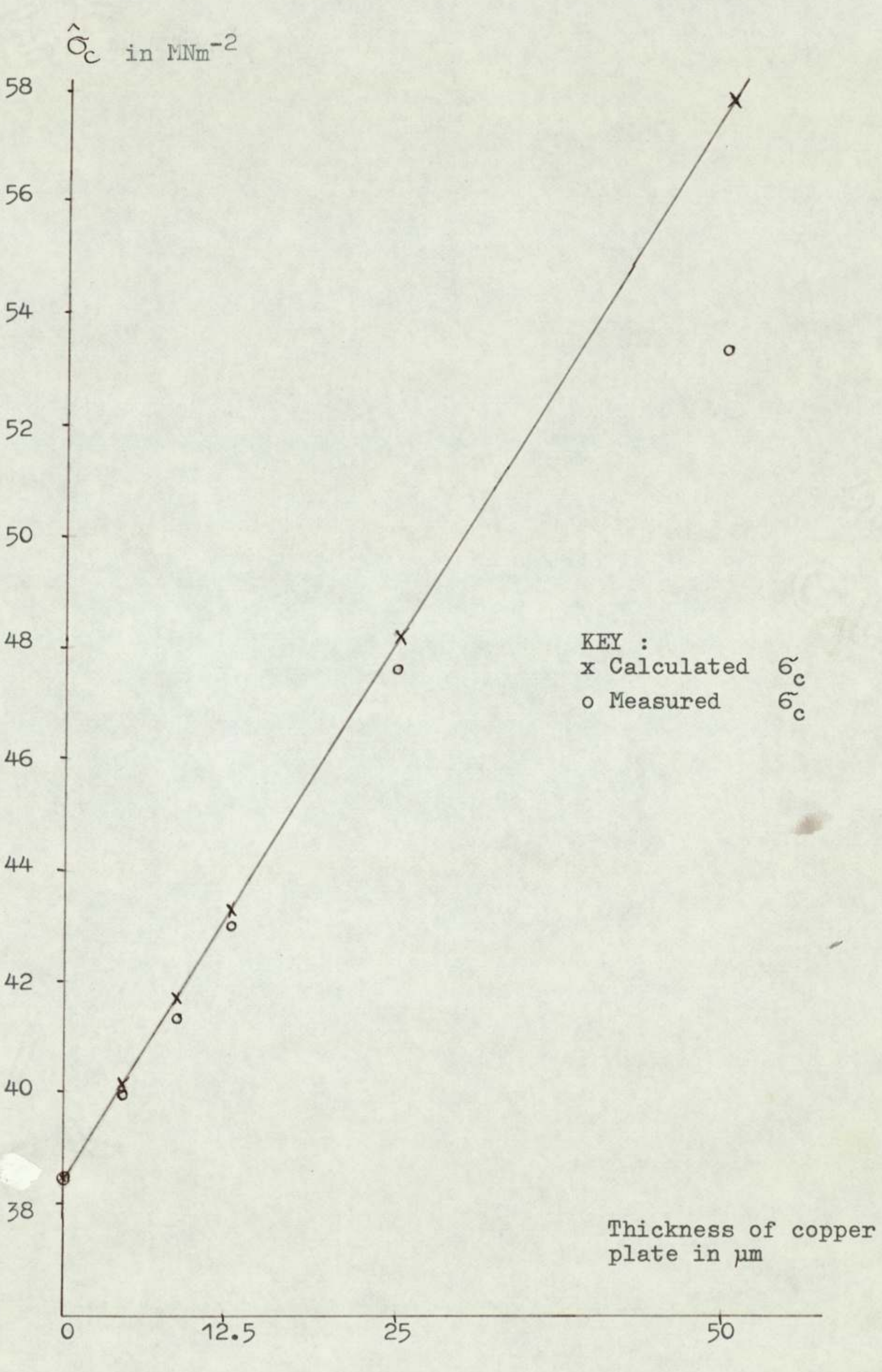
Grade of ABS	Adhesive	$\hat{\sigma}_{(p+a)}$ in MNm^{-2}
Z	Gloy	38.4
Z	Cow Gum	38.4
Z	Araldite	38.4

Table 4.7

Property	Polypropylene	Polypropylene with 25 μm of foil / side
$\hat{\sigma}_{calc}$ in MNm^{-2}		31.1
$\hat{\sigma}_{meas}$ in MNm^{-2}	24.2	24.2
I		0
Ductility (% R in A)	> 100%	> 100%

Table 4.8

GRAPH OF COMPOSITE STRENGTH v. COPPER PLATE THICKNESS



Graph 4.1

GRAPH OF COMPOSITE STRENGTH v NICKEL PLATE THICKNESS

$\hat{\sigma}_c$ in MN m^{-2}

80

70

60

50

40

38

36

34

KEY :
x Calculated σ_c
o Measured σ_c

Thickness of nickel plate in µm

12.5 25 50

Graph 4.2

4.4 Discussion

4.4.1. Effect of Metal Plate Thickness

4.4.1.1. Copper / ABS

It can be seen from Table 4.4 that increasing the thickness of the copper layers produced a composite with higher tensile strength. These results are comparable to those obtained by Matsunaga and Hagiuda.[134] Graph 4.1 shows that the relationship for plate thicknesses in the range 0 to 25 µm is roughly linear. There is good agreement between measured and calculated values, the interaction factor being greater than 0.6 in each case. Obviously as the metal thickness approaches zero any small errors in measurement etc. will have a large effect on the value of I. This may account for the seemingly low value of I for the composite plated with 4.2 µm of copper. Inasmuch, therefore, as adhesion affects the tensile strength of the composite, the metal to polymer adhesion is good. The actual magnitude of adhesion in this case is apparently sufficient to create a near isostrain situation with the theoretical stress distribution.

The rather larger deviation from the calculated composite strength value obtained with a 50 µm coating of copper cannot be due to differences of structure at the actual metal / polymer interface. It is possible that the lower tensile strength results from a larger volume of imperfections in the metal coating. More likely it is due to the greater stress gradient across the interface making it more difficult to achieve a uniform theoretical distribution of stress.

Table 4.5 indicates that all thicknesses of copper plate tested, resulted in embrittlement of the composite. This observation is in agreement with those of previous workers. [133,134,137] In the present investigation it was found that thicknesses of copper in the range 4.2 µm to 50 µm reduced the ductility of the composite to almost zero. Increasing the copper thickness had little or no effect. Using a different grade of ABS Matsunaga and Hagiuda [134] found that increasing this thickness from 21 µm to 43 µm produced a 0.5% improvement in ductility.

4.4.1.2. Nickel / ABS

In the case of the nickel plated composites, the tensile strength showed slight improvement as the metal thickness was increased from 4.2 µm to 50 µm (see Table 4.4) However, in each case the actual value fell far below the anticipated figure. This was probably due to the fact that isostrain conditions were not operating. Rather it seems likely that the stress distribution put an increased load on the metal plate. Consequently the metal failed under a lower applied stress. The non-isostrain conditions may have resulted from poor adhesion, such that the metal parted from the polymer and they extended by differing amounts locally. However, complete separation probably did not occur prior to fracture, as the samples failed in a brittle fashion, indicating that a crack, initiated in the nickel layer, could still propagate across the metal / ABS interface. In fact the composites plated with less than 50 µm of nickel failed at stress levels slightly less than those required to break the unplated polymer, yielding a

negative interaction factor. Although stronger than pyrophosphate copper, the nickel plate was much more brittle. It is possible that cracks propagated more readily, effectively notching the notch sensitive ABS, and so reducing its tensile strength. Alternatively the poor composite strength may have been due to localised high stress regions occurring over the surface, not from notches but resulting from variations in interfacial adhesion. In the case of copper plated composites, cracks did not propagate through the metal until the stress level exceeded the strength of the base polymer.

If I, the interaction factor, was purely a measure of a combination of interfacial parameters it should be constant for any given metal / plastic combination independent of variations in thickness of the metal. The values of I for the nickel / ABS composites with nickel thicknesses of 8.3 µm to 50 µm are quite similar indicating that I is largely dependent on interfacial factors. The low value obtained with a nickel thickness of 4.2µm may have been exaggerated as explained for the corresponding copper composite.

Table 4.5 shows that the nickel / ABS composites possessed almost zero ductility, independent of metal thickness. These results conflict with the observations of Morton and Baier,[142] who produced nickel plated polypropylene composites with ductilities of approximately 4%. Their composites also exhibited good peel adhesion. Since polypropylene like ABS is notch sensitive, it is

difficult to explain this retention of ductility, as the 8% ductility of the nickel used in their investigations was no greater than the ductility of the electrolytic copper used in the present work.

4.4.2 Effect of varying polymer substrate

The four grades of ABS tested had values of tensile strength ranging from 38.4 to 41.1 MNm^{-2}. In each case a 25 µm coating of pyrophosphate copper raised the strength of the composite to a level close to the calculated figure for maximum interaction factor. For R and U grades of ABS the measured values were slightly greater than those calculated. This anomaly may have been due to fluctuations in the metal thickness.

4.4.3. Correlation of peel test results and interaction factor for plated samples.

The peel tests were carried out on plaques with a metal coating, 50 µm thick. Since the tensile tests performed on metal plated composites indicated that the metal thickness affected the value of the interaction factor, those figures calculated for composites plated with 50 µm will be used for comparative purposes. From the results given in Table 4.2 and Table 4.4 it is clear that the large interaction factor of the copper composite corresponds to a relatively high peel strength, whilst the nickel plated ABS, with a very low peel strength value, has a low interaction factor. Some of the factors which determine the peel strength of the composite therefore probably affect the interaction factor.(57)

4.4.4. Effect of varying the level of adhesion in metal / ABS composites.

This variation was achieved by attaching metal foil with a series of glues, namely "Gloy", "Cow Gum", and "Araldite". For both copper and nickel foil sandwiched tensiles, with one exception, the correlation between measured tensile strengths and calculated values was poor, bearing in mind that for relatively thin metal coatings the polymer carried a large fraction of the total load, thus approaching the theoretical value for the composite. (See Table 4.6) This was probably due to low levels of adhesion between metal and polymer resulting in little distribution of load between the copper or nickel and ABS. In the case of araldited copper / ABS composites a level of tensile strength close to the calculated value was obtained and the value of interaction factor was close to unity. The low tensile strength figures and I values of copper/ABS composites correspond to high values of ductility for the composites (See Table 4.6). This is a further indication of low adhesion levels for those composites other than the araldited copper / ABS samples, which showed a marked reduction in ductility (45%) compared with the polymer substrate. The only other composite with a significantly lower ductility was the copper / ABS system employing the "Cow Gum" adhesive, corresponding to an interaction factor of 0.26. On the other hand nickel plated ABS with lower peel strength and I values than the copper plated composite, failed in a brittle manner. This may have been due to a greater load being transferred to the ABS when the nickel failed, the increased load resulting from the higher tensile strength of nickel and a non-uniform stress distribution.

Since, as seen from Table 4.7, the tensile strength of the ABS which was coated only with araldite showed no increase over the untreated polymer, the improvement in tensile strength of the copper /araldite / ABS composite was not due to load sharing by the adhesive. Therefore the equation

$$\hat{\sigma}_c = \frac{I\,\hat{\sigma}_m A_m + E_p e_p A_p}{A_c}$$

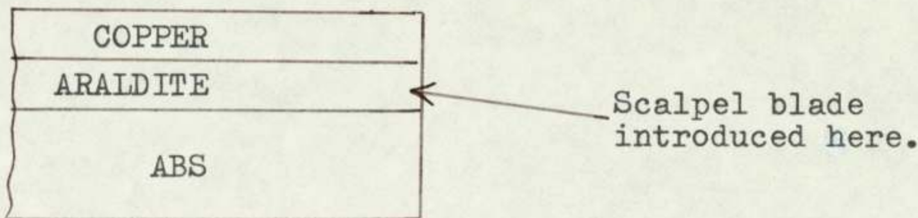
does not need to be modified to account for the strength of the araldite. This also applies to the other adhesives. It would appear in the case of araldited copper / ABS samples therefore, that load sharing between metal and polymer was permitted by a significant level of adhesion.

No glue tested on nickel / ABS samples produced a composite with significantly improved tensile strength, nor was there any marked reduction in ductility.

4.4.5 <u>Correlation of peel test results and interaction factors of glued ABS composites.</u>

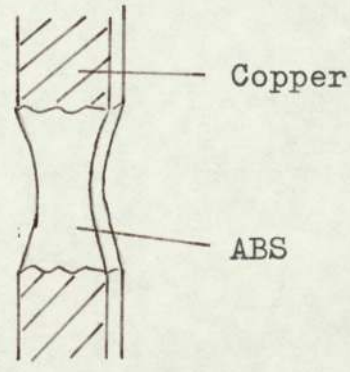
All peel tests indicated low levels of bonding between copper or nickel and ABS (See Table 4.6). Assuming that the interaction factor is a measure of adhesion (at least in part) for the case of the copper / ABS composite held together by araldite, a greater peel strength than that measured was anticipated. For other composites low interaction factors were found to correspond to low peel strengths.

The discrepancy observed for the araldited samples may have been due to their method of preparation. Slots were milled across the copper coated peel test plaque and the edge of the peeling strip was raised with a scalpel blade. This procedure may well have initiated a crack in the notch sensitive araldite, resulting in a lower peel strength, the actual failure occurring within the adhesive.



4.4.6. Nature of the failure of glued ABS composites

The failure of all the copper / ABS composites occurred as follows. Firstly the composite took the load and extended. When the level of stress reached a certain ~~level~~ value, the copper foils snapped and the ABS at this section of the test piece, continued to extend.



The copper continued to constrain that polymer to which it was still attached. As the stress was increased further, the copper began to part from the ABS along the length of the specimen. Separation generally took place at

the metal / adhesive interface. Some failure within the adhesive did occur. The constraint of the ABS by the copper was most marked in the case of the araldited composite. This corresponds to the larger value of tensile strength and lower ductility observed for this type of specimen. For the composite held together by "Gloy", parting of the copper and ABS occurred much earlier corresponding to little improvement in tensile strength or loss of ductility.

The nickel foil was rather less ductile than the copper foil. This led to a different failure mechanism of the nickel/ ABS composites. In this case the foil became completely crazed and tended to flake from the polymer substrate when put under stress. The whole composite gauge length extended, unlike the localised strain observed for the copper coated composites. This apparent lack of constraint by the foil paralleled the small improvement in tensile strength (compared with the calculated increase for perfect interaction between metal and polymer).

Separation of the nickel foil again occurred mainly at the metal / adhesive interface. The tensile strengths and moduli of the adhesives were closer to those values for ABS than for nickel or copper. Therefore when the composites extended the maximum stress on the adhesive would have been on the metal side of the adhesive. Hence failure at this interface was most likely.[143]

4.4.7 <u>Nature of the failure of araldited polypropylene composites.</u>

An applied stress extended the composites slightly until

the copper foils snapped. The polypropylene substrate elongated rapidly as it took on the load carried by the copper. The foils proceeded to debond from the copper along the whole gauge length, so that the polypropylene was not subjected to any significant constraint. Consequently there was no loss of ductility of the substrate. In spite of treating the polypropylene surface as described in Section 4.2, adhesion was insufficient to allow load distribution between metal and polymer, yielding a zero interaction factor.

4.5 Conclusions.

1. The simple "method of mixtures" formula for predicting composite tensile strength was limited to those composites where the interfacial adhesion was sufficiently great to permit the theoretical stress distribution.

2. For composites with low levels of adhesion it was necessary to incorporate an interaction factor, I, into the equation so that

$$\hat{\sigma}_c = \frac{I\,(\hat{\sigma}_m A_m) + (\hat{\sigma}_p' A_p)}{A_c}$$

(symbols as previously defined).

When I is less than unity the maximum composite strength is not achieved, since the applied load is not distributed theoretically.

3. Good correlation was found between interaction factor and peel strength, indicating that I is determined at least in part by factors affecting peel adhesion.

4. In the case of copper / ABS composites high values of interaction factor coincided with the production of brittle composites. If the generally accepted embrittlement theory is correct, then the interaction factor is related to interfacial adhesion. However nickel plated ABS composites of relatively low peel strength, and low I value still failed in a brittle fashion. In this instance the increased impact on the substrate when the nickel failed, compensated for the increased difficulty in crack propagation across the nickel / ABS interface. Therefore the mode of failure is determined in part by both non-uniform stress distribution, measured by I, and the minimum level of adhesion permitting crack propagation across the interface.

4.6 Suggestions for further work

1. Intermediate levels of metal to polymer interfacial adhesion might be produced for further tests of interaction factor I, by incomplete etching of an ABS substrate. It may be possible to determine the minimum peel strength to give an interaction factor of unity, for a given metal plate thickness.

2. By producing composites with greater volume fractions of copper the stress distribution on such composites may vary from the theoretical distribution, and the need to incorporate I into the composite strength equation might be further tested.

3. The effect of plating an intermediate, relatively ductile, metal layer e.g. indium between the electrolessly

coated ABS and copper or nickel plate might provide further information on the mechanism of composite embrittlement.

CHAPTER FIVE

Selective Area Plating

5.1. Introduction

The advantages of selective area plating have been well documented.[144,145] Saving of materials coupled with achieving desirable mechanical properties are foremost.

The many methods of carrying out selective plating on plastics will be examined, followed by a discussion of the mechanical properties of selective area plated composites.

5.1.1. Methods of Selective Area Plating

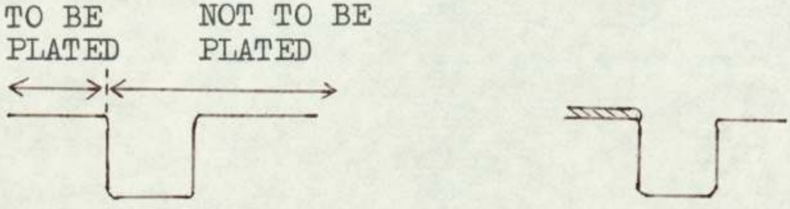
The simplest means of selective plating is to apply a coat of "stop-off" lacquer to those areas of polymer which are to remain unplated. This lacquer is immune to the electroless plating procedure, and no metal deposition takes place on it. Martin[144] has suggested that acrylic resins are the best stop-off materials. These materials are very resistant to mineral acids. After etching the polymer, Martin has recommended that it be treated with a chromating solution. This solution removes any acrylic degradation products which are capable of adsorbing the Pd-Sn complex during the catalysing stage.

Lacquers are available for use with a number of plastics materials.[145]

A range of chemicals have been patented as poisons to the reception of electroless copper.[146] These poisons are applied dissolved in an organic solvent together with a

resin binder. Useful poisons include organic and inorganic compounds of sulphur, selenium, tellurium, polonium and arsenic e.g. thiourea, MBT, sodium and potassium sulphides. There is a problem with surface imperfections on plastics substrates catalysing deposition where it is not wanted. This results from the trapping of ions by pores for instance. It is thought that the action of the poison is to prevent entrapment or to neutralise trapped ions.

A difficulty with the lacquer stop-off method is the production of precise stopped off zones. There is a tendency to form ragged edges, which grow more ragged during electroplating. Miller has suggested a solution to this problem. (147) Components should be designed with a masking groove, and the plated zone is ended at the "going down" edge of the groove to reduce current density.



This technique should produce a component of good appearance. However if the substrate is notch sensitive and the part is likely to suffer impacts in service, then mechanical failure might result from the incorporation of the groove.

Masking tapes are also available for stopping-off straight edges. A difficulty arises from the use of some tapes, however. It is possible that the chemical etching solution

used to prepare the polymer surface gets under the edge of the tape and remains there through the rinse. The etchant may then leach out and prevent deposition of the catalyst or electroless copper. This problem may be countered by applying the tape after etching, but new difficulties are encountered in applying the tape firmly without touching the adjacent polymer surface.

Many techniques for selective area plating, using radiation have been described. Schlesinger and Baylis[148] have selectively inhibited deposition of Shipley electroless metal on ABS by exposing areas of the polymer to U.V. radiation following immersion in the catalyst solution. The requisite pattern of plated and unplated regions was achieved by placing a negative mask between the ABS and the source of U.V. radiation. This technique is limited in terms of substrate, however, these workers being unable to achieve selective inhibition on glass.(149)

Means of selectively sensitising a polymeric substrate have been described in patent literature.[150] One such method is to treat the polymer with a sensitizer comprising a photo-sensitive compound of either Ni, Mn, U, Mo or W. Alternatively a combination of photosensitive species of Pd and In or Ce may be used. The sensitized surface is exposed to U.V. radiation through the appropriate pattern. The irradiated surface is then immersed in a solution of catalyst metal ions, which are reduced at the photosensitized regions. In the case of Pd-In and Pd-Ce sensitizers, the use of a further catalyst solution is unnecessary.

Selective sensitisation of polyimide has been patented.[151] This is carried out by subjecting the areas to be plated, to a natural gas flame played through a mask to give the required outline. Once sensitized the film is immersed in catalyst solution. Good adhesion and line definition have been claimed, but careful control of the process is necessary to prevent thermal degradation of the polymer.

An elegant chemical technique has been patented by DeAngelo and Sharp.[152] The substrate is first treated with a "photo-promoter" solution. This contains a metal salt in which:

(a) high energy radiation can alter the oxidation state of the metal

(b) either the original or altered oxidation state, but not both, is capable of reducing precious metal ions e.g. Pt, Pd, Rh

The substrate is then irradiated with U.V. through either a positive or negative pattern depending on which oxidation state is the reducing agent. The precious metal catalyst is then deposited. Examples of negative photo-promoters are mercuric oxalate and ferric oxalate. Stannous chloride, plumbous chloride and titanium(II) chloride act as positive photopromoters.

A patent for a similar system has been issued in which cupric acetate is reduced by the disodium salt of anthraquinone 2,6 disulphonic acid.[153] The latter radiant energy sensitive compound reduces the metal salt when exposed to U.V.

A further technique has been patented which involves the selective area, photolytic decomposition of a silver, palladium or copper salt of methacrylic acid.[111] Exposure to U.V. light liberates metal ions, which are reduced and form catalytic aggregates on the polymer surface.

Selective area plating of "Melinex" film has been claimed.[154] This water permeable polymer is impregnated with a salt of the following type:

$$\underset{\underset{R'}{|}}{\text{(Py)N}^+} \text{———} (CH{=}CH)_n \text{———} \underset{\underset{R^2}{|}}{\text{(Py)N}^+} \quad 2X^-$$

Where R = H, or hydrocarbon grouping

X = anion of a strong acid

n = 0-3

When exposed to U.V. radiation through the appropriate pattern, the salt breaks down and radical cations are formed. Immersion in silver nitrate solution results in the deposition of silver at the radical cation sites.

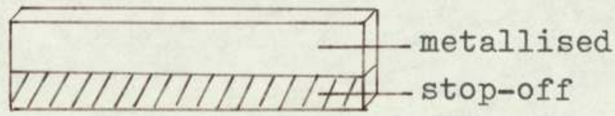
A brush plating technique for selective area plating on plastics has been described by Lupinski.[155] The technique of brush plating is being developed for selective area plating of metals, and advances in this area may lead to improvements in the brushplating on plastics process. Industrial procedures have been summarised by Rubinstein.[156]

Turner has reviewed the use of jet plating, anode placement and differential metal deposition as means of selective area plating.[157] Each of those processes is rather limited in its field of application and effectiveness.

5.1.2. Properties of Selective Area Plated Plastics

Metal plating on plastic produces a composite with many advantages over the bare polymer which have been summarised in a previous section. However, these improved properties have been achieved at the cost of certain adverse effects. Two important disadvantages are the brittleness of the composite, and the tendency for the metal coating to part from the polymer substrate. These effects are encountered when the polymer is completely encapsulated in metal.

Martin[144] has performed impact tests on unnotched Charpy test pieces, of bare polypropylene and ABS, totally encapsulated polymer, and selective area plated polymer. At temperatures of 20°F and 70°F the selectively plated polymers showed little reduction in ductility compared with the totally encapsulated test pieces. Unfortunately this worker did not describe the "stop-off" pattern but the lacquer appears to have been applied along the length of the test piece.



The impact strength of unnotched Charpy test pieces moulded in ABS and modified PVC, plated on one side only, have been determined.[158] The behaviour of these composites depended on which side of the test piece faced the hammer. When struck on the metallised side the bar deformed in a ductile manner, but when the hammer was directed at the side opposite the metallised face, the test piece fractured in a brittle fashion. These findings were accounted for as follows. When the bar was impacted the maximum stress concentration occurred at the face opposite to that which is struck. If the highly stressed face was the metallised one then cracks would initiate in the metal and propagate through the coating and across the metal / polymer interface, resulting in brittle failure. On the other hand, when the unmetallised side took the maximum stress of the impact the test piece could bend in a ductile manner.

Selective area plating has also been found to give better thermal cycling properties and outdoor service performance.[144] This is probably due to the break-up of large plated areas by stopped off regions and preventing the build up of stresses by permitting the plastic to expand and contract more freely.

No information on the tensile properties of selectively plated plastics was found in the literature.

For completely encapsulated specimens, a number of workers have shown that the strength of metal / polymer composites

can be determined from simple reinforcement theory, if the strengths of the individual components are known. This work is discussed more fully in Chapter 4. The composite strength may be calculated from the following equation:

$$\hat{\sigma}_c \phi_c = \hat{\sigma}_m \phi_m + \hat{\sigma}'_p \phi_p$$

where $\hat{\sigma}_c$ = tensile strength of the composite

$\hat{\sigma}_m$ = tensile strength of the metal

$\hat{\sigma}'_p$ = stress on the polymer at breaking strain of the metal

ϕ_c = volume fraction of the composite = 1

ϕ_m = volume fraction of the metal

ϕ_p = volume fraction of the polymer

Since this equation takes into account the volume fraction of the metal coating, it should be possible to predict the effect on tensile strength of altering ϕ_m by either thickening the layer of metal or by selective area plating.

5.2 Experimental Procedure

Tensile bars of Z grade ABS were moulded to ASTM specifications.[100] These bars were plated totally or partially, employing Shipleys electroless copper as described in the previous chapter followed by electrolytic copper plating to a thickness of 0.0254 mm in a pyrophosphate copper bath. Selective area plated bars were produced by applying "Sellotape" after the etchant

neutraliser treatment prior to catalyst deposition, to the areas of ABS to be masked from the plating solutions. Since the Sellotape was itself susceptible to plating, electrical contact between isolated regions of ABS, necessary for electroplating, was achieved without the need for a complex jigging arrangement. Once plated the Sellotape was simply peeled off. Using this procedure selective area plated bars were produced with the following features:

Type (i) Three horizontal umplated strips 12mm wide on each face; edges uncovered.

Type (ii). A central plated vertical strip 2.5mm wide on each face; edges uncovered.

Type (iii). A central plated vertical strip 5mm wide on each face; edges uncovered.

Type (iv). Faces completely covered; edges uncovered.

Unplated and completely encapsulated bars were also produced.

The dimensions of the bars and strips were measured with a hand micrometer and a travelling microscope, prior to pulling in an Instron tensile testing machine. The ultimate tensile strength of each specimen was determined at a strain rate of 5mm per minute and the dimensional changes were recorded.

At least four specimens of each type were tested.

5.3. Results

SPECIMEN TYPE	AVERAGE U.T.S. in MNm^{-2}	AVERAGE DUCTILITY $\frac{\text{CHANGE C.S.A.}}{\text{ORIG. C.S.A.}} \times 100\%$
Unplated	38.4	38.1%
Type (i).	37.7	20.7%
Type (ii).	39.3	3.2%
Type (iii).	44.2	2.4%
Type (iv).	46.4	0.8%
Encapsulated	48.2	0.8%

Table No. 5.1

MODE OF FAILURE	NO. OF SPECIMENS	AVERAGE UTS in MNm^{-2}	AVERAGE DUCTILITY
Within unplated zone.	4	38.3	22%
At edge of unplated zone.	2	36.5	18.1%

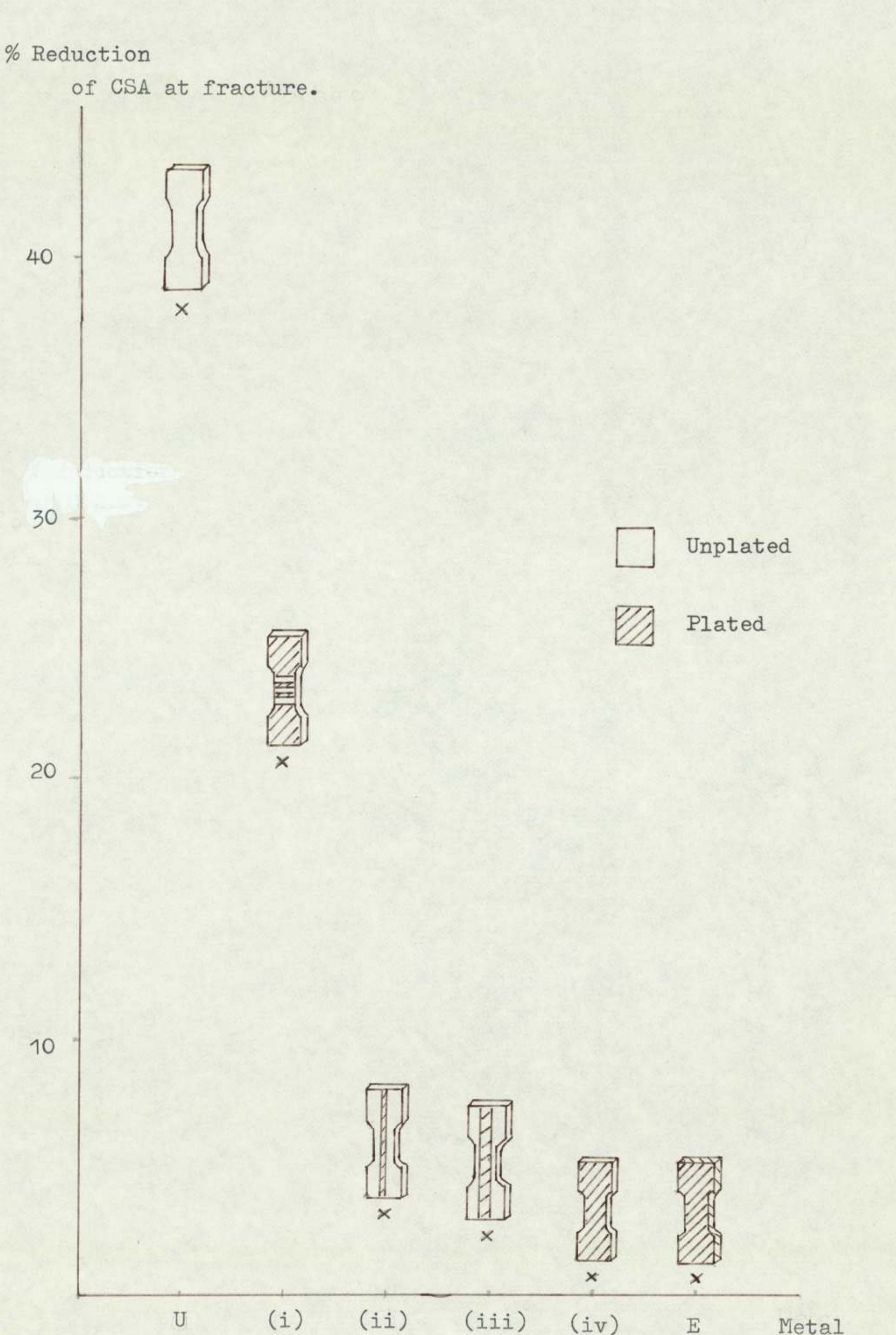
Table No. 5.2 Failure of Type (i) Composites.

SPECIMEN TYPE	VOLUME FRACTION OF METAL	CALCULATED UTS in MNm^{-2}	MEASURED UTS in MNm^{-2}
Type (i).	0.007	38.7	37.7
Type (ii).	0.003	36.3	39.3
Type (iii).	0.006	38.4	44.2
Type (iv).	0.015	44.6	46.4
Encapsulated	0.019	47.3	48.2

Table 5.3

GRAPH 5.1

EFFECT OF SELECTIVE AREA PLATING ON DUCTILITY.



GRAPH 5.2

EFFECT OF SELECTIVE AREA PLATING ON UTS

U.T.S. in MNm^{-2}

49

48

47

46

45

44

43

42

41

40

39

38

37

U (i) (ii) (iii) (iv) E METAL COVERAGE

Key:

Unplated

Plated

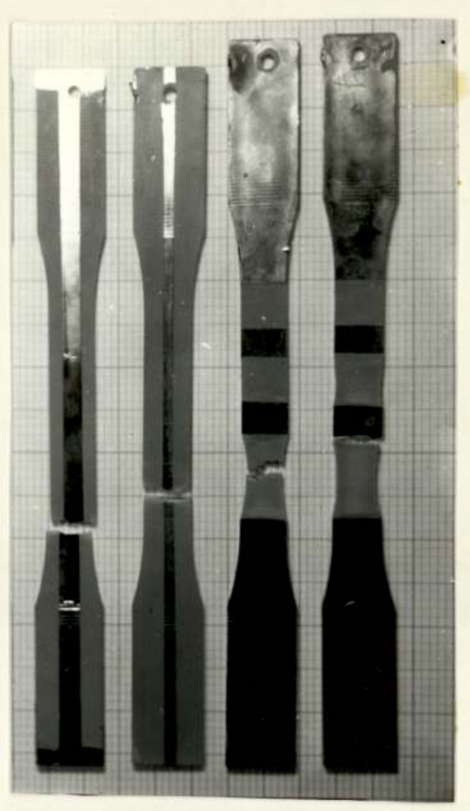


Plate 5.1

Fractured selective area plated composites.

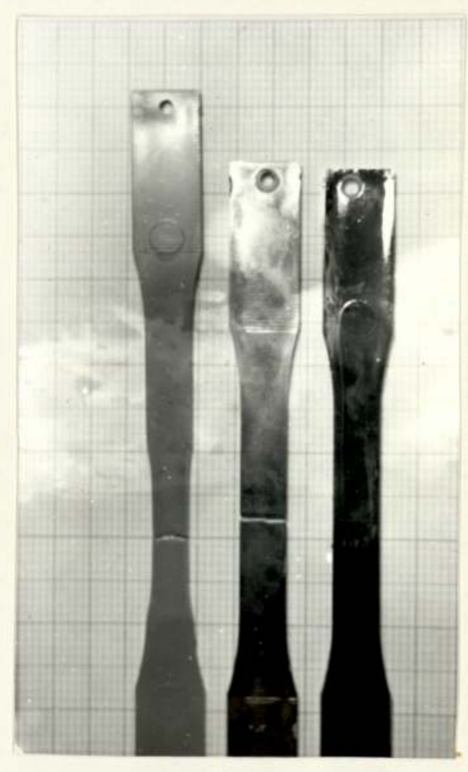


Plate 5.2

Fractured selective area plated composites.

5.4. Discussion

From Table 5.1 and Graphs 5.1 and 5.2 it can be seen that electroplating had a significant effect on the tensile strength and ductility of copper / ABS composites. Encapsulation of the polymer with only a 0.0254mm thickness of copper plate resulted in an almost 25% increase in ultimate tensile strength. However, as Tipping and Dennis [133] have shown previously, this improvement in strength was accompanied by a sharp loss in ductility. Whilst unplated bars underwent an average reduction in cross sectional area of about 38% prior to failure, a completely metallised specimen fractured before a 1% reduction was achieved. In the latter case the polymer was completely constrained in all directions, the copper plate possessing a much greater Young's modulus. Only when the copper had fractured was there a possibility of the ABS extending. However, the failure of the metal resulted in the sudden transference of load onto the polymer. Under these conditions it is thought that the crack initiated at the metal surface and propagated across the metal plate, can travel across the metal/ polymer interface if the interfacial adhesion is sufficient. Brittle failure of the whole composite will then occur.

In the case of those selectively plated specimens of types (ii), (iii), and (iv), an increase in tensile strength was observed together with a loss of ductility. These samples being constrained along their whole length in the direction of applied stress, were unable to extend until the copper plate had failed. The resultant impact on the polymeric substrate of type (ii) specimens would be rather less than on

on type (iv) bars, but this was sufficient for brittle failure of the composite. The change in impact force as the width of the constraining strip was reduced, produced a small improvement in ductility as expected. Also the tensile strength increased with the width of metal strip.

The results of tests on type (i) composites which were constrained intermittently in the direction of applied stress, showed some interesting features. As can be observed from Plate No. 5.1 the composite extended in a ductile fashion in those regions which were free of the metallic constraint.

The ultimate failure of these samples was found to occur at one of two places; either in the centre of a necked unplated region in which case no improvement in tensile strength was gained from the electroplate, or at the edge of the copper plating bordering on unplated zone (see Plate 5.1). Those failing in the second position had a considerably lower tensile strength about 36.5 MNm^{-2} which resulted in an average tensile strength for type (i) composites that was lower than the tensile strength of the unplated specimens. The reason for this second mode of failure may have been that the metal edge acted as a stress raiser and resulted in premature failure.

The ductility of the unplated zones of type (i) composites, reinforced the findings of Tipping that the embrittlement of the composite was not due to the etching of the polymer as had been previously suggested.

The application of reinforcement theory proved to be inaccurate. The predicted trends in tensile strength, for those specimens being completely constrained in the longitudinal direction were observed in practice, although the measured values differed from those calculated by as much as 15%. Also the measured values of composite tensile strength were greater than the calculated figures (See table 5.3). The reason for these discrepancies may have been due in part to inexact stopping off of the copper plate. Measurements taken on the width of the plated strips, using a travelling microscope, showed a tendency for the copper to encroach onto the stopped off regions. This would account for the greater tensile strength of the composite. Also since the outward growth of the metal strip was not uniform, the difference between the calculated volume fraction and that actually present would vary from sample type to sample type. Hence the percentage error in predicting the tensile strength of the composites would vary.

The reason for the failure of the horizontally striped specimens to come up to expectations has already been discussed. The reinforcement equation does not take into account the effect of stress raisers, which are probably present in these samples, and is therefore not applicable in this form. In fact the situation is similar to transverse fibre reinforcement, which does not produce a composite with strength greater than that of the matrix.

5.5 Conclusions

1. The problem of brittleness encountered in plated ABS has been overcome by judicious use of selective area plating, whilst retaining certain other advantageous composite properties.

2. The ductility of ABS was retained in the plated composite by "stopping off" areas of plastic in the direction transverse to the applied stress, in order to allow energy to be dissipated by plastic deformation of the unplated areas rather than by fracture of the composite.

3. In all cases where ABS bars were totally constrained in the direction longitudinal to the applied stress by a metal plate along their entire length, they failed in a brittle fashion. Reducing the width (and volume fraction) of this constraining metal strip did not give ductile composites.

4. It was not possible to apply composite reinforcement theory to those composites intermittently constrained in the direction transverse to the applied stress. This situation seemed analogous to transverse fibre impregnation of a matrix where no reinforcement is encountered.

5. For small volume fractions of metal plate the above theory was not accurately applicable to longitudinally selective area plated composites. Increasing the fraction of unplated plastic did reduce the tensile strength of the composite as predicted by the theory.

5.6. Suggestions for Further Work

1. Additional work on the application of reinforcement theory to selectively plated composites with increased metal thicknesses may provide further evidence of its validity.

2. The effect of varying the width of transversely stopped off regions might be usefully investigated for design purposes. Any relationship between the stopped off band width and ductility could be determined.

3. Also the differences in mechanical properties brought about by the use of several small unplated zones compared with a single large one, might be investigated.

CHAPTER SIX

ION BOMBARDMENT

6.1. Introduction

Little work has been carried out on the effects of bombarding polymer surfaces with ions accelerated by an electric potential with a view to implanting such ions into the surface.

Goldie [78] has described the effect of "corona bombardment" on a copolymer of tetrafluoroethylene and hexafluoropropylene. In an atmosphere of nitrogen the plastic was exposed to a high frequency, high voltage discharge. The stream of electrons was thought by this author to have produced free radicals on the polymer surface. The nitrogen atmosphere prevented combination of these radicals with oxygen. However adjacent radicals would not have been prevented from combining with each other. Any remaining free radicals may have been capable of forming a bond with other materials e.g. metals.

A process involving bombardment of low surface energy polymers with activated species of inert gases has been claimed to improve adhesion between such polymers and a metal coating. [159,77] This improvement was thought to be due to cross linking of the polymer, strengthening it and hence producing stronger mechanical keys between metal and substrate. Possible mechanisms have been suggested involving the formation of free radicals on the polymer chain prior to the formation of a three dimensional network. Bombardment by an activated

species of helium may have brought about the following changes:

$R_1H + He^* \longrightarrow R_1H^* + He$ (1) R= polymeric radical

$R_1H^* + R_2H \longrightarrow R_1R_2 + H_2$ (2)

cross-linking reaction

$R_1CH_2\ CH_2\ R_2^* \longrightarrow R_1\ CH = CH\ R_2 + H_2$ (3)

Unsaturation such as that produced in equation (3) was indeed observed in practice, which supports this mechanism. However, ESR studies indicated that the following mechanism was more likely:

$RH + He^* \longrightarrow R\cdot + H\cdot + He$ --- (4)

$R_1R_2 + He^* \longrightarrow R_1^{\cdot} + R_2^{\cdot} + He$ --- (5)

$H\cdot + RH \longrightarrow H_2 + R\cdot$ --- (6)

$R\cdot + R_1\cdot \longrightarrow RR_1$ --- (7)

$R\cdot + R_2\cdot \longrightarrow RR_2$ --- (8)

$R\cdot + R\cdot \longrightarrow RR$ --- (9)

Equations (7) (8) and (9) may have led to crosslinking.

The energy requirements for crosslinking various polymeric materials have been determined. Polystyrene was crosslinked by ionising radiations with a minimum energy of 855 eV. [160] ESR studies indicated the formation of the following radical:

$$-\underset{H}{\overset{H}{C}}-\underset{C_6H_5}{\overset{H}{C}}- + A^* \longrightarrow -\underset{H}{\overset{H}{C}}-\underset{C_6H_5}{\overset{\cdot}{C}}-$$

Two such radicals were capable of combining to form a crosslink as follows:

$$-\overset{H}{\underset{H}{C}}-\dot{C}(C_6H_5)- \;+\; -\overset{H}{\underset{H}{C}}-\dot{C}(C_6H_5)- \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{C_6H_5}{C}- \,/\, -\overset{H}{\underset{H}{C}}-\underset{C_6H_5}{C}-$$

Polybutadiene on the other hand was crosslinked by ionising radiations of very low energy. Values of 12.5 - 14 eV have been postulated. [160] The probable mechanism again involves free radical formation, for addition to take place.

$$-CH(=CH_2)-CH- \;+\; -\dot{C}H- \longrightarrow \dot{C}H-CH- \,/\, CH_2 \,/\, -CH-$$

1,2 addition product

Copolymerisation with polystyrene was said to increase the energy requirement to 17 - 18.5 eV when 23% polystyrene was included. Polyacrylonitrile further increased this figure.

Burlant and Taylor have reported that polyacrylonitrile is crosslinked by ionising radiation in the presence of nitrogen. [161] Chain scission occurs in an oxygen atmosphere, on the other hand. Crosslinking may have involved formation of the following radical species:

```
  H    H                         H
  |    |                    .    |
- C —— C —    + A* ——>    — C —— C —     + H·
  |    |                    |    |
  H    C ≡ N                H    C ≡ N
```

The energy requirement for producing such a radical has been quoted as 500 eV when hydrogen gas is evolved.[162]

It is clear then that in the case of ABS, bombardment by even low energy ions may result in crosslinking via free radical production.

Williams [163] has described a technique known as "ion plating" for metallising polymer substrates. This process, which has been claimed to give excellent metal to polymer adhesion, involved the implantation of high energy metal ions into the polymer surface. The ions themselves were accelerated under vacuum by a large potential difference across the ion source and a cathode plate held behind the plastics substrate.

A patent has been granted for the activation of soda glass, poly (methyl methacrylate) and poly (ethylene terephthalate) surfaces by bombardment with palladium ions prior to electroless plating.[164] These ions possessed very low energies in the range 100 - 300 eV and the dosages giving best results were from 1×10^{18} to 3×10^{19} ions m^{-2}. They became implanted in the substrate surface. To prevent build up of charge

which would repel low energy ions, alternate bombardment with metal ions and electrons was used. If higher energy species were employed, ion implantation beneath the surface occurred resulting in poor electroless metal coverage.

6.2. Experimental Procedure

Plaques of Z grade ABS were cut into squares of side 44mm. These squares were ion bombarded at Harwell's Nuclear Physics Division. The actual target area was a circle of diameter 25.4mm at the centre of each square.

Impregnation of the specimens with Ar+, O+ and Cu+ ions was carried out using dosages of 10^{18}, 3×10^{18}, 10^{19} and 3×10^{19} ions m^{-2} for each ion type. A low target current was applied to minimise overheating and resultant degradation of the ABS. The accelerating voltage employed was 150keV.

Each sample was treated with Shipley's electroless copper deposition sequence and the extent of copper plating and blistering was noted.

The chemical composition of the ion bombarded polymer surface was investigated by C,H,N analysis. Its solubility in acetone was tested.

6.3. Results:

The effects of ion bombardment on plateability and

adhesion of copper on ABS are tabulated. Unlike the untreated ABS, the ion bombarded polymer was insoluble in acetone, suggesting some chemical change.

The results of C, H, N analysis on a sample bombarded with Cu^+ ions (3×10^{19} m^{-2}) showed these elements to be present in the following quantities:

C 82% H 9.2% N 4.2%

This compared with calculated values for Z grade ABS of :

C 81.2% H 8% N 6%

Table 6.1

No.	Ion B. Treatment Ions m^{-2}	Appearance of I.B. Circle After Bombardment	After Plating	Appearance of Surround After Plating	Adhesion of Copper to Treated Circle	Adhesion To Surround	Notes
1	10^{18} O+	Pale Yellow	Blistered bright deposit	MATTE COPPER	20% flaked off in rinse	GOOD	Electroless Cu deposited on surround before treated circle
2	3×10^{18} O+	Golden	Blistered bright deposit		90% flaked off in rinse		" "
3	10^{19} O+	Dark Brown	No deposit		-		
4	3×10^{19} O+	Dark Brown	Blistered bright deposit		20% flaked off in rinse		" "
5	10^{18} Ar+	Pale Yellow	Blistered bright deposit		95% flaked off in rinse		" "
6	3×10^{18} Ar+	Yellow	No deposit		-		
7	10^{19} Ar+	Light brown	No deposit		-		
8	3×10^{19} Ar+	Dark brown	No deposit		-		
9	10^{18} Cu+	V. Pale Yellow	Blistered bright deposit		80% flaked off in rinse		" "
10	3×10^{18} Cu+	Pale Yellow	Blistered bright deposit		20% flaked off in rinse		" "
11	10^{19} Cu+	Golden	Blistered bright deposit		20% flaked off in rinse		" "
12	3×10^{19} Cu+	Brown	Blistered bright deposit		90% flaked off in rinse		" "

6.4. Discussion

In all cases the deposition of electroless copper to the treated ABS was affected. Bombardment with argon ions resulted in no deposit being able to form on surfaces with ion densities greater than 10^{18} ions m^{-2}. The lowest dosage permitted copper to deposit but this was so weakly adherent that it blistered extensively and 95% flaked off in the rinse.

Oxygen ion bombardment also resulted in deposits forming with very poor adhesion, the deposits being unable to adhere initially or being substantially removed during the rinse procedure.

Slightly greater adhesion was achieved as a result of copper ion bombardment, possibly due to some chemical interaction between the implanted species and the deposited metal. In all cases, however, the deposit blistered and partially fell off.

It was expected that the ions in the polymer surface would chemically interact with the subsequently deposited catalyst and electroless copper. These interactions may have been dipolar in nature, or possibly strong chemical bonds may have formed. If either type of bonding occurred then it is likely that increasing the ion dosage would improve adhesion, the number of interactions per unit area being increased. This clearly was not the case. However, if in addition to promoting adhesion, the presence of such ions increased the rate of electroless metal deposition, the consequent rapid evolution of hydrogen may

have caused blistering. The lack of a direct correlation between electroless metal coverage and ion dosage indicated that more than one factor was determining the former.

It should be noted that whenever a slightly adherent deposit did form, the surface of the copper was highly reflective, showing that the underlying polymer surface was smooth. In contrast the area of ABS unaffected by the ion beam was coated with an adherent matte deposit, typical of the etchant-roughened substrate. It seemed likely therefore that ion bombardment had in some way rendered the polymer resistant to the strongly oxidising "treacle etch".

Two possible mechanisms for the resistance to etching are:

(1) Formation of a thin carbon coating on the ABS. Such film may have resulted from degradation of the polymer itself or (more likely) from the breakdown of organic additives in the plastics surface. Discoloration of the treated polymer surface was observed in accordance with this mechanism.

(2) Crosslinking of the ABS, via the formation of free radical sites on the polymer, by the energetic bombarding ions, which combined to form a three-dimensional network. The high energy levels of the bombarding would have easily been capable of such a reaction. As already indicated, literature values of the order of

several hundred electron volts have been quoted [160, 161] for free radical formation and in this investigation ions with an energy level of 150 keV were employed.

Since bombardment took place under vacuum any radicals so produced could have combined either with the accelerated ions or with each other prior to being exposed to the atmosphere. Crosslinking was therefore likely to occur.

Treated areas were found to be insoluble in acetone. If these regions had simply undergone degradation resulting in the formation of a carbon film on the polymer surface, it might reasonably have been expected that the samples of surface removed would have dissolved in part, since ABS is soluble in acetone, leaving behind an insoluble carbon film for successive analysis. However, the samples remained almost completely unaffected by acetone and C,H,N analysis indicated that the material was not constituted solely of carbon. Rather this analysis showed a similarity between the chemical composition of the affected and unaffected polymer, which is consistent with the formation of crosslinked ABS.

It seemed therefore that the most likely result of bombarding ABS with high energy ions was the production of an etchant-resistant crosslinked network, possibly together with small quantities of degradation products to account for the discoloration. This may have included

some elemental carbon.

In order to produce a usefully impregnated surface it may well be necessary to use ions of lower energy. Whether or not the depth of penetration of such species would be sufficient for good bonding is open to question.

6.5. Conclusions

1. Bombardment of ABS with high energy argon, oxygen and copper ions (150 keV) rendered it immune to attack by a strong chromic / sulphuric acid etchant. This was probably due to crosslinking of the ABS, initiated by the high energy bombarding species.

2. Ion bombardment selectively stopped off ABS from subsequent electroless plating.

6.6. Suggestions for Further Work

Bombardment of plastics materials by low energy species, in the range 100 - 500 eV, might be carried out in order to impregnate the polymer substrate without crosslinking it. Bombardment with copper or palladium ions might result in catalysation of the polymer for electroless metal deposition.

CHAPTER SEVEN

General Conclusions.

1. Small amounts of the following complexes have been shown to promote adhesion between copper and ABS: Ni $(acac)_2$; Cr $(acac)_3$; Fe $(acac)_3$.

2. It was possible to incorporate these complexes into the surface layer of the ABS by dissolving each complex in a mild solvent for this plastics material, namely Shipley's organic conditioner.

3. A similar quantity of Cu $(acac)_2$, incorporated into the ABS in the same manner, apparently did not promote adhesion.

4. The lack of adhesion promoting activity of Cu $(acac)_2$ may have been due to its molecular geometry. The molecules of this β-diketonate, being more streamlined than those of the other complexes under examination, may have diffused into the bulk of the substrate. As a result no significant adhesion enhancement could have taken place.

5. For each adhesion promoting complex it was found that there was an optimum time of immersion in the complex containing solvent which produced the best adhesion enhancement.

6. For reducing copper salts incorporated in ABS dimethyl aminoborane was found to be the most convenient reducing agent, having a strong reducing action and no apparent adverse effects on the base polymer.

7. Copper (II) acetylacetonate proved to be the most readily reducible metal compound tested.

8. The most successful means of incorporating the copper (II) acetylacetonate for reduction and subsequent catalysation of electroless metal deposition was to mix it in to the molten plastics material. This gave approximately a 90% electroless metal coverage of the ABS. However this deposit was weakly adherent.

9. Application of copper (II) acetylacetonate with a binder or incorporation by the swelling technique also gave rise to electroless deposits with poor adhesion, but with a much lower coverage.

10. Increasing the immersion time in the copper (II) containing solution and also the metal complex concentration gave better electroless metal coverage, using the swelling technique. The optimum residence time in the reducing solution was found to be 2 minutes. Longer immersion times did not improve electroless metal coverage.

11. The simple "method of mixtures" formula for predicting composite tensile strength was limited to those composites where the interfacial adhesion was sufficiently great to permit the theoretical stress distribution.

12. For composites with low levels of adhesion it was necessary to incorporate an interaction factor, I, into the equation so that

$$\hat{\sigma}_c = \frac{I(\hat{\sigma}_m A_m) + (\hat{\sigma}_p A_p)}{A_c}$$

(symbols as previously defined)

When I is less than unity the maximum composite strength is not achieved, since the applied load is not distributed as expected theoretically.

13. Good correlation was found between interaction factor and peel strength, indicating that I is determined at least in part by factors affecting peel adhesion.

14. In the case of copper / ABS composites high values of interaction factor coincided with the production of brittle composites. If the generally accepted embrittlement theory is correct, then the interaction factor is related to interfacial adhesion. However nickel plated ABS composites of relatively low peel strength and low I value still failed in a brittle fashion. In this instance the increased impact on the substrate when the nickel failed, compensated for the increased difficulty in crack propagation across the nickel / ABS interface. Therefore the mode of failure is determined in part by both non-uniform stress distribution, measured by I, and the minimum level of adhesion permitting crack propagation across the interface.

15. The problem of brittleness encountered in plated ABS has been overcome by judicious use of selective area plating, whilst retaining certain other advantageous composite properties.

16. The ductility of ABS was retained in the plated composite by "stopping-off" areas of plastic in the direction transverse to the applied stress, in order to allow energy to be dissipated by plastic deformation

of the unplated areas rather than by fracture of the composite.

17. In all cases where ABS bars were totally constrained in the direction longitudinal to the applied stress by a metal plate along their entire length, they failed in a brittle fashion. Reducing the width (and volume fraction) of this constraining metal strip did not give ductile composites.

18. It was not possible to apply composite reinforcement theory to those composites intermittently constrained in the direction transverse to the applied stress. This situation seemed analogous to transverse fibre impregnation of a matrix where no reinforcement is encountered.

19. For small volume fractions of metal plate the above theory was not accurately applicable to longitudinally selective area plated composites. Increasing the fraction of unplated plastic did reduce the tensile strength of the composite as predicted by the theory.

20. Bombardment of ABS with high energy argon, oxygen and copper ions (150 keV) rendered it immune to attack by a strong chromic/sulphuric acid etchant. This was probably due to crosslinking of the ABS, initiated by the high energy bombarding species.

21. Ion bombardment selectively stopped off ABS from subsequent electroless plating.

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APPENDIX

Problems with Plating on plastics

1. Problems with the substrate

The plastics surface must be scrupulously clean, otherwise adhesion will be impaired. It is necessary to avoid the use of mould release agents which, by the nature of their function, reduce adhesion between polymer and metal. It is difficult to remove all traces, if used, as some will be absorbed into or adsorbed onto the polymer surface and cleaning will not remove it completely.

The choice of plastics grade is important for the same reason. If the formulation includes lubricants (internal or external) which have a tendency to exude to the plastics surface, adhesion will be impaired.

Handling of the mouldings should be kept to a minimum, and then carried out only with a gloved hand.

2. Problems with the Shipley Crownplate System

The hydrolyser should remove all surface impurities and render the surface hydrophilic. Slight dulling of the ABS should be noticeable. It is necessary to make up evaporation losses. Poor performance of this solution may be due to insufficient CrO_3. The concentration of CrO_3 should be in the range 520 - 550 g/l and can be checked by the following method:
Transfer 50 ml of approximately 0.1N ferrous ammonium sulphate solution into a 250 ml flask, add about 25 ml

10% sulphuric acid and dilute to about 100ml with distilled water. Titrate with 0.1N potassium permanganate until a faint pink colour is obtained. Call this titration value A.

Dilute a 10ml sample of hydrolyser to 250ml in a standard graduated flask. Transfer a 5ml sample of the diluted hydrolyser solution into a 250ml flask, add 50ml of the previously standardised ferrous ammonium sulphate and 25ml of 10% sulphuric acid. Titrate with 0.1N potassium permanganate until a faint pink colour is obtained. Call this titration value B.

Then chromic acid concentration = 16.6 x (A-B) g/l.

The effectiveness of the organic conditioner can be visually assessed by the further dulling of the ABS. The pH of this solution should be kept within the range 2-7. This is controlled by additions of 1% H_2SO_4 or 5% $NaHCO_3$ to lower or raise the pH respectively. Some chrome residues tend to be carried into the conditioner solution and need to be filtered out. It is important not to overheat the solution, as this results in breakdown of the emulsion.

When operating correctly the etch should produce a totally matte, water break free surface on the ABS. If it is not working correctly incomplete metal coverage or poor adhesion may result. The S.G. of the solution should not exceed 1.85

at 65°C. Higher values indicate that there is too much dissolved ABS and one quarter of the bath's volume should be replaced. The CrO_3 level should be maintained at 1140-1175 g/l. Additions of CrO_3 should be made as an 800 g/l aqueous solution.

Following immersion in the neutraliser, there should be no yellow stains on the plastics surface. Such stains indicate chromium remains, and further neutralisation is required. The solution itself should be colourless with a pH of 12.5 to 13.5 maintained by additions of 50% sodium hydroxide solution. If all chromium residues are not removed, incomplete metal coverage will result.

The precatalyst dip is pale yellow in appearance and produces no visible effect on the ABS surface. The S.G. of the solution should be maintained in the range 1.121 to 1.134 at 20°C.

The activator itself deposits a uniform distribution of palladium nuclei over the plastics surface. This should be apparent as an even tan coloration over the entire surface. This colloidal solution is dark brown in colour. It is susceptible to atmospheric oxidation and the bath should be fitted with a loose lid. Air agitation must be avoided. If decomposition occurs a layer of metallic palladium forms at the bottom of the bath leaving a colourless liquor.

The accelerator is a colourless, acidic solution. When

operating correctly it produces a lightening of the tan coloration brought about by the activator, and rapid coverage of electroless copper will occur subsequently. The pH of the solution should be kept within the range 0.7 to 1.1. If it becomes brown or cloudy it should be discarded.

Many problems can occur with the final electroless copper stage. This royal blue solution can readily passivate or decompose if incorrectly or infrequently used. The pH should be maintained between 11.3 and 12.3. If too low, the solution will passivate. On the other hand solution instability results from too high a concentration of hydroxyl ions, and total plating out of the copper may occur. Spontaneous deposition can be halted by the addition of dilute sulphuric acid. A passivated solution produces a yellow coloration on the catalysed ABS. It is possible to restore the plating activity by increasing the pH, if this is necessary, or by making an addition of formaldehyde. Any metallic copper must be removed from the walls of the bath by dissolution in 50% nitric acid. The bath must not be scrubbed as any roughness introduced this way promotes spontaneous decomposition of the solution. Particles of copper should be removed from the solution for the same reason, by filtration. Finally copper removed from the solution should be regularly replenished. Low levels of copper concentration reduce the rate of deposition and the blue coloration of the solution becomes much less intense.

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