FUNDAMENTAL MECHANISMS AFFECTING SERVICE PERFORMANCE OF ELECTROPLATED PLASTICS

by

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SUMMARY.

Ten grades of ABS and four grades of polypropylene have been plated with various copper + nickel + chromium coatings and subjected to a variety of tests. In corrosion studies the pre-electroplating sequence and plastics type have been shown to influence performance. One ABS pre-electroplating sequence was consistently associated with better corrosion performance; two factors were responsible for this, namely the more severe nature of the etch and the relatively more noble electroless nickel. Statistical analysis has indicated that order of severity of the corrosion tests was static-mobile-CASS, the latter being the least severe. In mechanical tests two properties of ABS and polypropylene, ductility and impact strength, have been shown to be adversely affected when electrodeposited layers were applied. The cause of this is due to a complex of factors, the most important of which is the notch sensitivity of the plastics. Peel adhesion has been studied on flat panels and also on ones which had a ridge and a valley moulded into one face. High adhesion peaks occurred on the flat face at regions associated with the ridge and valley. The local moulding conditions induced by the features were responsible for this phenonemon. In the main programme the thermal cycling test was shown to be more likely than the peel adhesion test to give an indication of the service performance of electroplated plastics.

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1. LITERATURE REVIEW.

Introduction.

The electrodeposition of metals on to non-conductors was an early development in the history of electroplating. For electrodeposition to be facilitated the surface of the article must be rendered electrically conductive and hydrophillic. Early methods devised to fulfil the first requirement utilised graphite in colloidal suspensions which was painted over the article or silver which was produced by chemical reduction. The second requirement was satisfied by mild mechanical abrasion, or by chemical etching. In present day plating on plastics processes the aforementioned conditions are satisfied using chemical etchants and an electroless copper or nickel deposit; the electroless solutions are initially catalysed by some noble metal such as palladium, but afterwards the deposited metal itself further catalyses the reaction and so appreciable thicknesses (0.25 µm) can be deposited 'autocatalytically'.

Initially electroplated non-conductors were used in very specialised applications, or more commonly for souvenirs such as leaves or shells. The electrodeposits encapsulated the object since no bond existed between the object and coating. Furthermore, large deposit thicknesses were necessary to ensure complete encapsulation and so the reproduction of fine surface details was not possible. In modern processes for electroplating plastics the electrodeposit has a measurable adhesion to the substrate and relatively thinner (and therefore less costly) deposit thicknesses are used.

Mainly due to these features the electrodeposition of metals onto plastics has become an established branch of the metal finishing industry.

1.1. General Considerations.

The question 'why plate plastics ?' cannot be answered adequately unless some of the advantages of using plastics instead of metallic substrates are examined. Plastics have a much lower density than metals and thus offer considerable savings in weight. Furthermore, intricately shaped plastics mouldings can be produced having a high surface gloss, this in conjunction with 'brightened' electroplating solutions favours the production of a bright decorative finish, eliminating expensive mechanical polishing operations. The cost of zinc base material is currently around £ 333 per tonne *(1) whilst plastics materials such as acrylonitrile butadiene styrene (ABS) have a cost of around £ 650 per tonne *(2). The advantages of depositing metals onto plastics have been adequately documented by Goldie (3). For example, the flexural modulus of the plated plastics part is higher than the unplated version. It is evident that other properties such as abrasion resistance and resistance to UV degradation are also improved when metallic coatings are applied to plastics. However, as will be discussed later some properties of plastics such as impact strength and ductility may be affected adversely by application of electrodeposited layers.

1.2 The Choice of Plastics Material.

At the present time many plastics have been successfully plated ; they include ABS, polypropylene,

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* Latest figures available in 1974.

polyphenylene oxide (PPO), polycarbonate, polyethylene and nylon. However, only two plastics, ABS and polypropylene are used to any great extent for electroplating purposes. The reasons for this are partly due to economic considerations partly due to the overall chemical and physical properties of the plastics and partly due to the relative ease with which the plastics can be electroplated.

The final choice of which plastics type to electroplate will be a matter of compromise. Some of the advantages of using polypropylene, such as its lower cost, lower density, higher peel adhesion values and good thermal cycling behaviour may be offset somewhat by other factors since it is more difficult to successfully electroplate polypropylene than ABS. A further advantage that ABS offers is that it exhibits superior moulding characteristics to polypropylene, shrinkage is much less and this favours the production of mouldings with a high degree of dimentional accuracy. Until polypropylene can be plated as satisfactorily and as consistently as ABS the latter plastics will continue to dominate the plated plastics market.

Many supply houses have available methods for plating the various plastics mentioned above and this alone bears witness to the amount of research that has been undertaken on the subject of electroplating plastics. Today electroplated plastics are being used in a number of functional as well as decorative applications. Such items as lamp bezels, car trim, hub caps, handles and a variety of bathroom fittings are frequently found to be plated plastics.

Despite the volume of plated plastics produced there has been surprisingly little effort to determine some of the more fundamental mechanisms that can affect the service life of plated plastics. The present work was intended to examine the effects of process variables, plastics types and deposit thicknesses and combinations on a number of properties of plated ABS and polypropylene.

1.3 THE CHEMISTRY AND STRUCTURE OF ACRYLONITRILE BUTADIENE STYRENE (ABS).

Three monomers, acrylonitrile, butadiene and styrene make up the terpolymer known as ABS. These three constituents all have quite different physical and mechanical properties which they can confer to the resulting terpolymer. The ratio of A:B:S can be varied over a large range resulting in a family of ABS plastics having widely differing properties.

1.4 ACRYLONITRILE ($CH_2 = CHCN$)

This constituent readily polymerises to form a crystalline, high melting point polymer. The material is highly resistant to chemical attack (3) and this is its main contribution to the properties of ABS. Atkinson et al (4) have stated that this constituent can have a pronounced effect on the reactivity of ABS towards etchants and thus the ratio of A:B:S should be carefully chosen. However, Wiebusch et al (5) maintain that the ratio is of little importance in influencing the plastics electroplating characteristics. The arguements of Atkinson et al (4) propounding that the acrylonitrile content can influence etching seems tenable since, as confirmed in this present work, ABS polymers having high acrylonitrile contents need longer etching times to ensure adequate adhesion.

1.5 BUTADIENE ($CH_2 = CH - CH = CH_2$)

Butadiene readily polymerises to form polybutadiene which is a rubber-like polymer at room temperature. The double bonds present in the structure lend themselves to cross linking and may even enter into metal to plastics bonding (6). At sub-zero temperatures the material becomes brittle. The property which it confers on the terpolymer is impact resistance, the cracks being arrested at the butadiene rich areas or being made to go around the butadiene phase. However, if the plastics has a sharp crack present, the behaviour of the plastics in impact testing is poor due to the notch sensitivity of the ABS terpolymer as a whole.

1.6 STYRENE ($C_6H_5 CH = CH_2$)

Styrene polymerises to form polystyrene which is a hard rigid transparent thermoplastic that exhibits good moulding characteristics. However, it has the drawbacks of being very brittle and having a comparatively low softening point. However, modifications to the basic styrene structure such as incorporating methyl (CH_3) groups on the benzene ring structure can increase significantly the heat distortion temperature.

The structure of ABS has been well documented (3, 7) and generally the accepted structure is one where the polybutadiene (graft rubber) particles are dispersed in a styrene-acrylonitrile copolymer matrix.

To obtain ABS polymers having acceptable properties copolymerisation techniques are used. Butadiene-acrylonitrile rubbers are compatible with styrene-acrylonitrile copolymers due to the high degree of polarity and mutual attraction exhibited by the acrylonitrile molecule in each phase.

Copolymers exhibit better mechanical properties than physical mixtures or polyblends due to the formers compatibility.

Many modifications can be incorporated into ABS polymers, inorganic fillers such as carbon and titanium dioxide are often added. The use of metallic stearates, lubricants and plasticisers has been shown (8) to affect the peel adhesion value obtained on plated ABS presumably due to their influence on the etching process. The size of the butadiene phase can also influence the peel adhesion value the maximum size favoured being ~ 1 μm.

It is evident that commercial grades of ABS can vary in composition and thus can be expected to exhibit a range of properties.

1.7 PROCESSING AND MOULDING OF ABS.

ABS terpolymers are amenable to processing in a variety of ways but they are generally injection moulded. Since ABS is known to absorb water (3,9) it is essential that the material is dried prior to moulding; 2 hr. at 80° C being a common treatment applied. If this precaution is not taken the mouldings are likely to exhibit blisters and splay marks which render them useless for decorative applications since subsequent electrodeposition serves to magnify the surface imperfections. Ellis (10) has studied the effects of various moulding parameters on the peel adhesion value subsequently obtained and found that an increase in melt temperature, a decrease in filling speed, an increase in mould temperature and a reduction in moulding pressure enhanced adhesion. Ebneth et al (11) have shown that even the choice of moulding machine can influence the peel adhesion obtained. They found that screw injection types gave more favourable results than plunger types, this being attributed to the better heat transference and mixing characteristics of the former types. Ebneth et al (11) and Ellis (10) are in agreement that although the temperature of the injection mould exerts only minimal influence on peel adhesion values (peel value increases with increasing mould temperature) it is of paramount importance with regard to plastics weld and surface gloss on the moulding. Weibusch et al (5) are in conflict with Ebneth et al (11) and Ellis (10) since they maintain that the mould temperature exerts a considerable influence on peel adhesion value. They state that an optimum mould temperature of 50° C is essential. However, since cold moulds result in poor surface finish mouldings and in parts having a higher degree of surface stress it is probable that the higher mould temperatures will favour the production of better quality mouldings. Furthermore, since mouldings having an internal stress do exhibit lower adhesion levels than stress-free mouldings it is difficult to reason why Ebneth et al (11) and Ellis (10) generally discount the influence of the mould temperature. One reason could be that they used higher mould temperatures than Weibusch et al (5) but examination of the results shows that Weibusch et al (5) found that peel adhesion levels decreased with mould temperatures over 50° C. The main factor in this conflict may be due to the fact that all different grades of ABS were used in each investigation, and as such a differ ent response to the moulding variables was encountered.

Weibusch (7) and Ebneth et al (11) have shown that peel adhesion values can be influenced by moulding configuration ; the thicker the section the higher the adhesion. This dictum does not always apply since it has been found that a decrease in local cross-section can also lead to an increased peel adhesion value. Care must be exercised in interpreting these conflicting views since variables other than section thickness such as localised moulding conditions may well influence the phenonemon. For instance the level of moulded in stress could vary with section thickness, this is known to greatly influence peel adhesion values (3, 11).

Although the use of mould release agents especially of the silicone type is generally depracated (3,12), Ebneth and Moll (11) and Dennis (13) reason that surface greases if not too severe may be readily removed by either pre-cleaning in a soap solution or by the oxidative action of the acids employed in the process sequence. However, if contamination does occur the extra process involved in removing it may add to overall production costs, the recommendation by a plastics manufacture (14) that mouldings should be handled with gloves and stored in plastics bags until required seems the best way to obtain readily plateable mouldings.

1.8 MECHANISM OF ABS PRE-ELECTRO PLATING PROCESSES.

Several routes may be adopted to facilitate electrodeposition onto the surface of the plastics. Modern ABS pre-electroplating process sequences involve a number of stages, the final of which results in the electroless deposition of either copper or nickel onto the surface. An important feature of this is that in addition to being electrically conductive, the electroless deposit is also bonded to the plastics substrate. A typical ABS process is outlined below :-

1) Etching in a chromic/phosphoric/sulphuric acid mixture (10 min. at 65° C).
   Swill in water.
2) Neutralising hexavalent chromium in sodium metabisulphite solution , (2 min. at 28° C).
   Swill in water.
3) Activating in a catalyst, usually a palladium chloride/ stannous chloride mixture in hydrochloric acid, (2 min. at 28° C).
   Swill in water.
4) Accelerating or rendering the catalyst in an active form; a solution which solubilises stannous salts is used, (2 min. at 50° C).
   Swill in water.
5) Electroless deposition; the palladium initially catalyses the reduction of either nickel or copper, the reaction proceeds autocatalytically, (7 min. at 30° C).
   Swill in water.
   Electrodeposition as required.

The function of each stage may be summarised in very broad terms as :-

1.8.1) <u>Etching.</u>

This renders the surface hydrophillic and also causes pits and fissures to develop in the surface; the etched surface providing 'anchoring' points for the subsequent electroless deposit.

1.8.2 Neutralisation.

This serves to prevent contamination of subsequent treatment solutions by hexavalent chromium.

1.8.3 Activation.

The catalyst for the electroless deposition is adsorbed onto the surface in this stage.

1.8.4 Acceleration.

The catalyst is rendered active due to the accelerators' action on the adsorbed catalyst complex.

1.8.5 Electroless deposition.

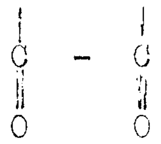
A thin layer of metal (or metal alloy) is reduced chemically in situ onto the surface of the plastics. The catalyst starting the initial reaction but as deposition occurs the metal itself further catalyses the reaction.

The effects of the above, except the etching stage, on the service performance of plated ABS have not received much attention from research workers. The influence of etchant compositions and operating conditions have frequently been related to the performance in the peel adhesion test only.

1.9 THE INFLUENCE OF ETCHANTS.

Etchants have been the most widely investigated stage of the pre-electroplating sequences used for ABS. It has been shown that the condition of the mouldings (degree of moulded-in stress) can influence the degree of etching sustained in a given etching solution. Ebneth et al (11) have shown that articles having a high degree of internal stress should be treated with etchants free from phosphoric acid. Weibusch et al (5) are in conflict with these views and maintain that mild phosphoric acid containing etches should be used always.

Weibusch et al (5) justify their arguments by stating that with highly stressed articles, etching will occur preferentially at low stress regions leaving stressed areas insufficiently etched; by using milder etching acids and longer immersion times all areas will receive adequate etching. This argument seems valid since poor adhesion is often encountered at highly stressed regions such as the injection gate area and these areas frequently need longer etching to ensure adequate adhesion. A mild etch (chromic/sulphuric/phosphoric acid) rather than a severe etch (i.e. straight chromic/sulphuric acid) will not severely over-etch those areas which are not stressed and therefore be susceptible towards etching. There are many variants on the formulations of etchants that are suitable for use on ABS plastics Lowenheim (15) has collated and critically reviewed a selection of etchants. The basic compositions of the etching acids consist of concentrated sulphuric acid (S.G. 1·84), water and chromic acid to saturation. Some solutions may contain phosphoric acid which it is claimed (5) acts as a buffer to the more severe etching action of straight sulphuric/chromic acid mixtures. If the ABS plastics are treated prior to etching with a reagent known to have a solvent action on them then it is claimed (16) that substantial increases in peel adhesion value results. While the mechanism by which the solvent pre-etch conditioner increases the effectiveness of the chemical etch cannot be completely explained, it is postulated (16) that the solvent selectively softens a portion of the styrene-acrylonitrile phase and thereby facilitates oxidation of the butadiene-styrene or butadiene-acrylonitrile "back bone". Heymann et al (17) and Ebneth (18) believe that the purpose of etchants is to preferentially attack the butadiene phase and create an extensive network of fine shallow pits on the surface of ABS. Weibusch (7) believes they form deep interlocking channels inside the plastics surface. Kato (19) has suggested that etching attacks the dispersed rubber particles in an entirely selective manner without affecting the matrix. In complete contrast to Kato (19) Logie and Rantell (20) have shown that etching of the styrene-acrylonitrile (SAN) can occur, but only at a slow rate, Rantell (21) considers a surface under-etched when the matrix is unattacked and over-etched when considerable attack of the matrix has occurred resulting in deep penetration into the surface. It may be that the type of attack depends on the composition of the etching acid, whether or not a solvent pre-treatment has been applied, the composition of the ABS and even the amount of moulded in stress in the ABS. Much conflict is in evidence as to the action of etching acids on ABS; what is agreed upon is that the etchants do serve to create a network of pits and cavities which can act as 'anchoring' points and thus facilitate adhesion between the plastics and electrodeposited layers. Saubestre and Khera (22) believe that the sulphuric acid content of the etchant serves as the active etching constituent, while the chromic acid oxidises the plastics surface resulting in the formation of C = C bonds; these they suggest serve to establish chemical bonding. This seems tenable since the C = C bond is often found in or near the surface of thermoplastics materials. This bond is relatively easily oxidised by oxidants, such as chromic acid to form the following :-



$$\overset{|}{\underset{\underset{O}{\|}}{C}} - \overset{|}{\underset{\underset{O}{\|}}{C}}$$

The unsatisfied oxygen linkages created are now available to enter into bonding. The incorporation of carboxylic (COOH) groups in ABS resins can result in increased peel adhesion (8) and so it is evident that the composition of the plastics may greatly influence the performance when plated.

A development on the theme of chemical solvent treatment prior to etching as described by Klinger et al (17) is discussed in the patent assigned to Saubestre and Baker (23). They describe how 'unreactive' ABS resins may be rendered 'active' and hydrophillic by treating them in an etching solution containing an aliphatic hydrocarbon monocarboxylic acid. The use of carboxylic radicles is likely to promote peel adhesion due to their contribution to the chemical component of adhesion (8, 16). Since styrene acrylonitrile (SAN) is resistant to chemical attack (3) it is unlikely that appreciable attack will occur on this phase; in view of this it is likely that Bogie and Rantell (20) are correct in stating that only slow attack occurs on SAN.

The depth of penetration of the etch pits is governed by a number of factors. Atkinson et al (4) have concluded that the depth of penetration is dependant upon the rubber (butadiene) content and composition of the ABS, rubber particle size and the orientation of rubber particles at or near the surface. Many workers believe that as far as peel adhesion is concerned, etching is the most important stage in the plating on plastics sequence. Saubestre (6) states that the level of adhesion of subsequent electrodeposits depends primarily on this stage. As will be shown later, little change in peel adhesion value occurs over a range of etch times once a minimum etch time has been exceeded.

In interpreting peel adhesion results it is prudent to examine the precise nature of the test, the process sequences employed and the plastics used. A minimum etch time may result in higher peel adhesion values since the surface layer will not be extensively attacked and weakened. Prolonged etch times may cause surface degradation resulting in low peel adhesion values. As will be discussed later, the time between plating and testing and the storage conditions may also influence the peel adhesion value.

It is evident that many factors can influence the action of etching acids on ABS plastics. The most likely changes that take place are the dissolution of butadiene, the slight attack of the SAN matrix and the creation of unsatisfied chemical linkages which serve to create a hydrophillic surface and sites where chemical bonding of the substrate to metal is possible.

1.10 THE INFLUENCE OF NEUTRALISING ON PERFORMANCE.

There is general agreement that neutralisation of hexavalent chromium is desirable after the etching stage. The function of neutralisation is to prevent Cr^{6+} being carried over to the subsequent pre-treatment stages and contaminating them. Surfaces that have Cr^{6+} on them will not respond correctly to the various treatment stages and areas of the plastics will not be covered in electroless metal; this results in 'skip' plating.

1.11 THE INFLUENCE OF THE CATALYST STAGE ON PERFORMANCE.

Although there has not been much published work concerning the role of catalysts in influencing service performance it is of interest to note that until recently the exact nature and function of these catalysts was not known. This is an example of the platers' art outdistancing theory. The catalyst stage is important in that insufficiently catalysed surfaces will not react with the electroless solution and will thus result in 'skip' plating. Rantell and Holtzman (24) have shown that, contrary to common belief, the modern palladium chloride/stannous chloride catalysts do not contain 'free' colloidal palladium. The palladium is only rendered active (and colloidal) after the final rinsing stage of the catalyst/accelerator treatment, when masking tin salts are leached away. The one-step type catalyst solutions since their inception in 1963 (25) have largely replaced the simple two-step stannous chloride sensitisers and palladium activators. The former offer many advantages over the latter since they provide a greater catalytic activity and facilitate selective or one-jig plating. The variables affecting the performance of these catalyst solutions have been documented by Goldie (3). The most important variables being the palladium content, the pH and temperature.

1.12 THE ROLE OF ACCELERATION.

Rantell and Holtzman (24) state that the function of accelerators is to convert hydrolysed adsorbed catalyst into active metallic palladium. They have found that several reagents will facilitate this function but a great variation in efficiency is detected. They state that acid accelerators can adversely affect catalytic activity due to their propensity towards etching out the active palladium nuclei. For this reason they favour alkaline accelerators such as ammonium hydroxide. Their results have largely explained the role of activators and have shown the importance of the rinsing stages in the process sequence.

1.13 ELECTROLESS DEPOSITION.

After the etching, activation and acceleration stages the ABS is capable of catalysing metal deposition onto its surface from solutions that can undergo a redox reaction; the metal ions in the electroless solution being reduced to the metallic state whilst some other constituent usually sodium hypophosphite is oxidised.

The mechanism involved in this reaction has given rise to much speculation; for although the reduction can be represented by the following equation :

$$Ni^{2+} + (H_2PO_2)^- + H_2O \rightarrow Ni^0 + 2H^+ + H(HPO_3)^-$$

the details of how this reaction occurs have not yet been finalised (26,27). Goldie (3) has suggested that the electroless decomposition of copper solutions using formaldehyde as the reductant can be represented as :

$$Cu^{2+} + HCHO + 3OH^- \rightarrow Cu^0 + HCOO^- + 2H_2O$$

The function of complexing agents in electroless nickel and copper solutions is primarily to prevent hydroxide precipitation and to control the free ion concentration. If the complexes formed are too stable then reduction will not be readily facilitated; this is why cyanides are not used for electroless copper solutions since the free ion concentration will be almost negligible, for example, a solution in which KCN is normal and the Cu^+ concentration decinormal has a free cuprous ion content of 5×10^{-29} (3).

Examination of the literature shows that electroless copper was originally favoured for plating on plastics but now it is used rarely. Electroless nickel solutions exhibiting high stability have found favour due to their tolerance to contamination and suitability for use in continual rather than batch processes.

1.14 SOME ASPECTS OF ELECTROLESS DEPOSITION AND THEIR INFLUENCE ON SERVICE PERFORMANCE.

1.14.1 Electroless Copper.

Electroless Copper baths are usually of the Fehling type which employ formaldehyde as the reductant and usually contain complexing salts other than Rochelle salts. For example E D T A acts as an accelerator and octyl mercaptan as a stabiliser (28). An important aspect regarding electroless copper is that the deposit is virtually pure copper; some oxide being the only other substance present (29). This is in contrast to electroless nickels which have appreciable quantities of phosphorous in them.

Electroless copper solutions are used at a pH in excess of 12 since the commonly used reductant (formaldehyde) will not function at lower pH values (3).

It has been found that electroless copper will give better resistance to corrosive attack (30) and in this respect has a great advantage over electroless nickel.

1.14.2 Electroless Nickel.

A nickel solution which was catalytic and deposited on a suitably prepared substrate was discovered by Brenner and Riddell in 1944. The results of their investigations were published in 1946 and 1947(31). They observed that when electrodepositing nickel from a bath containing sodium hypophosphite the cathode efficiency [illegible] higher than 100%, and it was then found that additional metal was being plated out by means of a chemical reduction reaction which supplied the necessary electrons. The Brenner and Riddell bath was alkaline and worked at 98° C. At such operating conditions ammonia volatilised rapidly and was extremely unpleasant.

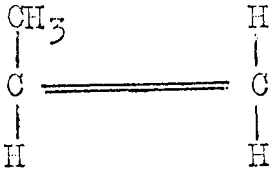
Modern electroless nickel plating solutions operate at room temperature and can be either of an acidic or alkaline nature. In contrast to electroless copper deposits electroless nickels are not 'pure' deposits but 'alloys'. Goldenstein et al(32) have postulated that electroless nickel is an amorphous solid, having a lamellar structure due to variations in dissolved phosphorous, this reverts to a crystalline structure at low temperature (below 890°C), being essentially a solid solution of nickel phosphide in a matrix of nickel. However, in contrast to Goldenstein et al(32) Graham et al(33) have shown that electroless nickel is not amorphous but is rather a supersaturated solid solution of phosphorous in crystalline nickel. Randin et al(34) have shown by differential thermal analysis that as plated electroless nickel is a supersaturated solid solution of phosphorous in nickel as a metastable intermediate state between that of a mixture of nickel plus phosphorous and the equilibrium system of nickel plus nickel phosphide.

In attempting to rationalise some of the conflicting evidence as to the structure of electroless nickel, it is best to examine those parameters that can influence the phosphorous content. For example Goldie (3) has stated that phosphorous content is dependant on temperature, pH and hypophosphite content. It is probable that a variety of structures can be developed in electroless nickel due to varying solution parameters, for example, the layered structure often exhibited by the electroless nickels has been shown to contain varying amounts of phosphorous (35). This layering effect can be influenced by agitation and so quite severe concentration gradients may exist across a deposit. It is highly probable that the dominant structure present in electroless nickel is the one cited by Randin et al (34) since electroless nickels can be heat treated to give very high hardness values in excess of 900 HV; the heat treatment on the super saturated solid solution serving to create precipitation of Ni_3P causing lattice straining and hence hardening.

Narcus (29) has presented the arguments in favour of electroless nickel and while not entirely discounting the use of electroless copper has shown that the latter solutions have several undesirable charecteristics; for example, electroless copper solutions are very sensitive and spontaneous decomposition and rack plating can occur. An interesting fact that emerges from Narcus' (29) discourse is that a 0.25 µm thickness of electroless nickel is more conductive than electroless copper of the same thickness.

1.15 THE CHEMISTRY AND STRUCTURE OF POLYPROPYLENE.

Until the discovery in 1953 of Ziegler catalysts, attempts to polymerise propylene resulted in rubbery sticky solids of no real practical use. The first high molecular weight polymers of propylene were prepared using Zeigler catalysts in 1954 and so useful polypropylene was synthesised. Polypropylene is a colourless, odourless thermoplastic material of high rigidity high chemical resistance and surface hardness; these properties it can retain at elevated temperatures. The basic structural unit of polypropylene is based on



$$\begin{array}{ccc} CH_3 & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

If polymerisation of propylene takes place without the use of special catalysts the resulting structure is amorphous and random in nature; such a structure is termed 'atactic'. The use of stereospecific catalysts such as trimethyl aluminium(36) induces the CH_3 (methyl) radicles to position in an ordered manner along the polymer chains. Two types of configuration are possible, the first being when the CH_3 groups are in the same relative position along the chain, (isotactic structure). The second when the CH_3 groups are positioned on alternate sides of the polymer chain, (syndiotactic structure). The former configuration is capable of a high degree of crystallinity and has good physical and mechanical properties (tensile, impact and chemical resistance). The atactic (random) structure is amorphous and has poor physical and mechanical properties. In commercially produced material all three types of structure are found in varying proportions. Goldie(3) states that commercial polymers commonly exhibit 65-75% crystallinity. As will be discussed later the presence of atactic areas in polypropylene are of importance with regard to the etching process. The relative proportions of atactic, isotactic and syndiotactic structure in the polypropylene have a great influence on the polymers' mechanical and physical properties. Goldie(3) states that physical properties depend on four main characteristics :-

1) Percentage of isotactic material present.
2) Molecular weight.
3) Type of crystalline structure.
4) Copolymerisation.

As the isotactic index increases so do the following :-

Yield stress, hardness, mould shrinkage, softening point, creep resistance and tensile strength. However, as crystallinity increases so does the possibility of stress cracking.

Propylene is frequently copolymerised with ethylene to yield polypropylene copolymers having enhanced properties compared to straight polypropylene homopolymers. As will be shown later, work carried out on a variety of polypropylene types has shown that, where a plated polypropylene is required to have resistance to impact the copolymer grade should be used.

In common with ABS polypropylene frequently contains inorganic fillers such as titanium dioxide. It is evident that commercial grades of polypropylene can vary significantly with respect to composition and therefore in response to the electroplating sequences to which they are subjected.

1.15.1 PROCESSING AND MOULDING OF POLYPROPYLENE.

Perrins and Pettett(37) have indicated that the successful plating of polypropylene depends primarily on good moulding practice. However, Perrins and Pettett base their conclusions on the effect of moulding pressure on peel adhesion value; the lower the injection pressure the higher the peel adhesion value. McGregor and Perrins(38) have shown that the addition of inert fillers in polypropylene plastics facilitate the production of a readily etchable material less dependant on moulding conditions. Although this may be generally desirable it is evident that the use of fillers is likely to increase the cost of the basic raw material. It is far better to use a cheaper material and to use the correct moulding conditions. The work described later will show that the moulding conditions certainly influenced the susceptibility of some grades of polypropylene to the etching process, but overall there was only a slight influence on service performance. It will be shown that the peel adhesion value on ABS can be influenced significantly by local mould configuration but the peel adhesion value on polypropylene is influenced only slightly. This highlights a difference between ABS and polypropylene, and this aspect has been ascribed(39) to the differences in structure between ABS and polypropylene.

1.15.2 MECHANISM OF POLYPROPYLENE PRE-TREATMENT PROCESSES.

The methods for applying an electroless deposit onto polypropylene are essentially the same as those adopted for ABS. However, there are some main differences which exist due to the resistance polypropylene shows to chemical attack. Certain non-polar solvents are known to attack and swell the amorphous regions in polypropylene. Such solvents are linseed oil and turpentine. The solvency action of these reagents enable the subsequent acid etch to create the etched surface generally observed.

A typical polypropylene pre-electroplating sequence is shown below :-

1) Non-polar solvent treatment (emulsion of turpentine and linseed oil at 70° C.)

Swill in Water.

2) Acid pre-etch and clean (dilute chromic/sulphuric acid solution S.G 1.25) 2 min at 65° C

3) Main acid etch (more concentrated chromic/sulphuric/ phosphoric acid mixture) 10 min at 80° C.

Swill in water.

4) Surface pre-activating treatment (usually a solution of an amine - this acts as a 'glue' to promote the adherence of the noble metal catalyst to the polymers' surface) 2 min at 28° C

Swill in water.

5) Catalyst treatment (palladium chloride/stannous chloride in hydrochloric acid) 5 min at 30° C.

Swill in water.

6) Acceleration (solution to solubulise tin salts) 2 min at 50° C.

Swill in water.

7) Electroless metal deposition 7 min at 30° C.

Swill in water.

Electrodeposition as required.

By comparing the process sequence schedules for

ABS and polypropylene it is evident that some differences exist. However, the use of the solvent treatment and a surface pre-activating stage is not entirely necessary since some commercially available processing sequences omit these stages.

1.15.3 THE INFLUENCE OF ETCHANTS ON SERVICE PERFORMANCES.

As in the case of ABS, the etchants serve to create surface conditions which favour the bonding of metal to the substrate. The amorphous areas are preferentially attacked leaving the crystalline (isotactic) regions relatively unaffected (40,41). In this context a parallel may be drawn with ABS, the amorphous areas corresponding to butadiene whilst the isotactic regions correspond to the SAN matrix. Due to the manner in which the amorphous regions are preferentially attacked the etch pattern resulting exhibits long deep fissures extending well below the surface of the polymer; this has been cited (40) as a reason why polypropylene generally exhibits higher peel adhesion values than ABS, the latter usually exhibiting relatively shallow pits and fissures after etching. McGregor and Perrins (38) when studying factors influencing the peel adhesion of electroplated copper to polypropylene demonstrated the interdependance of polymer composition and etching acid composition.
It is of interest to note that in addition to the importance of a well roughened surface they found that chemical bonding, involving chemically combined chromium was also necessary to promote good peel adhesion. An important

aspect regarding polypropylene etching solutions is the change of composition that occurs due to water evaporation. The problem is not so pronounced with ABS etching solutions since they operate at lower temperatures. McGregor and Perrins (38) state that polypropylene etching acids may rapidly change composition and hence their ability to effectively etch polypropylene will alter. They show that for maximum peel adhesion values to be obtained the composition of the acid must be rigidly maintained. This factor may well be responsible for the low peel adhesion values occasionally reported (39) for polypropylene.

It should be noted that phosphoric acid appears to be a necessary component of the etching acid in order to obtain selective attack. This is in contrast to the etching acids used in ABS solutions where the use of phosphoric acid-containing acids is only recommended for mouldings having negligible internal stress (11).

1.15.4 THE ROLE OF SURFACE PRE-ACTIVATING SOLUTIONS.

Due to the chemical inertness of polypropylene difficulty was encountered in obtaining a film of catalytic metal to adhere to its surface. The stannous chloride/palladium chloride complexes could not effectively adsorb onto the surface. Surfactants, usually based on amines were found to promote catalytic metal adsorption onto etched polypropylene substrates. These reagents act as 'glues' to retain the catalyst on the surface; their mode of action is due to the polar groups they exhibit which attract the catalyst complex (42).

1.15.5 THE CHOICE OF ELECTROLESS DEPOSIT.

While Narcus (29) has favoured the use of electroless nickel on plated plastics there is evidence that the use of electroless copper on polypropylene can, in certain cases result in increased peel adhesion values. Goldie (3) is in conflict with the views of Perrins and Pettett (37) and points out that copper is a catalyst for the thermal degradation of polypropylene especially at temperatures in excess of 60°C. It is partly due to this oxidative degradation that determines the final peel adhesion on polypropylene (37). However, it is postulated by Perrins and Pettett (37) that electroless copper is responsible for the generation of increased polarity at the polymer/metal interface which causes an increase in peel adhesion. They also found that if oxygen was allowed access to the plastics/metal interface the peel adhesion was increased. Furthermore, the increase in peel adhesion was much less when using electroless nickel rather than copper.

The oxidation process described by Perrins and Pettett (37) has been noted by the present author but since electroless nickel instead of electroless copper was used the magnitude of peel adhesion increase was less; this is due (37) to the relative efficiency of the metals in catalysing the process.

The published work frequently cites the peel adhesion test as the sole criterion for assessing service performance. There is little evidence of work carried out to detect the influence of other parameters on service performance. The production of an adherent metallic coating whilst seemingly highly important is not necessarily a measure of service performance. In tensile and impact tests on plated plastics adherent metallic coatings can cause embrittlement.

1.16 GENERAL FACTORS CONCERNED WITH THE PRE-ELECTROPLATING PROCESSES THAT INFLUENCE SERVICE PERFORMANCE OF ELECTROPLATED PLASTICS.

Factors other than those that influence peel adhesion must be taken into consideration when assessing mechanisms that affect the service life of plated plastics. The choice of pre-electroplating sequence may have a direct bearing on the corrosion and thermal cycling behaviour. Wiggle et al (43) have shown the importance of a well etched substrate in retarding the lateral spread of blisters due to corrosion. The response to etching depends on many factors and these have been discussed previously. A given process sequence may etch a grade of plastics in a different manner and therefore exert some influence on the rate at which blistering may spread on subsequent service exposure. The relative nobility of the electroless metals employed will also influence corrosion performance. These aspects are discussed in the following section.

1.17 EFFECT OF METALLIC LAYERS ON SERVICE PERFORMANCE.

1.17.1 Corrosion.

1.17.2 Influence of electroless layers.

Wiggle et al (43) have shown that the type of electroless metal can have a considerable influence on corrosion behaviour. By using anodic potential determinations they showed electroless nickel to be highly anodic, presumably due to the presence of phosphides. The reactivity of electroless nickel does seem to be partially due to the amount of phosphorous present in the deposit; this has been confirmed in the present work. It has been suggested (44) that the use of electroless copper can lead to an improved resistance to corrosive attack. Anodic potential determinations certainly suggest that this deposit should have superior corrosion resistance than electroless nickel. Furthermore, as will be seen later the corrosion service performance on statically exposed plated plastics was improved when an electroless copper rather than an electroless nickel underlayer was employed. This goes some way in showing the validity of anodic potentials in predicting likely service behaviour but due consideration should always be given to the precise conditions under which the determinations are made since slight variations in electrolyte composition, pH, temperature and even the agitation can influence the values (45).

1.17.3 Influence of electrodeposited layers.

The choice of electrodeposited layers was thought initially not to be of great importance since it was argued that, as the substrates were plastics, unsightly corrosion products from the substrates would not occur. However, corrosion of the multilayer coatings frequently resulted in disastrous losses of adhesion. The influence on service performance of various electroless and electrodeposited layers has concerned a number of authors over the last few years (45,46,47).

The choice of deposited layer will be governed by the service into which the component will enter. In BS 4601:1970 (48) a guideline is given as to the types and thicknesses of metal deposits to be used in typical service applications. In broad terms the more arduous the corrosive environment expected the thicker the layer of nickel. The use of microdiscontinuous chromium systems has permitted some relaxation of the standard with regard to nickel thickness; the discontinuous type chromium overlays can be used with thinner nickel deposits. It has been shown that plastics plated to the BS 4601:1970 (48) standard can perform badly in service tests. Crouch (46) has found that severe brown staining can occur quite early on in static outdoor exposure tests when relatively thin (6 µm) bright nickel layers are deposited onto copper and then plated with microdiscontinuous chromium overlays. Chadwick (49) has stated that the brown stain is due to cuprous sulphite formed when corrosive media breach the nickel deposit and allow sulphur dioxide access to the underlying copper. The present author using an X-ray energy dispersive technique has noted that the brown staining contains appreciable amounts of copper, sulphur and chlorine.

Flint and Melbourne (47,50) Dennis and Such (45) and Wiggle et al (43) have made studies with regard to the electrochemical activity of a variety of electroless and electrodeposited coatings. By determining the open circuit and anodic potentials of the metal deposits in various electrolytes some fundamental information may be derived as to the probable corrosion behaviour the metals will exhibit in service. While Flint and Melbourne (47,50) regard the main corrosion mechanism in Cu+Ni+Cr layers to be under cathodic control, Longhurst (51) disagrees with this stating that an increase in flaw density in the chromium layer will not necessarily increase corrosion resistance. In view of the beneficial corrosion protection that microdiscontinuous chromium deposits are known to give (46) it is difficult to see how Longhurst (51) can justify his argument. However, he points out that cathodic control is present on nickel with chromium overlays when a layer of water is over the chromium. As the thickness of the layer of water decreases then a reversal is likely and the process comes under anodic control. He cites Russian literature (52) to support his views. However, due consideration should be taken of the availability of oxygen, passivation effects (50) and the precise nature of the environments at the corrosion pits. The use of nitrogen atmospheres when determining anodic potentials is favoured by Flint and Melbourne(50) and Dennis and Such(45) since a condition of oxygen starvation is likely at the base of a corrosion pit due to the presence of corrosion products.

Anodic potentials are more likely than standing or open circuit potentials to indicate the electrochemical activity of multilayer coatings since in practice corrosion currents flow between the anodic and cathodic areas.

The corrosion behaviour of organically brightened electrodeposited nickel is partly dependant on the amount of sulphur present in the deposit(45), the higher the sulphur content the more base the deposit. Du Rose(53) noted that if a sulphur free nickel specimen was subjected to an atmosphere rich in SO_2 its anodic potential was more base than without the sulphur treatment. Only prolonged scratch brushing could restore the anodic potential to its original value. A further consideration when interpreting anodic potential determinations is the influence of stress in the deposit. Fully brightened nickel deposits may have high stresses; stressed metals are likely to exhibit anodic dissolution(54).

Although the use of anodic potential determinations in predicting corrosion behaviour has been demonstrated by several authors(43,45,47) some anomalies are encountered such as found in this present work where the preferential attack of bright copper instead of bright nickel when anodic potentials indicate that the latter should corrode preferentially. Great care must be excercised in the interpretation of such results since other factors may well overide the differences in anodic potentials.

1.17.4 INFLUENCE OF DEPOSITED LAYERS ON MECHANICAL PROPERTIES.

Literature regarding the mechanical properties of electroplated plastics is rather sparse (7,55,56,57) and this is no doubt due to the fact that electroplated plastics have been used mainly in decorative rather than functional applications. If more use is to be made of electroplated plastics then more fundamental knowledge regarding mechanical properties and modes of fracture will be necessary.

Clearly the addition of an adherent metal skin to plastics materials will produce composites with properties which bear little resemblance to those of their unplated counterparts.

Morton and Baier (56) show that the ductility of plated polypropylene is dependent on the metallic coating applied. They state that decorative nickel and chromium coatings are associated with high strength and low ductility ie they act elastically to applied stresses; the sharp yield point corresponding to the failure of the metallic skin. On the other hand they state that ductile electroplates yield composites which react plastically to applied stresses. Matsunaga and Hagiuda (57) whilst obtaining an improvement in tensile strength also showed that with ABS plated with nickel + decorative chromium, ductility increased with increasing deposit thickness. This appears in conflict with Morton and Baier (56) but it should be noted that Matsunaga and Hagiuda (57) carried out their tests on specimens cut from plated panels and hence no deposit was present on the edges of the specimens.

Comparing the results of Matsunaga and Hagiuda (57) with those of Morton and Baier (56) it is evident that the former tested a metal/plastics/metal 'sandwich'; it is likely that a different stress system would operate on such a composite compared to when a completely encapsulated plastics specimen is tested. This may explain the conflicting views propounded by Matsunaga and Hagiuda (57) and Morton and Baier (56). Since ABS and polypropylene are notch sensitive, the effects of electrodeposits on those plastics should be carefully studied. For example Morton and Baier (56) state that a ductile deposit will induce a ductile-type failure but care must be excercised when making such statements since the stress system in the composite may well induce a ductile material to fail in a brittle mode; triaxial stresses developed due to constraint effects being primarily responsible for brittle failure. An analogy can be made with regard to brittle failure of ferrite in steel. If large pearlitic regions surround the ferrite then a condition of physical restraint can induce brittle failure in a material that usually exhibits high ductility. Despite the loss of ductility that occurs when electrodeposited layers are applied to ABS and polypropylene the effect has been largely discounted by various workers (55,56,57). The reason for this may be due to a lack of more fundamental knowledge regarding the precise nature of the embrittlement and failure mechanisms.

It has been suggested that the loss in ductility is due mainly to the brittle nature of the electrodeposits (58).

Goldie (3) has stated that the impact resistance of plastics is improved when copper + nickel + chromium layers are deposited. Ebneth et al (11) are in conflict with this statement and demonstrate how electrodeposited coatings serve to embrittle the composite; they did not offer any reason as to the precise mechanism of embrittlement. In view of the notch sensitivity of ABS and polypropylene it is likely that when the metallic deposits fracture the crack will cause the embrittlement observed. Weibusch (7) has shown that the flexural modulus of plastics is improved by the application of electrodeposited layers. In applications requiring stiffness in flexure plated plastics are likely to be worth consideration, but it should be emphasised that the electrodeposited layers may also be a source of embrittlement.

1.18 FACTORS INFLUENCING THE PEEL ADHESION VALUE ON PLATED PLASTICS.

The Jacquet (59) peel adhesion test is often used to determine the adhesion of metal on plastics. The test involves peeling a strip of metal off the plastics substrate at a constant angle of 90° under standardised conditions. The validity of the test in assessing service performance has not been fully examined but Saubestre et al (60) conclude the test to be adequate in assessing the merit of plastics to metal bonds.

Much controversy has surrounded the peel adhesion test on plated plastics over the last nine years (20,60,61). The controversy has not only been concerned with the measurement and nature of the 'adhesive' bond but also the validity of the test as a realistic measure of service performance.

1.18.1 THE NATURE OF THE PLASTICS TO METAL BOND.

Many theories have been offered to explain the nature of the bond between plastics and metals and these can be grouped into two categories: those emphasising mechanical interlocking as the source of bonding and those which emphasise chemical effects as being responsible for the bonding.

1.18.2 MECHANICAL OR RHEOLOGICAL THEORY.

Bikerman (62) has observed that failure rarely, if ever, occurs at the plastics/metal interface and suggests that failure in the plastics subsurface is more likely. Saubestre et al (60) have shown that failure must occur in the subsurface if any appreciable bond exists. Logie and Rantell (20) confirmed these findings and also showed how the extent of the subsurface layer influenced the peel adhesion value. This weak layer is the result of the electroless layer partly blocking the cavities produced by the etchant. The butadiene when preferentially etched away leaves the surface covered with pits and fissures which serve to anchor the subsequent electroless deposit. Matsunaga (63) has shown that peel adhesion is directly related to the amount of mechanical interlocking.

1.18.3 CHEMICAL THEORY.

Logie and Rantell (20) have shown that a chemical factor is of importance to the final peel adhesion value obtained. By using replica techniques they produced surfaces corresponding to an etched surface. The peel adhesion value was low but a brief immersion in an acid etchant markedly increased the peel adhesion value.

Miksys and Saubanska (64) have also noted the importance of the chemical component in adhesion. McGregor and Perrins (38) have stated that for good electroplate adhesion on polypropylene chemically combined chromium in addition to a well etched surface is necessary. By an acid extraction technique they demonstrated how the peel adhesion value could be influenced by altering the concentration of hydrolysed chromate groups on the plastics surface. Perrins and Pettett (38) demonstrated the importance of an oxidation process on peel adhesion values on polypropylene. Saubestre (65) has further indicated the importance of chemically combined chromium in creating conditions favourable for good plastics to metal adhesion.

It is evident that no single theory adequately explains the mechanism of the bond between the plastics and metal, and that the real answer explaining the bond mechanism will contain elements of both mechanical and chemical theories.

When Saubestre et al (60) applied dimentional analysis to the peel test they considered that it was a measure of a complex of factors including the thickness of the electrodeposited metal, the thickness of the plastics yielding film, Youngs' Moduli of the electrodeposited metal and plastics yielding film and the tensile strength of the plastics yielding film. One feature which may be a flaw in their analysis is that they assumed Hooke's Law to be obeyed for the plastics film and the metal deposit. In the region undergoing the peel test very localised deformations are present; the metal layer is being bent through 90° and therefore is likely to undergo some plastic as well as elastic deformation. This is evident since a peeled foil is permanently deformed indicating plastic deformation. Similarly, the plastics film is bent through 90° and upon examination is found to be torn and distorted. Close scrutiny of the data presented by Saubestre et al (60) reveals some anomalies. For instance they find that the reading obtained in the Jacquet test (F) corresponds to the following equation :-

$$F = 1000 \times t_m^{\frac{3}{4}}$$

Where t_m is the thickness of the metal deposit and 1000 is a 'constant' derived from various parameters such as the Young's Moduli of the plastics and metal, deflection values and the thicknesses of the deposited metal and plastics yielding film. Later they show how this 'constant' varies with metal deposit thickness; it is evident that for any real meaning to be applied to such analyses the precise conditions must be stated. Rantell (66) when studying the influence of surface roughness and chemistry on peel adhesion derived an expression relating peel value to some chemical component, a geometric component and a polymer toughness component. This approach seems the more appropriate since the Saubestre et al (60) analysis failed to take into consideration the chemical component for adhesion. Atkinson et al (4) although acknowledging that the peel adhesion test measures a complex type of failure not necessarily related to stresses set up during service state that it is a useful comparitive method to determine the optimum conditions for processing and pre-treatment. They are in conflict with the Saubestre et al (60) analysis since they argue that it is unlikely that Hooke's Law will be obeyed in the severe deformation zones present in the subsurface layers. They put forward the theory that the peel value depends primarily on the mechanical properties of the polymers' surface. Arrowsmith (67) has indicated that higher peel adhesion values may be possible if the fracture toughness of the substrate could be improved; in this context he is in broad agreement with Atkinson et al (4). The analysis of Atkinson et al (4) shows that 'peel strength' F depends on the following equation :-

$$F = Wp + W_m$$

Where Wp is the work done in plastically deforming the plastics and Wm is the work done in plastically deforming the metal layer. The equation was found to give good agreement with observed peel values when appropriate values of Youngs' Moduli, radius of curvature of peeling foil and breaking elongation were used. However, this treatment does not include allowances for the chemical component of adhesion.

Much work has been expended in analysing the peel adhesion test and the nature of the plastics to metal bond but little has been done in assessing the peel adhesion test as a reliable method in determining service performance; the present author has found that the peel adhesion test does not necessarily indicate how a component will perform in service.

1.19 FACTORS INFLUENCING THE THERMAL CYCLING PERFORMANCE OF PLATED PLASTICS.

The thermal cycling test is frequently employed to assess the likely service performance of plated plastics. The test often used involves cycling the parts between - 40°C, room temperature and + 80° C allowing at least 1 hr. to elapse between each stage (48). The test, although providing a measure of adhesion does not measure the same property as the peel adhesion test since a layer of detached plastics is not associated with thermal cycling failures (60). As will be demonstrated later the thermal cycling test is likely to indicate more nearly the service performance of plated plastics.

Due to the difference in coefficient of thermal expansion between an ABS or polypropylene substrate and the electrodeposited layers it is necessary to utilise a ductile metal underlayer in order to 'buffer' thermally induced stresses. In the case of ABS the plastics are likely to expand up to six times as much as the metal layer in a given temperature interval; for polypropylene the ratio is higher. Although polypropylene has a higher coefficient of expansion than ABS it can pass thermal cycling tests with an all-nickel coating system whilst ABS cannot. This has been attributed (68) to the higher peel adhesion attainable on polypropylene.

Although Saubestre and Hajdu (69) find that the total number of articles failed in thermal cycling is proportional to the number of cycles, Crouch (70) does not; he found that articles could withstand a large number of cycles with little further deterioration providing satisfactory plating conditions had been used. Morton and Baier (56) state that the real key to thermal cycling resistance is the stress in the applied electrodeposits. This latter statement may be only partly true since it is articles that have been plated with thicker deposits that tend to fail early on in thermal cycling tests (71). As will be shown, thick chromium deposits are especially detrimental to thermal cycling performance but the effect is lessened when plastics having low coefficients of thermal expansion are tested. This is in conflict with the Morton and Baier (55) statement which discounts the effect of the substrate.

Such and Baldwin (72), Carter (73) and Crouch (70) are all in agreement that a ductile copper undercoat is a necessity if plated ABS is to pass the thermal cycling test as laid down in BS 4601:1970 (48). Narcus (29) whilst acknowledging the need for a ductile underlayer favours a ductile nickel layer deposited from a sulphamate bath. Carter (74) has demonstrated the validity of the thermal cycling test in predicting likely thermally induced service failures.

The chromium type as well as thickness may influence thermal cycling performance. Microporous chromium types usually exhibiting somewhat inferior performance than microcracked chromium types. This may be due to the stress raisers due to the presence of the inert particles in the microporous chromium surface and the stress relief due to the complete crack pattern in microcracked chromium surfaces.

Despite the volume of research work that has been undertaken on the subject of electroplated plastics, several factors have emerged from the literature review which suggest that more work is necessary if the behaviour in service of plated plastics is to be more fully understood. Conflicting arguments regarding the importance of moulding conditions, the role of etchants, the nature of the plastics to metal bond and the validity of the various tests in indicating service performance will only be rationalised when more fündamental data becomes available. It was one of the aims of this current work to investigate whether the corrosion resistance of plated ABS and polypropylene was influenced by the grade; it is of interest to note that most of the published work relates to a few grades of ABS and polypropylene only, this work has involved the investigation of ten grades of ABS and four grades of polypropylene. Another aim of the research programme was to use stqtistical analysis in order to investigate whether any relationships existed between laboratory tests and observed service performance.

2. EXPERIMENTAL PROCEDURES.

1) Manufacture of Plastics Injection Die.

A steel die was designed which utilised common top and bottom blocks but with interchangeable 'sandwich' pieces to produce the required shape of specimen, Fig 1. All surfaces of the die were highly polished and then chromium plated to ensure a good surface finish on the mouldings. The specimens produced were tensile test pieces to ASTM specification D638-71 (type I) (75), and impact test bars 12.0 cm x 1.3 cm x 0.65 cm. Two types of panels, 6.0 cm x 8.8 cm x 0.3 cm were also moulded, one having plain surfaces on each side but the other having a ridge 0.04 cm high and a valley 0.04 cm deep in one surface. The positions of the ridge and valley are shown in Fig.1b. The impact test bars were made to a size which enabled the production of specimens relatively free from surface and internal defects. Thin "flash" type injection gates were positioned to allow adequate melt ingress into the mould cavities. Other factors such as the need for melt turbulence in ABS moulding to prevent surface irregularities (known as "jetting") and the need to position injection gates remote from any critical testing areas or faces were also taken into consideration. The positions and relative sizes of the injection gates are shown in Fig 1b.

2) Pre-drying of Moulding Materials.

The manufacturers of the ABS grades used in the investigation recommended the materials (supplied as granules) to be dried in an air circulating oven at 80° C

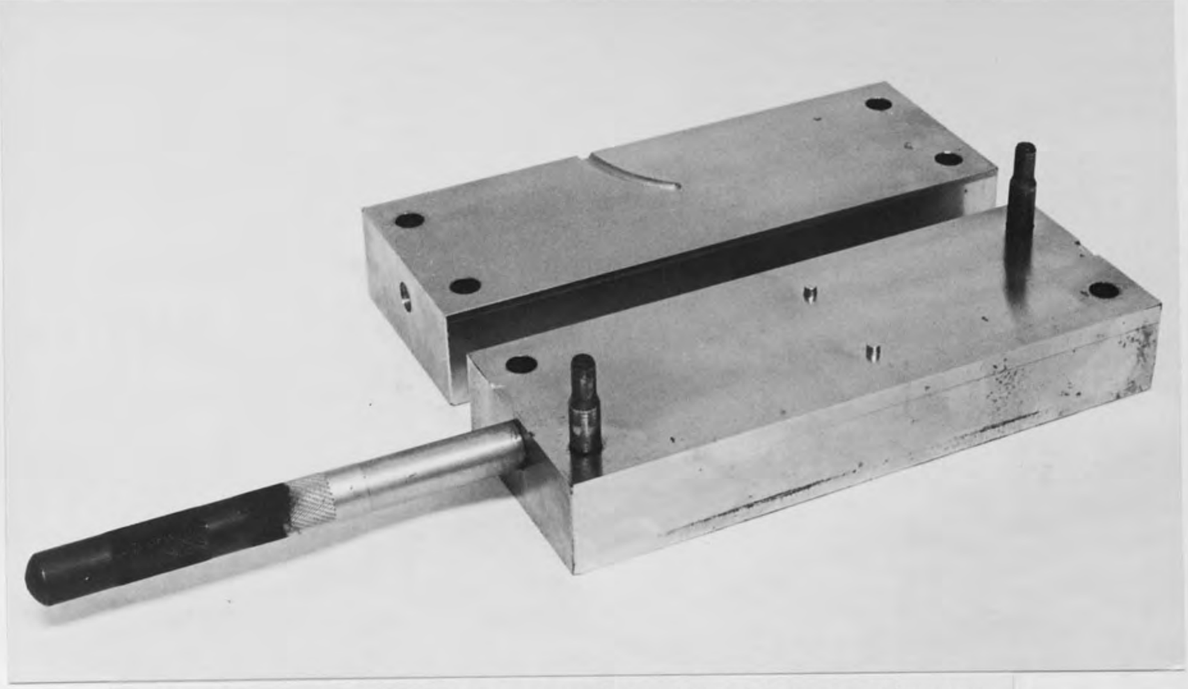


Fig.1a. Mould used to produce plastics specimens; common top and bottom blocks.

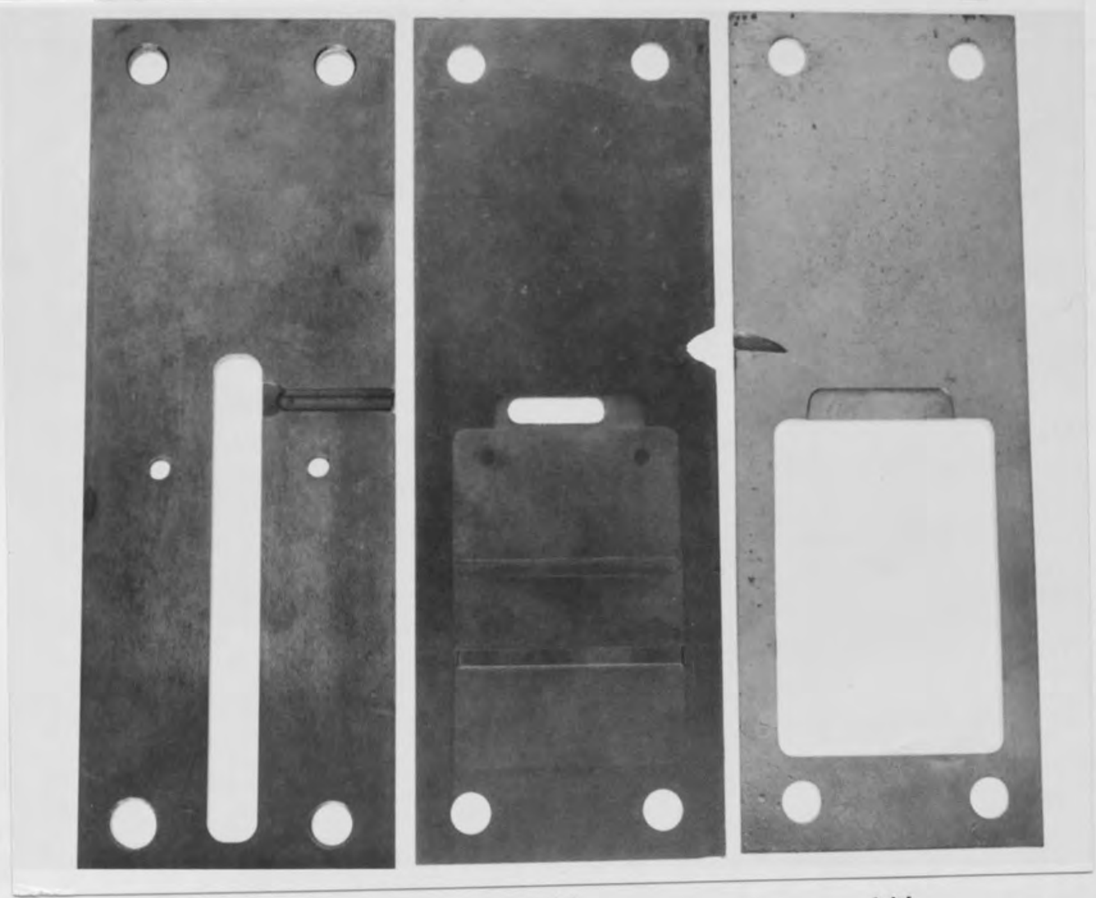


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Fig.1b. "Sandwich" pieces showing:-

i) Cavity for impact test specimens

ii) Cavity for ridged peel adhesion test panels

iii) Cavity for plain panels used for corrosion, peel adhesion and thermal cycling tests for a minimum of 2 hrs. before moulding. This precaution was taken since ABS absorbs water and can cause surface irregularities such as blisters and splay marks to form on moulding. The grades of polypropylene were also dried before moulding. Information regarding the various grades of materials is given in Table 1.

3) Moulding procedures.

This operation was carried out using the screw-injection type moulding machine shown in Fig 2. Ebneth et al (11) state that these types give efficient homogenisation of the melt which reduces heating and residence times in the machine, and so minimises the risk of thermal degradation to the plastics. Ebneth et al (11) have shown that with mouldings produced in screw-injection type machines a higher plastics to metal adhesion is possible compared to that obtained on mouldings produced in plunger types; presumably due to the more favourable heat transfer and mixing characteristics of the former types.

The moulding pressures were controlled by a hydraulic unit whilst the moulding temperatures were controlled by thermostats situated on the heater bands clamped to the barrel. The moulding conditions chosen were those expected to result in minimum stress levels for the various grades and types of plastics, Table 11. In one instance the effect of changing the moulding pressure on the performance in the tests of two grades of plated polypropylene was examined. The conditions

TABLE I. COMPOSITION, LINEAR COEFFICIENT OF EXPANSION AND MAIN ETCHING CONDITIONS FOR ABS AND POLYPROPYLENE

	Code	PROCESS SEQUENCE				COMPOSITION (APPROX) %			Coefficient of Thermal Expansion x10^{-5}/°C	Density Kg/m^3	General Comments
		A		B	C						
		Mins. Condi-tioner	Mins. Etch	Mins. Etch	Mins. Etch	Butadiene	Acrylo-nitrile	Constituents other than Styrene			
A B S	L	10	7	10		17	28			1120	Electroplating grade
	R	3	3	5		16	24		8	1040	General purpose grade, lubricated
	S	2	7	5		18	24		9.5	1070	Small particle size Graft Rubber, Plating grade
	T	3	3	5		20	27		7		High impact grade, high softening point
	U	4	7	20		6	28		6	1050	High modulus grade, lubricated
	V	4	7	7		16	24	Nitrile rubber	8		Plating grade
	W	6	8	20		15	25	α Methyl Styrene	7		High heat grade
	X	2	7	7		16	24		8		General purpose grade
	Y	20	6	20		11	27	Vinyl Pyridine	6		Plating grade, high heat resistance resin phase based on α Methyl Styrene
	Z	2	7	3		27	24		9	1090	High impact grade, lubricated
POLYPROPYLENE	M				5 and 10			Inorganic filler	11	945	Plating grade copolymer with ∿ 10% Ethylene
	N				5 and 10			Ethylene	11	940	Copolymer general purpose grade
	P				10			Inorganic Filler	11	920	High isotactic index
	Q				10			Inorganic filler	11	1010	High isotactic index

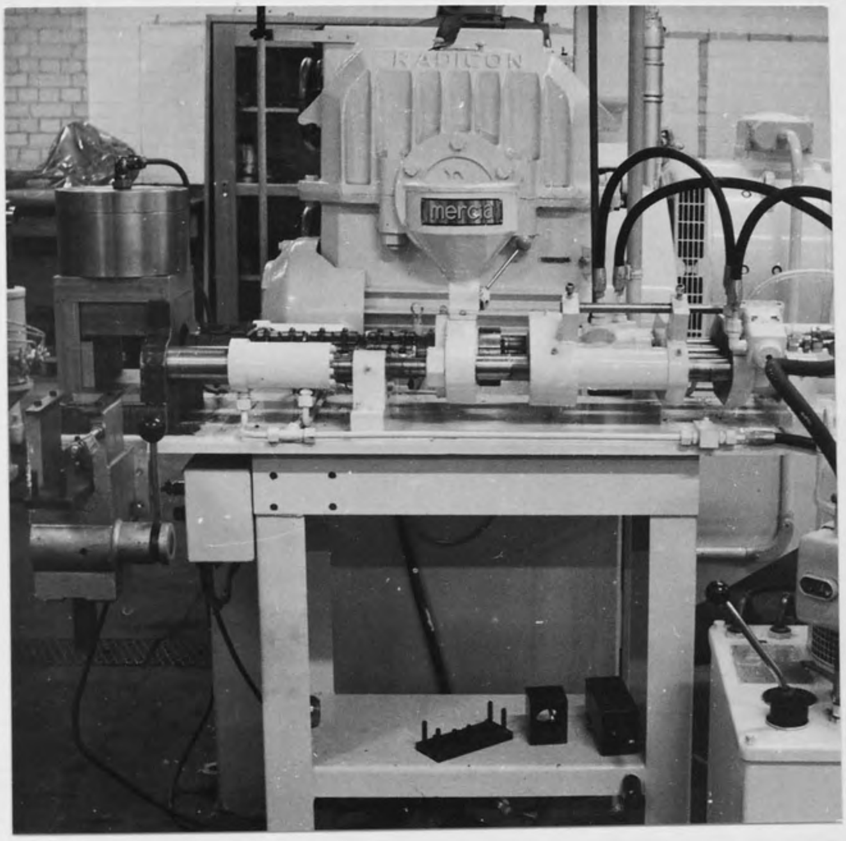


Fig.2. 'Manumold' plastics screw injection machine.

TABLE II. MOULDING CONDITIONS FOR ABS AND POLYPROPYLENE

Plastics Type	Plastics Grade	Temperature °C	Pressure kN/m^2
ABS	L	220	7000
	R	230	7000
	S	245	7000
	T	240	7000
	U	250	7000
	V	250	7000
	W	250	7000
	X	230	7000
	Y	270	7000
	Z	240	7000
POLYPROLYLENE	M	175	5500 (i)
	M	175	4500(ii)
	N	175	5500 (i)
	N	175	4500(ii)
	P	190	7000
	Q	190	7000

The figures quoted relate to the nominal settings on the *Manumold* Machine.

chosen were those which were likely to give different stress levels in the mouldings and were designated (i) and (ii), see Table 11. Values of temperature and pressure quoted were the nominal figures indicated on the Manumold screw injection machine. The moulding pressure is influenced by effects taking place at the tip of the nozzle at the instant of injection. A pressure in excess of that indicated on the machine is developed since the diameter of the injection nozzle is smaller than that of the ram. The melt temperature will increase due to the increase in pressure, gate geometry, melt internal friction and shearing and friction between the flowing melt and the nozzle. As the melt enters the cavity a pressure drop will then occur. The moulds were pre-heated to 40° C prior to use in order to promote good melt fluidity and to minimise surface stress (11).

4) <u>Precautions Taken after Moulding.</u>

All mouldings were removed from the die cavities and immediately placed in 'polythene' bags until required. This practice is recommended (14) to prevent absorption of water in the case of ABS and to prevent accidental surface contamination with grease and dust. All transference operations were performed with gloved hands.

5) <u>Quality Control on Mouldings.</u>

To ensure that the best possible quality mouldings had been produced samples were taken periodically from batches and subjected to two tests.

5a) Acetic Acid Stress Test.

It is well known (10, 60) that glacial acetic acid will induce stress cracking where internal stress is present in ABS. The affected areas manifest themselves as whitened patches. Much conflict is in evidence as to the conditions under which the test should be conducted and also the interpretation of the results so obtained. Ellis (10) suggests immersing the ABS moulding in glacial acetic acid for 30 seconds while Saubestre et al (60) favour a 2 min immersion period. Cox (76) however points out that not only immersion time but temperature must be specified, for example, 23° C. Goldie (3) has stated that the test is inconclusive and the results should be interpreted very carefully.

Test conditions of 2 min. immersion at 23° C were adopted in these tests since they appeared to be the best compromise.

5b) Radiographic Examination.

Specimens were subjected to 'soft' X-radiation and a high contrast film was used to facilitate detection of serious internal flaws.

6) Pre-electroplating Processing Sequences.

The plastics were processed using the appropriate pre-electroplating sequences which all involved the use of electroless nickel. Proprietary solutions were used and these were contained in 5 litre beakers in thermostatically controlled water baths. Periodic analysis and maintenance was carried out and adjustments made with the appropriate concentrates to ensure that the solutions were kept within the manufacturers specifications. It should be noted that only etching and conditioning times were varied in a given process sequence since these were chosen to suit the various grades of plastics, see Table 1. Details of the process sequences are shown below :-

2.6.1 Process Sequence A for ABS.

1) Alkaline cleaner - 3 min at 60° C
   Swill in water.
2) Hydrolyser - 3 min at 60° C
   Swill in water
3) Conditioner (organic emulsion) - appropriate time at 35° C
   Swill in water.
4) Etch (SG 1.80) - appropriate time at 65° C
5) Immerse in cold etch solution - 2 min at 20° C
   Swill in water.
6) Neutralise - 5 min at 43° C.
   Swill in water.
7) Hydrochloric acid dip (25% v/v) - 1 min at 20° C.
8) Catalyst - 2 min at 28° C.
   Swill in water.
9) Post catalyst treatment (accelerator) - 2 min at 43° C
   Swill in water.
10) Electroless nickel A -7 min at 28° C
   Swill in water.
   Electroplating as required.

2.6.2 Process Sequence B for ABS.

1) Acid cleaner (pre-etch, SG 1.20) - 2 min at 54° C
2) Etch (S.G. 1.45) appropriate time at 65° C

Swill in water.

3) Neutraliser - 1 min at 30° C

Swill in water.

4) Catalyst - 6 min at 30° C

Swill in water.

5) Post catalyst treatment (accelerator) - 2 min at 54° C.

Swill in water.

6) Electroless nickel B - 7 min at 30° C

Swill in water.

Electroplating as required.

2.6.3 Process Sequence C for Polypropylene.

1) Non-polar solvent treatment - 10 min at 72° C.

Swill in water.

2) Acid cleaner (pre-etch, S.G. 1.20) - 2 min at 54° C.

3) Etch (S.G. 1.45) - appropriate time at 82° C.

Swill in water.

4) Surface pre-activating treatment - 2 min at 28° C.

Swill in water.

5) Catalyst - 3 min at 30° C

Swill in water.

6) Post catalyst treatment (accelerator) - 2 min at 54° C.

Swill in water.

7) Electroless nickel B - 7 min at 30° C.

Swill in water.

Electroplating as required.

A very limited programme using ABS specimens having electroless copper underlayers was also undertaken. These were processed in sequence B but an electroless copper stage was substituted for the electroless nickel one. The electroless copper solution was proprietary, used formaldehyde as the reducing agent and worked at

30° C at a pH of 12.

The plastics panels were jigged on stainless steel rods for processing through all the pre-electroplating stages but were then transferred to conventional plastics coated jigs for electroplating purposes. To avoid damaging or contaminating the surfaces of the specimens this operation was performed while wearing rubber gloves which had been wetted with clean water.

Before commencing the main programme preliminary trials were carried out to determine the plating times required to give a particular thickness of deposit and to ensure that the arrangement of the specimens on the various jigs resulted in fairly uniform metal distribution. Wire 'robbers' were used for this purpose.

7) Determination of Electrodeposit Thickness.

The thicknesses of the electrodeposits were determined by two methods. The first method involved cutting cross-sections from various parts of specimens and after grinding, polishing and etching viewing the section under an optical microscope. This method had many drawbacks for plated plastics specimens since they could not be mounted in a block like metallurgical specimens since hot mounting in 'Bakelite'melted the plastics and cold curing mixtures attacked the plastics substrates. The development of a chamfered edge invalidates any thickness determination and so this method was abandoned. The BNF coulombmetric thickness tester was used to determine the thicknesses of the deposits. The essential feature of this method is the measurement of the total quantity of the charge required to anodically strip the metal deposit from a clearly defined area. The test is stopped after each metal layer is penetrated and the appropriate solution introduced for stripping the next metal. The instrument is designed to switch off automatically once the metal deposit is penetrated. The reading on the machine is taken and the thickness of metal relating to that figure is given in charts.

8) Electrodeposition.

All electroplating solutions were proprietary types and they were operated and maintained within the manufacturers specifications. The solutions' compositions and operating conditions are detailed in Table 111.
It was found that the thin electroless nickel deposit would 'burn off' if initially too high a current density was applied. Hence the precaution of applying only a low initial current density was adopted. It was then increased slowly over a period of two minutes. This procedure facilitated the deposition of a thin layer of copper which, as electrodeposition proceeded was capable of withstanding a higher current density. The specimens were rinsed thoroughly between stages when applying the multilayer coatings in order to prevent contamination of the solutions by 'carry over'. The coatings deposited are listed in each section of the various phases of the work.

Microporous chromium deposits were obtained using

TABLE III. OPERATING CONDITIONS OF PLATING SOLUTIONS

Plating Solution	Current Density A/dm^2	pH	Temperature ^{o}C	Agitation	Comments
Bright Copper-Pyrophosphate Bath	4	9.5	50	Air	Organically brightened
Bright Nickel	4	4.5	50	Air	Watts-type solution
Special Nickel containing inert particles	4	3.5	50	Air blowing downwards to keep particles in suspension	Watts-type solution Organically brightened
Semi-bright Nickel	4	4	55	Air	Watts solution + Coumarin
Bright Decorative chromium	10	-	38	None	
Micro-cracked chromium	19	-	42	None	Fluorosilicic acid Catalyst

the following procedure. After application of the bright nickel layer a 'special' thin nickel layer ($\sim$ 1 μm) was deposited from a solution containing inert particles of $\sim$0.02 μm diameter. The particles were kept suspended by vigourous air agitation. The 'special' layer contained the inert particles which co-deposited with the nickel; the solution contained several organic additives to brighten the deposit and to facilitate the co-deposition of the particles. After rinsing thoroughly a chromium layer was deposited using a conventional regular chromium plating solution on top of this 'special' layer. Deposition of the chromium was prevented at the sites of the inert particles.

9) Quality Control on Electrodeposited Layers.

Apart from periodic thickness determinations using the coulombmetric method described previously three other tests were applied to the various coatings in order to confirm that they had been plated within specification.

The first test was used to assess the ductility of the bright copper, bright nickel and semi-bright nickel deposits. This entailed depositing the metals onto annealed brass 'Hounsfield' tensile bars, chamfering the edges to remove the 'build up' regions due to high current density and marking a 5.0 cm gauge length on them. They were extended and the percentage elongation was taken as that extension on the gauge length at which the deposit first cracked, divided by the original gauge length x 100. The ductilities of the bright copper bright nickel and semi-bright nickel were 50%, 5% and 10% respectively.

Another test was carried out to see if the microcracked chromium had sufficient cracks to satisfy the standard given in BS 4601 : 1970 (48). The cracks per unit length were determined using a 'Vickers' projection microscope. The crack density was more than 250 cracks/cm^2

To ensure that the pore density in the microporous chromium deposit was sufficiently high enough to meet the requirements of BS 4601 : 1970 (48) a Dubpernell-type test was employed. Much controversy is in evidence as to the validity of this test since it is reported that this test tends to over-estimate the number of pores present. Further, the result can be influenced by the time allowed between plating and applying the test. The procedure adopted in this instance was that recommended by the supplier of the solutions necessary to produce the microporous chromium :-

1). A polished brass Hull cell panel was plated with 20 µm of bright nickel.

2). The panel was plated with the 'special' nickel containing particles for 2 min.

3). After rinsing in water the panel was chromium plated in a Hull cell for 4 min at 5 amps.

4). After rinsing and drying those areas of the panel not plated with chromium were masked off with PVC tape.

5). The masked panel was soak-cleaned in hot alkaline cleaner until the surface was water break free.

6). The panel was dead-loaded into an acid copper solution and plated at 0.5 A/dm^2 for 5 min.

After removal from the plating solution the panel was dried off in air. Using a bench microscope the density of the copper spots was noted at three positions on the panel. The thickness of chromium was determined at these three positions using the BNF coulombmetric tester and a plot of porosity (copper spot density) vs.chromium thickness was made. An extrapolation to a chromium thickness of 0.25 µm and 0.75 µm showed the 'porosities' likely to be present in the specimens used for the project. The pore density was found to be around 25,000 pores per cm^2 at a chromium thickness of 0.25 µm and around 18,000 pores per cm^2 at a chromium thickness of 0.75 µm.

10) Corrosion Tests.

Three types of corrosion tests were adopted, static and mobile outdoor exposure and the CASS test. The static test was conducted by mounting specimens at 45° on a rack facing south. This was situated on a roof in the centre of Birmingham. The panels were insulated from the framework with ceramic washers and fixed with nylon screws. In order to expose the required number of specimens on mobile sites it was necessary to utilise a number of cars. These all operated in the Birmingham area but nevertheless this did introduce an extra uncontrolled variable. The panels were fixed to badge bars with nylon screws and were mounted on the fronts of the cars. Due to the design of the various cars the test panels were not at a uniform height above the ground and this could lead to a slight variation in the corrosive environment encountered. The CASS test was performed according to the practice recommended in BS 4601 : 1970, Appendix G (48).

11) Assessment of Corrosion Behaviour.

All corroded specimens were assessed using the ASTM B 537-70 (77) method. This system was adopted since it affords scope for reporting both protection and appearance ratings.

12) Cleaning of Specimens Prior to Rating.

In accordance with the procedure given in ASTM B 537-70 (77) the panels were lightly cleaned with a mild soap solution prior to rating. The severe brown staining developed on some specimens was not removed by this procedure. When removal of this stain was desirable a mild abrasive, magnesium oxide suspended in water, was used.

Due to the different times material became available the outdoor tests were undertaken in two main phases. The first phase, designated the 'pilot' programme took place between 1/1/72 and 1/10/72. The results of this programme were used to determine some of the variables to be studied in the second phase, designated the 'main' programme. This programme commenced 1/10/72 and testing is still proceeding (1/9/74). A third phase, a limited programme using relatively thicker bright nickel deposits on a few grades of ABS and polypropylene, was started on

1/8/73 and testing is still proceeding (1/9/74).

13) Electrode Potential Determination.

In order to obtain information on the electrochemical activity of the individual metals comprising the multilayer coatings, an experimental technique was devised to determine the open circuit and anode potentials of these deposits. The method used was similar to the one employed by Dennis and Such (45) to evaluate the electrochemical activity of bright and semi-bright nickel deposits, the only difference being that a potentiostat was used as the current source. Specimens of electroless nickel and copper were prepared by depositing coatings onto ABS substrates in the usual manner since it would have been extremely difficult to prepare foils. Similarly specimens of electrodeposits were prepared by depositing onto an electroless underlayer. Potentials were determined in two solutions, acetic acid salt spray solution (48) and CASS (48) solution, and in two atmospheres, air and nitrogen. After deposition the specimens were washed thoroughly in water, clipped in a 'perspex' jig and immersed in the electrolyte as quickly as possible. Wetted rubber gloves were used for this transfer. The electrolytes had been subjected to a minimum of 1 hour agitation with either air or nitrogen before introducing the specimen into the vessel. All electrical connections were facilitated by platinum wire, the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was made from platinum foil.

The open circuit potential was noted after 5 min. and the specimen was then polarised anodically using the potentiostat. Values of current and voltage were recorded at 3 min. intervals when it was seen that a steady value was obtained. Little change occurred over the course of 1 hour for a given setting. Since the degree of agitation affects the potential of an electrode in a cell it was necessary to standardise the flow rate of the gas used for this purpose; a rate of 4 ml/s was used in these tests. After each determination the electrolytes were discarded. A possible source of error in the electrode potential determinations could have arisen from the small areas of electroless nickel exposed at the electroplating jig contact regions.

14). Mechanical Testing.

Two tests, the tensile and impact test were adopted in order to investigate the influence that the various processing variables and electrodeposited layers exerted on the mechanical properties of plated plastics.

14a) Tensile Tests.

An 'Instron' tensile testing machine was used for these tests. The rate of extension was standardised at 2 cm./min. This was chosen as a compromise since a preliminary investigation had shown that the plastics were not too strain rate sensitive within the range 0.5 - 5 cm./min. The choice of testing speed was also a compromise when comparing it to those recommended in the ASTM D 638-72 (75) procedure. The ABS plastics materials since their moduli of elasticity were greater than 686 MN/m^2 were classed as 'rigid plastics' according to the definition given in ASTM D 883-73a (78). As such the recommended rate of extension was 0.5 cm./min. The polypropylene plastics materials since their moduli of elasticity were less than 686 MN/m^2 were classed as 'non-rigid plastics' and the recommended rate of extension was 5.0 cm./min. The compromise rate of extension was chosen in order to eliminate a variable in the testing programme. The specimens were held in standard 'Hounsfield' wedge grips.

Some grades of unplated polypropylene exhibited very high ductility at low strain rates. Tensile strength was calculated using the true cross-sectional areas, that is allowance was made for the thicknesses of the various coatings deposited. The ductility of the specimens (on a 5.0 cm. gauge length) was calculated using two techniques. The first technique involved determining the elongation from the chart recorder and the second technique involved placing the fractured pieces together and measuring the increase in length. The latter method results in significant errors and renders the fractured surfaces useless for detailed examination. After an initial test programme this method was abandoned. It was found that more consistent results could be obtained by using the chart recorder technique.

14b) Impact Tests.

An 'Amsler' pendulum type machine which could be adjusted to provide a wide range of impacting energies was used to test the un-notched bars (12.6 cm. x 1.3 cm x 0.65 cm). The hammer (156J) had a striking nose of 0.2 cm radius and a 30° total included angle. The specimens were supported to give a 7 cm. span as recommended in BS 2782, 111, 1965 (79). Preliminary trials indicated the ranges that could be used in order to meet the requirements of this standard which states that the energy absorbed in breaking a specimen should be less than 80% but more than 10% of the impacting energy. It should be noted that this requirement could not be adhered to in all cases because some specimens were so brittle after plating that they absorbed less than 10% of the impacting energy even when the machine was set at its lowest capacity (10 J and 1.4 m/s). In contrast to this, some unplated grades of ABS and polypropylene were so ductile that they were not broken by the machine; consequently these results are recorded as "invalid" in accordance with the BS 2782, 111, 1965 (79) standard.

Certain grades of ABS and polypropylene were impact tested at - 40°C and + 80° C as well as at room temperature. They were cooled to - 40° C using a solid carbon dioxide/acetone mixture and heated to + 80° C in an air oven. The time allowed at temperature was 10 min. The specimens were all placed on the supports with the injection gate area on the left hand side; this practice was adopted since some variation in impact strength was seen to be due to the positioning of the impact bars. The energy absorbed in fracturing the specimens was recorded directly and as in the tensile tests the true cross-sectional areas were used to calculate the impact strengths.

15) Peel Adhesion Tests.

Two types of test panel 6.0 cm x 8.8 cm x 0.3 cm were used for this investigation. The first type had plain surfaces on each side but the other had a ridge and a valley moulded into one face. Preliminary trials on panels supplied by an ABS plastics manufacturer showed that a pattern on one surface could influence locally the peel adhesion value obtained on the other. The ridge was 0.04 cm high and corresponded to the size of a similar feature on the panels supplied by the manufacturer. The valley was 0.04 cm. deep to match the size of the ridge, (the positions of the features can be seen in Figs. 1b and 33).

The panels for peel adhesion testing were usually bright copper plated but a limited programme involving copper + semi-bright nickel layers was also undertaken. Plated panels were stored in the unslit condition for 10 days before slitting and testing. Since previous work had shown the adhesion of plated polypropylene to be partly dependant on the ease of access of oxygen, some panels were slit and then stored before testing. Peeling was commenced from the injection gate end, although peeling from the opposite end had no detectable effect on the values recorded.

Peel adhesion was determined using an 'Instron' tensile testing machine fitted with the attachment shown in Fig. 3 bolted to the bottom cross-head. The specimens were clipped to the trolley supported by roller bearings and by means of a thread attached to the trolley it was arranged that this moved forward as the lower cross-head descended. This mechanism ensured that a foil, 2.54 cm wide was peeled off at a constant angle of 90° with respect to the substrate. The width of the peeled foil was determined by milling parallel slits through the coating into the substrate, Fig.4. A tag of metal was then lifted off the substrate using pliers. Fluctuations in peel adhesion were registered by means of a load cell connected to the clamp that gripped the foil. The chart recorder was adjusted so that the chart speed was the same as the rate of peel; this was standardised at 2 cm./min.

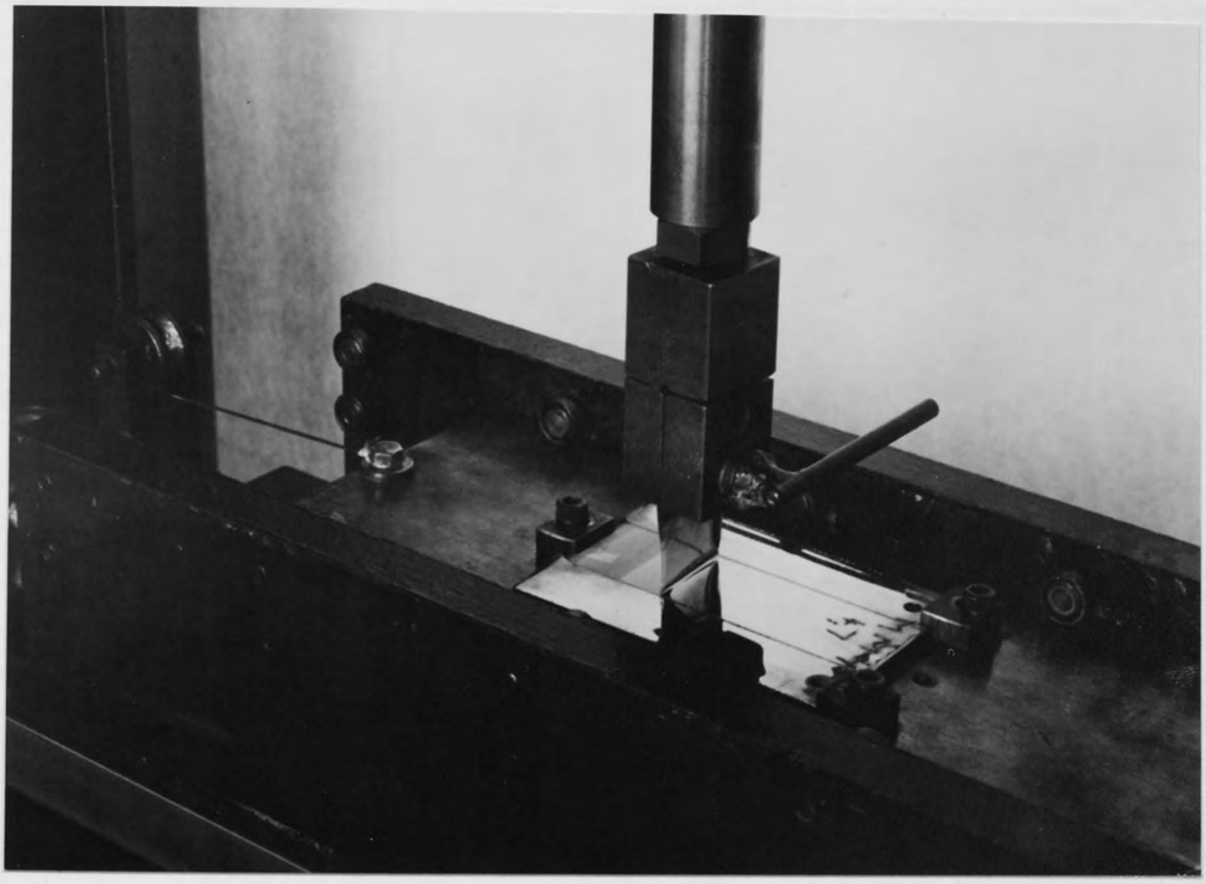


Fig.3. Peel adhesion test attachment used on 'Instron' tensile testing machine.

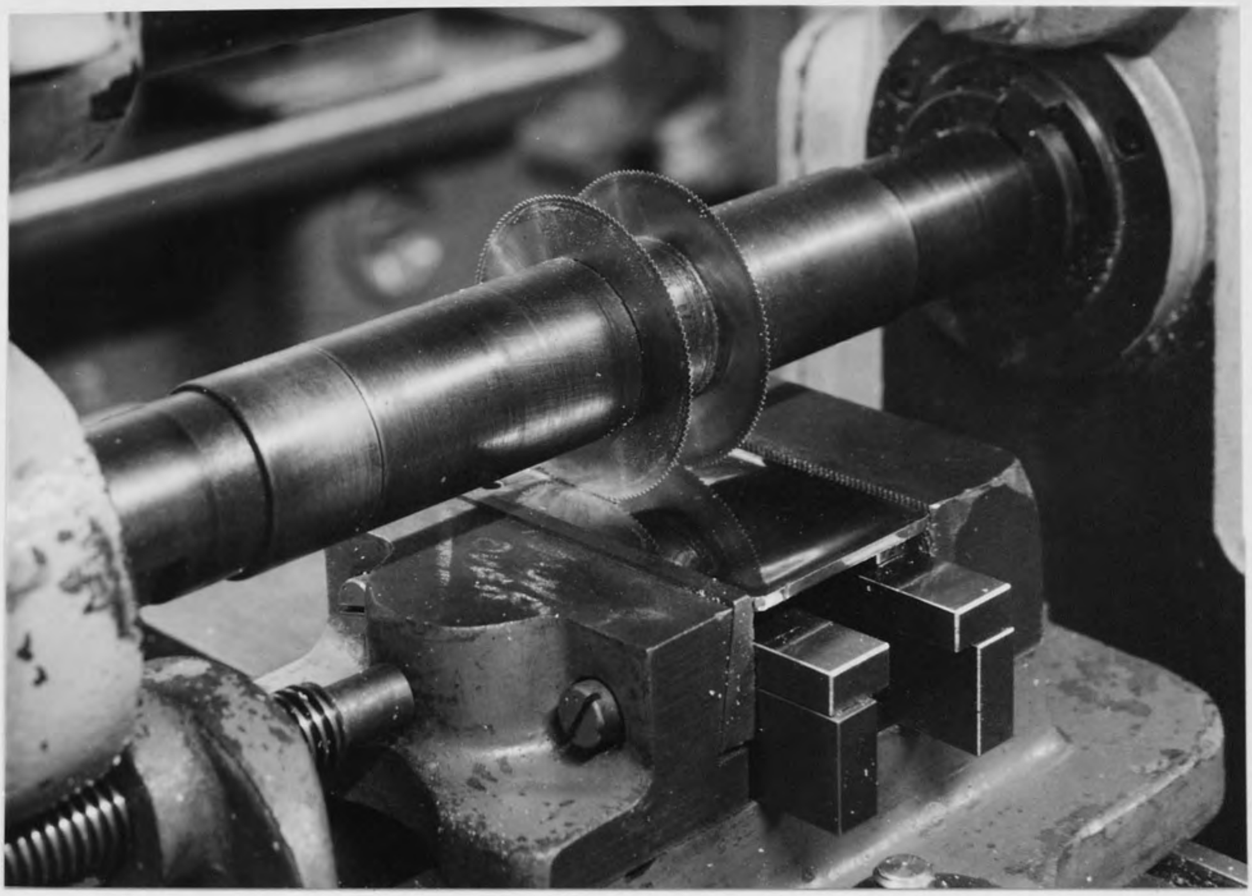


Fig.4. Milling machine attachment used for slitting panels for peel adhesion testing.

Average peel adhesion values were determined by measuring the areas under the curves by means of a planimeter . This gave a measure of work expended in detaching the foils from the substrates.

16) Determination of the Thickness of Plastics Film Detached During Peel Testing.

When a metal foil is detached from a plastics substrate by the peel test, failure occurs in the sub-surface layers if there is any significant bond between the metal and plastics. Saubestre et al (60) have proved by dimentional analysis alone that the bond must break at a point somewhat removed from the actual interface between metal and plastics. It was the object of this investigation to examine the effect of plating and moulding variables on the thicknesses of plastics films detached from several grades of ABS and polypropylene during the peel adhesion test.

The thicknesses of the plastics layers were determined by cutting sections 4 cm x 2.54 cm from identical areas of the peeled foils and dissolving the metals (electroless nickel, electrodeposited copper and in some cases semi-bright nickel) in 20% W/V ammonium persulphate at room temperature. The delicate plastics films were washed thoroughly in de-ionised water, placed on filter paper and dried in an oven at 50° C for eight hours. The dried films were weighed accurately and their thicknesses calculated by using appropriate values for the densities of the plastics, Tables I and XXIII. Errors in calculated thicknesses were inevitable since the densities of the bulk plastics were unlikely to be exactly the same as those of detached films. The surfaces of the plastics were subjected to etching prior to plating and so butadiene would have been removed from ABS and fillers may have been selectively etched out of ABS and polypropylene. Etching may have thus modified the effective densities of the films. In any case it is questionable whether true thicknesses can be reported for the plastics films since they are seriously distorted while being torn off the substrate during the peel adhesion test. However, results have been reported in terms of thickness but it may have been equally valid to have given the weight of plastics adhering to a unit area of foil.

17) Thermal Cycling Test.

This test was carried out in accordance with BS 4601, 1970, Appendix F[(48)] that is between - 40° C and + 80° C. The specimens were subjected to four cycles of the test and rated using an arbitary system each time they returned to room temperature. A value of 10 indicates no deterioration and 0 indicates disastrous failure. The system was weighted so that defects appearing early in the test qualified for greater penalties than those appearing after a number of cycles. Blisters and large areas of poor adhesion were regarded as serious defects while fine line sinks were considered less serious. Some test panels were supplied by an ABS plastics manufacturer; they were plain on one side but had a pattern on the other and so the plain side was designated a significant surface.

Consequently defects appearing on the plain surface warranted greater penalty points than those occuring on the patterned side. An outline of the rating system is given in Table IV.

18) Examination of Specimens.

18a) Corrosion Tests.

Corrosion sites were examined by three techniques: scanning electron microscopy, optical microscopy and electron probe micro-analysis (EPMA). A scanning electron microscope (SEM) with an energy dispersive X-ray attachment was also used to identify elements present in corrosion products. Dennis and Fuggle (80) have described the use of the SEM for the investigation of the morphology of corrosion pits in decorative nickel + chromium coatings on metallic substrates. The same procedure was adopted in this instance, appropriate sections were cut from the panels, vacuum coated with carbon and gold-palladium alloy and examined using the SEM. T he optical microscope and SEM were used to examine metallographically prepared cross-sections in order to observe the amount of preferential attack of underlying layers in the multilayer coatings. The electron probe microanalyser (EPMA) and the energy dispersive X-ray attachment fitted to the SEM were used to identify the elements present in the corrosion products that had exuded out of the corrosion pits onto the surface. The EPMA proved useful for the examination of the backs of foils stripped from the regions in which blistering had occurred. As will be described later in detail it was possible to prove that blistering resulted because

TABLE IV. RATING SYSTEM USED TO ASSESS TEST PANELS AFTER THERMAL CYCLING

TYPE OF DEFECT	PENALTY POINTS ALLOCATED ON FIRST APPEARANCE OF A DEFECT															
	1st cycle				2nd cycle				3rd cycle				4th cycle			
	- 40°C		+ 80°C		- 40°C		+ 80°C		- 40°C		+ 80°C		- 40°C		+ 80°C	
	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P
Distortion of Panel resulting in loss of adhesion	6½	5½	6½	5½	6	5	6	5	5	4	4	3	4	3	4	3
Cracked Plate	6	5	6	5	6	5	6	5	5	4	4	3	4	3	4	3
Blisters	5	4	5	4	4½	3½	4½	3½	4	3	3	2	3	2	3	2
Puckering of Plate	4	3	4	3	3½	2½	3½	2½	3	2	2	1	2	1	1½	1½
Gate sinking	3	2	3	2	2½	2	2	2	1½	1½	1½	1½	1½	1½	1	1
Line sinking	2	1	2	1	1½	1	1	1	1	½	1	½	1	½	½	½

F Refers to the plain surface of panel

P Refers to the patterned surface of panel

The test panels were rated at room temperature electroless nickel had been preferentially corroded away from a localised area.

18b) Mechanical Tests.

The fracture surfaces on tensile and impact specimens were examined in a similar manner to the corrosion specimens. The high resolution of the SEM enabled a detailed study of the surfaces and revealed areas where the metal deposits had been partly lifted off from the substrates.

The SEM proved useful when a study of the surfaces of etched ABS and polypropylene was made. The surface topographies of peeled panels and foils and the appearance of those substrates over which the metallic coating had blistered during thermal cycling were also studied using the SEM.

The SEM with the X-ray energy dispersive analysis attachment was used to detect the distribution of palladium on samples cut from ridged panels after the catalyst stage in the process sequence. The specimens used for this investigation were vacuum coated with carbon only. When standard operating conditions were employed, the technique was sufficiently sensitive to show that the palladium concentration was greatest in regions where the highest adhesion was known to occur. It had been noted with the naked eye that preferential adsorption of catalyst occurred giving rise to dark bands on the plain side of ridged ABS and polypropylene panels. These dark bands corresponded to regions of high adhesion in the case of ABS but the effect was not so apparent for polypropylene. Differences in the amounts of fillers in the plastics could also be detected at regions associated with the ridge and valley, eg. titanium and calcium indicating the distribution of titanium dioxide and calcium carbonate.

19). Transmission Electron Microscopy (TEM).

The shape, size and distribution of butadiene particles in specimens cut from different parts of ridged ABS mouldings was evaluated by transmission electron microscopy (TEM). It should be noted that only two grades were examined, U and R, containing 6% and 16% butadiene respectively, see Table I . Osmium tetroxide stains butadiene and the method employed was similar to that used by Kato(81) . Small pieces of ABS plastics were soaked in osmium tetroxide for 10 days then thin specimens not more than 1000 Å thick, were sliced from them using an ultramicrotome. These were dried before examining at 60 kv using a transmission electron microscope.

20). Statistical Analysis Techniques.

The use of statistical analysis was considered opportune in view of the large numbers of variables and specimens used in the investigation. Three techniques were adopted; the analysis of variance, correlation and regression analysis and the comparison of means or 't' test. All these tests are described fully in "Facts from Figures" by Moroney(82) and "Basic Statistical Methods for Engineers and Scientists" by

Neville and Kennedy (83).

Analysis of Variance.

This test involved the use of a standard 'statspackage' from the computer library. Suitably presented data was processed to indicate which variables were affecting the property being measured.

Correlation and Regression Analysis.

This test was used in order to assess whether any relationship between data obtained in the various corrosion tests existed. A standard program was selected for use on an 'Olivetti Programma 101' desk computer. The data was presented in a form which ensured a high number of degrees of freedom which is desirable if the analysis is to be meaningful.

Comparison of Means or 't' test.

The paired data technique was applied to data (84) obtained from the mechanical testing programmes. Aston has shown that this method is extremely sensitive for detecting the effects of variables. The condition for homogeneity of variances is not required if this version of the 't' test is applied; this technique is not influenced by random effects due to non-homogenous variances.

2.20 GLOSSARY OF STATISTICAL TERMS.

1). Analysis of variance is a study of the effects of all the variables in the experiments and examination of these variables in order to determine whether they affect the property being measured.

2). Coefficient of Correlation (r)

Correlation indicates that some interdependance between data exists and the correlation coefficient gives a measure of the interdependance between variates. A value of + 1 indicates a perfect relationship, 0 indicates no relationship and - 1 indicates a perfect inverse relationship.

3). Degrees of Freedom (ν).

Degrees of freedom can be defined as the number of choices of values that exist in a set of data.

4). Null Hypothesis.

In statistical significance tests the null hypothesis is set up which states there is no significant difference between sets of data or that no significant association exists between two sets of data coming from two different sources. If the statistic used to test the hypothesis lies outside acceptable limits then the null hypothesis is rejected.

5). Regression Analysis.

Regression analysis is the fitting of the 'best' line through a set of data where a dependant variable y is being estimated by an independant variable x. The value of x is taken to be free from error while y is the observed or measured quantity, subject to errors which have to be 'eliminated' by the regression technique.

6). Significance.

An effect is significant if the value of the statistic used to test it lies outside acceptable limits.

7). Significant First Order Interactions.

The combined contributions of two variables that affect significantly the property being measured are known as significant first order interactions.

8). Significance Level.

Significance level indicates the risk of being incorrect in stating that a relationship or association exists between two variables or that genuine differences exist between sets of data. For example, at the 5% level of significance there is a risk of stating incorrectly 5 times in every 100 that a relationship exists. At the 1% and 0.1% levels the risks are 1 in 100 and 1 in 1000 respectively. Consequently, the lower the significance level the more justifiable the statement that relationships and/or genuine differences exist between sets of data.

9). Comparison of Means or 't' test.

The 't' test is applied to the null hypothesis that the two samples being compared are drawn from the same population. The probability of the difference |average of sample 1 - average of sample 2| having a value as large or greater than observed is taken as a measure of any justifiable acceptance (or rejection) of the null hypothesis.

VARIATES.

Variates are the values that vary.

3. RESULTS.

3.1 Corrosion Tests - First Phase; Specimens on Outdoor Exposure 1.1.72 to 1.10.72.

Mouldings of three grades of ABS, X,Y and Z were supplied by a plastics manufacturer for this pilot corrosion testing programme. Two proprietary ABS pre-electroplating sequences (A and B) were also used. Information regarding the compositions of the ABS grades is given in Table 1. It should be noted that a common etch time of 7.min.was used on all grades of ABS in either process A or B. A compromise conditioner time of 2 min. was also used in process sequence A. The etch times were standardised to avoid another variable being introduced into the programme.The coating systems applied are given in Table V.

The histograms shown in Fig.5 indicate the corrosion protection and appearance ratings,using the ASTM two number system (77), of plated ABS panels after mobile and static outdoor exposure and after one 16 h cycle of the CASS (48) test. All specimens used in the first programme were taken off test on 1/10/72 in order that a detailed examination could be undertaken.

3.1.1.1 CASS TEST.

a) Bright Nickel + Decorative Chromium.

The main feature exhibited by this group of specimens was the fairly severe nature of the corrosive attack,the types of failure included stripping of the coating from the substrate,blistering, extensive pin-hole attack and cracking. It was noted that specimens processed using sequence B tended to blister more than those having an identical coating but processed in sequence A. Plastics type Y,when processed using sequence B,was particularly susceptible to blistering.In Fig.6 the metallic coating had been peeled from the substrate to reveal the size of corrosion pits in the case of plastics Y and Z.

TABLE V. COATING SYSTEMS APPLIED TO ABS

Tests	Coating Code Number	THICKNESS OF DEPOSIT - µm				
		Bright Copper	Bright Nickel	Special Nickel containing Particles	Decorative Chromium	Microcracked Chromium
First phase of corrosion and thermal cycling tests	1	20	12		0.25	
	2	20	12		0.50	
	3	20	6		0.25	
	4	20	6		0.50	
	5	20	12			0.75
	6	20	12			1.25
	7	20	6			0.75
	8	20	6			1.25
	9	20	12	1	0.25	
	10	20	12	1	0.50	
	11	20	6	1	0.25	
	12	20	6	1	0.50	

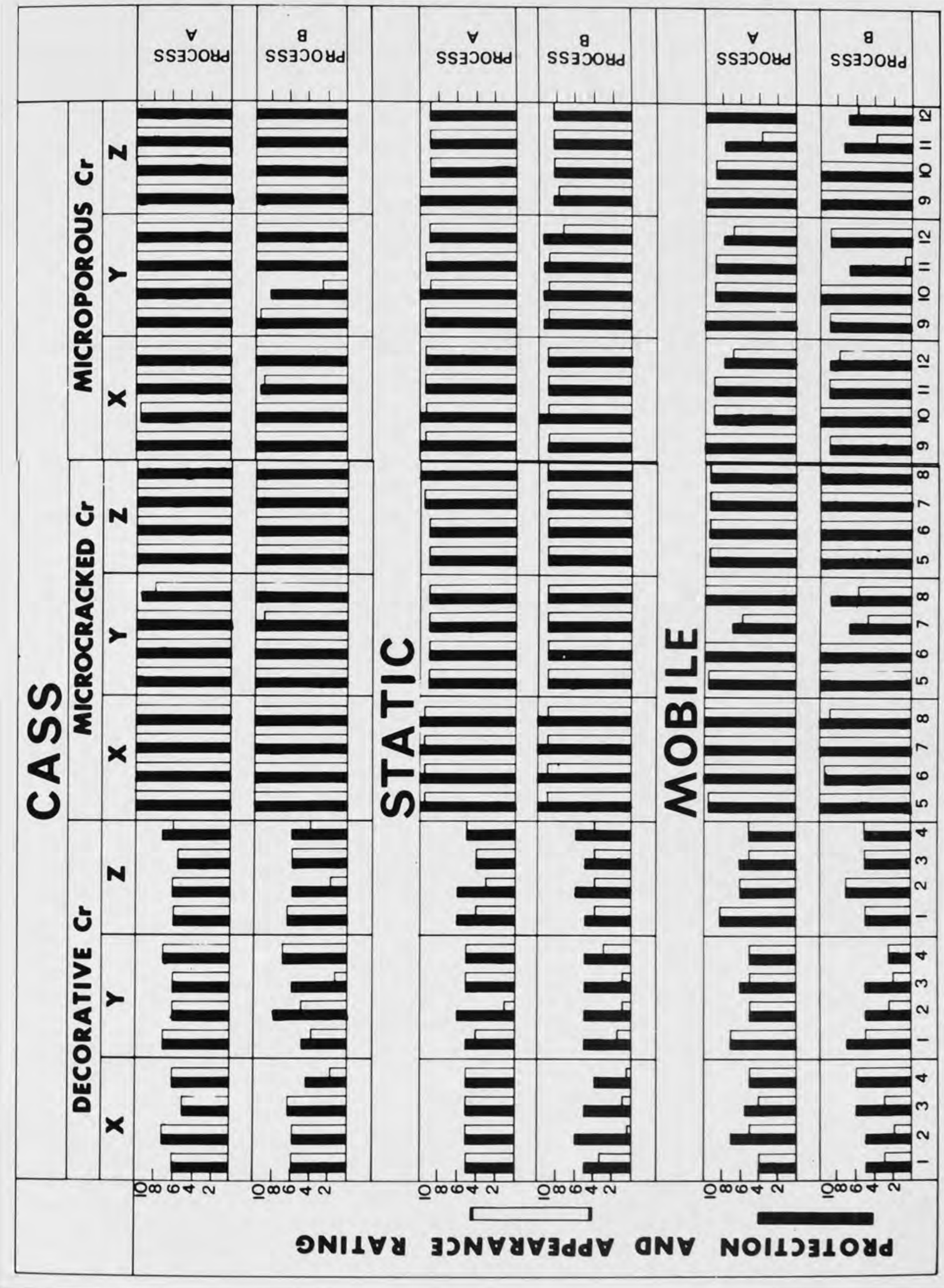
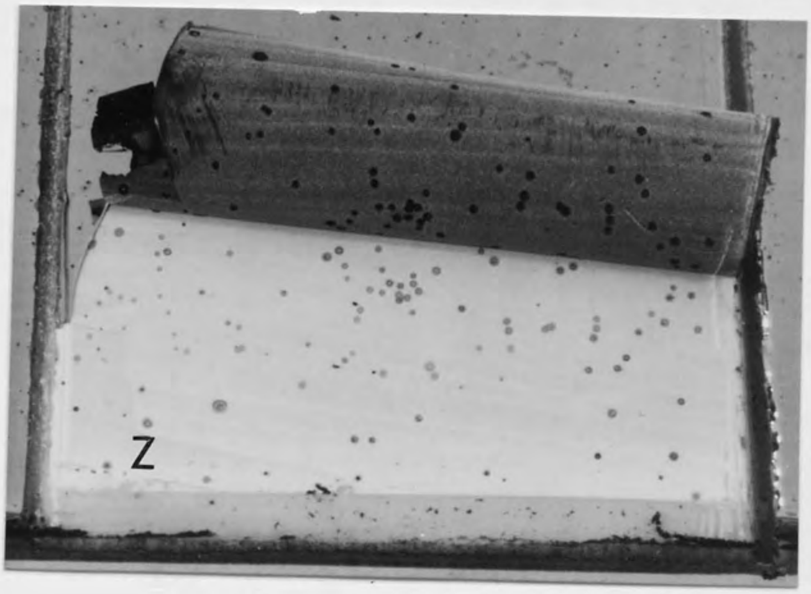


Fig.5. Ratings of plated ABS panels after corrosion tests, CASS test 16 hr., outdoor tests 9 months exposure, 1.1.72 to 1.10.72.

Numbers 1 to 12 at the bottom ofthe figure indicate the coating code numbers - see Table V.



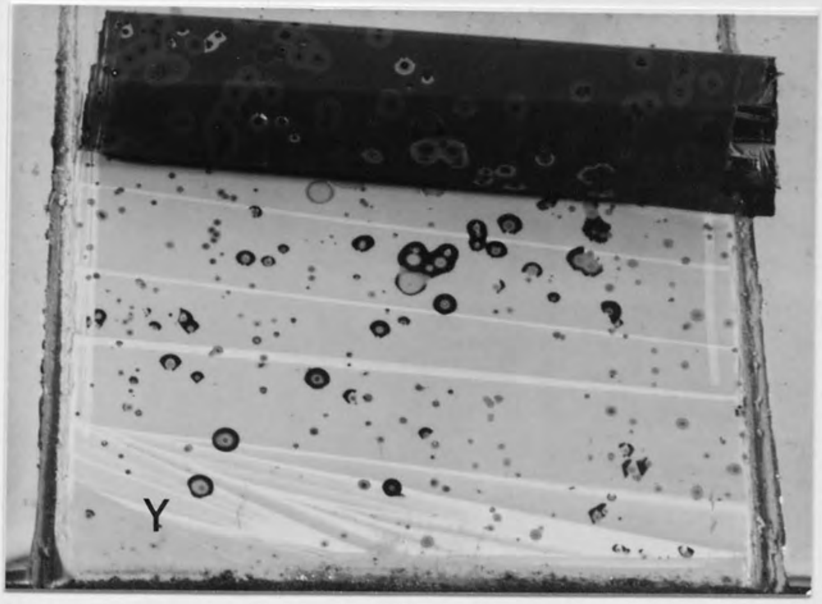


Fig.6. Coatings peeled off to show the size of corrosion sites. Process sequence B, coating system No.1., 16 hr CASS test. Magnification x 3.

The back of a metal foil and the ABS surface from which it was stripped is shown in Fig.7. The feature illustrated is a corrosion site at which penetration to the substrate had occurred. Preferential attack of underlying metal had resulted in the development of a blister. Examination of the back of the foil revealed a bright circular area of copper indicating that electroless nickel had been corroded away. Wiggle et al (43) have observed a similar effect after service exposure.

By electron probe microanalysis it was possible to prove that electroless nickel had been completely dissolved away by the CASS solution. Fig.8 shows a nickel X-ray photograph taken from the area of metal depicted in Fig.7. The diameter of the blister matched exactly the diameter of the circular area revealed on stripping off the metal foil. At higher magnification it was apparent that the boundary at the edge of the 'corrosion circle' was clearly defined, as shown in Fig.9. On the right hand side of the figure the ABS surface is covered with a layer of corrosion products while on the other side the surface has the typical appearance of a plastics surface from which a metallic coating has been stripped. This indicates that blister formation was due to corrosion and not to poor adhesion of the coating to the substrate. The surface of the ABS would not have a torn and distorted appearance unless fairly good adhesion had been achieved. Fig.10 shows the back of a metal foil stripped from a plastics substrate, the area on the

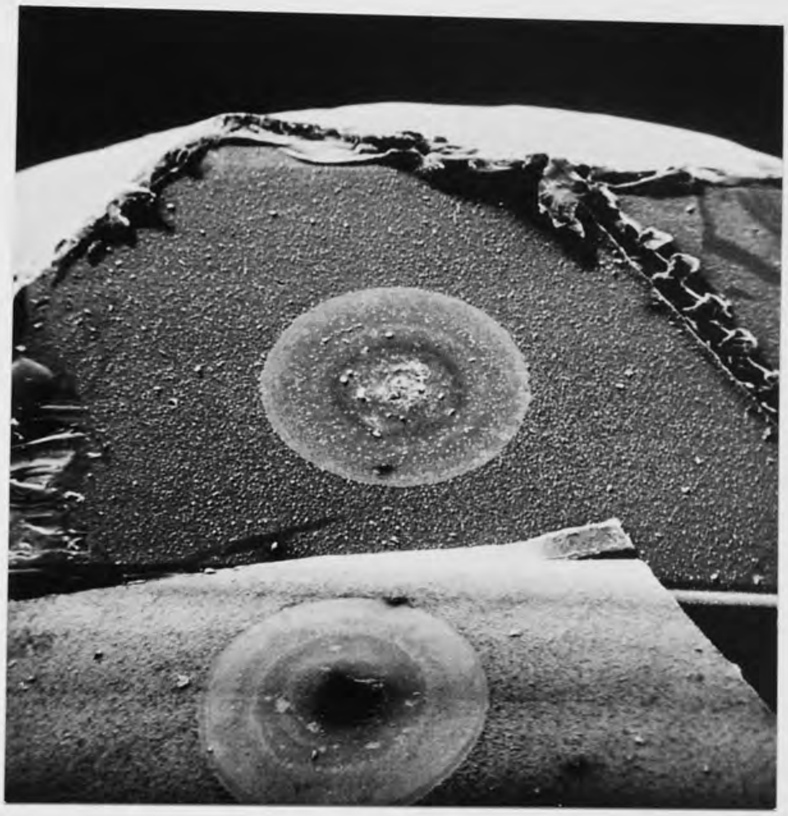


Fig.7. Scanning electronmicrographs of the back of a metal foil and the ABS surface from which it had been stripped. This illustrates that electroless nickel had been preferentially corroded away. Plastics Grade X, process sequence B, coating system No.4, 16 hr. CASS test. Magnification x 25.

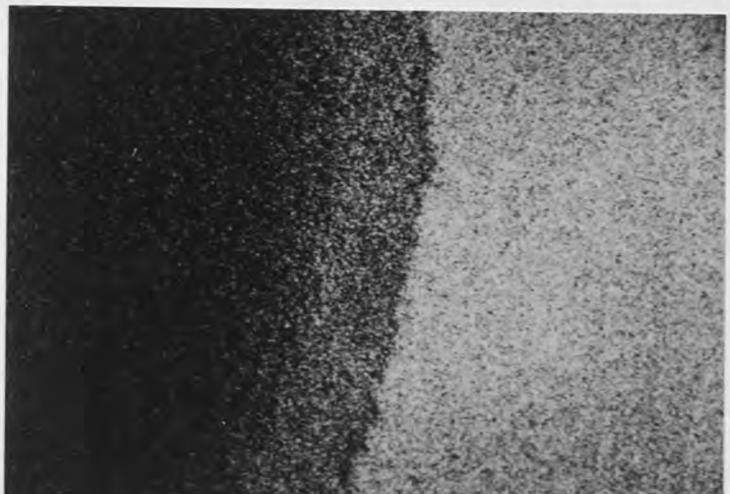


Fig.8. Electroless nickel X-ray picture of the back of a metal foil at the locality of a corrosion blister. This shows that the deposit had been dissolved away. Magnification x 750.

Fig.9. Edge of "corrosion circle". Corrosion products present where electroless nickel had been attacked and torn ABS surface where the coating had still been bonded to the substrate. Plastics grade X, process sequence B, coating system No.4., 16 hr CASS test.
Magnification x 1300.

Fig.10. Edge of "corrosion circle" on the underside of the metal foil, after peeling from substrate. A thin layer of plastics was present in the region unaffected by corrosion. Foil stripped from plastics grade X, process sequence B, coating system No.4., 16 hr CASS test.
Magnification x 1300.

left illustrates a region denuded of electroless nickel and that on the right a region of good adhesion. A thin layer of ABS can be seen adhering to the metal foil and once again the edge of the blister is marked by a clearly defined boundary.

Macrocracks developed in some coatings particularly when deposited onto ABS grade Z and extended for quite long distances across the surfaces (for example up to 1.5 cm). Fig. 11 illustrates the junction of two such cracks and shows that undercutting of the coating had also taken place. Examination of a cross-section cut from this area revealed that the copper deposit had been severely attacked once the nickel layer had been penetrated. In some places the copper layer had also been penetrated to expose the electroless nickel and then the attack on the copper was reduced since the electroless nickel was more readily corroded. Usually macrocracks did not lead to blister formation as did the pin holes, probably due to the difference in shape of the corrosion cell.

An example of the most catastrophic type of defect encountered is illustrated in Fig.12. At this corrosion site three blisters had joined together so that a large area of copper was exposed. This was then preferentially attacked so that the other layers of the coating were undermined. In some areas only the chromium layer remained.

Fig.11. Cracks in bright nickel + decorative chromium coating after 16 hr. CASS test. Plastics grade Z, process sequence B, Coating system No.2.
Magnification x 750.

Fig.12. Severe corrosion site produced by CASS testing. Copper had been preferentially corroded and chromium was flaking off. Plastics grade X, process sequence B, coating system No.2. 16 hr. CASS test.
Magnification x 300.

3.1.1.2. Bright Nickel + Microcracked Chromium.

In general this group of specimens exhibited very good resistance to the CASS test. The main cause of deterioration was due to surface dulling or light staining. Some small blisters and a limited amount of edge cracking occurred on a few test panels.

Scanning electron micrographs of the surface of corroded specimens confirmed that this type of coating system had behaved in a similar manner on ABS substrates to when plated on metallic ones (80). Consequently this accounted for the good corrosion resistance observed. Examinations of cross-sections showed that the nickel deposit had been penetrated rarely, although relatively thin layers had been used in this programme. It is not surprising that blister formation had been prevented on most panels since little opportunity had been afforded for attack of the layers of the coating most likely to corrode, that is electroless nickel and electrodeposited copper.

3.1.1.3 Bright Nickel + Microporous Chromium.

To the naked eye, most specimens plated with this coating system appeared to be almost perfect. However, low power optical microscopy or scanning electron microscopy revealed minute pits, cracks and blisters. Plastics Y was again the most unsatisfactory; blisters and small edge cracks could be observed when this grade of ABS was processed on either pre-electroplating sequences. Cross-sections suggested that the nickel layer had not been penetrated although a section cut from one of the more severely stained areas revealed that penetration was about to occur. However, penetration must have occurred at a few points to result in blister formation. Fig.13 shows typical corrosion sites at somewhat different stages of development and it also indicates the density of such sites.

3.1.2 OUTDOOR STATIC EXPOSURE.

3.1.2.1 Bright Nickel + Decorative Chromium.

The main features observed were the large corrosion sites and the voluminous corrosion products; this emphasises the aggressive nature of a British industrial environment and the poor resistance to corrosive attack that this coating system exhibits. The morphology of the corrosion sites was almost the same as for those occurring during the CASS test but the degree of corrosion was more severe. When the metallic coating was stripped off, the same type of circular markings were revealed and the EPMA indicated that electroless nickel had been preferentially corroded away again.

Cracking and gross blistering was particularly prevalent in the case of plastics Y processed using sequence B. As far as could be ascertained, the processing sequence had little effect on the frequency with which corrosion pits penetrated to the substrate, but blistering was more severe when sequence B was used.

3.1.2.2 Bright Nickel + Microcracked Chromium.

After about six weeks exposure the surface of these specimens became covered with a persistent brownish green stain even though they were washed with mild soap solution

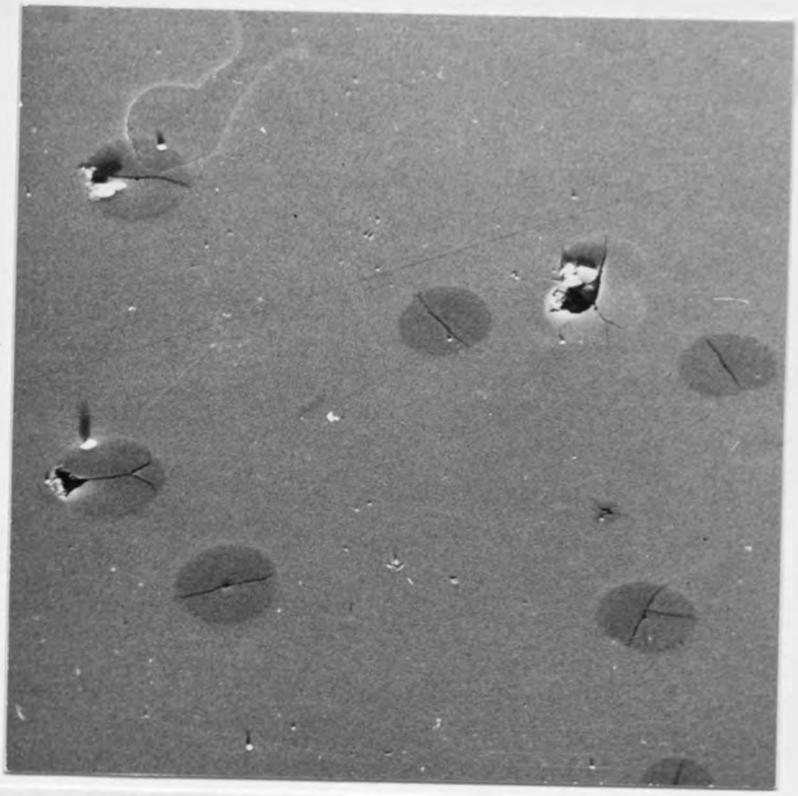


Fig.13. Corrosion sites in bright nickel + microporous chromium coating. Plastics grade Z, process sequence B, coating system No.11., 16 h.r. CASS test.
Magnification x 600.

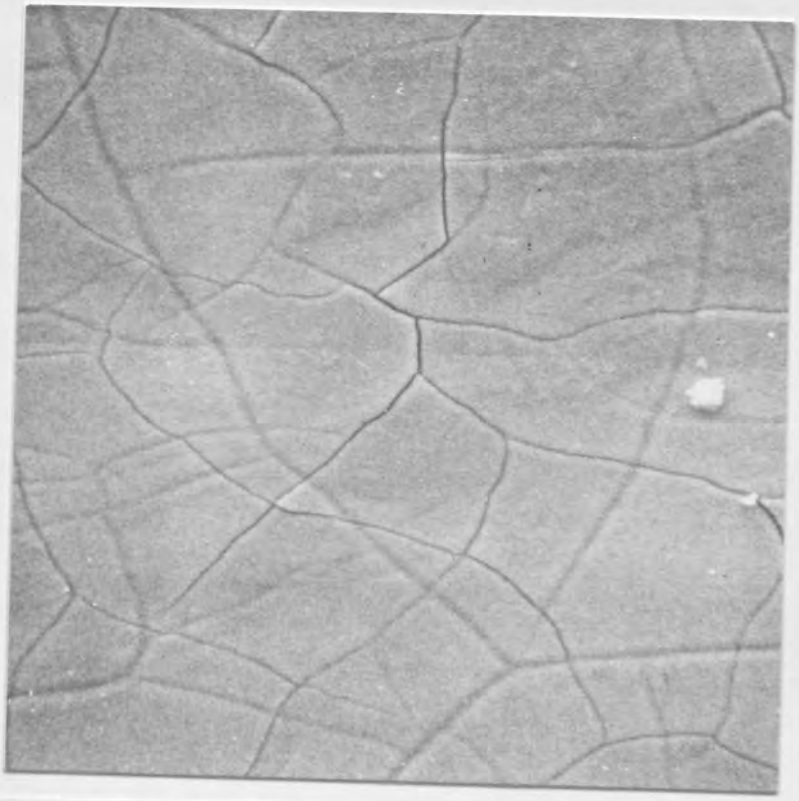


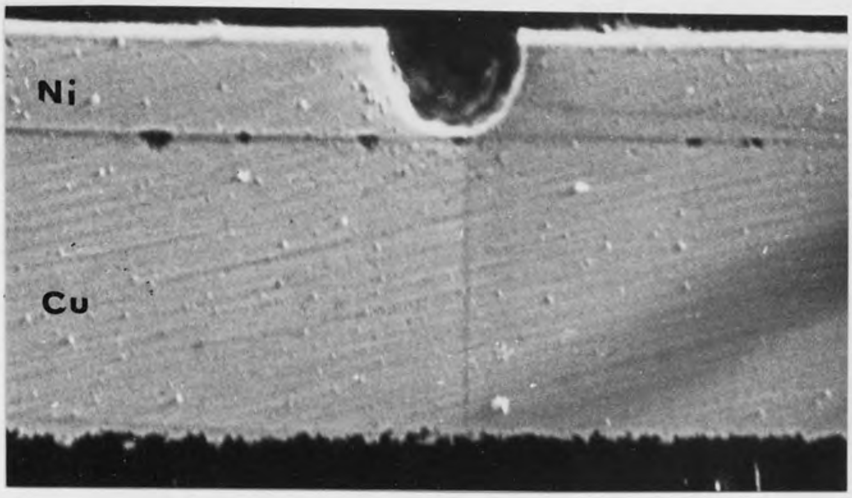
Fig.14. Bright nickel + microcracked chromium coating after 9 months static outdoor exposure, slight corrosion had taken place at some cracks. Plastics grade Y, process sequence B, coating system No.8.
Magnification x 1500.

before each rating, that is approximately once per month. At the end of the exposure period the microcracked pattern could not be resolved with either optical or scanning electron microscopy due to quite a thick layer of corrosion products. By means of the EPMA, the presence of copper was identified in this film indicating that the nickel layer had been penetrated. Confirmation was obtained by examination of cross-sections, although these showed that severe attack of the copper had not taken place at this stage. When the layer of corrosion product was removed using a mild abrasive such as magnesium oxide the surface was relatively bright and the crack pattern could be observed as shown in Fig.14. The appearance of the specimen shown in the photograph is typical of a bright nickel + microcracked chromium coating subjected to a moderate degree of corrosion. Some healed up cracks are visible but others have opened up somewhat due to the corrosion of the underlying metal. Dennis and Fuggle(80) have noted this effect when metallic substrates having bright nickel + microcracked chromium overlays have been subjected to corrosive attack.

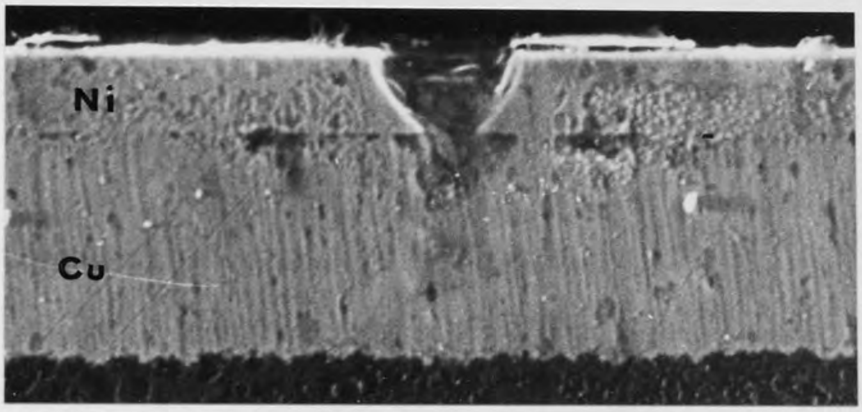
3.1.2.3 Bright Nickel + Microporous Chromium.

The brownish green stain appeared on these samples after about the same exposure period as in the case of the plastics plated with bright nickel and microcracked chromium. Other features observed included small edge cracks, mainly at jigging points, and the usual type of fine pitting. One panel which appeared quite bright near the edge but which became progressively less bright towards the centre was examined in detail in order to attempt to relate appearance to the degree of attack of the copper layer. Fig.15 shows cross-sections prepared from various parts of the panel. It was apparent that where the attack on the copper was most severe the brown stain was most noticeable. Although precautions were taken to obtain a uniform metal distribution it is obvious that the coating was thicker near the edge than in the centre and that the variation in thickness had caused the differences in appearance. In the case of the section cut from the centre of the panel the nickel had been anodically protected due to preferential attack of the copper. Areas of the surface adjacent to the sections shown in Fig.15 were examined using the SEM.

In the bright region the micropores had developed to only a limited extent, the chromium layer was still overhanging the pits. In an area having light brown staining the pitting was more severe, the chromium layers had been undermined and corrosion products were exuding from the pits. Finally in the area of most severe staining the degree of pitting had also reached the most advanced stage. The frequency of pitting was greater and the chromium layer had either been completely removed from the corrosion sites or had collapsed into them, in either case considerable corrosion of the underlying layers had taken place.



EDGE



1·5 cm FROM EDGE

CENTRE

Fig.15. Corrosion pits developed at various parts of a microporous panel plated with bright nickel + microporous chromium. Plastics grade X, process sequence B, coating system No.10, 9 months static outdoor exposure. Magnification x 1300.

3.1.3 OUTDOOR MOBILE EXPOSURE.

3.1.3.1 Bright Nickel + Decorative Chromium.

Failures observed in this instance were pin hole attack, cracking and blistering. Fig.16 shows a large corrosion site on a bright nickel + decorative chromium coating. Several pits have joined together and this has resulted in the undermining and cracking of the chromium. Other defective regions examined exhibited the blister effect shown in Figs. 6 and 7 after CASS testing. The same corrosion mechanism appears to have operated in all three tests. The electroless nickel was preferentially attacked in all three tests once the corrosion pit had penetrated to that layer. In each case blister formation then occurred.

3.1.3.2 Bright Nickel + Microcracked Chromium.

The overall performance of these specimens was excellent. The only defects observed were minute blisters on a few specimens and depressions arising from mechanical damage caused by flying debris from the road. The latter were characterised by localised macrocracking of the chromium. Many of the specimens had high rating values at the end of the exposure period and the staining experienced in the static test rarely occurred. In a few instances a brown tinge of stain could be detected after 9 months exposure. It is likely that more severe staining would have occurred if the test had been continued long enough for pits to penetrate sufficiently deep to cause significant attack of the copper layer.

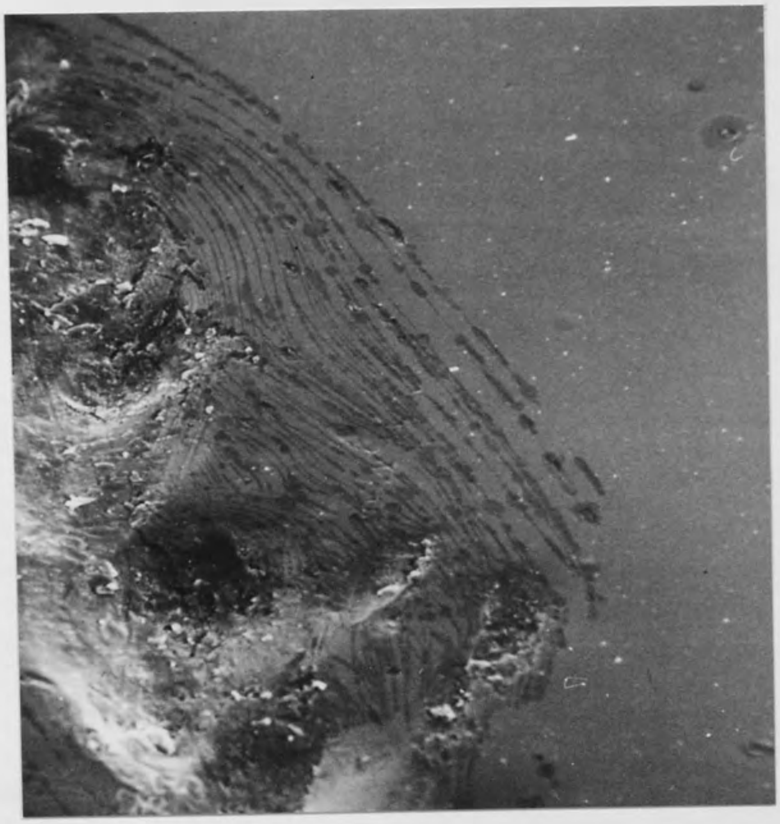


Fig.16. Large corrosion site developed in bright nickel + decorative chromium coating on mobile exposure. Plastics grade Z, process sequence B, coating system No.3. Magnification x 300.

3.1.3.3 Bright Nickel + Microporous Chromium.

The results for this type of coating system were very similar to those obtained for bright nickel + microcracked chromium. Most of the specimens retained their lustrous appearance and staining was only observed on a few samples. Surface deterioration was due to fine pitting and slight edge cracking. The pits were similar in shape to those occurring in the other corrosion tests. Fig.13. Examinations of cross-sections revealed that in most instances the nickel layer had not been penetrated and so little copper corrosion had occurred.

3.2 Corrosion Tests - Main Phase ; Specimens on Test from 1/10/72.

Tests were commenced on 1/10/72 and are continuing. This programme was a more detailed extension of the pilot programme. Additional grades of ABS together with four grades of polypropylene were used. It will be noted that two grades of ABS, Y and Z which had been previously investigated were also included in this programme. The performance of grade Y in the earlier corrosion test programme had been noted as unsatisfactory. Blistering frequently occurred over all the surfaces of plated specimens, particularly when process B was used. For this reason the degree of etching was increased in this programme. A limited exposure programme using electroless copper underlayers instead of electroless nickel was also undertaken. The electroless copper was applied to ABS grade Y and two etch times, 7 and 21 min. were also used.

The effect of electroless copper underlayers was investigated in the static tests only, using process sequence B.

In contrast to the pilot corrosion testing programme when only a compromise etch time was used on the ABS grades, the etch times in this programme were chosen to suit the different grades employed; these times were those which previous work had indicated as those giving an acceptable peel adhesion value. The pre-electroplating sequences, etch times and butadiene contents are listed in Table 1, together with some information on the grades of polypropylene. The types and thicknesses of the multilayer coatings used are given in Table V1. For polypropylene grades M and N the moulding pressure was changed in order to see whether this had any influence on corrosion behaviour. The moulding conditions (i) and (ii) are given in Table 11. In addition to varying the moulding pressure the effect of a shorter and longer etch time was also investigated, Table 1.

It must be noted that although this phase of work is still continuing the detailed assessment and analysis presented in this section relates to ratings obtained on 31/3/74. The last section deals with corrosion performances of the specimens up to 1/9/74.

The histograms shown in Figs. 17 and 18 indicate the protection and appearance ratings using the ASTM

TABLE VI. COATING SYSTEMS APPLIED TO ABS AND POLYPROPYLENE - MAIN CORROSION TESTING PROGRAMME

Comments	Code Number	THICKNESS OF DEPOSIT - µm				
	Coating Code number	Bright Copper	Bright Nickel	Special Nickel containing particles	Decorative Chromium	Microcracked Chromium
Identical coating systems used in thermal cycling tests	3*	20	6		0.25	
	13*	20	15		0.25	
	8*	20	6			1.25
	14	20	15			1.25
	11*	20	6	1	0.25	
	15	20	15	1	0.25	
	16*	20	6	1	0.75	
	17	20	15	1	0.75	

* Denotes coating systems used in mechanical test programme

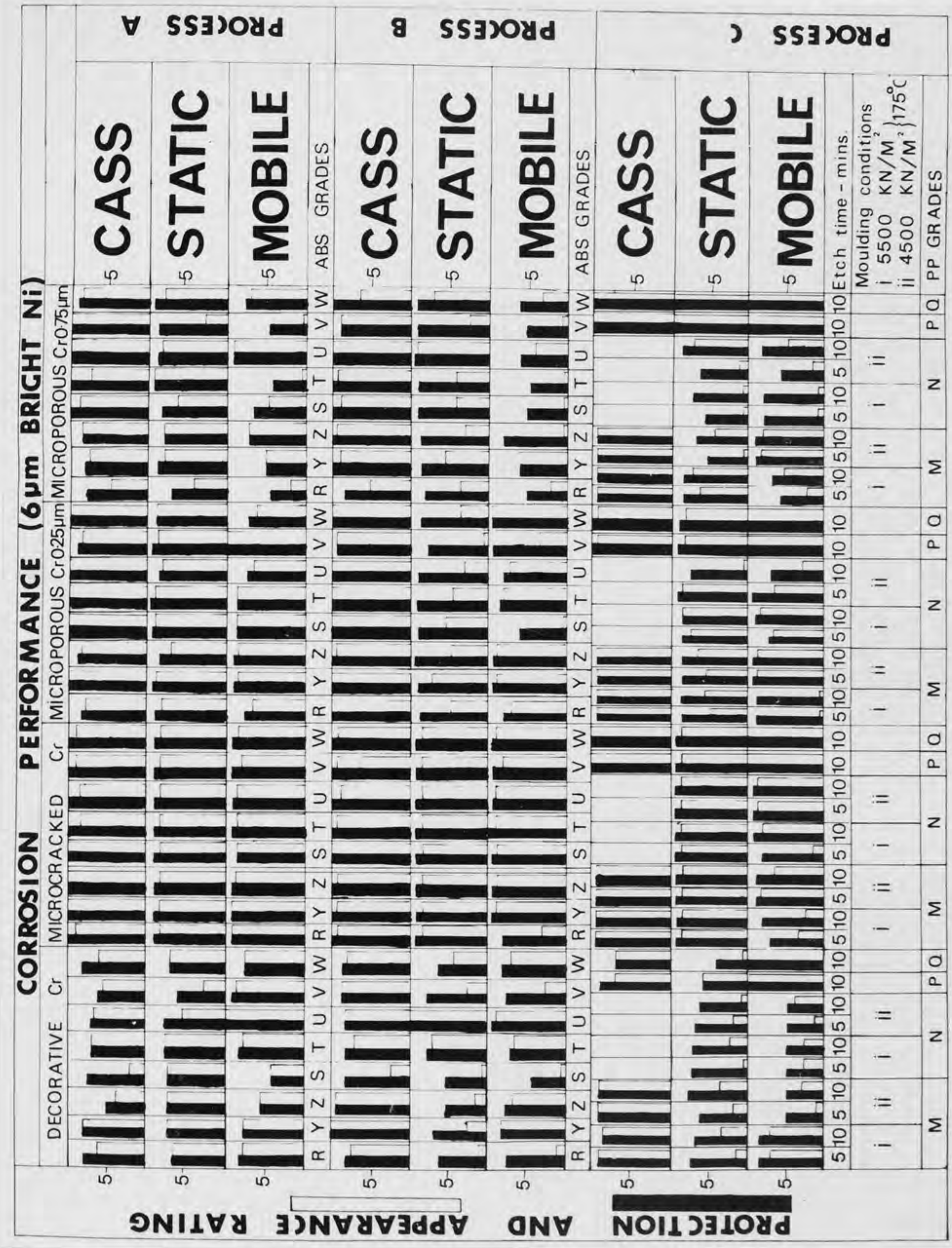


Fig.17. Ratings of plated ABS and polypropylene panels after corrosion tests - 6 µm bright nickel. CASS test 16 hrs. All outdoor tests 18 months exposure from 1.10.72 to 31.3.74 except polypropylene grades P and Q, which had 8 months exposure from 1.8.73 to 31.3.74.

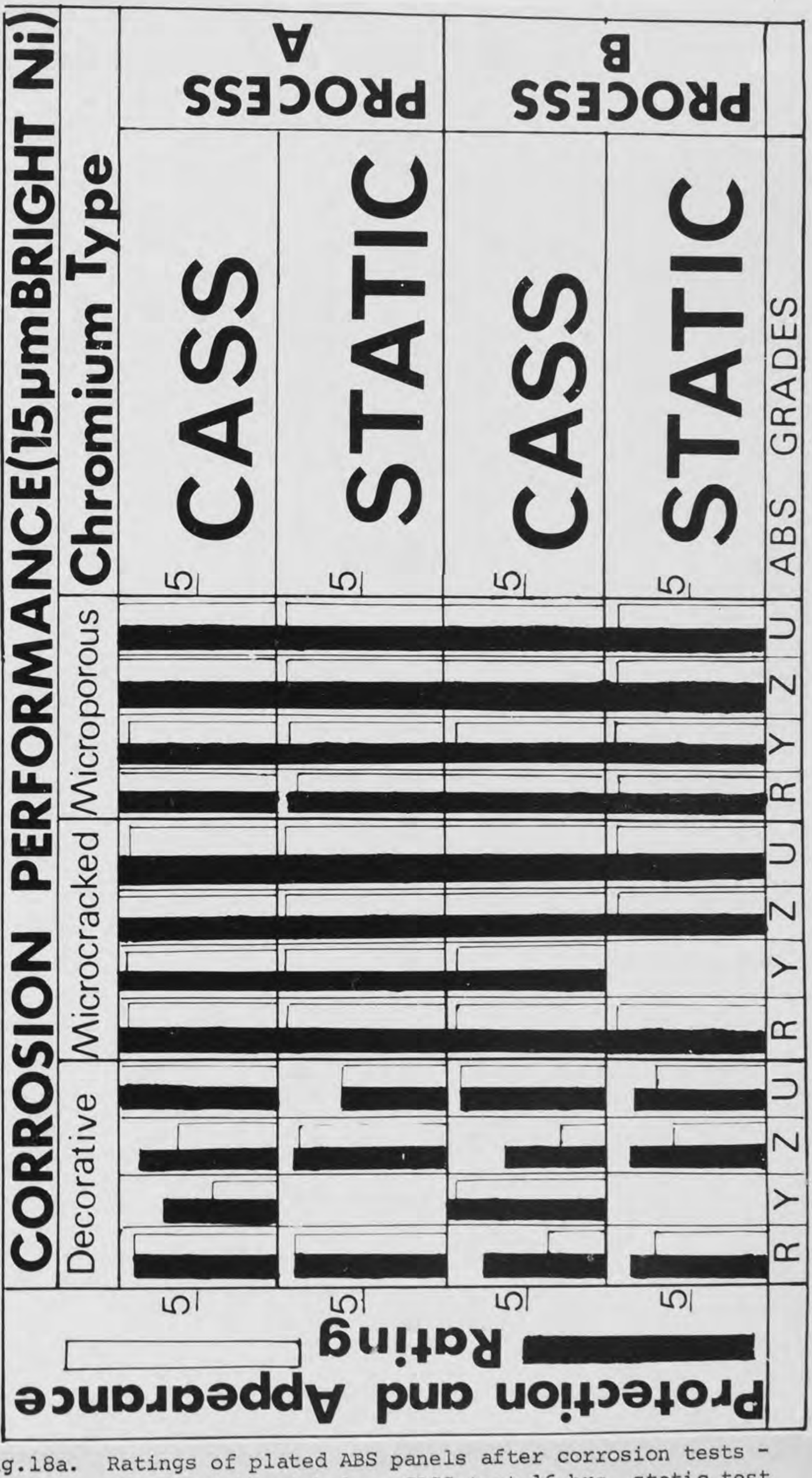


Fig.18a. Ratings of plated ABS panels after corrosion tests - 15 µm bright nickel. CASS test 16 hrs, static test 8 months exposure from 1.8.73 to 31.3.74. Microporous chromium 0.25 µm thick.

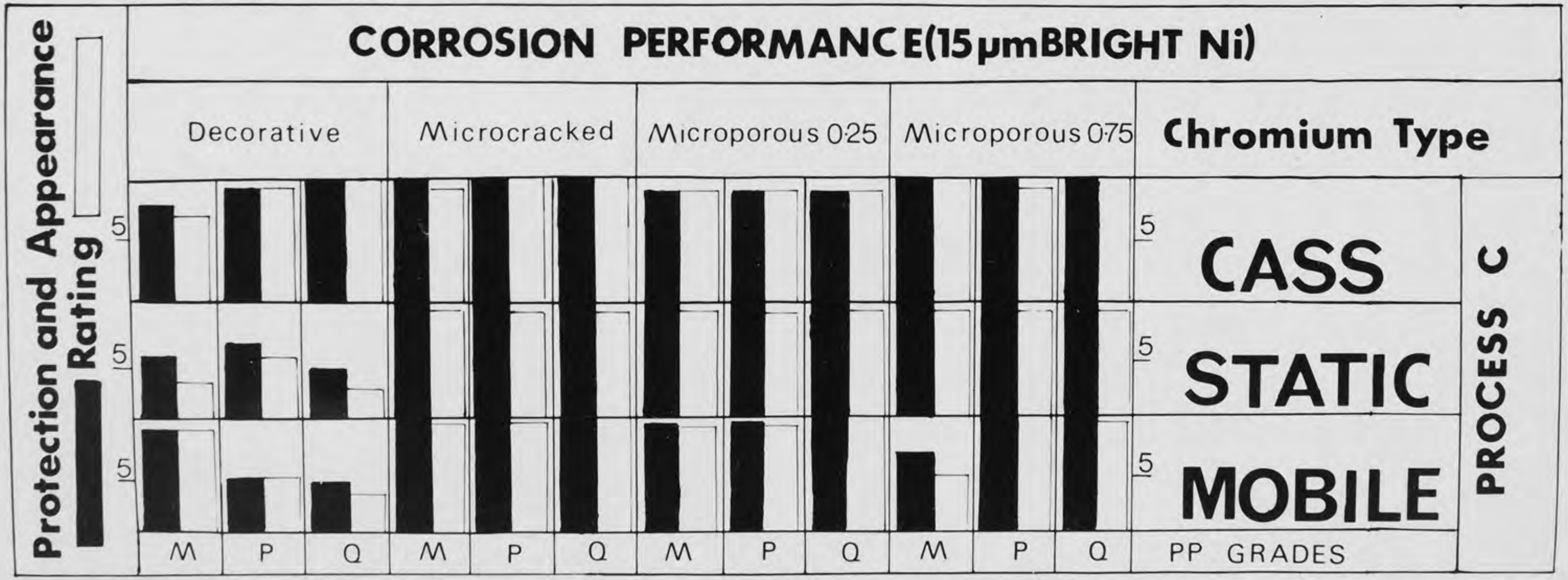


Fig.18b. Ratings of plated polypropylene panels after corrosion tests - 15 µm bright nickel, CASS test 16 hrs, outdoor tests 8 months exposure from 1.8.73 to 31.3.74.

two number system (77) of plated ABS and polypropylene panels after mobile and static outdoor exposure and after one 16 hr. cycle of the CASS (48) test. All test panels having bright nickel coatings 6 µm thick except polypropylene grades P and Q were exposed for 18 months from 1/10/72 to 31/3/74. All panels having 15 µm of bright nickel and polypropylene grades P and Q with a 6 µm coating were exposed 8 months from 1/8/73 to 31/3/74.

3.2.1. CASS Test.

3.2.1.1 Bright Nickel + Decorative Chromium.

This group of specimens exhibited typical corrosion failures for the coating system but blistering was not too severe. This was indicative of the relatively mild nature of the CASS test and agreed with previous findings. (43) The extent of blistering was minimised since mostly optimum etch times were used throughout. Overall pitting attack and green staining were the features observed on those specimens having 6 µm of bright nickel but little staining was evident on those having 15 µm of bright nickel. Although polypropylene grade M was moulded at two conditions (see Table 11), no significant difference in behaviour of test panels subjected to the CASS test could be detected. This may have been due to the limited amount of corrosion that had occurred. Polypropylene grade N was not evaluated in this test.

3.2.1.2 Bright Nickel + Microcracked Chromium.

Although a coating of only 6 µm of bright nickel was plated onto most of the ABS and polypropylene samples very little deterioration occurred during the test. There was no discernable difference between samples having 6 µm and 15 µm bright of nickel. In the case of all grades of ABS and polypropylene substrates, the only deterioration in coating appearance was due to a greenish white bloom which could be removed easily by mild cleaning. In no instance was brown staining observed. This was in contrast to the results of static outdoor exposure where the staining of microdiscontinuous chromium systems was caused by copper corrosion products (46)

3.2.1.3 Bright Nickel + Microporous Chromium (0.25µm).

The performance of this coating system was similar to that of microcracked chromium. The features exhibited by both ABS and polypropylene specimens were fine micro-pits and consequently some surface dulling.

3.2.1.4 Bright Nickel + Microporous Chromium (0.75 µm)

Very fine edge cracks developed on most of the specimens for both nickel thicknesses. In the most severe case, (plastics W/process B), the cracks emanated for 1.2 cm. from the top jig point area. Similar features, although more severe were noted on specimens after outdoor static exposure.

3.2.2 OUTDOOR STATIC EXPOSURE.

3.2.2.1 Bright Nickel + Decorative Chromium.

Blistering occurred on both ABS and polypropylene substrates due to penetration of the multilayer coatings and preferential dissolution of the electroless nickel layers. The degree of blistering depended on the grade of

ABS or polypropylene and, in the case of ABS, on the processing sequence. Process A resulted in less blistering than process B as illustrated by the photographs shown in Fig.19. Since more appropriate etch times were used in this programme for ABS, the amount of blistering in the case of grade Y, was negligible compared to the behaviour observed in the first phase of corrosion tests, when only a compromise etch time was used. The performance of grade Y when having an electroless copper underlayer was superior to similar specimens but having electroless nickel underlayers. The extent of blistering was less, even on those specimens having a 7 min. etch. This indicated the importance of choosing the correct electroless metal deposit as well as sufficient etch times. Polypropylene grade N was very susceptible to blistering but this was not a recommended plating grade. The ease with which polypropylene grades M and N could be etched was found to be influenced to some extent by the moulding conditions; this variable was not investigated for grades P and Q. At a given etch time the grades of polypropylene were etched more severely if moulded at condition (ii), see Table 11, as shown by the scanning electronmicrographs in Fig.20. Consequently, blistering was less likely to occur when samples were moulded at condition (ii).

3.2.2.2 Bright Nickel + Microcracked Chromium.

A persistent greenish brown stain developed after about 7 weeks exposure on this coating with either ABS

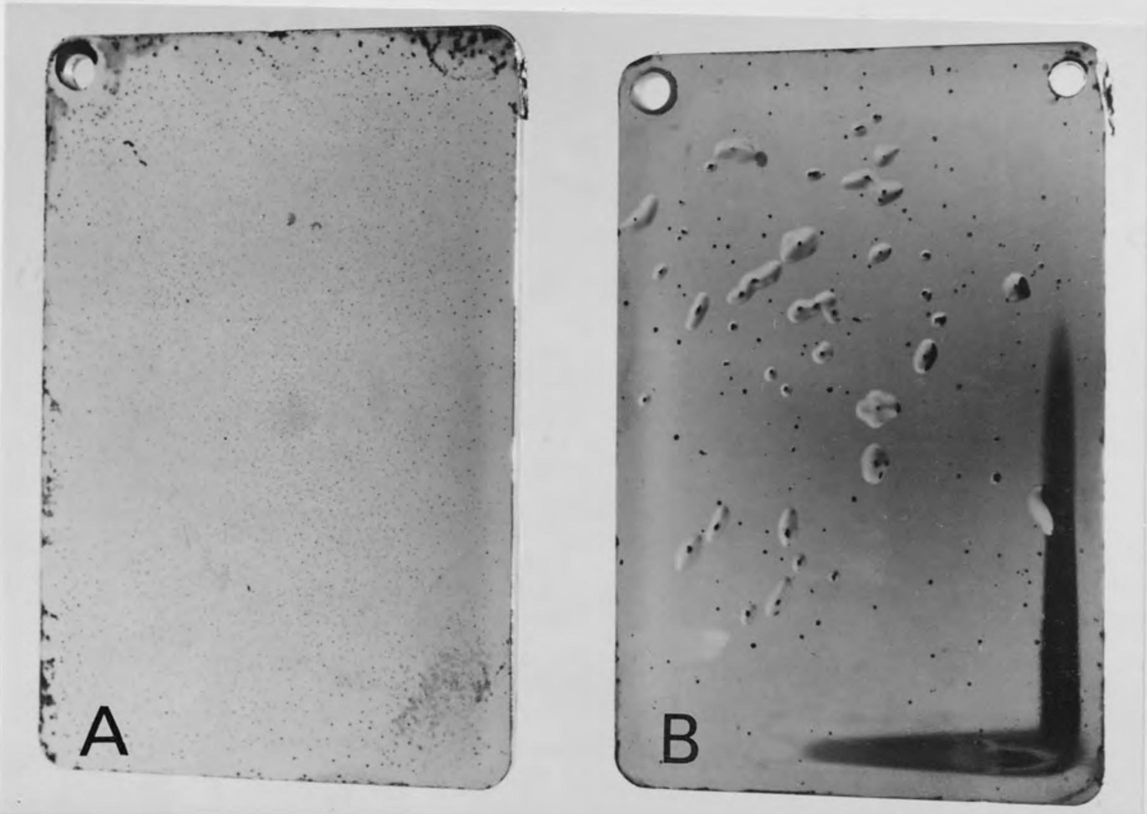


Fig.19. Panels of ABS plastics grade V, plated with 6 µm bright nickel + 0.25 µm decorative chromium, after 18 months static exposure. More severe blister formation is apparent after the use of process sequence B.
Magnification x 1.

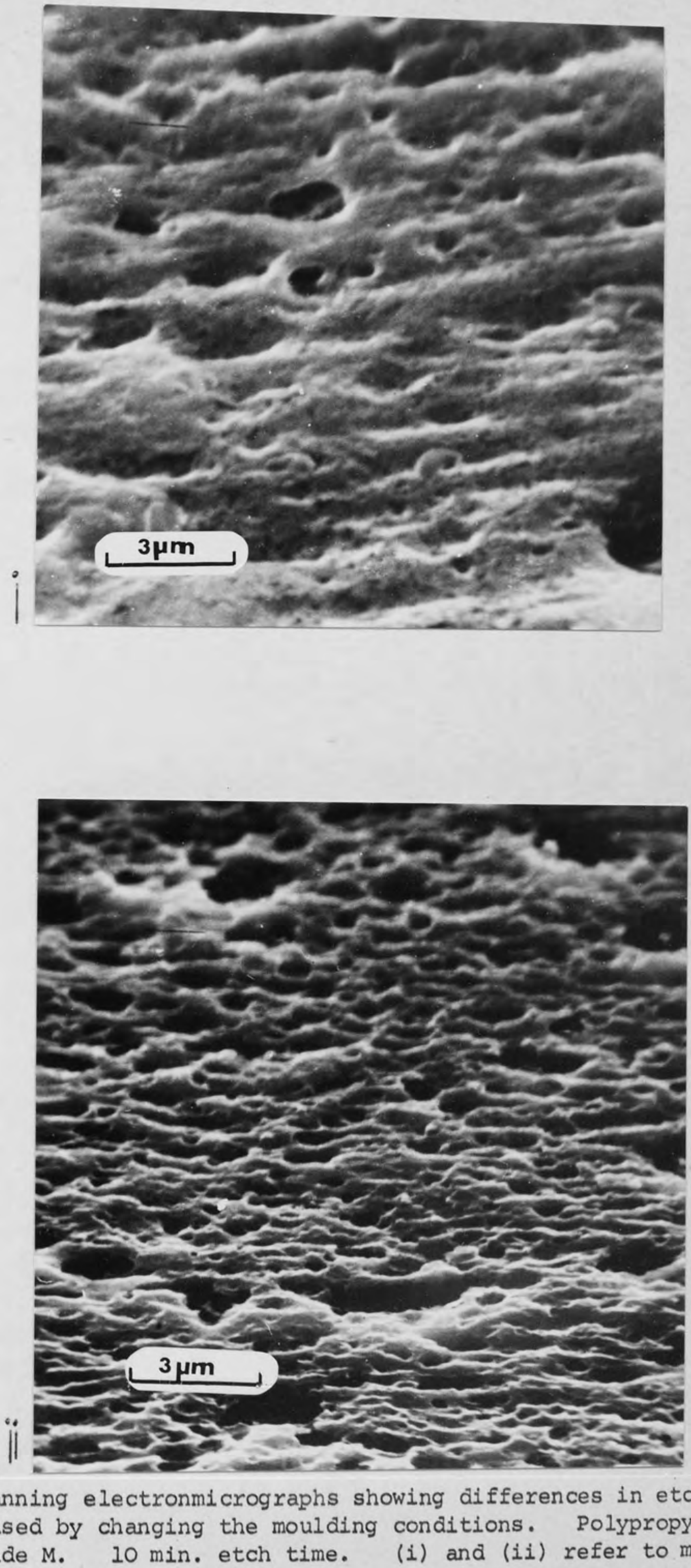


Fig.20. Scanning electronmicrographs showing differences in etching caused by changing the moulding conditions. Polypropylene grade M. 10 min. etch time. (i) and (ii) refer to moulding conditions, see Table II.

or polypropylene substrates having the 6 µm thick nickel layer. The samples having the thicker nickel layer were not stained after this period of exposure. Examination of cross-sections revealed that brown staining was an indication of attack of the copper layer. A SEM fitted with an energy dispersive X-ray analysis attachment was used to identify the elements present in the stain. Appreciable quantities of copper, sulphur and chlorine were detected. After removal of the stain the specimens appeared bloomed but otherwise the coatings had performed quite well. There was little evidence of blister formation even for the 6 µm nickel coatings on the most unfavourable substrates and even when the etch time was inadequate, for example polypropylene grade N etched for 5 min. Specimena are still under test in order to observe whether blistering will occur on prolonged exposure.

3.2.2.3 Bright Nickel + Microporous Chromium (0.25 µm)

In general the performance of this coating system was good and once again comparable to the microcracked chromium system. The greenish brown stain appeared after the same exposure period (7 weeks) in the case of the thinner nickel samples. There was a greater tendency for blister formation when ABS of all grades was processed using sequence B than when using sequence A. Polypropylene type N, particularly when moulded using condition (i) (see Table 11) was more susceptible to blistering than any of the other grades of polypropylene plated.

3.2.2.4 Bright Nickel + Microporous Chromium (0.75 µm)

This coating system provided some interesting features in that quite severe edge cracking occurred on most grades of ABS and polypropylene. The greenish brown staining was again in evidence on those specimens having only 6 µm of bright nickel. Cracks associated with corrosion sites were also observed.

3.2.3 OUTDOOR MOBILE EXPOSURE.

3.2.3.1 Bright Nickel + Decorative Chromium.

The features observed on plated ABS and polypropylene specimens subjected to this test included fine pitting, blooming, severe attack with blistering and impact damage caused by flying debris from the road. Again ABS specimens processed using sequence A performed better than those in B. Polypropylene grade N was most unsatisfactory in that the coating frequently blistered over the whole of the specimen surface.

3.2.3.2 Bright Nickel + Microcracked Chromium.

Slight brown staining, blooming, blistering and impact damage were noted on ABS and polypropylene specimens plated with this coating system. Most of the ABS specimens performed very well but polypropylene grades M and N plated with 6 µm of nickel produced disappointing results.

Large blisters were formed, mostly associated with corrosion sites that appeared to have been initiated by impact damage. Polypropylene grades P and Q, both nickel thicknesses still had a high rating after 8 months exposure.

3.2.3.3 Bright Nickel + Microporous Chromium (0.25 µm)

Once again the behaviour of this system was almost identical with that of bright nickel + microcracked chromium.

3.2.3.4 Bright Nickel + Microporous Chromium (0.75 µm)

The severe edge cracking which was so prevalent on static outdoor exposure was not so apparent on mobile exposure. The extent of edge cracking was similar to that experienced in the CASS test. A typical corrosion site is shown in Fig.21; the crack has propogated around the original corrosion site.

3.3 CORROSION TESTS UP TO 1/9/74.

Very little change had taken place in the specimens after a further period of exposure. The severe brown staining was however, less pronounced and specimens including those having decorative chromium overlays with 15 µm of bright nickel still exhibited good performance. The further period of exposure from 31/3/74 to 1/9/74 included the relatively milder weather of Spring and Summer, and this could be an important factor in the degree of corrosion taking place on the specimens.

3.4 STATISTICAL ANALYSIS OF CORROSION RESULTS.

Statistical analysis of the corrosion results was carried out by running computer programs designed to show which variables were of significance in each test. The results were assessed using two techniques namely the analysis of variance and regression analysis. The former technique gives an indication of which variables exert most influence on the corrosion behaviour whilst the second can be used to assess the relative severity

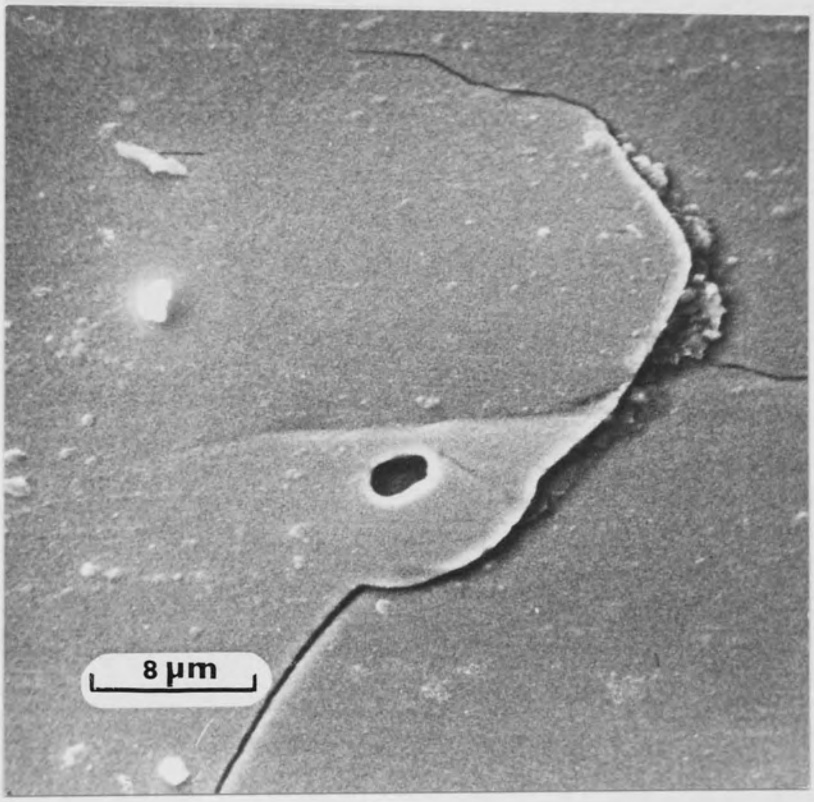


Fig.21. Cracks developed in a 6 µm bright nickel + 0.75 µm microporous chromium coating after mobile testing. Polypropylene grade N. Moulding condition (i) - see Table II. 5 min. etch time.

of the various tests used.

The results are presented in two sections ; the first section relates to the pilot corrosion programme and the second relates to the main programme.

Since the rating values of the specimens on 1/9/74 were virtually identical to those obtained on 31/3/74 it was considered that a statistical analysis on the 'final ratings' was not worthwhile.

3.4 STATISTICAL ANALYSIS ON FIRST PHASE OF CORROSION WORK - (Specimens on Exposure 1/1/72 to 1/10/72.

Computer programs for the analysis of variance yielded the information listed in Table V11.

3.4.1 Protection Ratings.

Chromium type and nickel thickness were the variables shown to have the greatest influence on protection ratings. Their effects on corrosion performance are obvious and require no further discussion. Processing sequence did not appear either as an individual variable of significance or as a first order interaction with other variables. Plastics type occurred as a significant variable in the most severe environment and as a significant first order interaction in the static and mobile tests.

3.4.2 Appearance Ratings.

Appearance rating was shown to be influenced primarily by chromium type but process sequence was found to be of significance on CASS testing and after static outdoor exposure. It had been observed t specimens plated using process B tended to blister more than those plated using process A, particularly on

TABLE VIII. SUMMARY OF VARIABLES AFFECTING PERFORMANCE ON CORROSION TESTING

Type of Test	*PROTECTION*				*APPEARANCE*			
	Significant Variables	*Per cent Significance level*	*Significant 1st Order Interactions*	*Per cent Significance level*	*Significant Variables*	*Per cent Significance level*	*Significant 1st Order Interactions*	*Per cent Significance level*
CASS	Chromium type	0·1	Chromium type with chromium thickness	5	Chromium type Processing sequence	0·1 1		
Static Outdoor Exposure	Chromium type Nickel thickness Plastics type	0·1 1 1	Plastics type with chromium type Nickel thickness with chromium type	1 1	Chromium type Processing sequence Plastics type	0·1 0·1 1	Processing sequence with chromium type Processing sequence with plastics type Plastics type with chromium type Plastics type with nickel thickness	0·1 1 1 1
Mobile Outdoor Exposure	Chromium type Nickel thickness	0·1 1	Plastics type with nickel thickness Nickel thickness with chromium type	5 5	Chromium type Nickel thickness	0·1 1	Nickel thickness with chromium type	5

static outdoor exposure. The reasons for the superior performance of process sequence A were the more noble nature of the electroless nickel and the more severe etching which made it more difficult for the electroless nickel to be dissolved away from a rough plastics/metal interface(43). Plastics type was found to be significant at the 1% level after static exposure and to be involved in some first order interactions after that test. In general, process sequence and plastics type were shown to be of greater significance with respect to appearance ratings than to protection ratings. For the coating/substrate systems concerned a reduction in appearance rating can be associated mainly with the extent of blister formation.

3.4.3 INFLUENCE OF ABS PRE-ELECTROPLATING PROCESS SEQUENCE ON CORROSION BEHAVIOUR.

Standard programs for correlation and regression analysis were used to assess the influence of the pre-electroplating sequences. The information was processed so that all coating systems on the three grades of ABS were considered. The equations quoted in Table VIII relate the behaviour, in a particular test, using sequence A to that using sequence B. By substituting specimen values in the equations concerned with protection rating it is apparent that processing sequence has no significant effect. This is not surprising since the protection value is dependant primarily on the coating system, it provides only an assessment of the number and size of corrosion pits that penetrate to the substrate.

Table VIII . INFLUENCE OF PRE-ELECTROPLATING PROCESS SEQUENCE ON CORROSION BEHAVIOUR

	Rating numbers		*Equation* $y = a + bx$	*Calculated value of r, the correlation coefficient*	*Level of significance, %*	*Superiority of process sequence*
	x	*y*				
PROTECTION	*CASS* A	*CASS* B	$y = 0{\cdot}5 + 0{\cdot}9x$	0·93	$> 0{\cdot}1$	A slightly superior to B
	Mobile A	Mobile B	$y = 1{\cdot}0 + 0{\cdot}9x$	0·85	$> 0{\cdot}1$	B slightly superior to A
	Static A	Static B	$y = 0{\cdot}6 + 0{\cdot}9x$	0·96	$> 0{\cdot}1$	A slightly superior to B
APPEARANCE	*CASS* A	*CASS* B	$y = -2{\cdot}2 + 1{\cdot}2x$	0·78	$> 0{\cdot}1$	A markedly superior to B
	Mobile A	Mobile B	$y = -1{\cdot}1 + 1{\cdot}0x$	0·81	$> 0{\cdot}1$	A markedly superior to B
	Static A	Static B	$y = -2{\cdot}3 + 1{\cdot}2x$	0·92	$> 0{\cdot}1$	A markedly superior to B

All coating systems were considered in this analysis.
34 degrees of freedom.
Value of r at 0·1% significance level equals 0·55.
x represents process sequence A results.
y represents predicted process sequence B results.

In general, when values are substituted in the equations concerned with appearance rating, sequence A is shown to result in significantly better performance than sequence B. As discussed previously, blister formation was more in evidence when process B was employed and since appearance rating evaluates deterioration due to defects such as blisters this is the reason why process B was shown to be inferior by this analysis.

3.4.4 RELATIONSHIP BETWEEN RESULTS OBTAINED IN CORROSION TESTS.

Having assessed a relatively large number of specimens after corrosion testing, it was decided to use statistical techniques to determine whether any relationships existed between the results obtained in the three corrosion tests. For example, it would be most useful if relationships could be evaluated between the CASS test and outdoor exposure since then an accelerated test could be used to predict the results of a lengthy outdoor exposure programme. However, it must be emphasised that any relationships derived are dependant on the actual information processed and so will be dependant on variables such as severity of the weather conditions during the exposure period. Nevertheless if relationships can be shown to exist it is likely that these can be used with reasonable confidence if similar experimental conditions prevail.

Correlation and regression analysis of the data was carried out and the resulting information is summarised in Table IX. The data was split in several ways

TABLE [illegible] RELATIONSHIP BETWEEN *CASS* AND OUTDOOR CORROSION TEST RESULTS

	Coating system	Rating number		Equation $y = a + bx$	Degrees of freedom	Calculated value of r, the correlation coefficient	Level of significance	Value of r (from tables) at significance level quoted	Severity of tests
		x	y						
PROTECTION	All systems	*CASS* A	Mobile A	$y = 0{\cdot}7 + 0{\cdot}9x$	34	0·83	> 0·1	0·55	*CASS* more severe than Mobile
	All systems	*CASS* B	Mobile B	$y = 0{\cdot}6 + 0{\cdot}9x$	34	0·79	> 0·1	0·55	Mobile ,, ,, *CASS*
	All systems	*CASS* A	Static A	$y = -1{\cdot}5 + 1{\cdot}1x$	34	0·95	> 0·1	0·55	Static ,, ,, *CASS*
	All systems	*CASS* B	Static B	$y = -0{\cdot}9 + 1{\cdot}0x$	34	0·94	> 0·1	0·55	Static ,, ,, *CASS*
	All 12 µm Ni systems	*CASS* A	Mobile A	$y = -0{\cdot}1 + 1{\cdot}0x$	16	0·92	> 0·1	0·71	Mobile ,, ,, *CASS*
	All 12 µm Ni systems	*CASS* B	Mobile B	$y = 0{\cdot}3 + 0{\cdot}9x$	16	0·80	> 0·1	0·71	Mobile ,, ,, *CASS*
	All 12 µm Ni systems	*CASS* A	Static A	$y = -1{\cdot}0 + 1{\cdot}1x$	16	0·94	> 0·1	0·71	Static ,, ,, *CASS*
	All 12 µm Ni systems	*CASS* B	Static B	$y = -0{\cdot}7 + 1{\cdot}0x$	16	0·90	> 0·1	0·71	Static ,, ,, *CASS*
	All 6 µm Ni systems	*CASS* A	Mobile A	$y = 1{\cdot}1 + 0{\cdot}8x$	16	0·75	> 0·1	0·71	Mobile ,, ,, *CASS*
	All 6 µm Ni systems	*CASS* B	Mobile B	$y = 0{\cdot}8 + 0{\cdot}8x$	16	0·80	> 0·1	0·71	Mobile ,, ,, *CASS*
	All 6 µm Ni systems	*CASS* A	Static A	$y = -1{\cdot}8 + 1{\cdot}1x$	16	0·97	> 0·1	0·71	Static ,, ,, *CASS*
	All 6 µm Ni systems	*CASS* B	Static B	$y = -1{\cdot}1 + 1{\cdot}0x$	16	0·97	> 0·1	0·71	Static ,, ,, *CASS*
APPEARANCE	All systems	*CASS* A	Mobile A	$y = -0{\cdot}2 + 0{\cdot}9x$	34	0·80	> 0·1	0·55	Mobile more severe than *CASS*
	All systems	*CASS* B	Mobile B	$y = 2{\cdot}7 + 0{\cdot}5x$	34	0·51	> 1	0·45	Mobile ,, ,, *CASS*
	All systems	*CASS* A	Static A	$y = -3{\cdot}2 + 1{\cdot}3x$	34	0·93	> 0·1	0·55	Static ,, ,, *CASS*
	All systems	*CASS* B	Static B	$x = -0{\cdot}6 + 0{\cdot}9x$	34	0·79	> 0·1	0·55	Static ,, ,, *CASS*
	All 12 µm Ni systems	*CASS* A	Mobile A	$y = -0{\cdot}8 + 1{\cdot}1x$	16	0·91	> 0·1	0·71	Mobile ,, ,, *CASS*
	All 12 µm Ni systems	*CASS* B	Mobile B	$y = 2{\cdot}8 + 0{\cdot}6x$	16	0·58	2	0·54	Mobile ,, ,, *CASS*
	All 12 µm Ni systems	*CASS* A	Static A	$y = -6{\cdot}0 + 1{\cdot}5x$	16	0·96	> 0·1	0·71	Static ,, ,, *CASS*
	All 12 µm Ni systems	*CASS* B	Static B	$y = 0{\cdot}5 + 0{\cdot}8x$	16	0·69	1	0·59	Static ,, ,, *CASS*
	All 6 µm Ni systems	*CASS* A	Mobile A	$y = 0{\cdot}5 + 0{\cdot}8x$	16	0·65	1	0·59	Mobile ,, ,, *CASS*
	All 6 µm Ni systems	*CASS* B	Mobile A	$y = 2{\cdot}5 + 0{\cdot}5x$	16	0·48	5	0·47	Mobile ,, ,, *CASS*
	All 6 µm Ni systems	*CASS* A	Static A	$y = -1{\cdot}1 + 1{\cdot}0x$	16	0·96	> 0·1	0·71	Static ,, ,, *CASS*
	All 6 µm Ni systems	*CASS* B	Static B	$y = -1{\cdot}6 + 1{\cdot}0x$	16	0·89	> 0·1	0·71	Static ,, ,, *CASS*

x represents the result from the *CASS* test, using either process sequence A or B.
y represents the predicted result for either the mobile or static test, using either process sequence A or B.

in order to investigate the relationship between the various tests and to give as many pairs of results as possible for each analysis. The latter ensured a high value for ν , the number of degrees of freedom and hence a more accurate and meaningful correlation if this existed. The validity of a particular relationship is reported in terms of level of significance.

Consideration must be given to the confidence with which these equations can be used. Normally protection and appearance values of less than 7 are of little practical interest. Since most of the values used to compute the above equations were in the range 5 to 10 it can be assumed that their accuracy will be good for the practical range of rating values. However, the accuracy of the equations is limited because rating values were assessed in increments of half a unit. The order of severity of the three tests indicated by the analysis showed the static test to be the most severe while the CASS test was the least severe.

3.5 STATISTICAL ANALYSIS ON MAIN PHASE OF CORROSION WORK: SPECIMENS ON EXPOSURE 1/10/72 to 31/3/74 .

The results are summarised in Tables X and XI.

3.5.1 Analysis of Variance Test.

3.5.1.1 a) ABS substrates - 6 µm bright nickel coatings.

The importance of chromium type in affecting both protection and appearance ratings was indicated. Furthermore, plastics type was shown to be of significance in influencing both ratings. The role of plastics

TABLE X. SUMMARY OF VARIABLES AFFECTING PERFORMANCE ON CORROSION TESTING - 6 µm BRIGHT NICKEL

	Type of Test	PROTECTION				APPEARANCE			
		Significant Variables	Significance Level %	Significant First Order Interactions	Significance Level %	Significant Variables	Significance Level %	Significant First Order Interactions	Significance Level %
	CASS	Chromium Type Plastics Type	>1.0 >1.0			Chromium Type Plastics Type	>1.0 1.0		
	Static	Chromium Type	>1.0			Processing sequence Chromium Type Plastics Type	>1.0 >1.0 1.0	Processing sequence with Chromium Type	1.0
	Mobile	Chromium Type Plastics Type	>1.0 1.0	Chromium Type with Plastics Type	1.0	Processing Sequence Chromium Type Plastics Type	>1.0 >1.0 1.0		
	CASS	Chromium Type	5.0			Chromium Type	5.0		
	Static	Chromium Type	>1.0			Chromium Type	>1.0		
	Mobile	Chromium Type	>1.0	Plastics Type with Moulding conditions Moulding conditions with Etch time Plastics Type with Etch time Moulding conditions with Chromium Type	>1.0 >1.0 1.0 1.0	Chromium Type Plastics Type	1.0 5.0		

> Indicates that the level of significance was better than the figure quoted.

TABLE XI. SUMMARY OF VARIABLES AFFECTING PERFORMANCE ON CORROSION TESTING 15 µm BRIGHT NICKEL. (RESULTS UP TO 31/3/74)

	Type of Test	PROTECTION		APPEARANCE	
		Significant Variables	Significance Level %	Significant Variables	Significance Level %
ABS	CASS	Chromium Type	>1.0	Chromium Type	>1.0
		Processing Sequence	>1.0	Processing Sequence	1.0
		Plastics Grade	1.0	Plastics Grade	1.0
	Static	Chromium Type	>1.0	Chromium Type	>1.0

All plated polypropylene panels still had a high rating after 8 months exposure outdoors and after 1 cycle Cass. Consequently a worthwhile statistical analysis could not be carried out.

Analysis of ABS results relates only to Grades R, Y, Z and U.

> indicates that the level of significance was better than the figure quoted.

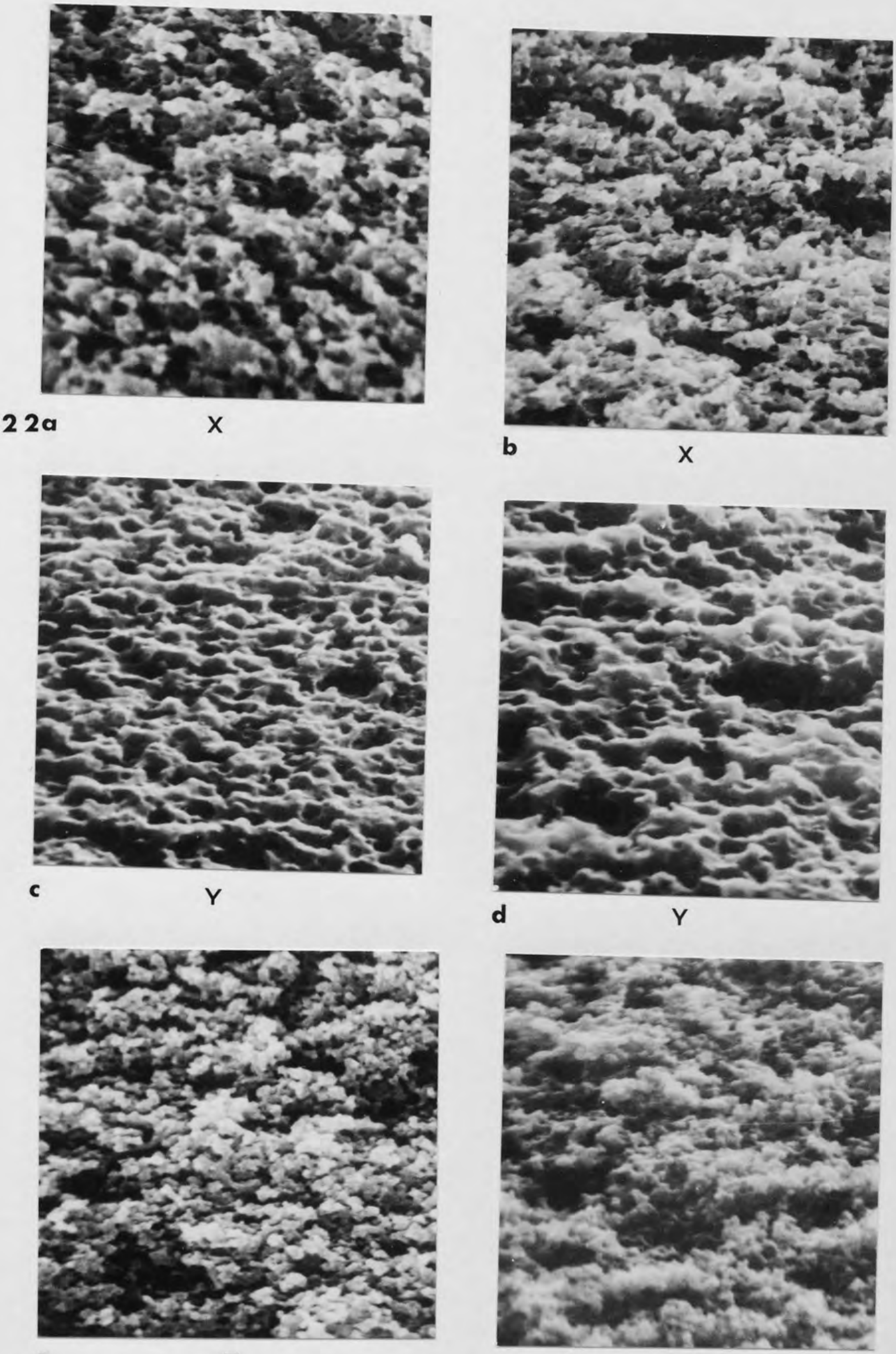
type in affecting protection ratings is probably associated to some extent with its effects on peel adhesion and blister formation. If a low peel adhesion value occurs then it is likely that the coating will lift so that subsequently cracking will result and corrosive environments will have access to the underlying layers. Both plastics type and processing sequence were shown to be significant with regard to appearance ratings. This can be explained in terms of the relative severity of the etching on a given plastics type resulting from the use of process sequence A compared with that given by B for a similar etch time. This effect is illustrated in Fig.22. Wiggle et al (43) have noted that blister size may be minimised if the plastics substrate is well etched.

3.5.1.2 ABS substrates - 15 μm bright nickel coatings.

In this limited programme the mobile outdoor test was omitted and grades, R,Y,Z and U only were evaluated. Chromium type was indicated as being of significance, in both the CASS and static outdoor tests, in affecting protection and appearance ratings.

3.5.1.3 Polypropylene substrates - 6 μm bright nickel coatings.

As anticipated, chromium type was again shown to be significant in affecting protection and appearance ratings in all tests. First order interactions of moulding conditions, etch time and grade of polypropylene were indicated as being of significance in affecting protection ratings on mobile testing. The same effects were not detected at the end of the exposure periods in the CASS and static outdoor tests.


2 2a
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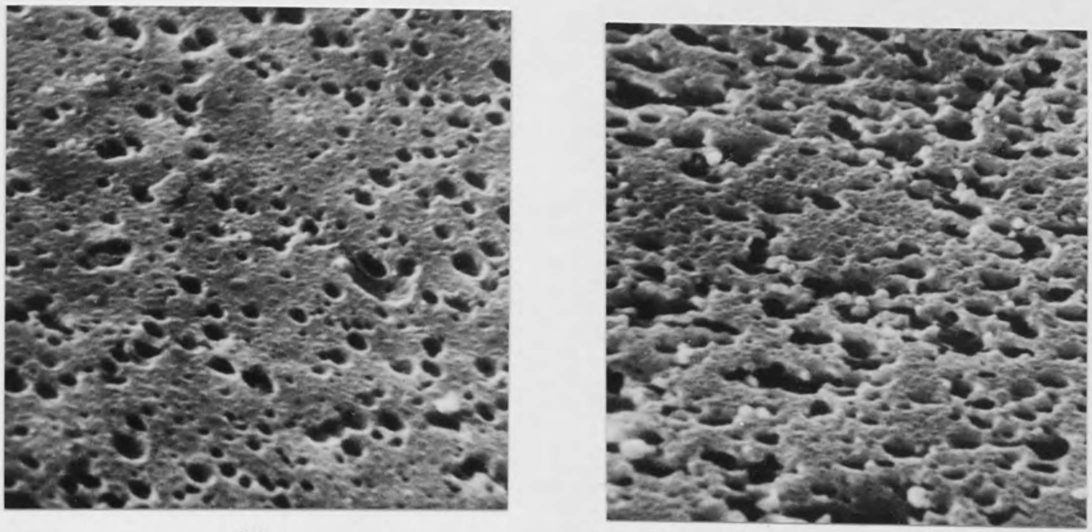


g Y

h Y

Fig.22. Degree of etching of ABS grades X, Y and Z after 7 and 21 min. treatment.
Magnification x 6000

The CASS test was relatively mild and all specimen groups had similar ratings hence discrimination between specimens within particular groups was not possible. On analysis of results at earlier stages in the static outdoor test, moulding conditions and etch time were shown to be significant in influencing protection ratings. The static test is the most severe of the corrosion tests employed and the relative differences in coating performance were greater after a particular time of exposure than at the end of the period. As corrosion proceeded the rating values allotted to the inferior coatings could not continue to decrease very much but the more satisfactory ones could so that their rating values became more similar. The mobile test was of intermediate severity between the CASS and static tests and hence at the end of the exposure period it did show certain variables to be of significance in influencing performance.

3.5.1.4 Polypropylene substrates - 15 μm bright nickel coatings.

All four grades of polypropylene were exposed to the three corrosion tests but at the end of this exposure period corrosion was not sufficiently advanced to indicate performance trends.

3.5.2 INFLUENCE OF PRE-ELECTROPLATING PROCESS SEQUENCE ON CORROSION BEHAVIOUR.

Correlation and regression analysis was carried out to investigate whether the ABS process sequence had exerted any influence on the corrosion behaviour.

The information obtained is given in Table X11. The overall trend indicated by the analysis was that once again the use of process A would lead to a better performance in corrosion testing with regard to appearance ratings than process B. The process sequence was not detected as influencing the protection ratings and as such agreed with the findings in the pilot programme.

3.5.3 RELATIONSHIP BETWEEN TESTS OBTAINED IN MAIN PROGRAMME CORROSION TESTS.

3.5.3.1 ABS substrates.

The equations obtained by correlation and regression analysis are listed in Table X111. For this exposure programme the order of severity of test was static - mobile - CASS, static being the most severe. The points raised in the previous section dealing with the validity and use of these equations remain pertinent here. However, this analysis proved useful in assessing the severity of the tests when large numbers of specimens had been tested.

3.5.3.2 Polypropylene substrates.

The statistical analysis on the performance of polypropylene grades in various tests showed that there was little evidence of any association between the tests. The analysis failed to yield a sufficiently high enough value of r, the coefficient of correlation, for the degrees of freedom available.

TABLE XII. INFLUENCE OF PRE-ELECTROPLATING PROCESS SEQUENCE ON CORROSION BEHAVIOUR.
ABS GRADES R, Y, Z, S, T, U, V AND W, 6μm BRIGHT NICKEL SYSTEMS

	Rating Number		Equation $y = a + bx$	Calculated value of r, the correlation coefficient	Level of Significance %	Superiority of Process Sequence
	x	y				
PROTECTION	CASS A	CASS B	$y = 6.11 + 0.40x$	0.59	> 1.0	B slightly superior to A
	STATIC A	STATIC B	$y = -2.00 + 1.20x$	0.65	> 0.1	A slightly superior to B
	MOBILE A	MOBILE B	$y = 0.71 + 0.90x$	0.80	> 0.1	A slightly superior to B
APPEARANCE	CASS A	CASS B	$y = 3.10 + 0.68x$	0.76	> 0.1	B slightly superior to A
	STATIC A	STATIC B	$y = 0.13 + 0.70x$	0.41	> 5.0	A markedly superior to B
	MOBILE A	MOBILE B	$y = 0.13 + 0.80x$	0.55	> 1.0	A markedly superior to B

30 degrees of freedom

x represents process sequence A results

y represents predicted process sequence results

TABLE XIII. RELATIONSHIP BETWEEN CASS AND OUTDOOR TESTS ON ABS SUBSTRATES - 6 μm BRIGHT NICKEL SYSTEMS

		Rating Number		Equation $y = a + bx$	Degrees of Freedom, ν	Calculated value of r, the correlation coefficient	Level of Significance %	Severity of tests
		x	y					
ABS *	PROTECTION	CASS A	STATIC A	$y = 2.80 + 0.62x$	30	0.71	> 0.1	Static more severe than CASS
		CASS B	STATIC B	$y = -8.10 + 1.67x$	30	0.69	> 0.1	Static more severe than CASS
		CASS A	MOBILE A	$y = 3.53 + 0.51x$	30	0.36	5.0	Tests of similar severity
		CASS B	MOBILE B	$y = 1.20 + 0.69x$	30	0.29	10.0	Mobile more severe than CASS
	APPEARANCE	CASS A	STATIC A	$y = 4.43 + 0.35x$	30	0.40	1.0	Tests of similar severity
		CASS B	STATIC B	$y = 1.03 + 0.43x$	30	0.28	10.0	Static more severe than CASS
		CASS A	MOBILE A	$y = 3.09 + 0.51x$	30	0.39	5.0	Tests of similar severity
		CASS B	MOBILE B	$y = 1.20 + 0.78x$	30	0.39	5.0	Mobile more severe than CASS

A similar analysis on polypropylene did not give sufficiently high enough values for r to justify that there was any association between the CASS and outdoor tests.

*ABS grades R, Y, Z, S, T, U, V, and W considered.

x represents CASS test result
y represents predicted outdoor exposure results

3.6 ELECTRODE POTENTIAL DETERMINATION

The open circuit potentials of the relevant electrodeposits and electroless deposits, determined in acetic acid salt spray and CASS solutions, are listed in Table XIV while the results of anode potential determinations are shown in Figs. 23 to 26. The most noticable feature of these results was that the two electroless nickel deposits were much less noble than all the electrodeposits. They were also considerably less noble than the electroless copper deposit. The order of nobility of the deposits was more or less the same in both electrolytes when using either air or nitrogen agitation but certain anomalies were observed. In acetic acid salt spray solution electroless nickel from process A (6.35% P) was found to be more noble than the electroless nickel from process B (6.72%P) but in the CASS solution when using air agitation, their relative electrochemical activities were reversed on application of a polarising voltage. This was almost certainly due to the galvanic deposition of copper on to the surface of the electroless nickels. The formation of a copper coloured film could be detected easily with the naked eye and the more base the specimen immersed in the CASS solution the more readily the galvanic reaction took place. The anode potential value obtained could be influenced by the amount of copper deposited on the specimen surface and so spurious results due to this 'mixed surface' effect were recorded. Another example of the problems encountered when using the CASS solution is highlighted by the results shown in Table XIV and Fig.26 for the behaviour of bright nickel when employing

TABLE XIV. OPEN CIRCUIT POTENTIALS

DEPOSIT	OPEN CIRCUIT POTENTIAL mV v S C E			
	Acetic Salt Spray Solution		CASS Solution	
	Air agitation	Nitrogen agitation	Air agitation	Nitrogen agitation
Bright Copper	- 252	- 248	- 158	- 172
Bright Nickel	- 265	- 263	- 178	- 267* - 146*
Special Nickel containing particles	- 250	- 270	- 175	- 192
Electroless Nickel A	- 370	- 418	- 400	- 390
Electroless Nickel B	- 475	- 490	- 422	- 401
Electroless Copper	- 258	- 272		

* Two ranges were obtained in this instance, see Fig. 26, and Page 124

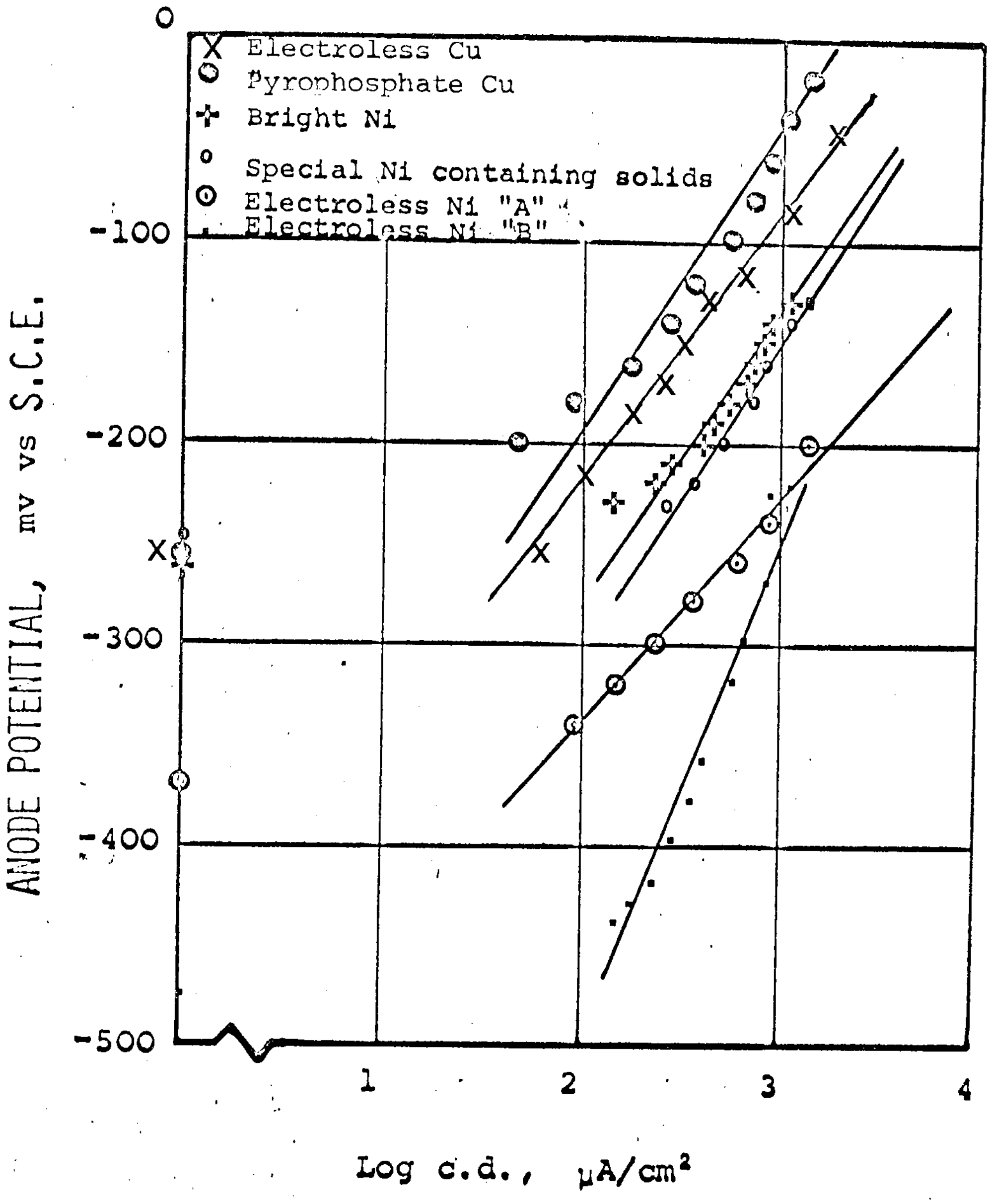


Fig.23. Relationship between applied current density and anode potential for the relevant electroless and electrodeposits. Acetic acid salt spray solution, pH 3.2, air agitation, 4 mℓ/s.

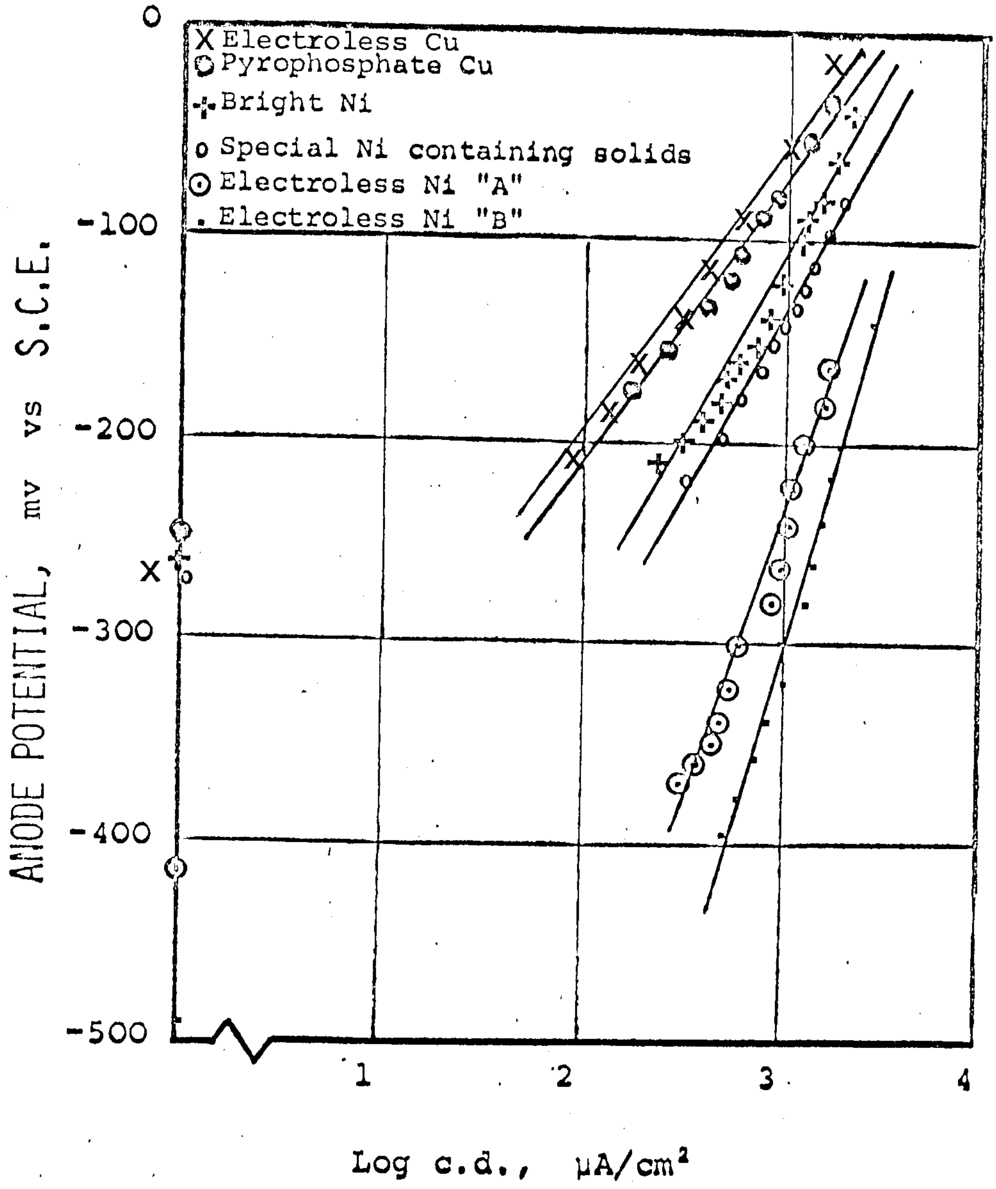


Fig.24. Relationship between applied current density and anode potential for the relevant electroless and electrodeposits. Acetic acid salt spray solution, pH 3.2, nitrogen agitation, 4 mℓ/s.

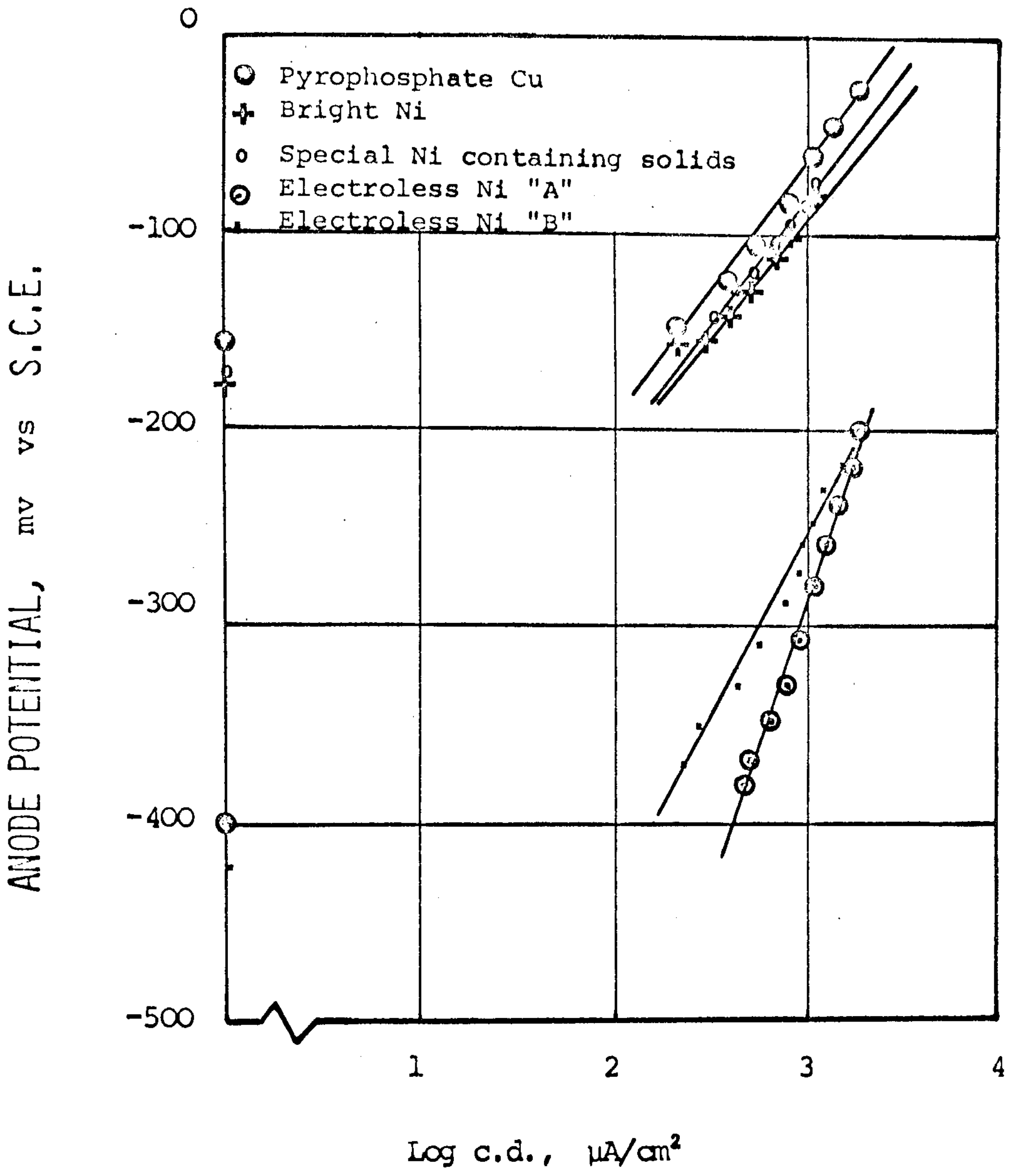


Fig.25. Relationship between applied current density and anode potential for the relevant electroless and electrodeposits. CASS solution, pH 3.2, air agitation, 4 mℓ/s.

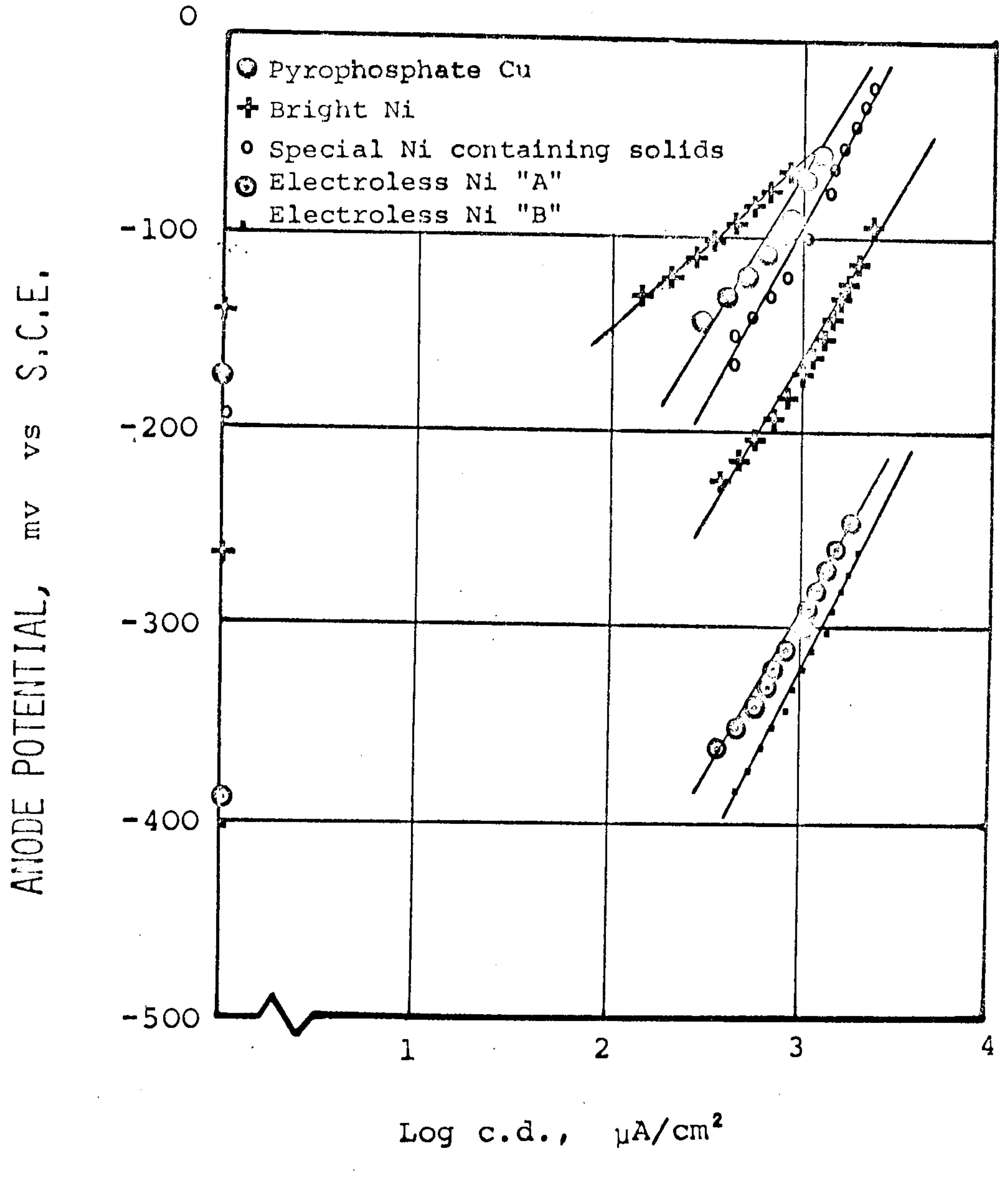


Fig.26. Relationship between applied current density and anode potential for the relevant electroless and electrodeposits. CASS solution, pH 3.2, nitrogen agitation, 4 m ℓ /s.

Note: Two ranges of values were observed for bright nickel in CASS solution when using nitrogen agitation, see Table XIV and p 124.

nitrogen agitation. Two ranges of results were obtained and it appears that intermittent passivity occurred. This effect may be similar to that reported by Dennis and Such (45) when investigating the anodic potentials of semi-bright nickels in nickel sulphate solution. The results obtained in acetic acid salt spray solution are simpler to interpret but it was considered worthwhile to undertake the study using CASS solution since this was the accelerated test used in this work. Even in the CASS solution the electroless nickel deposits were shown to be less noble than the electrodeposits.

The object of determining open circuit and anode potentials was to compare fundamental information to the behaviour of the relevant deposits when employed as layers in composite coatings subjected to outdoor exposure or CASS testing. The study of the morphology of the corrosion pits had shown that the bright copper was attacked in preference to the bright nickel once a corrosion pit had penetrated to that layer, see Fig. 15. Subsequently when the copper was attacked to such an extent that the electroless nickel layer was exposed, the latter was preferentially corroded away as shown in Fig.7 and blister formation then occurred.

The results of the anode potential study certainly suggest that preferential corrosion of the electroless nickel layers should take place. Also since electroless nickel B is less noble than type A it would appear likely that blister formation should occur more readily when plastics are processed using sequence B. This phenomenon was observed particularly after static exposure of plastics having a top coat of decorative chromium. In general, the type of process sequence had little effect on protection rating of test panels but it did have some influence in terms of appearance rating. The electroless copper deposit exhibited somewhat more noble behaviour than the electroless nickel deposits. The behaviour in corrosion testing on ABS grade Y when having an electroless copper underlayer was found to be superior to similar specimens having electroless nickel layers.

The electrode potential determinations do not provide such a straight forward explanation of the mechanism for preferential attack on the electrodeposited copper layer since the anodic potential values indicate that the copper deposit is more noble than the bright nickel. The behaviour of copper + nickel + chromium coatings on metallic substrates is a problem that has concerned a number of authors(45,47,85), in recent years and conflicting information has been reported. It has been shown that the mode of attack on the copper layer is governed by the type of chromium overlay, that is when a discontinuous type of chromium is used the anodic current density at the corrosion site is lower than when a few large defects are present in the chromium layer. However, in the present work preferential attack of copper took place in all instances, regardless of chromium type. Crouch (46) has also noted this effect on ABS having microdiscontinuous chromium overlays. Dennis and Fuggle (80) have also observed the same corrosion mechanism in the case of zinc alloy substrates. The corrosion mechanism is obviously governed by the conditions prevailing at the bottom of a corrosion pit and in the present case the bright nickel must passivate or oxidise so that the underlying copper is preferentially corroded away. This effect may well overide the differences in potentials which suggests that bright nickel should be attacked in preference to copper.

3.7 MECHANICAL TESTING.

Four grades of ABS (R,S,U and Z) and three grades of polypropylene (M, P and Q) were investigated;details of these materials are listed in Table 1 together with the etch times employed. The coating systems deposited onto the plastics were the same as those used in the main corrosion testing programme(see Table V1).

3.7.1 Tensile Tests.

The tensile strengths and ductilities exhibited by ABS and polypropylene as moulded, etched and when plated with various coatings are recorded in Tables XV and XV1. Each value represents the average of two determinations. By studying the information in Tables XV and XV1 it is apparent that although etching led to a slight decrease in U.T.S, it resulted in an increase in percentage elongation with respect to the 'as moulded' condition. The etch pits produced did not result in

TABLE XV . UTS OF ABS AND POLYPROPYLENE

			U T S - MN/m^2										
					COATING SYSTEMS								
		Type & Grade of Plastics	As moulded	Etched i) Shorter time ii) Longer time	Electroless nickel (∿0.25μm)	Bright copper (20μm)	Bright copper (20μm) + Bright nickel (6μm)	Bright copper (20μm) + Bright nickel (15μm)	Bright copper (20μm) + Bright nickel (6μm) + Decorative chromium (0.25μm)	Bright copper (20μm) + Bright nickel (15μm) + Decorative chromium (0.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microcracked chromium (1.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microporous chromium (0.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microporous chromium (0.75μm)
PROCESS A	ABS	R	47.32	i) 45.32 ii) 44.68	46.05 45.68	56.92 56.49	58.18 58.00	69.89 63.08	47.92 46.85	44.56 43.14	51.76 49.50	48.63 47.38	48.37 47.74
		S	43.98	i) 41.94 ii) 41.12	41.85 42.12	54.88 54.25	53.27 56.31	46.24 41.73	40.33 40.25	40.84 40.93	46.40 41.52	42.92 41.13	41.94 42.21
		U	45.25	i) 41.82 ii) 41.46	42.91 42.55	58.55 56.86	53.27 54.73	53.42 54.00	51.89 45.06	41.53 42.52	52.35 52.35	45.42 47.38	46.85 47.38
		Z	42.03	i) 40.21 ii) 40.30	41.12 40.12	42.77 48.42	44.71 51.58	55.01 44.29	41.13 39.26	39.16 41.81	41.41 41.94	40.33 41.76	41.94 38.82
PROCESS B	ABS	R	47.32	i) 46.50 ii) 44.22	46.59 42.67	59.90 60.53	46.85 51.31	63.43 49.17	47.74 47.74	48.28 45.27	51.85 52.65	50.60 52.20	49.44 49.97
		S	43.98	i) 43.04 ii) 42.40	42.67 42.95	55.06 49.86	49.92 46.13	58.47 46.95	41.49 46.22	45.89 41.19	46.76 56.66	46.85 45.06	51.58 42.46
		U	45.25	i) 42.03 ii) 41.94	45.13 42.40	60.98 53.89	51.76 52.74	46.51 46.07	45.06 44.44	41.46 46.83	53.63 47.38	48.19 46.40	44.71 47.47
		Z	42.03	i) 41.12 ii) 40,76	40.21 40.85	43.04 46.46	41.76 43.66	40.31 48.90	40.33 41.23	39.60 42.52	46.40 47.71	42.12 43.28	44.62 44.62
PROCESS C	POLYPROPYLENE	M	29.5	i) 27.69 ii) 27.22	27.86 26.94	36.47 31.92	40.45 33.61	38.27 27.64	32.36 24.43	27.40 27.16	37.68 39.26	37.48 34.31	28.60 29.15
		P	34.06	i) 33.74 ii) 33.74	34.01 33.55	40.80 36.41	35.25 34.27	35.97 35.44	37.24 35.07	35.08 35.08	37.72 39.26	38.79 32.39	32.75 32.71
		Q	31.46	i) 29.68 ii) 29.63	31.09 30.73	37.39 37.66	33.73 33.40	46.30 32.16	32.12 32.12	31.63 32.51	32.60 33.61	33.28 33.64	31.41 31.68

TABLE XVI. DUCTILITY OF ABS AND POLYPROPYLENE

			DUCTILITY	(PERCENTAGE	ELONGATION	ON	5 cm GAUGE	LENGTH)						
					COATING SYSTEMS									
		Type & Grade of Plastics	As moulded	Etched i) Shorter time ii) Longer time	Electroless nickel (∿0.25μm)	Bright copper (20μm)	Bright copper (20μm) + Bright nickel (6μm)	Bright copper (20μm) + Bright nickel (15μm)	Bright copper (20μm) + Bright nickel (6μm) + Decorative chromium (0.25μm)	Bright copper (20μm) + Bright nickel (15μm) + Decorative chromium (0.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microcracked chromium (1.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microporous chromium (0.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microporous chromium (0.75μm)
PROCESS A	ABS	R	11.5	i) 13.0 ii)18.0	16.3 19.0	1.5 2.0	0.3 0.7	1.5 0.7	1.0 1.0	1.3 0.8	1.2 1.5	0.8 0.8	1.0 2.0
		S	10.6	i) 15.0 ii)15.0	10.0 8.0	1.3 1.1	1.3 1.3	0.8 1.5	0.3 1.7	0.2 0.2	1.0 0.9	1.3 1.1	1.6 1.2
		U	12.8	i) 17.0 ii)16.0	10.5 11.5	1.7 1.9	1.4 1.2	1.8 0.3	2.0 0.7	0.3 0.6	1.0 0.8	0.2 0.5	1.8 2.0
		Z	14.5	i) 15.0 ii)18.0	9.0 10.5	1.5 0.7	0.7 1.2	1.7 1.3	0.4 1.5	0.8 1.1	0.8 1.2	1.4 0.9	1.8 2.0
PROCESS B	ABS	R	11.5	i) 22.0 ii)11.0	8.0 16.5	2.0 1.8	1.0 0.5	0.9 2.0	1.7 1.0	0.5 0.7	1.0 1.0	1.7 2.0	1.5 1.5
		S	10.6	i) 17.0 ii) 8.5	5.5 7.5	1.7 1.3	0.3 0.7	0.7 1.0	0.4 0.3	1.0 1.0	1.0 0.6	1.4 2.0	1.5 1.0
		U	12.8	i) 15.0 ii)14.5	8.0 8.0	2.0 0.2	0.3 0.2	1.5 2.0	0.5 1.0	1.7 1.0	1.7 1.1	1.7 1.0	1.0 1.0
		Z	14.5	i) 18.0 ii)13.0	19.0 14.0	1.0 1.5	1.0 1.0	2.0 1.0	0.5 0.2	2.0 1.9	0.3 1.3	2.0 1.0	1.0 0.6
PROCESS C	POLYPROPYLENE	M	300†	i) 300 † ii) 300 †	300 † 300 †	4.0 14.6*	8.0* 14.5*	13.0* 29.0*	10.0* 10.0*	5.0 5.0	2.5 4.0	6.0 4.0	12.0* 16.0*
		P	17.5	i) 28.5 ii)20.5	23.0 21.0	2.0 2.5	0.2 0.4	1.0 2.5	1.3 3.0	3.5 1.5	1.3 1.2	0.8 4.0	1.3 8.5
		Q	31.1	i) 54.0 ii)38.0	53.0 27.0	3.0 2.0	4.0 1.0	0.4 5.0	11.0 9.0	7.0 4.0	1.6 1.7	15.0 3.5	22.0 8.0

† Denotes value at which test was stopped.

* Denotes invalid result due to low adhesion.

premature failure and so presumably were not sufficiently large to act as centres of stress concentration. Since the processing solutions were operated at elevated temperatures it was decided to evaluate the effects of heating specimens in either air or water for periods corresponding approximately to the immersion times in the processing solutions. The conditions chosen for the two plastics types were as follows :-

ABS - 10 min. at 65° C

Polypropylene - 10 min. at 65° C followed by
10 min. at 80° C.

The results obtained did not differ significantly from those on as moulded samples. Neither the relatively low temperature heat treatment nor the possible absorption of water (14) had any effect.

The electroless nickel layer was quite thin, approximately 0.25 µm, and the application of this coating had little further effect than etching on U.T.S, but in many instances led to a moderate fall in ductility. More severe changes in both properties occurred as a result of depositing a copper coating 20 µm thick. The U.T.S. increased by between 10 - 30% compared to the 'as moulded' condition but the elongation fell to 2% or less for all grades of ABS and to only slightly higher values for polypropylene, with the exception of grade M. The effect on U.T.S. was as anticipated since the plastics substrate was reinforced by a metallic shell but the severe reduction in percentage elongation was more surprising since the copper deposit had a ductility of approximately 50% when plated onto an annealed brass substrate.

However, the stress system present during the tensile test in the case of a plastics substrate encapsulated by an adherent layer of copper is different to that when a copper/brass/copper 'sandwich' is tested. In the former case a triaxial state of tensile stress will be generated in the copper since in addition to the longitudinal tensile stress a transverse stress component will also be induced as the copper 'necks down' onto the plastics substrate; this process is physically constrained by the substrate and thus the transverse stress is generated. It is well known that a triaxial state of tensile stress can result in brittle failure (86). Other factors such as edge reinforcement effects may also favour the generation of a transverse tensile stress.

In the case of a copper/brass/copper 'sandwich' being subjected to a tensile stress only a plane stress situation is present; edge reinforcement effects are eliminated since edges are chamfered off prior to testing.

Variable results were obtained for U.T.S. when bright nickel layers were plated onto electrodeposited copper. In comparison with the results for copper alone the strength decreased in about two thirds of the cases. Application of chromium overlays on nickel resulted in lower values than for copper alone; in many instances they were similar to those obtained for the etched condition.

For all grades of ABS, ductility was low when copper + nickel + chromium coatings were applied. The results were rather more favourable for polypropylene although somewhat erratic. The highest values were achieved with grades M and Q, particularly with a microporous chromium overlay. The types of fractures changed when different coatings were deposited on the plastics substrates. The examples shown in Figs.27 and 28 show the ductile failures of ABS and polypropylene after testing in the etched condition and the brittle nature of the fractures when the same materials were plated with copper + nickel + microporous chromium.

Percentage elongation was determined by two methods. The first method involved measuring the gauge length before and after testing. The final measurement was made after reassembling the broken specimens but this procedure led to significant errors for both large and small extensions.

It was difficult to position the two pieces of ductile specimens in close contact while for brittle ones a small error in the measurement of extension resulted in a relatively large error in percentage elongation. Furthermore, this procedure rendered fractured faces useless for SEM examination since the fine surface details were likely to be damaged.

The method using the load-extension plot out on the chart enabled calculation of the elongation without damage to the fractured faces.

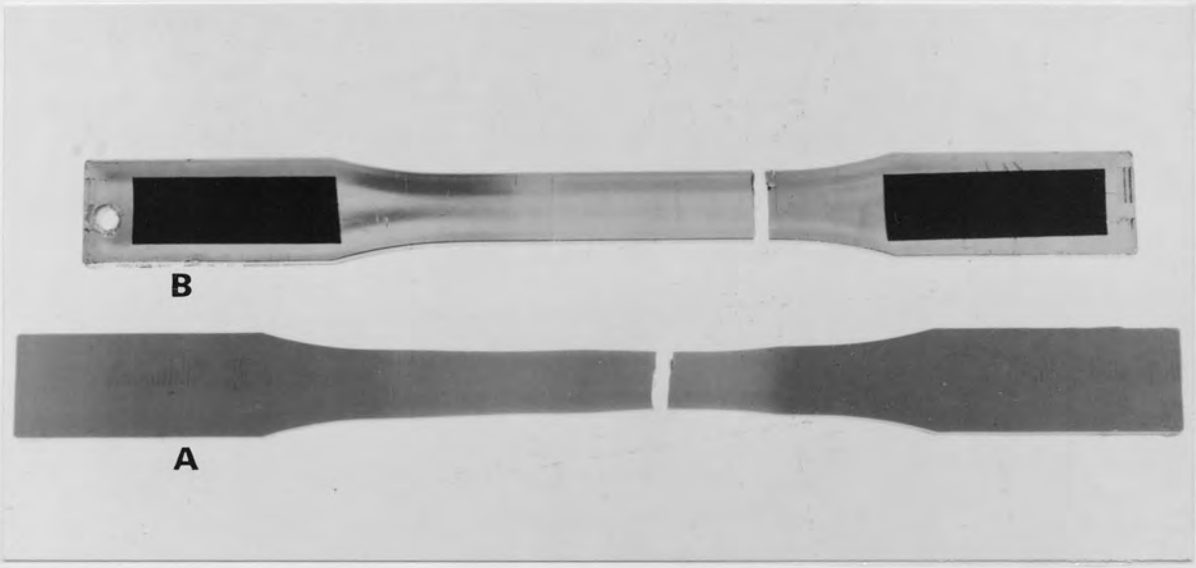


Fig.27. Fractured ABS tensile specimens. The unplated sample (A) exhibits whitened areas where considerable plastic deformation has taken place whereas the plated sample (B) exhibits brittle failure. ABS grade Z, process sequence A. Magnification ∿ x ¾. (A) etched for 7 min., (B) plated with 20 µm copper + 6 µm bright nickel + 0.25 µm microporous chromium.

Fig.28a. Scanning electronmicrographs of fractured face of polypropylene grade P after tensile test; specimen in the etched condition. Magnification x 20.

Fig.28b. Scanning electronmicrographs of fractured face of polypropylene grade P after tensile testing; specimen plated with 20 μm copper + 6 μm bright nickel + 0.25 μm microporous chromium. Magnification x 20.

The ductility of strip-type plated plastics may have been influenced by edge effects. The coatings were thicker at the edges than on flat surfaces and so cracks were likely to be initiated at the edges and premature failure could have occurred. When the ductility of an electrodeposit is determined by plating onto a metallic substrate this problem is eliminated by chamfering the edges to remove build up from high current density regions. This procedure could not be adopted with confidence on plastics substrates due to the lower adhesion levels involved. As previously mentioned the form of the test piece may also influence the results since different stress systems will be established. In the present work the plastics substrate was encapsulated with an adherent rectangular tube of metal but Matsunanga and Hagiuda(57) used specimens cut from plated panels. Consequently they tested a metal/plastics/metal 'sandwich' since the edges of the substrate would not be coated with metal.

Some typical examples of the load-extension graphs exhibited by plated ABS and polypropylene are shown in Figs. 29 and 30.

3.7.2 Impact Tests.

The results obtained at room temperature are listed in Table XV11 and those at - 40°C and + 80°C in Table XV111. In general these results followed a similar pattern to the ductility results obtained in the tensile tests in that when any of the electrodeposited coatings were applied the impact strength was reduced significantly. In many instances zero impact strength

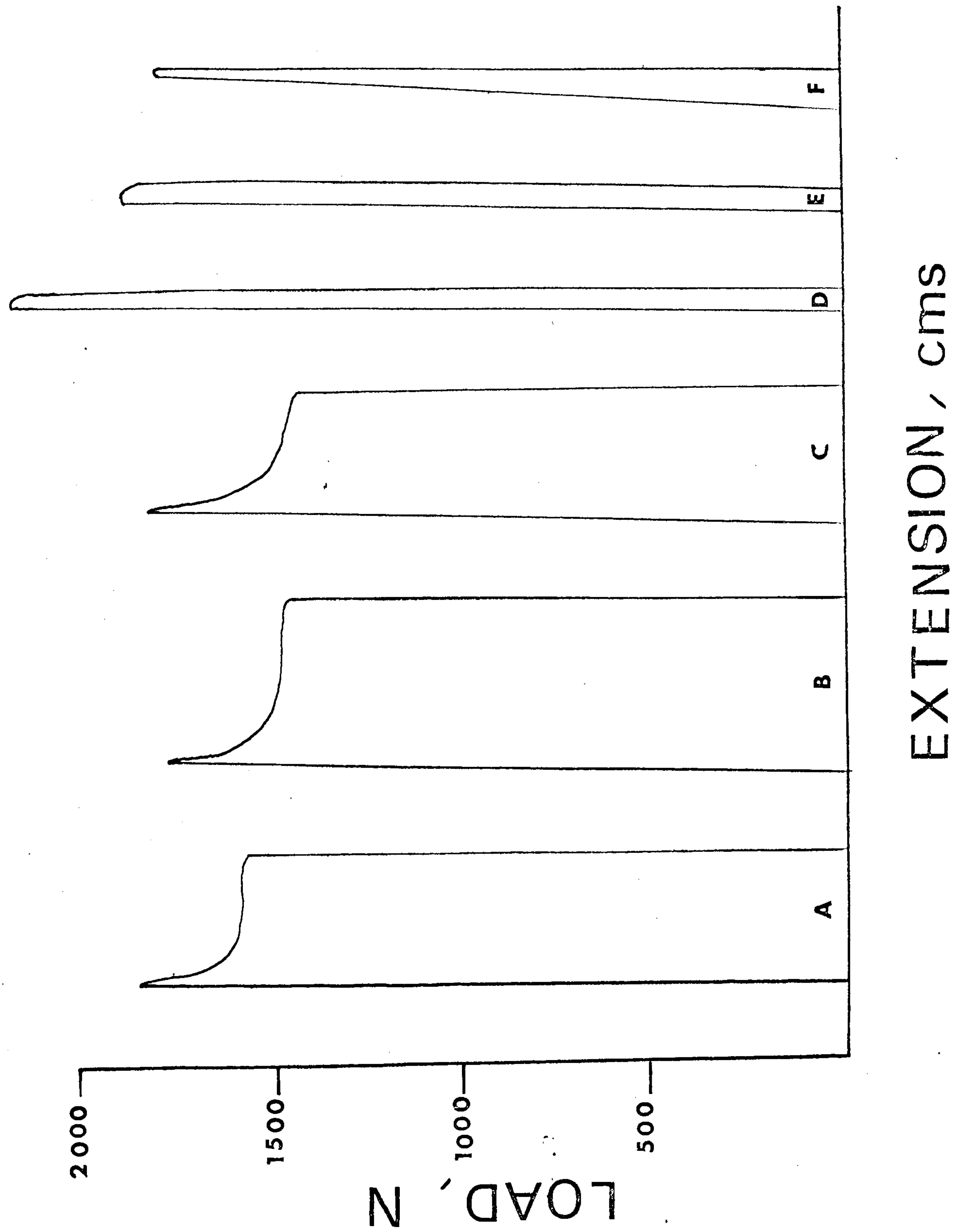


Fig.29. Load extension curves for ABS grade Z plated using sequence B. a) As moulded, b) etched for 3 min., c) etched for 3 min + ∿ 0.25 μm electroless nickel, d) plated with 20 μm copper, e) plated with 20 μm copper + 6 μm bright nickel + 0.25 μm decorative chromium, f) as moulded, with 45° V notch 25 μm deep. Similar curves are present at conditions e) and f) indicating that a cut notch may affect the plastics in a similar manner to electrodeposited layers.

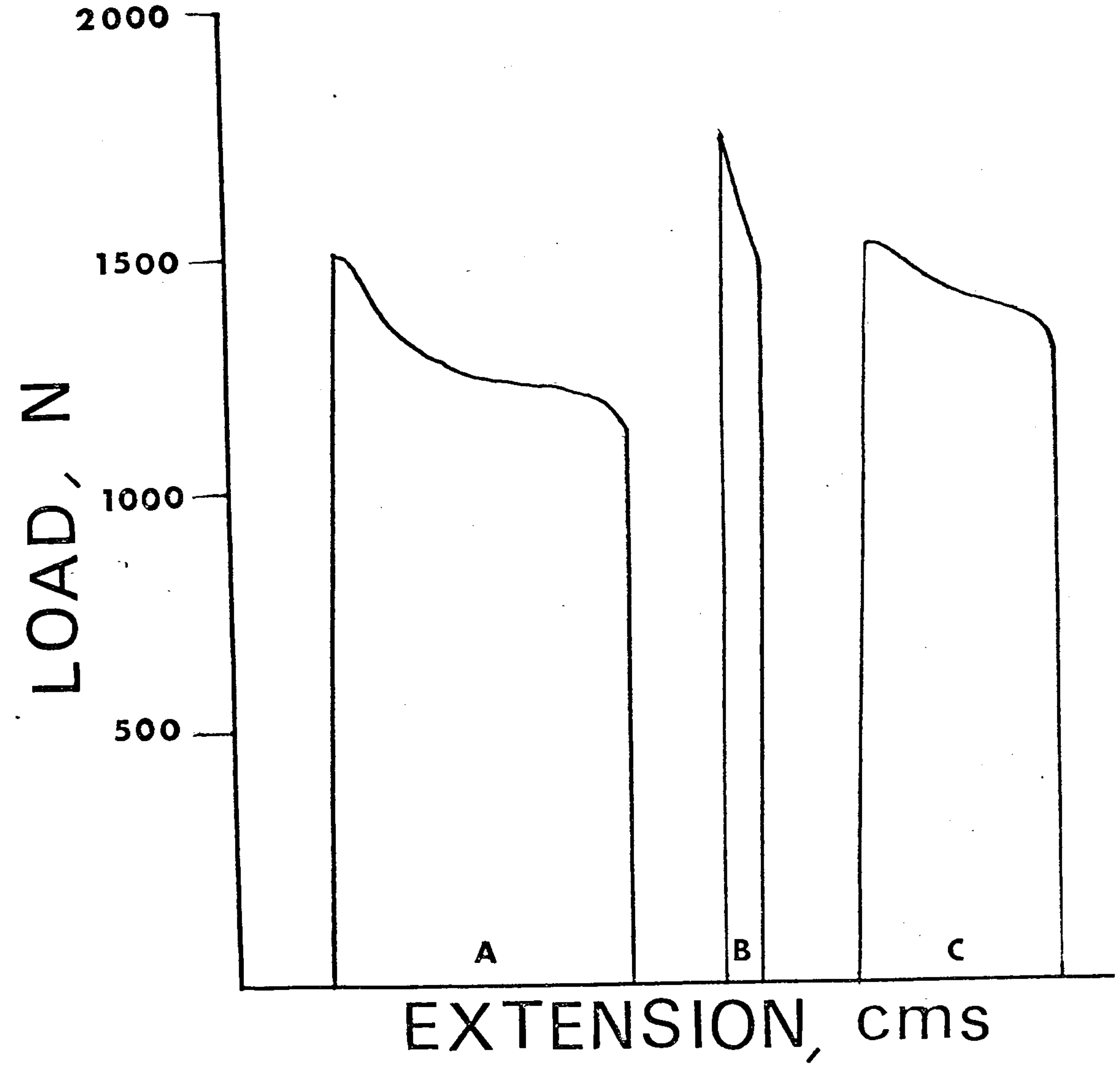


Fig.30. Load extension curves for polypropylene grade Q.
a) as moulded, b) plated with 20 μm copper, c) plated with 20 μm copper + 6 μm bright nickel + 0.75 μm microporous chromium.

TABLE XVII. IMPACT STRENGTH OF ABS AND POLYPROPYLENE AT 23^{O}C

					IMPACT STRENGTH AT 23^{o} C - J/cm^{2}									
					COATING SYSTEMS									
		Type & Grade of Plastics	As moulded	Etched i) Shorter time ii) Longer time	Electroless nickel (∼0.25µm)	Bright copper (20µm)	Bright copper (20µm) + Bright nickel (6µm)	Bright copper (20µm) + Bright nickel (15µm)	Bright copper (20µm) + Bright nickel (6µm) + Decorative chromium (0.25µm)	Bright copper (20µm) + Bright nickel (15µm) + Decorative chromium (0.25µm)	Bright copper (20µm) + Bright nickel (6µm) + Microcracked chromium (1.25µm)	Bright copper (20µm) + Bright nickel (6µm) + Microporous chromium (0.25µm)	Bright copper (20µm) + Bright nickel (6µm) + Microporous chromium (0.75µm)
PROCESS A	ABS	R	9.65	i) 7.32 ii) 7.34	6.17 5.13	1.00 0.84	1.66 1.25	1.82 1.24	1.12 1.41	2.07 2.07	1.58 0.87	1.08 1.25	1.12 0.83
		S	15.30*	i) 12.40* ii) 11.95*	8.02* 9.11*	1.41 1.33	1.66 1.49	1.74 1.40	1.62 1.12	1.49 1.59	1.25 0.91	0.95 1.16	1.33 0.83
		U	6.39	i) 3.53 ii) 4.10	2.52 1.98	0.29 0.29	0.83 0.99	0.95 0.99	0.37 0.00	1.28 0.58	0.49 0.00	0.58 0.24	0.0 0.58
		Z	16.2*	i) 9.82* ii) 15.14*	16.15* 14.04*	1.29 0.88	1.87 1.41	1.24 1.45	1.49 0.70	1.45 1.28	1.03 0.78	0.87 1.58	0.87 1.37
PROCESS B	ABS	R	9.65	i) 9.00 ii) 6.29	5.20 3.87	0.71 1.25	0.81 1.58	1.24 0.95	0.75 0.66	0.60 0.87	0.54 1.03	0.95 1.41	1.82 0.90
		S	15.30*	i) 15.47* ii) 14.20*	11.99* 8.41*	1.67 1.08	0.61 0.36	0.99 1.41	0.58 0.79	0.41 0.16	0.83 0.83	0.55 0.91	0.83 0.83
		U	6.39	i) 3.70 ii) 3.15	3.78 2.31	0.71 1.54	0.83 0.58	1.74 0.57	0.00 0.00	0.00 1.45	0.17 0.40	0.71 0.21	0.00 0.66
		Z	16.2*	i) 16.20* ii) 13.90*	13.54* 14.05*	2.08 2.29	1.03 1.25	1.28 1.17	1.66 1.04	0.79 0.99	1.23 1.24	0.80 1.45	2.16 1.57
PROCESS C	POLYPROPYLENE	M	14.07*	i) 12.65* ii) 12.61*	12.79* 12.65*	0.78 0.87	0.00 0.00	0.00 0.00	0.86 1.12	0.46 0.50	0.35 0.00	1.17 0.00	0.24 0.83
		P	2.50	i) 2.98 ii) 2.80	3.00 4.42	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00
		Q	4.90	i) 4.12 ii) 6.09	2.63 3.48	0.17 0.17	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.14

* Denotes invalid result - specimens failed to break

TABLE XVIII. IMPACT STRENGTH OF ABS AND POLYPROPYLENE AT -40°C AND +80°C

IMPACT STRENGTH AT - 40° C AND + 80° C - J/cm²														
						COATING SYSTEMS								
		Type & Grade of Plastics	Test Temper-ature °C	As Moulded	Etched i) Shorter time ii) Longer time	Electroless Nickel (∼0.25μm)	Bright copper (20μm)	Bright copper (20μm) + Bright nickel (6μm)	Bright copper (20μm) + Bright nickel (15μm)	Bright copper (20μm) + Bright nickel (6μm) + Decorative chromium (0.25μm)	Bright copper (20μm) + Bright nickel (15μm) + Decorative chromium (0.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microcracked chromium (1.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microporous chromium (0.25μm)	Bright copper (20μm) + Bright nickel (6μm) + Microporous chromium (0.75μm)
PROCESS A	ABS	U	-40	0.00	i) 0.00	1.51	0.42	0.00	0.83	0.00	0.00	0.00	0.00	0.00
					ii) 1.66	0.00	0.84	0.32	0.99	0.00	0.00	0.00	0.00	0.00
			+80	14.32	i) 10.93	10.93	1.08	5.83	0.00	0.17	0.83	0.00	0.00	0.00
					ii) 13.96	10.93	0.84	0.00	1.66	0.66	3.30	0.00	0.17	0.33
		Z	-40	3.80	i) 1.69	1.69	0.84	0.66	0.83	0.83	0.50	0.33	0.50	0.42
					ii) 1.34	0.67	0.84	0.83	1.24	0.42	0.00	0.00	0.33	0.00
			+80	15.21*	i) 11.10*	10.10*	1.67	1.25	0.33	0.83	0.00	0.00	0.00	0.42
					ii) 8.92*	9.26*	1.08	3.32	1.49	0.17	0.00	0.00	0.17	0.00
PROCESS B	ABS	U	-40	0.00	i) 0.00	1.60	0.92	3.15	0.83	0.00	0.17	0.24	0.22	0.33
					ii) 0.00	0.92	0.00	1.0	1.24	0.00	0.17	0.33	0.50	0.00
			+80	14.32	i) 11.35	10.26	2.33	0.00	2.15	0.17	0.26	0.33	0.17	0.33
					ii) 10.09	10.43	2.50	0.02	0.00	0.33	0.24	0.34	0.00	0.17
		Z	-40	3.80	i) 4.03	3.03	1.08	0.83	0.83	0.00	0.00	0.83	0.00	0.83
					ii) 4.17	2.52	1.48	0.00	0.99	0.83	0.00	0.00	0.83	0.83
			+80	15.21*	i) 9.67*	9.08*	3.00	0.91	1.65	1.24	0.00	3.07	1.16	1.66
					ii) 9.67*	8.92*	2.92	1.16	1.47	0.66	1.65	0.75	1.00	1.16
PROCESS C	POLYPROPYLENE	M	-40	5.12	i) 4.38	5.96	0.03	0.00	1.72	0.00	0.00	0.00	0.00	0.86
					ii) 3.50	3.52	0.00	0.69	0.00	0.00	0.00	0.00	0.00	0.00
			+80	7.84*	i) 3.68*	3.85*	7.11	6.02	5.95	6.14	5.51	6.06	5.53	6.04
					ii) 4.03*	4.03*	6.24	6.05	6.71	5.88	6.02	5.96	5.10	6.48
		P	-40	0.73	i) 0.61	0.35	0.17	0.00	0.00	0.43	0.00	0.00	0.86	0.00
					ii) 0.61	0.90	0.87	0.00	0.43	0.00	0.00	0.00	0.00	0.00
			+80	5.59	i) 5.25	5.25	0.87	1.73	0.69	4.15	0.86	1.69	0.95	0.95
					ii) 5.25	4.99	1.65	0.95	0.86	0.86	0.69	0.35	1.12	1.64

* Denotes invalid result - specimens failed to break

was recorded for polypropylene at room temperature. For both types of plastics the highest values were generally obtained at + 80°C although even these were low for the plated samples.

Some grades of plastics M, S and Z could not be evaluated in the as moulded, etched and electroless plated conditions because they were so ductile that their test bars were pushed past the supports by the hammer without being broken. These results have been designated 'invalid' since according to BS 2782:1965 (79) the specimens must be fully broken. The value recorded shows the energy expended in bending the bars and their subsequent transport past the supports. The results have been included merely to indicate how ductile these particular grades were and to show how they were subsequently embrittled by electroplating. Typical fractures are shown in Figs. 31 and 32.

3.7.3 STATISTICAL ANALYSIS OF MECHANICAL TESTING RESULTS.

The results were assessed to see whether the various treatments had influenced the properties measured. The test used was the 'comparison of means' or 't' test.

A summary of the variables indicated by the analysis as influencing performance in tensile and impact tests is given in Tables XIX and XX. In statistical significance tests the level of significance indicates the degree of certainty with which an inference can be made. The lower the value of significance the more justified the inference; usually the 5% level is

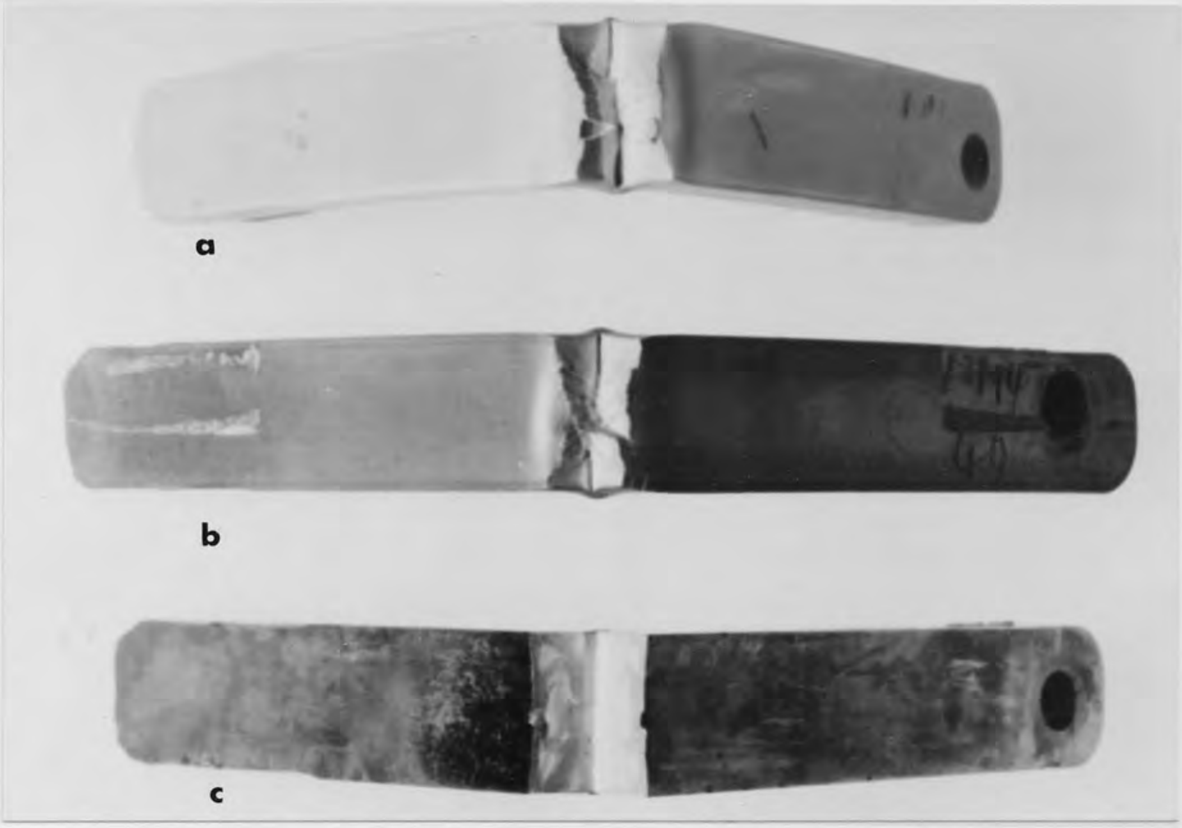


Fig.31. Appearance of ABS grade U after impact testing at 23° C. Process sequence B, 40 min. etch. Magnification x 1½. a) as moulded, b) etched for 40 min. + ∿ 0.25 μm electroless nickel, c) plated with 20 μm copper. Considerable embrittlement results after the application of an electrodeposited layer.

Fig.32. Appearance of polypropylene grade M after impact testing at + 80°C. Etched for 10 min., plated with 20 μm copper + 6 μm bright nickel + 0.25 μm decorative chromium. Magnification x 1½. Severe embrittlement has not resulted. Note the poor adhesion of the electrodeposited layers to the substrate; this may be partly responsible for the ductile fracture of the specimen.

TABLE XIX. Summary of variables affecting performance in tensile tests

	Variable being tested	Grade of plastics	U. T. S.		DUCTILITY	
			Significance Level %		Significance Level %	
			Process A	Process B	Process A	Process B
ABS	Effect of etching time within a given process sequence	R	>5	5	NS	NS
		S	NS	NS	NS	NS
		U	NS	NS	NS	NS
		Z	NS	>5	NS	NS
	Effect of process sequence	R	>5 (Process sequence A associated with the higher average UTS)		NS	
		S	NS		NS	
		U	NS		NS	
		Z	NS		NS	
POLYPROPYLENE			PROCESS C		PROCESS C	
	Effect of etching time	M	>5		NS	
		P	10		NS	
		Q	NS		>5	

> indicates that the level of significance was better than the figure quoted.

NS denotes no significance detected.

TABLE XX. SUMMARY OF VARIABLES AFFECTING PERFORMANCE ON IMPACT TESTING

Variable being tested	ABS Grade	SIGNIFICANCE LEVEL %			
		Process A	Process B	Polypropylene Grade	Process C
Effect of etch time within a given process sequence (-40°C results compared)	U	NS	NS	M	>10 (Etch(i) associated with higher average impact strength)
	Z	>10 (Etch(i) associated with higher average impact strength)	NS	P	>5 (Etch (i) associated with higher average impact strength)
Effect of etch time within a given process sequence (+23°C results compared)	R	>10 (Etch (i) associated with higher average impact strength)	NS	M	NS
	S	NS	NS	P	NS
	U	NS	NS	Q	NS
	Z	NS	NS		
Effect of etch time within a given process sequence (+80°C results compared)	U	NS	NS	M	NS
	Z	NS	NS	P	NS
Effect of test temperature (-40° and +80°C results compared)	U	>10 (Higher average impact strength at +80°C)	NS	M	>1 (Higher average impact strength at + 80° C)
	Z	NS	>5 (Higher average impact strength at +80°C)	P	>5 (Higher average impact strength at + 80° C)
Effect of process sequence (-40°C results compared)	U	NS			
	Z	NS			
Effect of process sequence (+23°C results compared)	R	NS			
	S	NS			
	U	NS			
	Z	NS			
Effect of process sequence (+80°C results compared)	U	NS			
	Z	NS			

> Indicates that the level of significance was better than the figure quoted

NS Denotes no significance detected

taken as probably significant (82,84). It can be seen that in many cases no effects could be detected due to the plating variables but where they could, the level of significance was found in most cases to be better than 5%.

3.8 PEEL ADHESION.

These results are reported in three sections. The first section deals with the peel adhesion determinations on the three grades of ABS (X, Y and Z) used in the pilot corrosion testing programme. The second section presents the peel adhesion results obtained on the grades of ABS and polypropylene used in the main corrosion testing programme(i.e. ABS grades R,Y,Z,S,T, U, V and W, and polypropylene grades M,N,P and Q.) The effects of changing the moulding conditions on the peel adhesion values on polypropylene grades M and N are also given. The first two peel adhesion investigations were carried out in order to determine whether there was any relationship between the peel adhesion value and the performance of plated ABS and polypropylene in corrosion tests. The third section presents the results of a more detailed investigation into the factors affecting the peel adhesion value on ABS and polypropylene. ABS grades L, R, U and Z, and polypropylene grades M,P and Q were used for this investigation. The thicknesses of the detached plastics films are also given.

3.8.1 Peel Adhesion Results on ABS Grades X, Y and Z.

These specimens were all plated with 50 µm of bright copper and peel adhesion was determined at three etch times in addition to the standard 7 min. etch used for the corrosion programme. For specimens processed in sequence A the conditioner time was kept constant at 2 min. The results are summarised in Table XX1. Samples processed in sequence A usually exhibited higher peel adhesion than those processing in sequence B. It appeared that the 7 min. etch was insufficient to achieve maximum peel adhesion in the case of grade Y, particularly when using sequence A. In three out of four of the remaining plastics type/processing sequence combinations, the variation in etch time over the range investigated resulted in only slight changes in peel adhesion. Previous work (8) carried out on a wide range of ABS formulations had indicated that in most instances realistic variations of etch time did not have a great deal of influence on peel adhesion once a critical time had been exceeded. However, the surface topography is changed considerably as the etch time increases. Fig.22 shows some examples of the degree of etching after 7 and 21 min. treatment. All grades of plastics were etched rather more severely after a particular time in process A than in process B. By comparison of Figs. 22c and 22h, it can be seen that type Y was etched more severely after 7 min. in process A than after 21 min. in B.

3.8.2 Peel Adhesion Results on ABS Grades, R,Y,Z,S,T,U, V and W, and Polypropylene Grades M, N, P and Q.

All specimens were plated with 50 µm of bright copper and the peel adhesion values for the grades studied are listed in Table XX11. All plated test panels were allowed to age by storing for ten days.

TABLE XXI . PEEL ADHESION ON ABS - FIRST PHASE OF TESTS

Grade of ABS Code	PEEL ADHESION kN/m							
	Etch time 3.5 min		Etch time 7 min		Etch time 14 min		Etch time 21 min	
	A	B	A	B	A	B	A	B
X	2.3	0.8	2.4	0.9	1.4	1.0	1.8	0.7
Y	0.8	1.2	0.7	1.6	2.8	1.9	2.4	2.0
Z	2.8	2.2	3.0	2.2	2.6	2.4	2.8	2.4

A and B indicate the process sequences used

Process sequence A - Common conditioner time 2 mins.

TABLE XXII . PEEL ADHESION OBTAINED ON ABS AND POLYPROPYLENE TEN DAYS AFTER PLATING - MAIN CORROSION PROGRAMME

Code	Peel Adhesion KN/m	
	Process A	Process B
R	0.57	0.55
Y	1.05	0.85
Z	2.90	2.16
S	3.35	2.51
T	2.01	1.82
U	0.92	1.39
V	0.93	0.87
W	1.21	1.20

PROCESS C

Code	Moulding Condition	Etch Time Mins	Peel Adhesion KN/m
M	i	5	0.74
	ii	10	0.74
	i	5	0.85
	ii	10	0.69
	ii	5	3.46*
N	i	5	0.21
	ii	10	0.09
	i	5	0.20
	ii	10	0.06
	ii	5	2.92*
P		10	2.62
Q		10	1.54

* Denotes values obtained from specimens slit one year before testing

at room temperature before slitting and peel adhesion testing. The results of pre-slitting polypropylene grades M and N are also shown. In both ABS process sequences the highest peel adhesion values were obtained on ABS grades S,Z and T whilst the lowest occurred on grade R. It should be noted that for grade Y processed in sequence A the increased amount of etching improved the peel adhesion but the value achieved was not as high as that obtained in the first phase of work when using prolonged etch times. The moulding conditions and etch times used had little influence on peel adhesion values obtained on polypropylene grades M and N after storing for ten days. Grade N was not a recommended plating grade and the peel adhesion values were extremely low. Much higher peel adhesion values were obtained on polypropylene grades P & Q than on M and N ; these grades which were specifically formulated for electroplating, etched readily and were easy to treat in process sequence C. It was observed that maximum peel adhesion values occurred near jig contact points on all grades of polypropylene. This was in agreement with the results of Perrins and Pettett (37) who considered the phenonemon was due to an increase in polarity resulting from an oxidation process. In the case of grade P the adhesion was so great at oxygen access points that areas of electroless nickel adhered to the substrate in these regions after peeling off the electrodeposited copper. It is of importance to note that in the peel adhesion investigations electroless nickel was employed throughout as the initial metal layer. The peel adhesion values obtained on polypropylene grades M and N ten days after plating are similar to those obtained by Perrins and Pettett (37) when processing similar grades of polypropylene using electroless nickel as the initial layer and determining peel adhesion after a similar ageing period on uncut plaques. Polypropylene grades M and N which had been slit ready for testing but then stored for one year before peeling exhibited much greater adhesion than similar specimens tested after ten days storage, Table XX11. This was also in agreement with the results of Perrins and Pettett (37). It should be emphasised that the rate of increase in adhesion on storage is less when electroless nickel is used rather than copper since the latter metal is more efficient in catalysing the oxidation reaction. It is also dependant on the ease of access of oxygen: this is facilitated by defects in the coating at jig contact points or by slitting the coating well before the peel test is performed.

3.8.3 Peel Adhesion Results on ABS Grades L,R,U and Z, and Polypropylene Grades M, P and Q.

In this programme the effect of copper + semi-bright nickel layers, etch time and mould geometry (using ridged panels) on peel adhesion was studied. Details of the etch times used are shown in Table XX111 and the types and thicknesses of the

TABLE XXIII. COMPOSITION, DENSITIES AND ETCHING CONDITIONS FOR ABS AND POLYPROPYLENE

	Code	PROCESS SEQUENCE				MAIN CONSTITUENTS % (APPROX)		DENSITY Kg/m^3	General Comments
		A		B	C	Butadiene	Acrylonitrile		
		Conditioner min	Etch min	Etch min	Etch min				
ABS	L	10 10	7 14	10 20		17	28	1120	Electroplating grade
	R	3 3	3 6	5 10		16	24	1040	General purpose grade, lubricated.
	U	4 4	7 14	20 40		6	28	1050	High modulus grade, lubricated.
	Z	2 2	7 14	3 6		27	24	1090	High impact grade, lubricated.
POLYPROPYLENE	M				10 20			945	Plating grade. Copolymer with approx. 10% ethylene.
	P				10 20			920	Isotactic polymer
	Q				10 20			1010	Isotactic polymer. High resistance to thermal cycling Crystalline and amorphous structure.

electrodeposits are listed in Table XXIV. Two types of panels, 6.0 cm x 8.8 cm x 0.3 cm. were used in this investigation. One was the usual form having plain surfaces on each side but the other had a ridge and a valley in one surface. The positions of these features are shown in Figs. 1 and 33. ABS panels of both types were subjected to the acetic acid test for 2 min. at 23° C. Areas associated with high adhesion peaks on ridged panels were least affected by the test (see Fig.33b). Typical graphs obtained by peel testing the various plastics types and grades are shown in Fig.34. It was noted that all graphs obtained on a particular grade of plastics had a charecteristic shape. ABS grade L was included in the programme since from earlier work (8) it was known to exhibit the "slip stick" failure mechanism in the peel adhesion test. Examination of the plastics surface after peeling off the coating revealed the presence of parallel bands over part of the peel length, particularly when process B was used. The graphs shown in Figs. 34a and 35 illustrate how the peel adhesion values increased and decreased periodically. The expanded graph shown in Fig.35 was obtained by increasing the chart speed and this illustrates that the load increased periodically up to a critical value at which peeling could occur. The radius of curvature of the metal foil at the line of peel became smaller as the

TABLE XXIV. COATINGS DEPOSITED ON PLAIN PANELS OF ABS AND POLYPROPYLENE

Coating Code	Type of coating	Thickness, µm
1	Copper	50
2	Copper	100
3	Copper + semi-bright nickel	25 Cu + 25 Ni
4	Copper + semi-bright nickel	50 Cu + 50 Ni

All copper deposits were plated from a pyrophosphate bath.

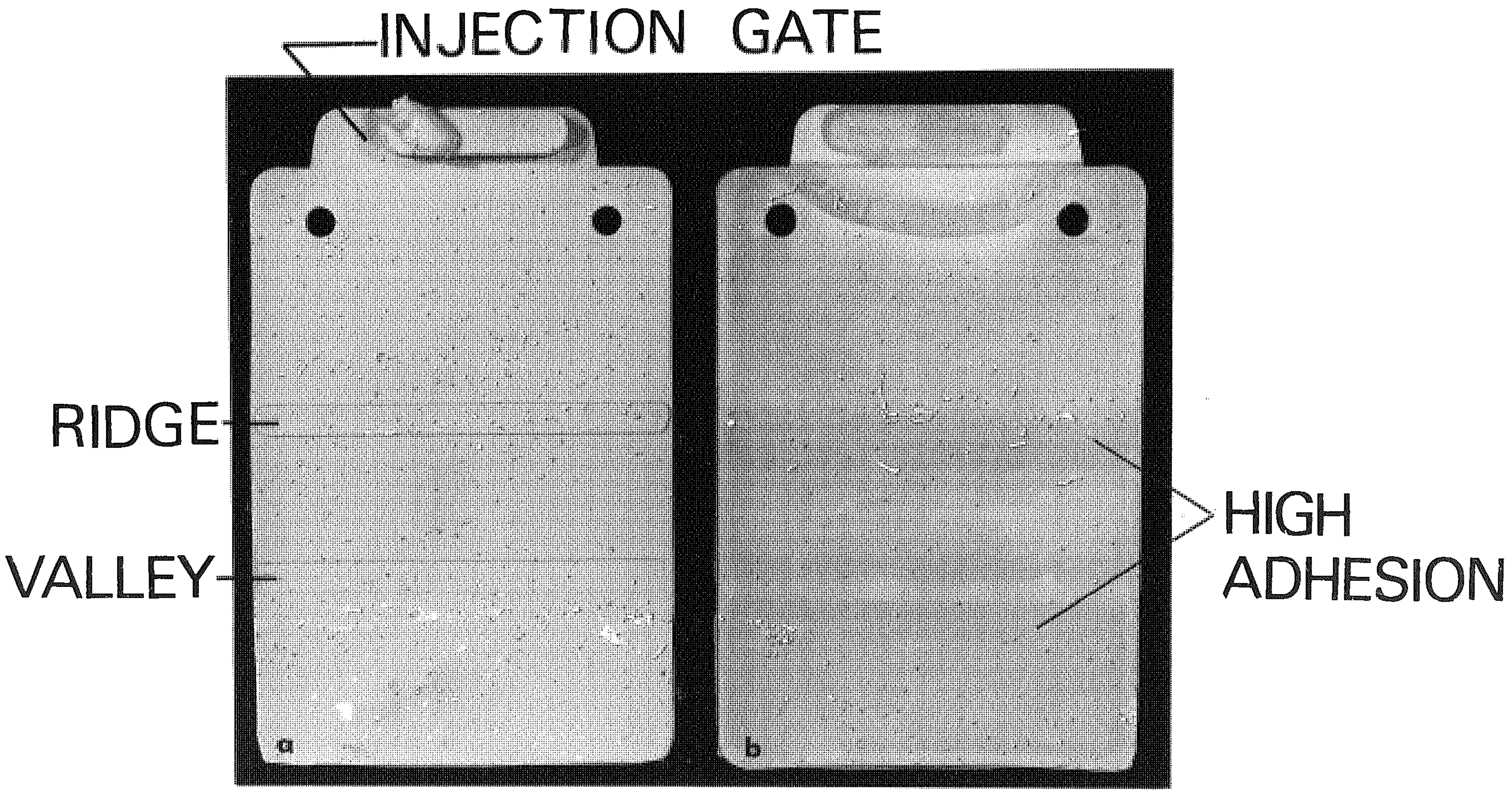


Fig.33. Ridged panels.
a) Positions of injection gate ridge and valley are indicated.
b) Plain side of panel after acetic acid test; the bands correspond to high adhesion regions.

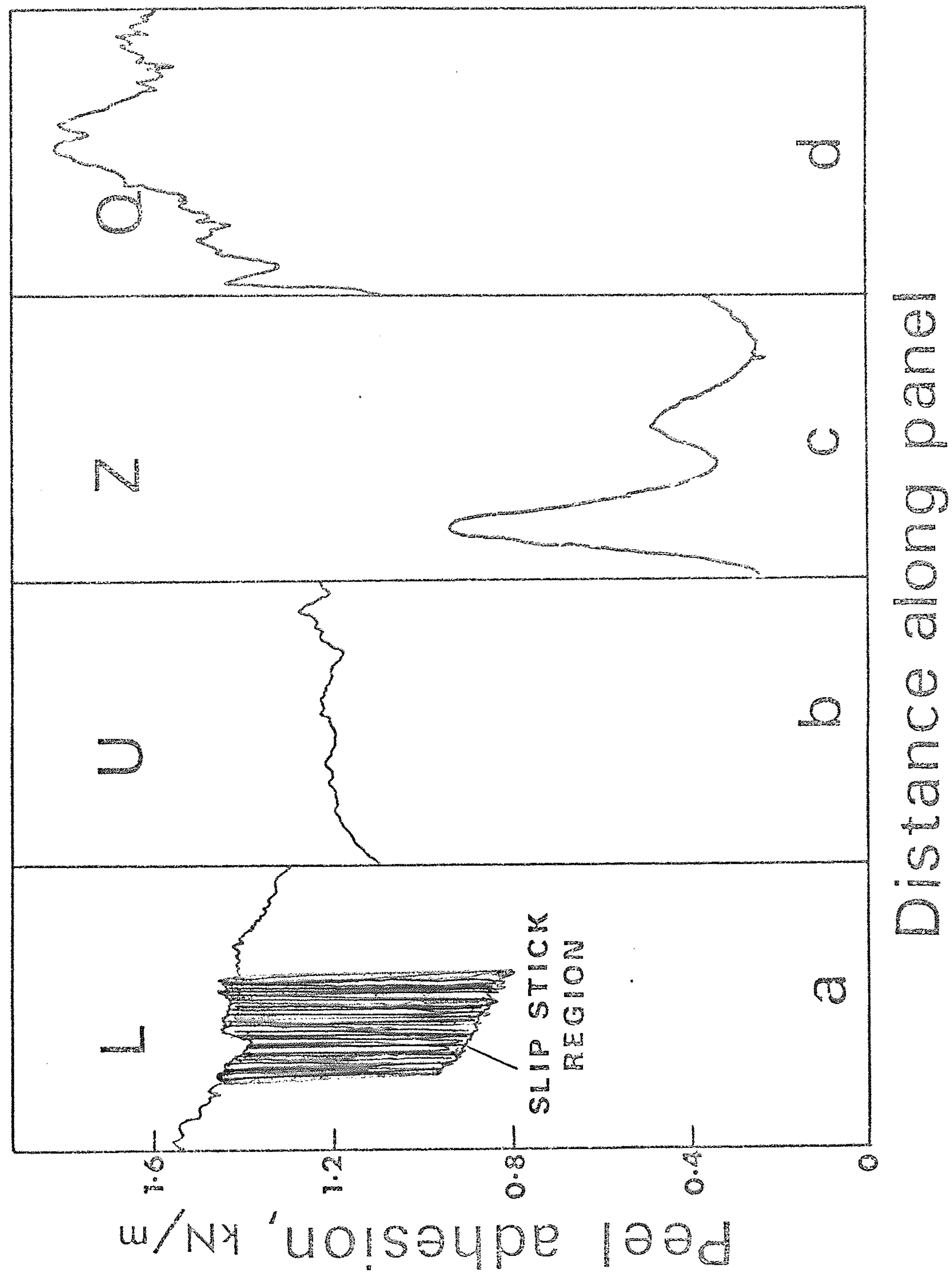


Fig.34. Typical peel adhesion curves obtained on plain panels. All samples were plated with 50 μm copper. ABS grade L processed in sequence B, etch (i). ABS grades U and Z processed in sequence A, etch (i). Polypropylene grade Q processed in sequence C, etch (ii).

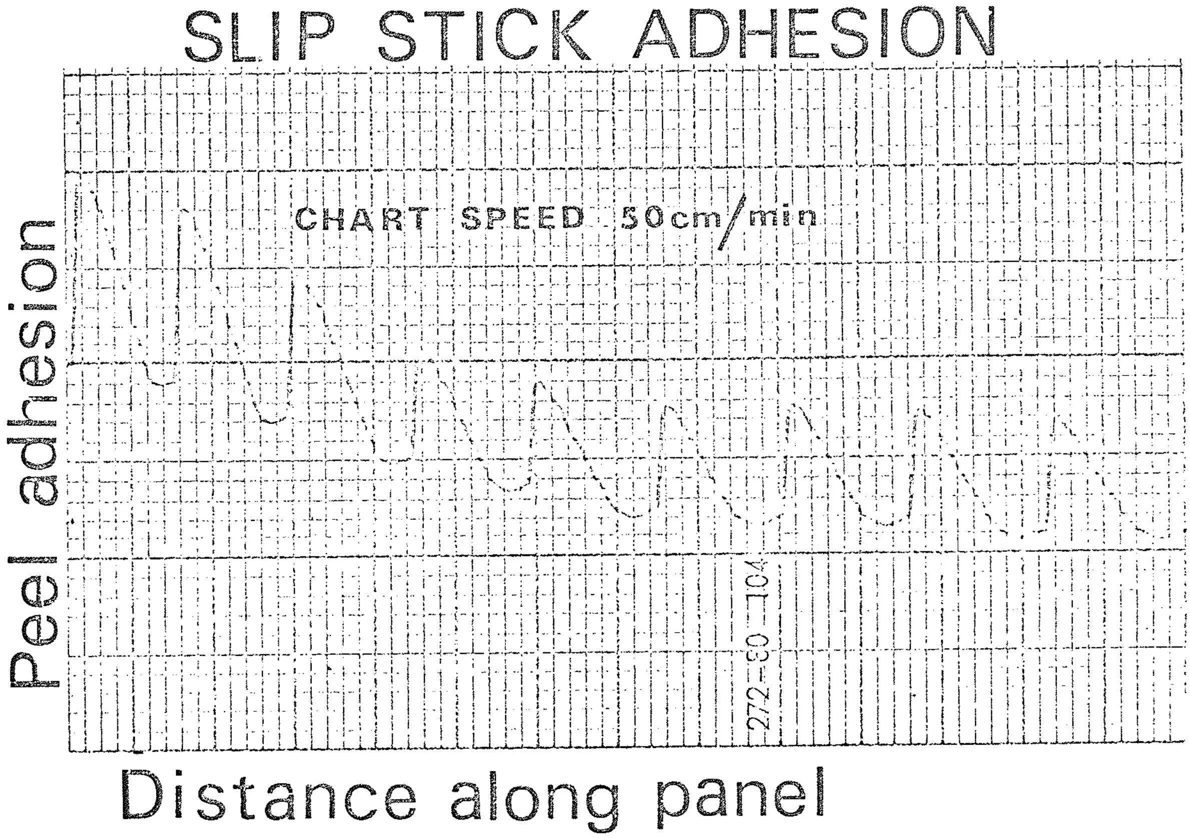


Fig.35. Peel adhesion curve for ABS grade L. The expanded scale illustrates the "slip stick" mechanism.

load increased and consequently the stress field became more intense. At a certain load and radius the stress field was sufficiently high to shear away the area of plastics within the field. This caused a sudden relief of the force on the plastics and the load dropped sharply. Consequently the term "slip stick" was applied to this failure mechanism. Stopping the test and then restarting it did not prevent this mechanism occurring on this grade of plastics. Fig.36 shows the appearance of the band effect on the substrate and on the back of a detached metal foil. It is apparent that a somewhat different failure mechanism took place in the two areas and that a sharp demarcation occurred between them. None of the other plastics included in this investigation exhibited this effect but the shapes of the peel adhesion graphs were thought to be dependant on the properties of the plastics and their moulding characteristics.

The relationships between peel adhesion and the thickness of plastics layers adhering to the metal foils are plotted in Figs. 37 and 38. These results are also listed in Table XXV in order that some comparisons can be made more readily. It should be noted that results could not be plotted in Fig.38 for polypropylene grade M since no detectable layer of plastics was present on metal foils peeled from this material. Each value in Figs. 37 and 38 represent an average of two results.

Although not correct for each specific case the general trends of behaviour can be summarised as indicated below.

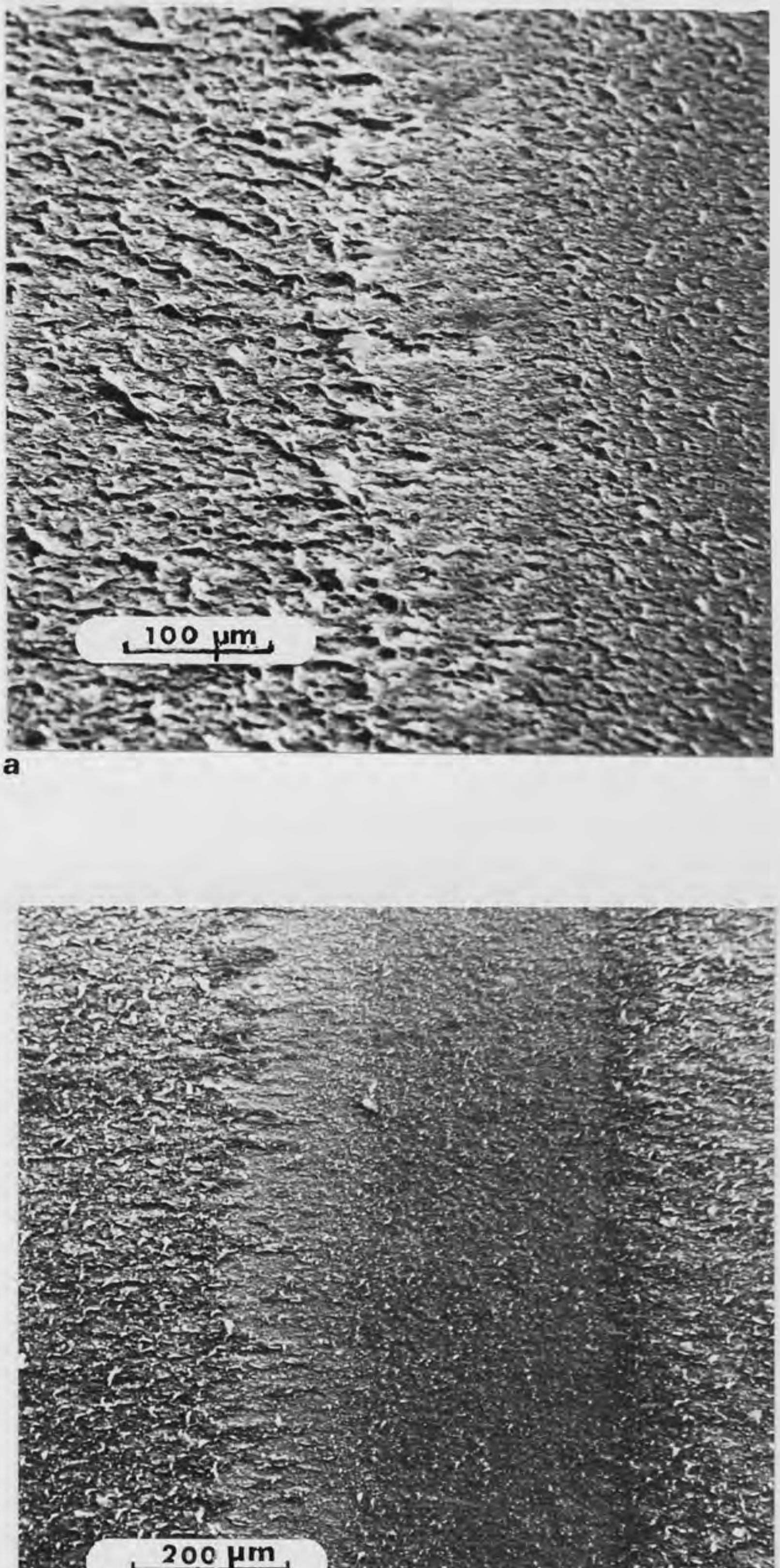


Fig.36. Scanning electronmicrographs of:-
a) The surface of ABS grade L after the peel adhesion test,
b) the back of the peeled foil.
Process sequence B, 10 min. etch.

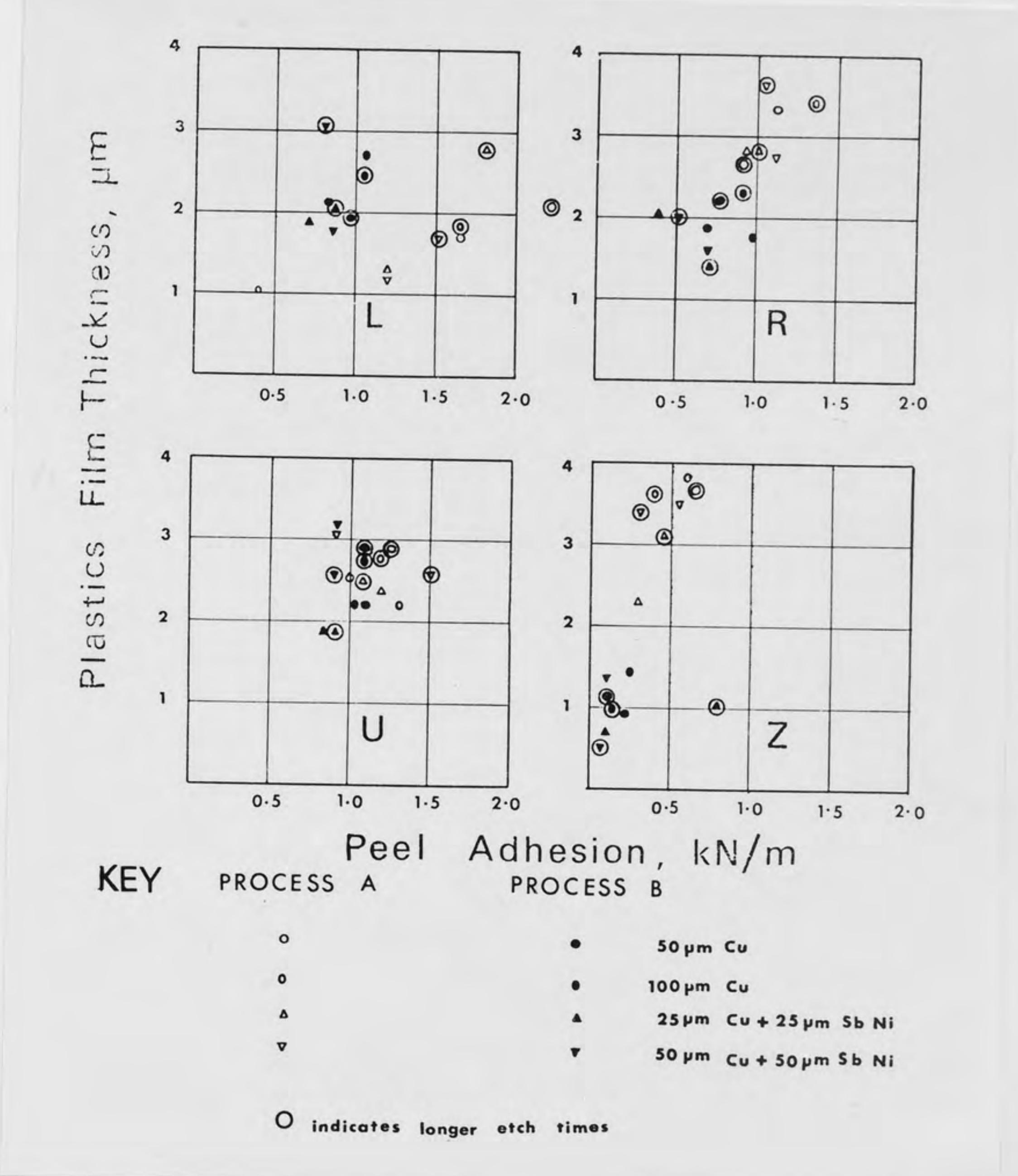


Fig.37. Relationships between peel adhesion and thicknesses of ABS films detached from plain panels.

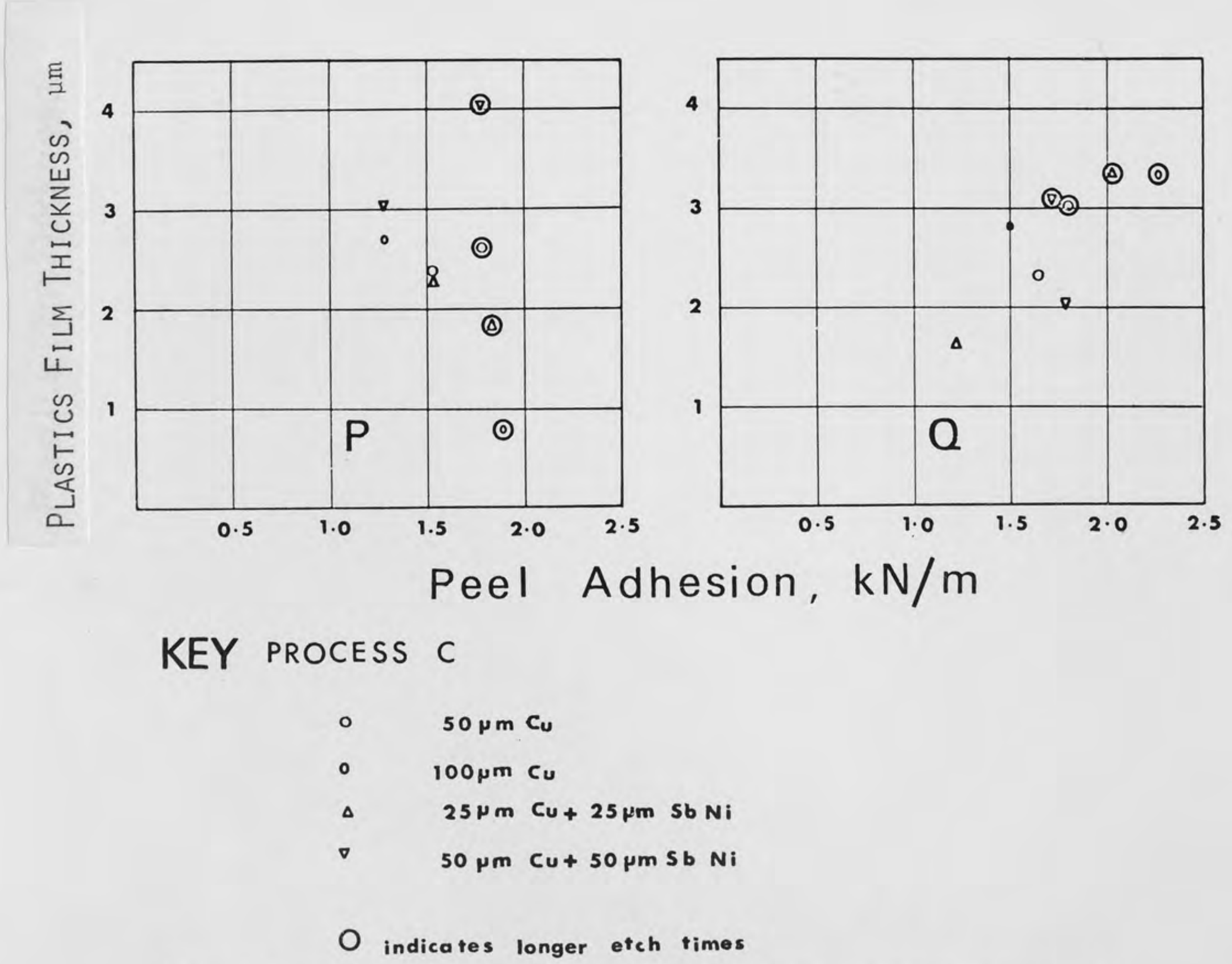


Fig.38. Relationships between peel adhesion and thicknesses of polypropylene films detached from plain panels.

TABLE XXV. PEEL ADHESION ON PLAIN PANELS AND THICKNESS OF PLASTICS FILM ADHERING TO DETACHED FOIL

	Plastics Code	Coating Code *	Peel Adhesion, kN/m.						Thickness of detached plastics film, μm.					
			Process A		Process B		Process C		Process A		Process B		Process C	
			Etch(i)	Etch(ii)	Etch(i)	Etch(ii)	Etch(i)	Etch(ii)	Etch(i)	Etch(ii)	Etch(i)	Etch(ii)	Etch(i)	Etch(ii)
A B S	L	1	1.67	2.19	0.86	0.97			1.7	2.1	2.1	1.9		
		2	0.41	1.65	1.04	1.05			1.0	1.8	2.7	2.5		
		3	1.20	1.80	0.70	0.86			1.3	2.8	1.9	2.1		
		4	1.19	1.50	0.89	0.78			1.2	1.7	1.8	3.1		
	R	1	1.13	0.90	0.69	0.76			3.3	2.7	1.9	2.2		
		2	1.06	1.27	0.97	0.82			4.3	3.4	1.8	2.4		
		3	0.90	0.97	0.39	0.70			2.8	2.8	2.0	1.4		
		4	1.12	1.06	0.70	0.50			2.8	3.6	1.8	2.0		
	U	1	1.03	1.23	1.17	1.14			2.5	2.9	2.2	2.9		
		2	1.06	1.21	1.32	1.07			2.2	2.8	2.2	2.8		
		3	1.47	1.02	0.88	0.89			2.4	2.5	1.9	1.9		
		4	0.92	1.45	0.90	0.91			3.1	2.6	3.2	2.6		
	Z	1	0.59	0.65	0.23	0.17			3.8	3.7	0.9	1.1		
		2	0.42	0.45	0.25	0.14			3.6	3.6	1.4	1.0		
		3	0.31	0.48	0.09	0.81			2.3	3.2	0.7	1.0		
		4	0.53	0.33	0.13	0.09			3.5	3.4	1.4	0.5		
POLYPROPYLENE		1					1.14	1.10					0	0
		2					0.70	0.70					0	0
		3					1.25	0.95					0	0
		4					0.63	0.90					0	0
	P	1					1.53	1.58					2.4	2.6
		2					1.34	1.89					2.7	0.7
		3					1.53	1.84					2.3	1.8
		4					1.28	1.77					3.1	4.1
	Q	1					1.67	1.81					2.3	3.0
		2					1.50	2.31					2.8	3.3
		3					1.22	2.03					1.6	3.3
		4					1.80	1.73					2.0	3.1

(i) and (ii) refer to single and double etch times given in Table XXIII for each plastics grade

* see Table XXIV

3.8.3.1 PLAIN PANELS.

3.8.3.1.1. ABS Substrates.

Process sequence A usually resulted in higher peel adhesion than B. This effect had been noted in the previous peel adhesion investigations (see previous sub-section). For grades R and Z the thicknesses of detached plastics films were greater for process A than for B. However, in the case of grade Z the peel values were all quite low and so there was not much difference between the peel adhesion results obtained in process A and B even though there was a considerable difference in the thicknesses of detached plastics films.

2). An increase in etch time did not have a very significant effect in most instances on either peel adhesion or the thickness of detached plastics films.

3). No definite trend was established for the relationships between either peel adhesion or detached plastics film thickness and increase in coating thickness.

4). In the majority of cases peel adhesion and thickness of detached plastics film were greater, for a particular coating thickness, when a single copper layer was employed instead of one consisting of copper + semi-bright nickel.

5). The relationship between peel adhesion and thickness of detached plastics film depended on the grade of plastics. For grades R and Z there was an indication that the thickness of the detached plastics film increased as the peel adhesion increased.

3.8.3.1.2 Polypropylene substrates.

1). The longer etch time resulted in somewhat higher peel adhesion for grades P and Q.

2). An increase in coating thickness usually resulted in lower peel adhesion values but thicker detached plastics films.

3). The relationship between peel adhesion and thickness of detached plastics film depended on the grade of plastics (Fig.38). In the case of grade M no film was detected.

3.8.3.2. RIDGED PANELS.

The influence of mould geometry on peel adhesion is illustrated clearly in Figs.39 and 40. When copper coatings 50 µm thick were peeled from the plain surface of ABS, adhesion peaks occurred at positions corresponding to the ridge and a region just beyond the valley. Small peaks were also noted directly opposite to the valley feature . The highest peel values were obtained at the region just beyond the valley, the maximum adhesion recorded as being as much as seven times the average value. Light coloured bands could be seen on the plastics surface indicating the areas at which greater forces had been involved in tearing the metal foil from the substrate. The direction of peel was reversed on a few specimens in order to check whether this had any effect on the values obtained. The peaks occurred at the same positions and peel values were in good agreement with those obtained in the main programme. A few panels of each grade of ABS were annealed at 80°C for 2 hours before plating but this had no effect on the position or magnitude of the adhesion peaks.

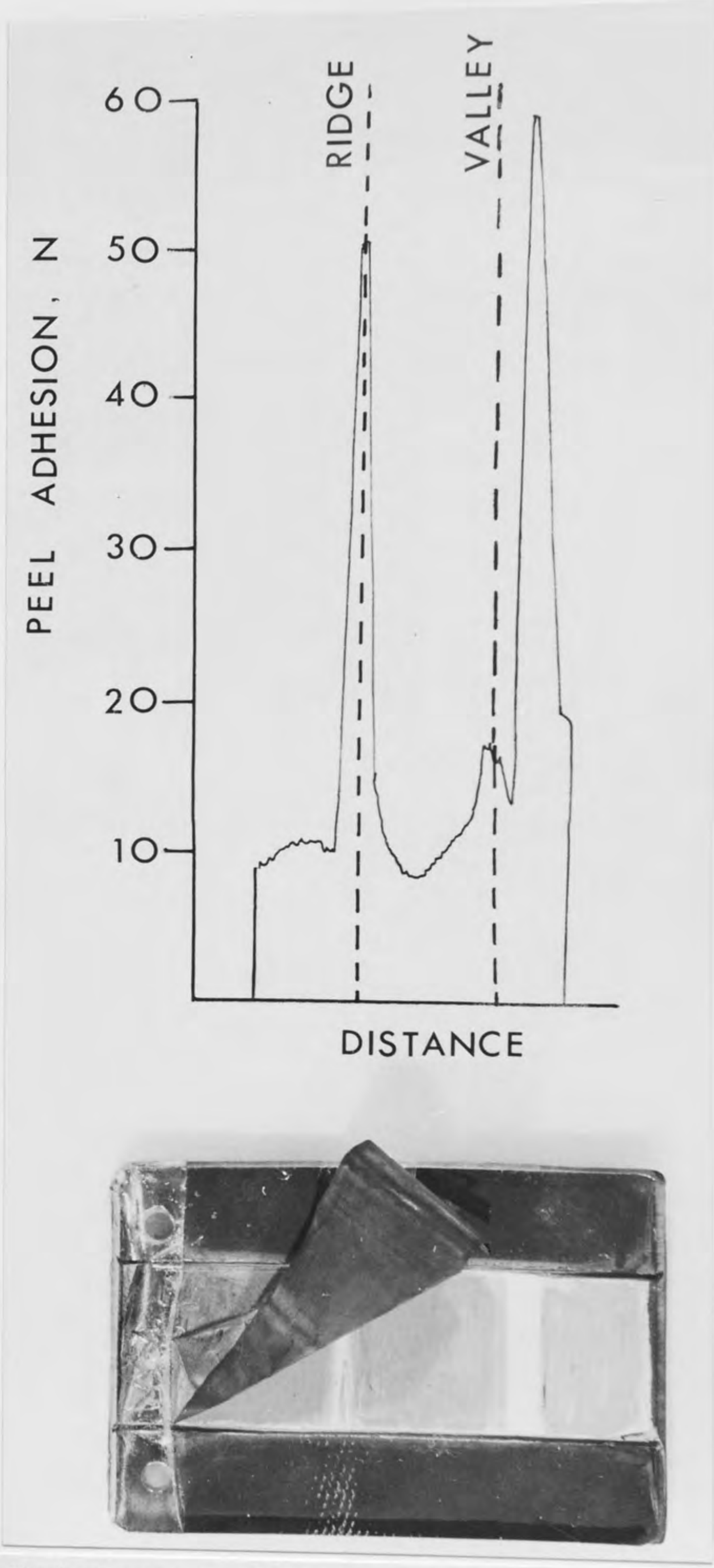


Fig.39. Typical peel adhesion curve obtained on ridged panel of ABS grade U. Light coloured bands can be seen on the panel and underside of the peeled foil corresponding to the peak adhesion regions. The vertical scale represents the load required to detach a foil 2.54 cm. wide.

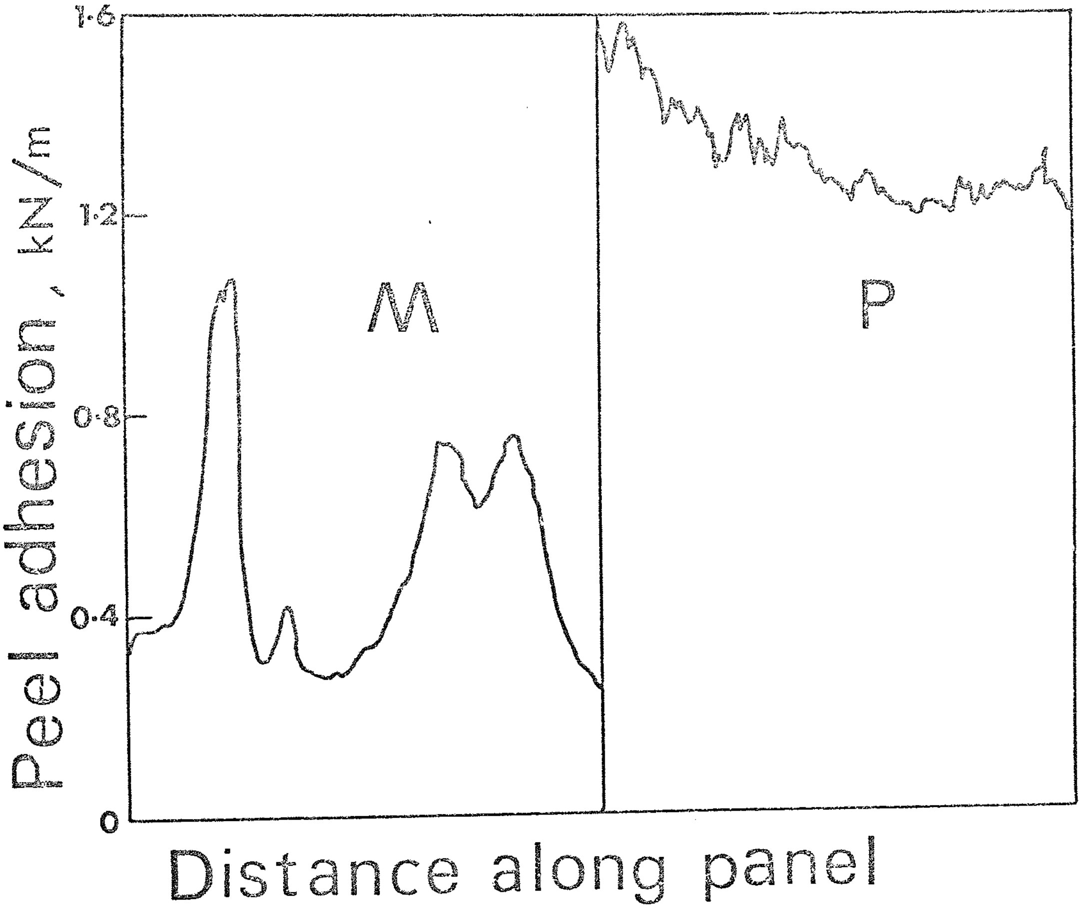


Fig.40. Typical peel adhesion curves obtained on ridged panels of polypropylene grades M and P. Both samples plated with 50 m copper, 10 min. etch. Peaks occurred on grade M but not on grade P.

The results for average and maximum peel values are recorded in Table XXV1 together with the thicknesses of detached plastics film. The SEM investigation on ABS revealed that the degree of etching varied along the plain side of ridged panels and that this was related to features on the reverse side of the mouldings. It was evident that the etch patterns in low adhesion areas were oriented in the direction of melt flow during moulding and that those areas exhibiting high adhesion were etched more uniformly. The true surface area was much greater in these latter regions and so provided more scope for mechanical keying. Also, it was noted that the palladium catalyst was adsorbed more readily at these regions and that electroless nickel deposition also occurred more rapidly, presumably due to the presence of a greater concentration of catalyst. Although greater concentrations of titanium dioxide filler were detected at the high adhesion regions using the energy dispersive X-ray analysis technique, it is unlikely that they would have had very much effect on adhesion(8).

The results of the TEM investigation confirmed that adhesion was lowest where the butadiene phase was present in an elongated form. At the ridge and valley regions it occurred as spheroids. Measurement of the "diameters" of the butadiene phase will indicate the "orientation factor" ϕ. This factor is obtained by dividing the larger "diameter" of an elongated butadiene particle by the smaller "diameter". It is obvious that the more elongated a butadiene particle is the higher the value of ϕ. A value of unity will describe a perfectly spherical

TABLE XXVI. PEEL ADHESION ON PLAIN SIDE OF RIDGED PANELS AND THICKNESS OF PLASTICS FILM ADHERING TO DETACHED FOIL

(50 μm copper coating only)

	Process Sequence	Plastics Code	Etch Times		Peel Adhesion kN/m				Adhesion Ratio Peak : Average		Ave:thickness of detached plastics film μm
			Conditioner min.	Etch min.	Average including peaks	Average excluding peaks	Peak opposite ridge	Peak just beyond valley	Ridge	Valley	
A B S	A	R	3	3	0.61	0.49	1.34	1.50	2.7	3.1	3.1
			3	6	0.74	0.60	1.51	1.93	2.5	3.2	3.6
		U	4	7	0.48	0.35	1.34	1.54	3.8	4.4	3.3
			4	14	0.44	0.34	1.04	1.22	3.1	3.6	2.6
		Z	2	7	0.56	0.44	1.62	1.69	3.7	3.8	1.3
			2	14	0.69	0.45	1.98	2.32	4.4	5.2	0.9
	B	R		5	0.77	0.53	1.88	2.03	3.5	3.8	1.5
				10	0.66	0.46	1.62	1.94	3.5	4.2	3.3
		U		20	0.41	0.34	1.05	1.27	3.1	3.7	2.2
				40	0.49	0.34	1.46	1.34	4.3	3.9	2.3
		Z		5	0.45	0.35	2.54	2.35	7.3	6.7	2.1
				10	0.57	0.34	1.77	1.77	5.2	5.2	2.1
POLYPROPYLENE	C	M		10	0.58	0.39	0.77	0.85	1.9	2.8	0
				20	1.44	1.16	1.25	1.70	1.1	1.5	0
		P		10	2.60	2.20	2.34	2.38	1.1	1.1	4.8
				20	2.40	2.05	2.17	2.27	1.1	1.1	9.3
		Q		10	2.25	2.24	2.70	2.70	1.2	1.2	0
				20	1.49	1.49	1.39	1.70	0.9	1.1	0

X

butadiene particle. The values of ϕ obtained on ABS grade along various locations of a ridged panel are listed in Table XXV11. It is evident that values of ϕ approach unity near the ridge and valley features indicating that less orientation was present. Typical TEM electromicrographs are illustrated in Fig.41. The large white areas are due to the embedding resin and the dark phase is the butadiene.

Examination of the backs of peeled foils showed that the amount of detached plastics varied along the length of panels, usually being greatest at the high adhesion regions. This effect is depicted in Fig.39.

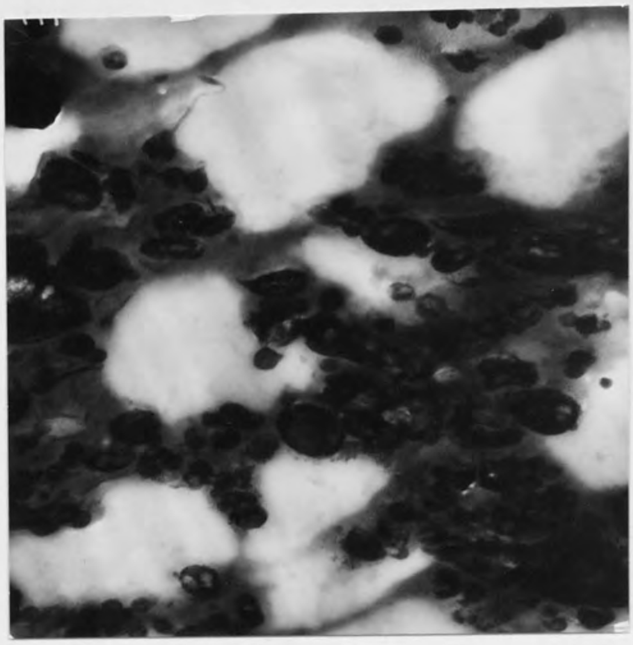
Polypropylene did not exhibit such great fluctuations in peel adhesion as ABS. In many instances peaks were barely detectable even though preferential adsorption of palladium took place on the plain surfaces of panels opposite the ridge and valley regions. The etch pattern also seemed more uniform at these parts of the mouldings. It is probable that variations in adhesion were not so marked in the case of polypropylene because it has a different structure to ABS. The latter contains one phase, butadiene, that is etched in preference to the rest while the etching of polypropylene is dependent on the relative etching characteristics of amorphous and crystalline regions, together with any effects due to fillers. Films of polypropylene could not be detected on the backs of any of the metal foils stripped from grades M and Q unless they had been stored in the slit condition. A more detailed examination of

TABLE XXVII. ORIENTATION FACTORS OF BUTADIENE AT DIFFERENT LOCALITIES ON THE PLAIN SURFACE OF RIDGED PANELS

ABS Plastics	Typical Peel Adhesion Value KN/m	Butadiene Orientation Factor ϕ	Comments
R	0.3	4.24	1 cm in from injection gate
	1.4	1.67	Opposite ridge
	1.7	1.29	Just past valley
	0.5	3.1	8 cm from injection gate
U	0.3	3.82	1 cm in from injection gate
	1.3	1.37	Opposite ridge
	1.6	1.81	Just past valley
	0.4	2.85	8 cm from injection gate

ABS Grades R and U both processed in sequence A, shorter etch times used - see Table I.

NB Peel adhesion value obtained from different panels to those used for TEM examination since etching, plating and peeling renders the surfaces of panels useless for TEM examination.



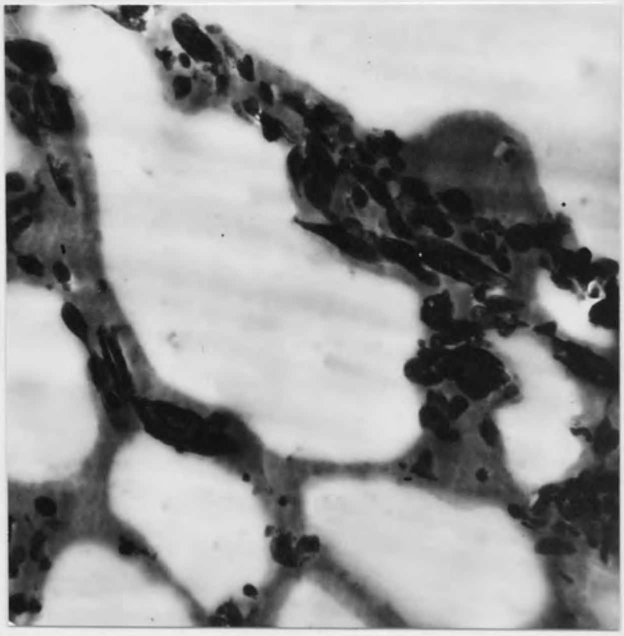


Fig.41. Transmission electronmicrographs of ABS grade U.
a) Shape of butadiene phase at surface of panel at peak adhesion area (ridge),
b) shape of butadiene phase at surface of panel at average adhesion area.
Magnification x 20,000

grade M showed that adhesion had been due solely to a 'press stud' effect. The electroless nickel appeared to have been pulled out of the holes produced by etching. It was rather surprising that an appreciable plastics layer was not present on foils stripped from grade Q since the adhesion was quite high and measurable plastics layers were detached from flat panels of this material. A few ridged specimens were slit one month before testing, plastics films could then be observed on the backs of metal foils stripped from all types of polypropylene and the adhesion values were higher than those obtained on panels stored for ten days in the unslit condition. As mentioned previously the adhesion of electrodeposited metal on polypropylene depends partly on the ease of access of oxygen.

3.9 THERMAL CYCLING

These results are presented in two sections. The first section deals with a limited programme on three grades of ABS (X, Y and Z) only. These three grades which were also used in the pilot corrosion testing programme were subjected to the "compromise" etch time of 7 min. in either process A or B. They also had the same coating systems deposited on them as used in the pilot corrosion testing programme since it was intended to see whether any relationship between the thermal cycling and corrosion tests existed; the coating systems applied are listed in Table V. The second section presents results obtained on the eight grades of ABS and four grades of polypropylene used in the main corrosion testing programme;

these also had identical etch times and moulding conditions and coating systems as used for the main corrosion testing programme, see Tables 1, 11 and V1.

3.9.1 Thermal Cycling Results on ABS Grades X,Y and Z.

The results after four cycles of the thermal cyling test are shown in Fig.42. The use of the arbitary rating system enabled assessment to be made of the extent of deterioration of test panels. It was shown that the type of ABS and processing sequence employed had a significant effect on behaviour during thermal cycling. Many of the specimens still had a high rating even after four cycles of the test but overall plastics X was slightly superior to Y while both were considerably better than Z. Processing sequence A resulted in more satisfactory behaviour than B, particularly in the case of plastics Z.

The influence of the chromium coatings on thermal cycling behaviour provided rather unexpected results. The microporous system was found to be the most unsatisfactory while decorative and microcracked chromium gave almost identical results. The latter two chromium deposits have little similarity, the microcracked was much thicker than the decorative and contained a high density of discontinuities. On the other hand, the microporous chromium was the same thickness as the decorative but had a high density of discontinuities. A tenable explanation for this behaviour has been put forward by Carter (44). He suggested that the reduced performance in thermal

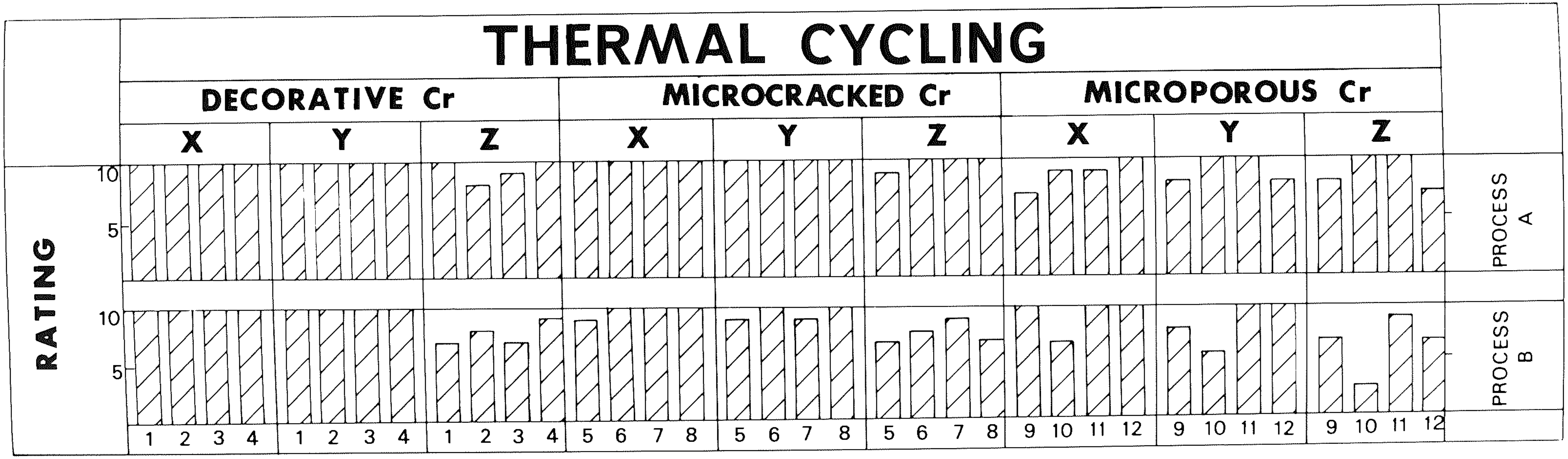


Fig.42. Ratings of plated ABS panels after four cycles of the thermal cycling test.
Numbers 1 to 12 at the bottom of the figure indicate the coating code number - see Table V.

cycling tests of microporous chromium systems may be due to the presence of the inert particles acting as stress raisers. He also suggested that the complete crack pattern in microcracked chromium may serve to act as stress relievers thus accounting for this systems' superior thermal cycling performance.

It was noted that there was no detached plastics film present on the backs of the deposited layers where a blister or other defect had manifested itself. This is in contrast to the peel adhesion test where it is common to find a detached plastics film on the backs of peeled foils. Saubestre et al (60) have also noted this effect and conclude that the thermal cycling and peel tests each measure a different property of the plastics/metal composite.

3.9.1.1 STATISTICAL ANALYSIS OF THERMAL CYCLING RESULTS OBTAINED ON ABS GRADES X, Y AND Z.

Programs for the analysis of variance yielded the information which is summarised in Table XXV111. It appeared that the ABS plastics grade and processing sequence were of greater significance in thermal cycling than in corrosion tests.

3.9.2 Thermal Cycling Results on ABS Grades R,Y,Z,S,T,U,V, and W, and Polypropylene Grades M,N,P and Q.

The results after four cycles of the thermal cycling test are shown in Fig.43. The present results showed that all grades of ABS were more satisfactory when processed using sequence A than when processed in sequence B. Thus not only were the earlier findings

TABLE XXVIII. VARIABLES AFFECTING PERFORMANCE OF ABS GRADES X, Y, Z ON THERMAL CYCLING

Significant Variables	Per Cent Significance Level	Significant First Order Interactions	Per Cent Significance Level
Plastics Type	0.1	Plastics Type with Process Sequence Type	1.0
Process Sequence Type	0.1		
Chromium Type	0.1		

See Table V. for coating systems applied.

TABLE XXIX. VARIABLES AFFECTING PERFORMANCE ON ABS GRADES R, Y, Z, S, T, U, V, W AND POLYPROPYLENE GRADES M, P AND Q ON THERMAL CYCLING, 6 μm BRIGHT NICKEL DEPOSITS

	Significant Variables	% Significance Level
ABS	Process Sequence	1
	Plastics Type	1
	Chromium Type	1
Polypropylene	Plastics Type	5

See Table VI . for coating systems applied

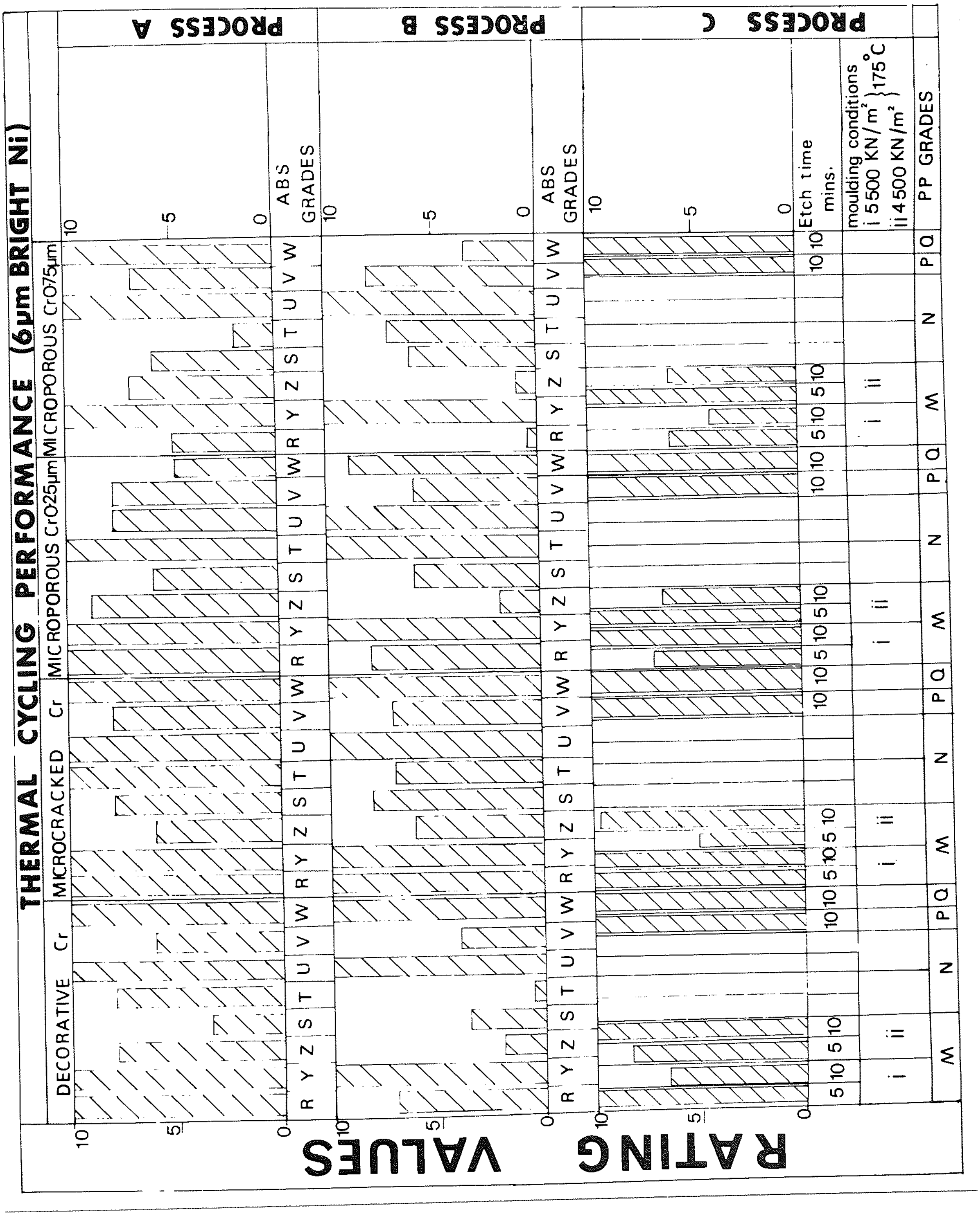


Fig.43. Ratings of plated ABS and polypropylene panels after four cycles of the thermal cycling test - 6 µm bright nickel.

confirmed in a general manner but plastics type Z was again shown to be the least resistant to thermal cycling. It failed predominantly due to blister formation around the injection gate area. Microporous chromium 0.75 µm thick did not perform well since edge cracks developed, in many cases after the first hot cycle. These cracks were similar in form to the ones observed in the corrosion studies. On examination of the results of the thermal cycling of plated polypropylene it is evident that it performs better than plated ABS in this test.

There was a tendency for coating systems having a 15 µm bright nickel layer to perform in an inferior manner to those having a 6 µm bright nickel layer. This is probably a result of greater stresses being developed between the fairly rigid coating and the substrate due to thermal expansion and contraction.

3.9.2.1 STATISTICAL ANALYSIS OF THERMAL CYCLING RESULTS OBTAINED ON ABS GRADES R,Y,Z,S,T,U,V and W, and POLYPROPYLENE GRADES M,N,P and Q.

Computer programs for the analysis of variance yielded the information listed in Table XXlX.

Processing sequence, grade of plastics and chromium type were shown to be significant in the case of the 6 µm thick bright nickel coatings on ABS but for polypropylene only the grade was important; even this was significant only at the 5% level since all grades of polypropylene regardless of chromium type, moulding conditions or etch time exhibited good resistance to thermal cycling failure. As indicated later in the discussion of the analysis of corrosion test results, it is not possible to discriminate between variables if there is a great similarity in the results.

4 DISCUSSION OF RESULTS.

This discussion is presented in three sections. The first section deals with the corrosion test results and the second with the mechanical test results; the peel adhesion and thermal cycling results are discussed at the end of the mechanical test section. Comparisons and relationships between the various tests in the light of overall service performance trends are discussed in the third section.

4.1 Corrosion Tests.

The pilot corrosion testing programme using only three grades of ABS (X, Y and Z) two ABS pre-electroplating sequences (A and B) and a compromise etch time of 7 min. highlighted some of the problems encountered in attempting to relate the results of laboratory tests to service behaviour. The same corrosion mechanism occurred in all three corrosion tests although inevitably the rate of attack varied. The equations listed in Table X1 enable a reasonable estimate of performance in an outdoor test to be calculated from CASS test results. Process sequence A was shown to lead to better results in all three corrosion tests. Two phenomena are of importance regarding the process sequence : A etches a particular grade of ABS more severely than B in a given time and the electroless nickel used in process A was more noble than that used in process B. Both effects are likely to result in better performance when using process A, as long as the ABS is not grossly over-etched. Since electroless nickel B is less noble than A its use is more likely to result in blister formation. Wiggle et al (43) have shown the importance of a well etched surface in retarding blister formation. Consequently, the extent of blister formation in a corrosive environment is not just associated with the strength of the bond between the coating and substrate.

Plastics type Z had the highest butadiene content, etched most readily and performed well in corrosion tests. Adequate or even slight over-etching occurred in the 7 min. allowed; this resulted in the production of a well roughened surface which discouraged the lateral spread of attack of corrosive electrolyte.

Plastics X and Y were of similar composition but Y contained an extra additive - vinyl pyridine. They behaved in a similar manner when plated except after corrosion testing. This was almost certainly due to the greater resistance to etching of type Y.

As a result of visual and microscopic examination, the grade of ABS and process sequence were considered to be of greater significance with regard to corrosion behaviour than was suggested by the statistical analysis. The latter did indicate clearly the significance of nickel thickness and chromium type. The effect of process sequence on corrosion behaviour has been discussed earlier and the results summarised in Table VIII illustrate that it is of significance only in relation to appearance ratings. The reason for plastics type not being shown to be of significance may be that the eye and the microscope are more sensitive than the numerical rating system, or possibly may be due to the way in which the system was employed.

The corrosion results obtained from the main test programme confirmed most of the earlier findings on ABS substrates and provided information on four grades of polypropylene. ABS grade Y which had proved disappointing in the pilot corrosion testing programme when given a standard 7 min. etch now performed considerably better when etched more severely, blister formation did not occur so readily during corrosion tests. This illustrates the importance of determining the correct processing treatment for each grade of plastics. In the case of polypropylene a limited programme was undertaken to investigate the effect of moulding conditions on etching characteristics and corrosion performance. Fig.20 shows that the degree of etching was certainly influenced by the moulding conditions and so emphasises the need for precise control at all stages in the production of plated plastics components. However, in spite of their influence on etching characteristics the variations in moulding conditions investigated had surprisingly little effect on corrosion behaviour. On balance, moulding condition (ii) (see Table 11) which produced mouldings more susceptible to the etching process was associated with better corrosion performance.

In the case of ABS, process sequence A was usually superior to B with regard to corrosion resistance even though mostly optimum etch times were used for either process. This suggests that the surface roughness effect is not the sole factor of importance in influencing performance. The relative nobilities of the electroless nickels used in the processes were known also to have a significant effect on blister formation in a corrosive environment. The limited programme undertaken using electroless copper instead of electroless nickel on ABS grade Y and two etch times, 7 and 21 min. showed that it was superior to electroless nickel in static corrosion tests. Even when the shorter etch time was used in sequence B it was noted that gross blister formation did not occur, even on specimens having a decorative chromium overlay. The anodic potential behaviour of the electroless copper deposit showed it to be considerably more noble than either of the electroless nickels, Figs.23 and 24. There has been much dispute over the years with regard to the type of electroless deposit which should be used. Marcus (29) has favoured electroless nickel so that the "all nickel" systems can be used. These he has claimed have several advantages over electroless copper + electrodeposited copper systems. He states that the total elimination of copper is desirable from a corrosion stand point since if "all nickel" systems are used then there is likely to be little difference in the corrosion potential set up in the multilayer coatings. However, as shown earlier the present author has found that the differences in potential between the electroless nickels and the electrodeposited nickel was quite large, for instance up to 210 mV with respect to the S.C.E. when using air agitated acetic acid salt spray solution. This is in contrast to the suggestions of Marcus (29). A further aspect which leads Marcus to favour electroless nickel is the ease of bath operation and maintenance of those solutions compared to electroless copper ones. Carter (44) has suggested the use of boron-type electroless nickels which exhibit good bath stability, covering power and a more favourable anodic potential; this seems a reasonable avenue to pursue if maximum freedom from blistering is required.

The corrosion results obtained when using microporous chromium deposits 0.75 μm thick were less satisfactory than when a deposit 0.25 μm thick was used. This was due to the development of edge cracks which probably resulted from too great a thickness of chromium being deposited despite the use of 'robbers'. The cracks may also have been propagated by flexural effects caused by relative differences in the coefficients of expansion of metals and plastics substrates. It can be observed in Fig. 43 that some grades of ABS performed much better than others having an overlay of thick microporous chromium. It is possible that a thickness intermediate between 0.25 µm and 0.75 µm may be the best compromise in that when exposed to a corrosive environment surface dulling due to excessive fine pitting and staining would be delayed without the formation of visible cracks.

At the detailed corrosion assessment of the main corrosion programme on the 31/3/74 it was evident that polypropylene grades P and Q were the most successful and that they were superior to even the best grades of ABS.

The last detailed examination of the main programme which took place in September,1974 showed that not only were the polypropylene grades P and Q still superior to ABS but also that the specimens having a 15 µm thick bright nickel layer were still relatively unaffected this was especially the case on specimens having a decorative chromium overlay since those having micro-discontinuous chromium overlays still exhibited good performance. It is of interest to note however, that the specimens having the thinner nickel deposit and a microdiscontinuous chromium overlay were severely stained indicating that some penetration to the copper layer had occurred.Similar specimens but having 15 µm bright nickel layers were still not stained after this exposure programme. It is indicated that thicker nickel layers are needed beneath microdiscontinuous chromium layers if a copper undercoat is employed ; this will retard the rate at which the staining will appear. In general, doubling a given nickel thickness will quadruple the time needed for penetration by a corrosive environment.

The use of microdiscontinuous chromium overlays and their influence on corrosion have been adequately discussed by several authors (45,46,73). There seems to be little choice between microcracked or microporous chromium since both afforded good protection to the underlying layers. However, as previously discussed if too great a thickness of microporous chromium is employed cracking may well appear; this will afford the corrosive environment access to the underlying layers which could result in blistering. A point of interest to consider when assessing the relative merits of microcracked or microporous chromium for corrosion resistance is their cost. Microcracked chromium solutions must be operated at precise conditions in order to obtain a satisfactory crack pattern. Also the current density required is very high (17 - 19 A/dm^2) and the times of deposition are around 15 min. Thus a microcracked chromium deposit is likely to be expensive to apply due to the cost of rectifiers having the necessary capacity. In contrast, microporous chromium can be relatively easily produced by the addition of a thin "special nickel" layer immediately after the bright nickel deposit but before the chromium is applied. The deposition of the chromium is carried out using standard decorative chromium plating conditions with current densities around 10.0 A/dm^2 and plating times of 7 min. Hence microporous chromium appears to be the better layer to apply from economic considerations. However, the final choice of deposited layer must be made with regard to the other functions an item must undertake. For instance, this present work has shown that microporous chromium can exert an unfavourable influence in thermal cycling tests.

4.2 MECHANICAL TESTING.

4.2.1 Tensile and Impact Tests.

The investigation illustrated that two properties of ABS and polypropylene, ductility and impact strength, were adversely affected by the application of electrodeposited coatings. Even the U.T.S. of many plastics plated with copper + nickel + chromium coatings was no greater than that of the same grade of plastics in the etched condition.

In the tensile test the electrodeposited coatings always cracked first followed by rapid brittle failure of the substrate. The metal layers were the first to crack because their Young's Moduli were greater than those of the plastics substrates and so the application of a given strain resulted in a greater increase in stress in the metal than in the plastics. The cross-sectional areas of the coatings were small compared to those of the substrates and so the fracture stress of the metallic layers was reached quickly. It was noted that a single crack occurred in copper and copper + bright nickel deposits whilst coatings having various chromium overlays usually exhibited multiple cracking. Dennis (87) has noted this effect on metallic substrates, the density and severity of cracking was related to the type and thickness of the chromium layer ; microporous chromium 0.75 µm thick was particularly susceptible to multiple cracking - See Fig.44. Initially it was thought that sudden load transference together with an associated high induced strain rate was responsible for the brittle behaviour observed. By using the concept of compound bar theory (88) a model was established to examine how a given load would be shared by the plastics substrate and copper coatings of varying thickness. The portions of the load borne by the substrate and metal are dependant on their Young's Moduli and cross-sectional areas. By reference to Fig.45, it can be seen how the theoretical proportions of the loads borne by copper layers vary with increasing thickness. At a copper thickness of 20 μm it was shown by calulation that the substrate (grade Z) supports only 49% of the total load. Fig.45 was constructed by making the following assumptions :-

i) A good bond exists between the coating and substrate.

ii) Load supported by substrate + Load supported by coating = Total load.

ie $(\sigma_p \times A_p) + (\sigma_m \times A_m)$ = Total load.

Where σ_p represents the stress in the plastics;
A_p represents the cross-sectional area of the plastics;
σ_m represents the stress in the metallic coating;
A_m represents the cross-sectional area of the metallic coating.

iii) $$\frac{\sigma_p}{\sigma_m} = \frac{\text{Young's Modulus of Plastics } (E_p)}{\text{Young's Modulus of Metallic Coating } (E_m)}$$

The Young's Modulus for copper was assumed to be 103×10^3 MN/m^2 and for ABS plastics grade Z 1.66×10^3 MN/m^2.

Fig.44. Tensile fracture of polypropylene grade M. The loss in adhesion of the coating to the substrate has resulted in loose 'collars' of electrodeposit forming along the gauge length. The specimen exhibited a ductile mode of failure. 10 min. etch plated with 20 µm copper + 6 µm bright nickel + 0.75 µm microporous chromium.
Magnification ∿ x 1¾.

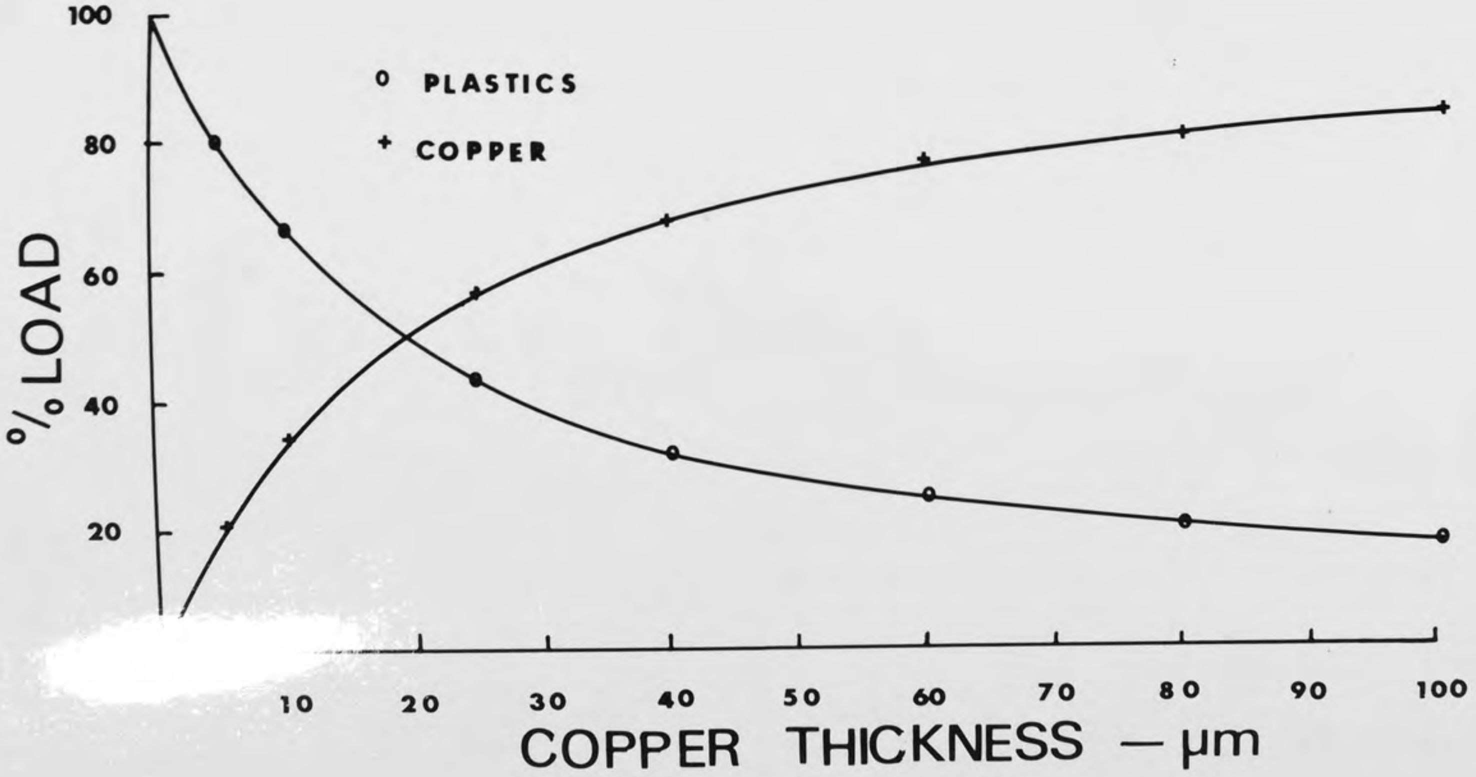


Fig.45. Calculated relationship between the percentage of load borne by the plastis substrate (grade Z) and copper coatings of varying thicknesses, in the tensile test.

If for example the fracture load of a specimen of ABS grade Z plated with 20 µm of copper were 1846 N, then the respective loads carried by the two materials would be 907 N by the plastics (stress 24 MN/m^2) and 939 N by the copper (stress 1514 MN/m^2). The fracture stress of this grade of plastics in the unplated condition was 42 MN/m^2 but at the instant of failure of the copper coating, when that portion of the load borne by the metal is rapidly transferred to the substrate, the latter would be stressed above its fracture value. In the example quoted the stress induced on failure of the coating would be about 49 MN/m^2. The strain rate would also be high and so both these effects are likely to induce brittle failure.

The model predicts that with very thin copper deposits most of the load is borne by the substrate and this suggests that in such situations the load transference effect should be insignificant on failure of the copper layer. Specimens of grade Z were plated with 2 µm of copper and tested but they all failed in a brittle manner. It should be noted that specimens coated with electroless nickel failed at a somewhat lower ductility when unplated. Grade Z was also plated with 500 µm of copper so that a large proportion of the load would be carried by the coating. Brittle failure again occurred, the ductility being only slightly greater for specimens plated with 20 µm of copper. Matsunaga and Hagiuda (57) noted a more significant increase in ductility with increase in copper thickness but they only deposited coatings up to 126 μm thick. It is also important to note that they tested metal/ plastics/metal 'sandwiches' and as such the stress system existing in their tests would be different to the stress system present in these tests. This may well account for the higher elongation values they recorded.

The UTS was increased in the case of the 500 μm thick coating, the stress at fracture for the composite specimen being 106 MN/m^2 compared to about 48 MN/m^2 when plated with 20 μm of copper.

Fig.46 was constructed to indicate how the distribution of the load between substrate and coating would be influenced by variation in the ratio of the Young's Moduli of plastics and copper at a particular coating thickness of 20 μm. Lines have been drawn in Fig.46 to indicate the values relevant to the four grades of ABS used in the investigation. Since a range of values exists for the Young's Moduli of the various grades, the load distribution varies significantly for different plastics/copper combinations. These models have been constructed for single layers of copper but it is obvious that the situation is much more complicated for multilayer coatings having widely different Young's Moduli.

From the results reported it is evident that a sudden load transference effect is not solely responsible for the brittle behaviour observed. A series of unplated ABS and polypropylene tensile test pieces had notches machined at 90° to their gauge lengths. V (45°) and U shaped notches were machined to depths of 25,

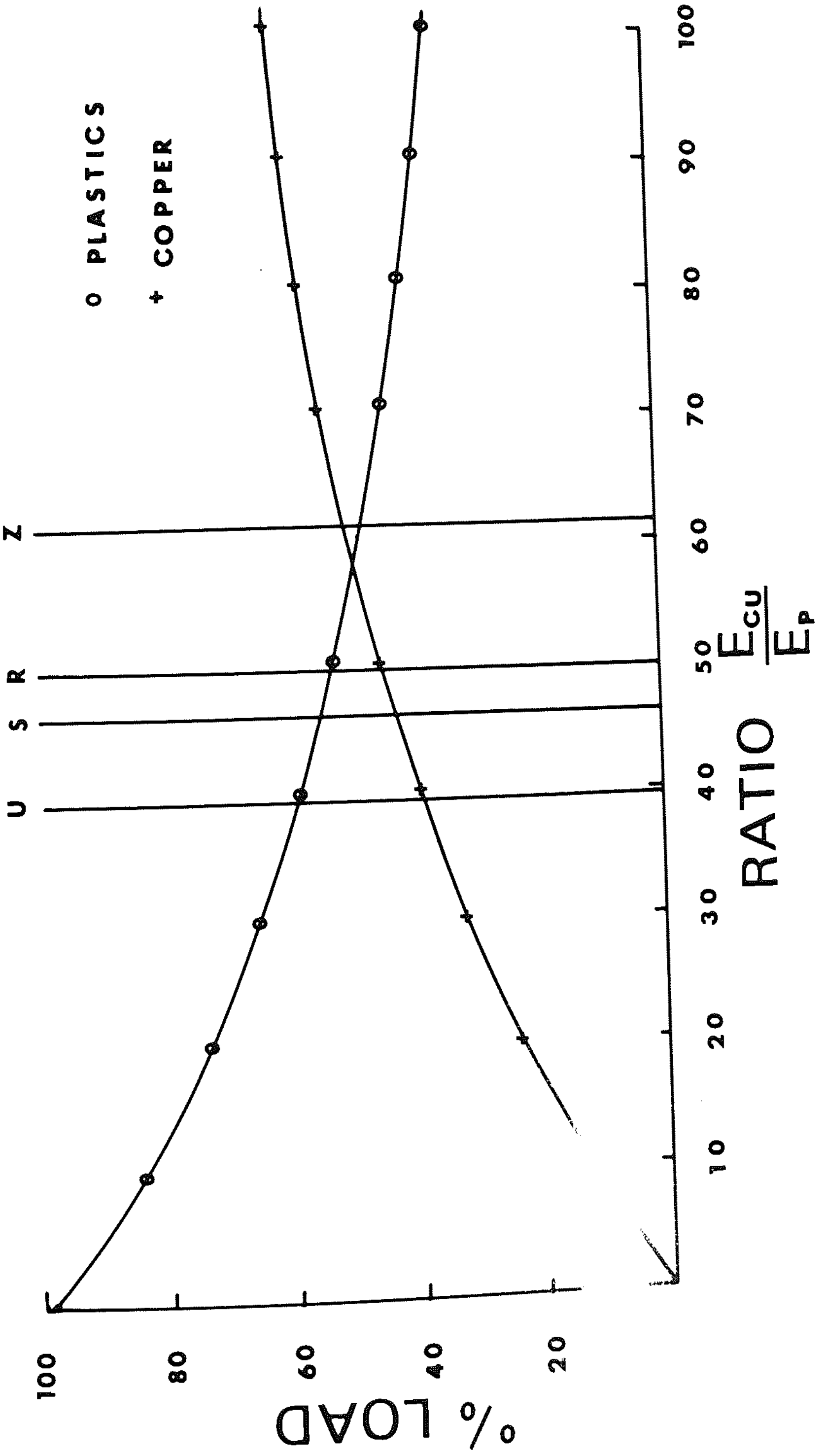


Fig.46. Influence of variations in the Young's Moduli of plastics substrates on the distribution of the load carried by plastics tensile specimens plated with 20 μm of copper.

The ratios $\frac{E_{cu}}{E_{pl}}$ and the load distributions relating to the four grades of ABS used in the investigation are indicated.

75 amd 150 μm. A similar series of impact specimens were also produced. In all cases the notches caused a reduction in ductility and impact strength thus demonstrating that all the plastics were to some extent notch sensitive. In both tests V notches had a greater effect than U shaped ones and the deeper the notches the more severe their effects. Polypropylene grade M was affected less than any of the other plastics by the presence of notches but was still embrittled a significant amount. This grade of polypropylene was a copolymer containing about 10% ethylene and it is known(3) that propylene/ethylene copolymers are more resistant to notched impact testing than homopolymers. Grade M also exhibited somewhat more favourable behaviour than other plastics on ductility and impact testing when plated.

The notch sensitivity investigation suggested that brittle failure of plated plastics was at least partly due to the initiation of cracks in the coating and their subsequent propagation into the substrate. Due to the degree of notch sensitivity of the plastics this is probably the dominant mechanism. However, the sudden load transference phenomenon would assist the propagation of cracks due to the release of energy at the tip of the crack. Propagation of cracks from the coating to the substrate is more likely to take place if there is good adhesion between the two materials. This effect was illustrated when tensile tests were undertaken on polypropylene grade M, which the peel adhesion tests had shown exhibited a very low peel adhesion value. Many of these specimens were not severely embrittled but during tensile testing they "necked down" so that loose collars of electrodeposit were formed along the gauge length as shown in Fig.44. In regions where the coating became detached the test was effectively being carried out only on the substrate and should be considered invalid (see Tables XV1 and XV11). Further tests were carried out on tensile specimens that had been coated with a resist, on top of the electroless nickel layer, over part of their gauge length in order to prevent deposition of copper in that region. Examination during testing revealed that "necking down" was prevented where the copper coating was present but the unplated portion had extended a considerable amount. Non-uniform extension can also result in low ductility. If a crack propagates from the metal layers to the substrate, it can be envisaged that a minute 'gauge length' of plastics is exposed at the tip of the crack. The substrate is pinned in these regions if the metal to plastics bond is good on either side of the crack. Although the percentage elongation of the plastics may be relatively high, for example about 15% the actual extension possible on the 'gauge length' exposed at the bottom of the crack would be extremely small.Consequently the overall ductility of a plated specimen would appear to be low due to this effect. Examination of the fractured ends of plated samples showed that in virtually every case whitening of the plastics due to plastic deformation had not taken place under the electrodeposits.

A copper plated ABS specimen, grade Z, was stripped using 20% W/V ammonium persulphate solution at room temperature and then subjected to the tensile test. The ductility value obtained was similar to that exhibited by an etched sample of the same material thus indicating that the heating and immersion operations involved in copper plating and stripping had had no residual effect on ductility.

There are obvious differences between the tensile and impact tests. The rate of application of the load is non-uniform and rapid in the impact test and one side of the specimen is in compression while the other is in tension. However, since failure always occurred from the side in tension it is probable that similar arguments can be used to explain the brittle behaviour encountered in both tests.

4.3 PEEL ADHESION TESTS.

The study of factors influencing the peel adhesion value on plated ABS and polypropylene provided information regarding detached film thickness and the effects of multilayer coatings.

Saubestre et al(60) have discussed in detail the use of the peel test for determining the adhesion of electrodeposits to plastics. They concluded that the resulting numerical reading was not a true measure of adhesion but was actually a measure of a complex of factors including the thickness of the electrodeposited metal, Young's modulus of the yielding plastics film and the tensile strength of the yielding plastics film. By mathematical analysis they showed that to a first approximation $F = Kt_m^{\frac{3}{4}}$, where F is the measured peel adhesion, t_m is the thickness of the electrodeposited metal and K is a constant. Consequently, according to this equation higher peel adhesion values should be obtained as the thickness of the electrodeposited layers is increased. However, their practical results showed that K decreased as the thickness of the metallic coating, t_m, increased. They considered that K was a better measure of real adhesion than F since the latter can be 'artificially' increased by increasing t_m.

Some of the results obtained in the present work are not in agreement with those found by other authors'(7,60). As just described, Saubestre et al (60) showed both on a theoretical and practical basis that peel adhesion was governed by the metallic coating thickness for a particular grade of ABS treated in a given process sequence. The results given in Table XXV do not show this trend. Grade of plastics was shown to influence the results as illustrated in Figs. 37 and 38. Peel adhesion and thickness of detached plastics film are likely to be influenced by the extent of chemical and mechanical bonding, in turn these will be affected by factors such as composition of the plastics material, process sequence, ease of access of oxygen to the metal/plastics interface and moulding conditions. Consequently, test conditions must be specified precisely if peel adhesion values are to be of any significance. This was taken into consideration by the ASTM, committee B8, when evaluating test methods with a view to developing an ASTM Recommended Practice on plating on plastics. In the present work a fair scatter of results was encountered even when precautions had been taken to standardise the test conditions and a doubt still remains as to whether or not the peel test is a realistic measure of adhesion in relation to service performance. A copper coating is normally employed for the peel test while in practice copper + nickel + chromium coatings are applied for most applications. Inspection of the curves shown in Fig.34 indicates how changes occurred in peel adhesion, even on plain flat panels, as a foil approximately 4 cm long was peeled off. For example, in the case of grade Z processed in sequence A and plated with 50 µm of copper, the maximum value was 0.9 KN/m and the minimum 0.2 KN/m. Problems were encountered in reproducing peel adhesion results when changing from one batch of mouldings to another. This may have been due to slight changes in moulding conditions or to slight modifications in the batches of commercial materials. It had been observed that minor changes in the composition of a particular grade of plastics had a significant effect on peel adhesion (8).

This was especially true in the case of ABS grade R. After the first peel adhesion tests had been completed subsequent supplies of this material had a slightly different lubricant/plasticiser system. Consequently peel adhesion values were significantly different to those obtained before this modification to the composition.

The choice between the peel adhesion test and the thermal cycling test as a means of assessing the anticipated service performance of plated plastics is still open to dispute. Carter (74) has demonstrated the validity of the thermal cycling test in indicating likely service performance. In view of the disadvantages of the peel adhesion test and since commercial mouldings as well as specially prepared panels can be subjected to the thermal cycling test, it was probably a wise choice to include the latter in BS 4601:1970 (48) (Specification for electrodeposited coatings of nickel + chromium on plastics materials) instead of the peel adhesion test.

The thickness of plastics film adhering to a detached foil did not seem to be too important but it did appear to be associated with the particular type and grade of plastics employed. For example, ABS grade L processed in sequence A and plated with 50 µm of copper had a relatively high peel value (1.67 KN/m) but a low plastics film thickness (1.7 µm); this may have been due to the 'slip stick' peel mechanism exhibited by this grade.

The converse was true for grade Z which had a peel value of 0.59 KN/m and a plastics film thickness of 3.8 µm. A layer of plastics was detached from all grades of ABS, even when the adhesion was low, but the least successful grade of polypropylene, M, only failed in the subsurface layers of the plastics if slit and aged before testing. For a particular grade of plastics there was no definite relationship between the thickness of the plastics film detached from the plain and ridged panels.

The ridged panels illustrate the range of variations in peel adhesion that are likely to be encountered on commercial mouldings. As illustrated, a contoured profile on one surface of a moulding can affect the level of adhesion on the other side of the section. The results obtained appear to indicate that polypropylene mouldings are less likely than ABS ones to suffer wide variations in adhesion. However, the effect demonstrated should be regarded with caution since it may be due to the specific shape of the mould and the moulding conditions employed. That peaks of adhesion should appear where they do is a matter of conjecture since little is known about the mechanisms of mould filling. However, it is likely that turbulence effects in the localities of the ridge and valley features played some part in the disruption of orientation, since the butadiene in ABS mouldings was seen to be less oriented in the high adhesion areas.

A further point of interest is provided by the fact that although the two features were exactly opposite in configuration, they both were associated with peaks of adhesion. This is in conflict with Weibusch (7) who states that only an increasing cross-section results in higher adhesion. It is also of interest to note that the higher adhesion peak was always associated with the thinner cross-section. An explanation for this behaviour is that the constriction in the mould may result in an isostatic state of compression in the moulding at the adhesion peak locality. This seems tenable for two reasons; firstly, by considering the direction of melt flow it is probable that the protuberance (which causes the valley) will cause an 'overshoot' effect in the melt resulting in a band of disturbed (disorientated) material at a distance somewhat removed from the feature, this was seen to be the case in the acetic acid stress test, the TEM studies and the peel adhesion tests; secondly it is likely that the material will be in a state of compression at this locality since the constriction in the mould will locally increase the moulding pressure. It is known that compression moulded ABS exhibits much higher peel adhesion values than does injection moulded material (8).

Comparison of the peel adhesion values listed in Tables XXV1 and XXV11 indicates that the average values obtained on ridged panels were lower than those achieved on the plain ones. This suggests that overall peel adhesion may be lower on commercial mouldings than on specially prepared test panels having a minimum residual stress.

4.4 THERMAL CYCLING TESTS.

The use of the thermal cycling test in assessing likely service behaviour is illustrated when the results of this test are compared to the corrosion tests. As mentioned previously agreement appears quite good. Saubestre and Hajdu (69) indicate that the thermal cycling results can be influenced by the number of cycles applied and the temperature ranges employed; they found that the number of failures depended on the number of cycles applied, Crouch (70) did not find this trend. Such and Baldwin (72) when investigating this test found that the results could be influenced by either subjecting the plated plastics to the hot cycle or the cold cycle first; the latter proved to down-grade performance and was regarded as the more appropriate test since heating to + 80° C or more can increase peel adhesion values; their findings were largely adopted for inclusion in BS 4601: 1970 (48). It is of interest to note that although the polypropylene grades had larger coefficients of expansion than ABS they generally performed better than the ABS grades, this effect has been noted by Innes et al (68). This behaviour appears different to that observed on ABS specimens where these grades having a relatively low coefficient of expansion (Y,T and U) were superior to the other grades having relatively higher coefficients of expansion (Z and S). The role which the coefficient of expansion plays in thermal cycling can be explained using the concept of differential thermal expansion (or contraction) coefficients (88). It can be shown that in a metal/plastics composite which is heated the differences in their respective coefficients of expansion will induce stresses in both materials; the metal having a lower coefficient of expansion than the plastics will be stretched,i.e. subjected to a tensile stress, whilst the plastics will be restrained from expanding its full amount and therefore be subjected to a compressive stress. This concept assumes that a good bond exists between the metal and plastics. When the composite is cooled the stress system is reversed. This explains the appearance of blisters in the metallic overlay during cold cycles and cracks during the hot cycles. The average difference between the coefficients of expansion of ABS and plated copper + nickel + chromium is about 6, i.e. the ABS is likely to expand 6 times more than the metallic overlay in a given temperature interval. Obviously, when the ABS and metal are in the form of a 'composite' a compromise situation is reached. The concept however, fails to explain why polypropylene having a larger coefficient of expansion should exhibit superior thermal cycling performance to ABS when plated. Arguments put forward by Innes et al (68) concerning the peel adhesion values on polypropylene being greater than ABS would not explain the phenonemon adequately since the better the bond the more likely the efficient transfer of stress. A possible explanation of the phenonemon concerns the nature of the differences between the etched substrates. Etched ABS can be envisaged as having a predominantly SAN surface layer since most of the butadiene will be removed during the etching procedure (20). SAN is very brittle and will not absorb flexural effects generated by thermal cycling and rupture is likely to be induced. On the other hand, the surface of etched polypropylene is likely to contain a high proportion of isotactic (crystalline) regions since it is the atactic(amorphous) regions that are preferentially etched away. As mentioned in the literature review , isotactic polymers have extremely good overall mechanical properties,including impact resistance. Thus the surface layers of polypropylene when plated are likely to absorb thermally induced flexural effects more readily despite the greater difference between the plastics/metal coefficients of expansion. This explanation goes some way towards explaining the superior behaviour of plated polypropylene in thermal cycling. However, previous work has shown (8) that when pure SAN is plated and subjected to the thermal cycling test its performance is very good; it should be noted that both the coefficient of expansion and the peel adhesion values were extremely low. This latter statement tends to support the theory put forward concerning the effect of the coefficient of thermal expansion on ABS substrates but is in conflict with the effect of surface mechanical properties. In the case of SAN, although it is brittle there would be little induced stress in thermal cycling due to its relatively low coefficient of expansion. This would be conducive to a high thermal cycling performance.

It is obvious that the factors influencing thermal cycling performance are complex. It is indicated that if a mechanically tough substrate is present after etching then good thermal cycling performance is likely. Furthermore, if this requirement can be satisfied as well as having a plastics substrate with a low coefficient of expansion few thermally induced failures within the range - 40° C to + 80° C should occur.

4.5 GENERAL CONSIDERATIONS

This investigation has indicated that many variables are likely to affect the service life of plated ABS and polypropylene plastics. The statistical analysis techniques did much to confirm experimental inferences and also indicated where other variables were likely to influence the properties being assessed. The results of the statistical analysis are summarised at the end of each relevant section.

It was seen that the moulding conditions and mould shape could influence peel adhesion values but the limited investigation into the effects of moulding on corrosion behaviour did not indicate any trends, despite the fact that in the cases examined, (polypropylene grades M and N), moulding conditions did affect their propensity towards etching and, this is known to retard blister formation (43). Early assessments on the corrosion behaviour of these grades of polypropylene did show that etching time and moulding conditions were influencing performance. This highlights an important consideration regarding corrosion testing and assessment since if corrosive attack is allowed to progress too far then even the ratings of corrosion resistant systems may approach those allotted to poorly resistant ones. As the rating values approach one another it is difficult to differentiate between the performances of the coatings. The influence on corrosion performance of ABS processing sequence was seen to be associated with the relative severity of the etch and also the activity of the electroless nickel used in either sequence. ABS specimens processed using sequence A were consistently superior to those processed in B since the former process etched more severely thus retarding lateral spread of blisters (43) and also employed a more noble electroless nickel. The performance of specimens having an electroless copper underlayer was found to be good, even when having decorative chromium top coats. The anodic potential determinations certainly suggested that the electroless copper was considerably more noble than either of the electroless nickels. That microdiscontinuous chromium deposits conferred excellent corrosion resistance was not surprising since the virtues of these types have been known for some years. By providing numerous potential corrosion sites these systems effectively reduce the corrosion current and so the attack is confined to shallow pits all over the surface of the article, hence penetration to the underlying layers and substrate is retarded. The use of 'thick' deposits of microporous chromium is to be avoided since stress cracks frequently manifested themselves in corrosion and thermal cycling tests.

The mechanical testing results, in complete contrast to the corrosion results, showed that the etching times and process sequences employed had little influence on the performance. The plastics were all notch sensitive and this feature appeared to dominate the test results. Polypropylene grade M being a propylene/ ethylene copolymer exhibited somewhat more favourable behaviour in mechanical tests since copolymers are less notch sensitive than homopolymers. However, its performance in corrosion and peel adhesion testing was generally unsatisfactory. In contrast to this, polypropylene grades P and Q exhibited good performance in corrosion testing but their ductilities and resistance to impact were adversely affected by the application of electrodeposited layers; both of these grades were homopolymers with inorganic fillers. It is of interest to note that both these grades exhibited relatively high peel adhesion value. The latter feature may well have been instrumental in causing the severe embrittlement observed during tensile and impact testing due to the efficient transference of the crack from the metallic layers to the substrate. The performance of plated ABS and polypropylene in impact tests at sub and elevated temperatures was largely as expected, but electrodeposited layers still rendered the plastics brittle even at elevated temperatures. The peel test was found not to give realistic assessment of service performance. In the first phase of the investigation when only ABS grades X,Y and Z were used it was indicated that the peel test would give a better 'measure' of performance; however, in the main programme which involved eight grades of ABS and four grades of polypropylene it was found that the thermal cycling test was more valid than the peel adhesion test in indicating those plastics/metal composites which were likely to give inferior service performance.

The thermal cycling test results were obtained using the arbitary system outlined in Table IV since the no other way of 'quantifying' the results exists. The variables indicated as influencing the performance in the test were different for ABS and polypropylene substrates. The former were influenced by processing sequence (process sequence A generally superior to B), plastics grade (ABS grades having lower coefficients of thermal expansion and those having proportions of . α methyl styrene in their resin phases superior to other grades) and chromium type (microporous chromium inferior to other types). The performance of polypropylene was only influenced by the grade of polypropylene but the statistical evidence for this inference was relatively low (5% level of significance). This was due to the fact that all grades of polypropylene exhibited good thermal cycling performance.

The factors influencing the thermal cycling performance appear complex but those plastics having low coefficients of expansion and tough subsurface layers after etching are likely to resist thermally induced service failures.

The relative performances of the grades of ABS and polypropylene are summarised in Tables XXX and XXX1. The plastics are arranged in order of performance in each test; it will be noted that a reasonable fit exists between the corrosion tests and the thermal cycling tests when the eight grades of ABS are considered ; this is in contrast to the trend shown in Table XXX1, when only three grades of ABS were considered. The reason for this is most probably the use of the 7 min. compromise etch time for ABS grades X,Y and Z and the fact that grade Y exhibited low peel adhesion as well as poor corrosion performance. Table XXX1 gives an insight to the validity of the various tests in predicting service performance. The outstanding feature is that although ABS plastics grades S and Z had a relatively high peel adhesion value they exhibited poor thermal cycling and corrosion performance despite the use of more appropriate etch times. In contrast, polypropylene grades P and Q had good peel adhesion values and also performed well in corrosion and thermal cycling tests. This tends to suggest that polypropylene is the better plastics to use. However, polypropylene grades P and Q proved disappointing in tensile and impact

TABLE XXX. GENERAL TRENDS OF BEHAVIOUR OF THREE GRADES OF PLATED ABS (X, Y and Z) AND TWO PRE-ELECTROPLATING SEQUENCES (A and B)

TEST	ORDER OF PERFORMANCE OF ABS GRADES				ORDER OF PERFORMANCE OF PRE-ELECTROPLATING SEQUENCES		
	1st	2nd	3rd	Comments	1st	2nd	Comments
Corrosion	Z	X	Y	X and Z very similar	A	B	
Thermal cycling	X	Y	Z	X and Y very similar	A	B	
Peel adhesion	Z	X	Y	X and Y very similar. Order shown relates to 7 min. etch.	A	B	In case of Y, at etch time used for other tests, process B gave a higher peel adhesion value than A.

TABLE XXXI. GENERAL TRENDS OF BEHAVIOUR OF PLATED ABS AND POLYPROPYLENE IN CORROSION, THERMAL CYCLING AND PEEL TESTS. ABS GRADES R, Y, Z, S, T, U, V and W AND POLYPROPYLENE GRADES M, N, P AND Q.

	TEST	Nickel Thickness µm	ORDER OF PERFORMANCE 1st	2nd	3rd	4th	5th	6th	7th	8th	COMMENTS
A B S	Corrosion	6	Y	W	T	U	Z	V	S	R	
		15	U	R	Y	Z					Order based on CASS results only
	Thermal Cycling	6	Y	U	W	R	T	V	S	Z	Y and U similar R, T and V similar
		15	W	Y	T	R	Z				
	Peel Adhesion		S	Z	T	W	U	Y	V	R	Order based on peel results obtained ten days after plating
POLYPROPYLENE	Corrosion	6	P	Q	M	N					P and Q far better than M and N
		15	P	Q	M						Little deterioration after 8 months.
	Thermal Cycling	6	P	Q	M						All good
		15	P	N	Q	M					All good
	Peel Adhesion		P	Q	M	N					Order based on peel results obtained ten days after plating

Order shown relates to performance at 31/3/74 testing where it was found that their ductilities and impact resistance suffered adversely by the application of electrodeposited layers.

5 CONCLUSIONS.

The importance of choosing the correct processing conditions and grade of plastics has been demonstrated. ABS process sequence A was associated with superior corrosion performance to B since it employs a more severe etch and a more noble electroless nickel; both factors have been shown to lead to better corrosion performance. The use of electroless copper instead of electroless nickel is likely to result in a further increase in corrosion performance. If a copper layer is present then an increase in bright nickel thickness will retard the appearance of unsightly staining due to copper corrosion products.

The use of microdiscontinuous chromium overlays resulted in an increase in corrosion performance but if too thick a deposit of microporous chromium layer were employed then edge cracking may occur resulting in a decrease in corrosion performance. Decorative chromium overlays were unsatisfactory for outdoor service conditions; this was particularly true when thin layers of bright nickel were used.

Two mechanical properties of ABS and polypropylene, ductility and impact strength, have been shown to be adversely affected when electrodeposited metal layers were applied. The mechanisms responsible for these phenomena appear to be due to a complex of factors, the most important of which is the degree of notch sensitivity exhibited by the various plastics. The use of propylene/ethylene copolymers is likely to result in better performance but until a more satisfactory level of adhesion can be obtained it is prudent to regard the results with caution since a high adhesion value may well adversely affect the results.

The level of peel adhesion on ABS and polypropylene seemed relatively unchanged over the range of etch times used in the investigations; the peel adhesion value on polypropylene was found to be partly dependant upon the ease of access of oxygen to the polymer/metal interface.

In situations involving thermal cycling those grades of plated ABS having relatively high coefficients of thermal expansion are likely to be inferior to those having lower coefficients,particularly if these grades have a proportion of α methyl styrene in their resin phase. Plated polypropylene was superior to plated ABS in thermal cycling despite the former plastics higher coefficient of expansion; the nature of the differences between the etched surfaces of ABS and polypropylene could explain the phenonemon. Polypropylene is expected to have a high proportion of isotactic material in the surface layers after etching whereas ABS will have a high proportion of SAN, the isotactic material is more likely than SAN, to absorb thermally induced stresses.

Overall, the thermal cycling test results were shown to be more reproducible than the peel adhesion test results. The former test provided a better assessment of service performance in the main programme. Since the peel adhesion test conditions have to be specified precisely if any meaningful interpretation is to be derived from the test the use of the thermal cycling test appears to be more favourable.

In the main programme ABS grades Y,W,T and U gave better service performance, especially if processed using the pre-electroplating sequence A. ABS grades S and Z although exhibiting reasonably high peel adhesion values would not be as satisfactory for use in service applications involving thermal cycling between - 40°C and + 80° C.

The choice of plated ABS grade for functional applications seems unimportant in that apart from initial differences in tensile and impact strengths the ductilities and resistance to impact were very similar once an electrodeposited layer had been applied. The pre-electroplating sequences and etch times used in the investigation exerted only a small influence on the tensile and impact test values ; this is in contrast to the corrosion test results where process sequence and etch time both exert considerable influence.

Until more fundamental knowledge is obtained regarding the mode of crack formation and subsequent propagation in plated ABS and polypropylene plastics, it is probable that good design practices such as the use of generous radii at sharp corners and reinforcement struts in highly stressed regions can do much to offset the embrittlement phenomenon.

Polypropylene grades P and Q when plated exhibited superior performance to even the best grades of ABS in corrosion, peel adhesion and thermal cycling tests. However, examination of the mechanical test results showed that they were markedly inferior to ABS, especially in impact testing. These grades of polypropylene were homopolymers and as such exhibited poor resistance to crack propagation. Polypropylene grade M was a propylene/ethylene copolymer and had a measurable resistance to impact failure when plated, yet its performance in corrosion and peel adhesion testing was generally poor. Polypropylene grade N was not a recommended plating grade and it was difficult to plate successfully. It performed badly in corrosion and peel adhesion tests but its performance in the thermal cycling test was adequate. The result of the mechanical tests suggests that polypropylene copolymers may have some advantages for functional applications.

The choice of processing sequence, plastics type and grade and electrodeposited layers must all be considered in the light of the proposed function that the plated part has to perform in service.

6 SUGGESTIONS FOR FURTHER WORK.

A corrosion test programme where ABS specimens that had been processed in sequence A but had a layer of electroless nickel from process B, or vice versa, may indicate the relative dominance of the severity of the etch and the electrochemical activity of the electroless nickel.

A mechanical test programme involving fracture toughness measurements on ABS and polypropylene specimens having a variety of additives such as stearates, paraffins and in the case of ABS, different size distributions of butadiene may yield some fundamental information regarding the fracture toughness and notch sensitivity of these materials.

A tensile and impact test programme involving cylindrical rather than rectangular cross-sectional test specimens may indicate the effect that shape of specimen has on the embrittlement; the influence that the edges exert in causing constraint and reinforcement effects could then be evaluated.

The use of the three point bend test could provide further information regarding the effect of the different metallic coatings. The stress system is similar to that in the impact test but the rate of application of the load can be much slower in the bend test. In this test it is likely that the failure of the individual metallic layers could be monitored and fundamental data obtained regarding the importance of the velocity of crack propagation in causing the brittle fractures commonly observed in the tensile and impact tests.

It would be of interest to alter the size and position of the injection gate in the mould which was used to produce the ridged panels. The locality of the peel adhesion peaks may have depended on the positioning of the injection gate. With the direction of the melt flow altered the occurrence and magnitude of the peel adhesion peaks may be influenced; it may be that the peaks would vanish or more probably they would move to other localities where the appropriate moulding conditions are induced. Moulding conditions other than those used in this investigation may also influence the peel adhesion values obtained on the ridged panels. A further extension of this work would be to investigate the minimum sizes of ridge and valley necessary to induce the peak peel adhesion effect; on the other hand, a programme designed to investigate the maximum sizes of ridge and valley at which the effect either vanishes or reaches a limiting value may also provide information regarding the phenonemon, especially if more TEM studies were undertaken at the peak adhesion areas. The TEM studies on the shape and distribution of the butadiene phase may provide an indication of the manner in which mould filling occurs. This could indicate the effects that sectional changes and injection gate positioning have on the behaviour of commercially plated plastics.

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