TITLE: A FUNDAMENTAL STUDY OF SURFACE PROTECTION BY POWDER COATING

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SYNOPSIS

The thesis examines the fundamental factors governing the corrosion protection properties of powder coatings on various steel and aluminium substrates. A corrosion testing programme involving static outdoor roof exposure and salt spray fog testing has been carried out and the results related to potential-time measurements. The powder coatings studied were a polyester, a mixed polymer and various epoxy coatings including a low-bake formulation and a matt-textured coating on substrates in conditions including grit blast, iron and zinc phosphated and chromated. A study of adhesion was carried out and attempts made to develop a good quantitative test for powder coatings.

The curing stage in the production of powder coatings was studied with differential thermal analysis and a hot stage microscope technique. The hot stage microscope technique studied the flow behaviour of the molten particles on various substrates and it was found that flow varied according to powder type, the substrate and the condition of the powder. Differential thermal analysis was used to study the differences in curing behaviour between fresh and stale powders, and also as a tool to evaluate the degree of curing in a study on the effects of partial curing. Scanning electron microscopy was used to examine the powders, the substrates and the surface of the cured coating.

The discussion brings together these studies with previous studies cited in the literature to elucidate the factors governing the corrosion of powder coated articles.

KEYWORDS Powder coating, thermo-setting, hot-stage microscopy, corrosion, adhesion, Differential thermal analysis.

LIST OF TABLES AND FIGURES

LITERATURE REVIEW

CHAPTER 1

1.1 Introduction

Powder coating is the technique of applying plastic materials to products, where the coating materials are in powder form and contain 100% solids,(1-29). A number of techniques are available for applying the coating. These include the fluidised bed, electrostatic fluidised bed, electrostatic spray, flock coating, flame spraying, cloud chamber and many other methods. The most important commercially are the fluidised bed and electrostatic spraying techniques. A technical description of these will be given later.

The technical, economic and environmental advantages of powder coatings over wet paints can be attributed to the lack of solvent. Wet paints contain approximately 50% solvent, and therefore require twice as much storage space as powders, hence storage costs are lower for powders. Air pollution by solvents is eliminated and there is a reduction in health and fire hazards during spraying. Ventilation and building heating costs are also reduced. Solvent blisters do not occur in the final coating; there are no sags and runs; and a more continuous, pore-free film is produced. Powder is ready for use, whereas wet paints involve expensive preparation or checking of viscosity and flow characteristics.

Overspray presents few problems in powder coating as it can be recovered and recycled. In this way material utilisation can be over 95%, compared to 50-80% for wet systems where overspray cannot be recovered. There are no solid waste disposal problems, and booth cleaning costs are greatly reduced. Labour costs are also reduced because relatively there is little skill required for powder coating.

Powder coating materials are more expensive due to higher raw material costs and more expensive capital equipment. Final coating costs, however, may be less due to more material utilisation and less expensive safety precautions. Recent developments, (29), have meant that very thin epoxy powder coatings can be applied, (12-50 microns thick), that are also pin-hole free. Again, this type of development may result in lower final coating costs.

The main disadvantage of powder coatings is associated with colour. Changing from one coloured powder to another is slow and contamination is likely to occur. Unlike liquid paints powders cannot be mixed to give different colours. During production, colour matching one batch of powder with another is difficult.

The object to be coated must be able to withstand the curing time and temperature, and as such, powder coatings cannot be used as a direct substitute for air drying systems. Epoxy coatings are liable to chalk when used in outdoor applications, resulting in a reduction in gloss, and white coatings tend to discolour when exposed to ultra-violet light.

1.2 Powder production

There are three main methods of producing powder: dry, melt and wet processing,(30-48).

Dry processing involves dry blending of the raw ingredients, pigment, resin and other additives, in a ball mill for 12-18 hours. This technique produces a mechanical mixture only of separate particles of the various ingredients. It produces a cured coating of lower gloss than a melt blended powder coating. It is difficult to control the particle size and shape of dry blended powders, and there can be problems in recovery and re-use of overspray. However, the initial cost is low and it can be suitable for low performance applications.

Melt processing consists of softening a dry blended mixture by heating and mixing thoroughly in a Z-blade mixer or an extruder. There is more intimate contact between resins and additives than with dry blending only. The heating cycle has to be controlled such that the temperature is not so high that curing reactions take place, and not so low that an homogeneous mixture is not produced. The molten mixture is poured onto a table and allowed to solidify and is pulverised to give the desired particle size. The powders produced have a fairly wide particle size distribution, which is reduced by screening, the coarser particles being returned to the mill. The cured finish has a higher gloss than dry blended powders, the extrusion blended product having a higher gloss than the Z-blade mixed product. Although the initial cost per unit weight is higher than dry blended powder, melt mixed powders can be used for higher performance applications.

In wet processing the ingredients are dispersed in a solvent to form an homogeneous mixture. The solvent can be extracted by a number of techniques. It can be evaporated so that a solid results which can be micro-pulverised, freeze dried or spray dried. Spray drying eliminates the intermediate steps such as granulation and pulverisation, and produces spherical shaped particles of uniform size. A spray drier is a large chamber in which the solution is atomised. A volume of gas sufficient to completely evaporate the liquid is fed into the chamber. Some solvent may be trapped within the particles which can cause problems such as agglomeration of the powder in use. Inevitably the re-introduction of solvent into the process negates some of the advantages of solvent elimination in powder coating.

Thermoplastic and thermosetting powders are available for powder coating. The thermoplastic resins used include polyvinyl chloride, polyvinyl butyral, nylons, polyesters, acrylics, and certain high molecular weight epoxy resins. Thermoplastic powders are normally applied by fluidised bed because of the problems of grinding at ambient temperatures to produce a fine particle size suitable for electrostatic deposition. Thermosetting resins include polyesters, acrylics, and epoxies, which are normally applied by electrostatic deposition.

Various additives can be made to the finished powder to improve its performance. 0.1% silica reduces caking and improves fluidity. Cellulose acetate butyrate reduces the caking tendency of heat sensitive powders and can enhance exterior durability. Ultra-violet screening agents can be added to impart resistance to breakdown by light.

Powder coatings can be formulated to give special surface effects such as low gloss satin finishes, texture effects and metallic finishes. To achieve a textured finish the flow of the powder during curing has to be restricted in a controlled manner. This is done by having a high pigment loading, or adding extenders such as barium sulphate. This technique gives the desired decorative effect but there is much lower flexibility and impact resistance in the finished film. The use of two hardeners with different gel times gives a fine textured appearance, due to a particle containing hardener 'A' having gelled whilst an adjacent particle containing hardener 'B' is still flowing. Low gloss can be achieved by adding incompatible film formers such as ethyl cellulose, the reduction in gloss being proportional to the amount added. The chemical and solvent resistance of the coating is reduced as the amount of ethyl cellulose increases. The techniques for producing low gloss in a solvent system cannot be applied to powder. The addition of substances such as stearates which float to the surface during film formation cannot be used because the viscosity is not low enough for long enough to allow for complete flotation. The addition of substances of very high oil absorption leads to an unacceptable level of orange peel.

1.3 Metal surface pretreatment

Many early papers suggested that properties obtained using powder coatings on a degreased substrate were equivalent to those obtained from wet systems having a conversion coating beneath them, (12, 19 & 74), and this was given as a cost advantage of powder coatings. It was shown later (50, 51, 52, 53, 55, 59, 60, 61, 63, 65, 67, & 69), that like wet paint systems, maximum adhesion and corrosion resistance can be obtained only after a thorough schedule, including the use of conversion coatings. The first requirement is to have a surface free from grease, carbonaceous deposits, scale and rust. Alkaline cleaning and solvent degreasing will remove oils and grease. Alkaline cleaning removes soil by one or a combination of the following mechanisms:-

saponification - the conversion of animal or vegetable oils into soap;
emulsification - the break up of oil into droplets suspended in the cleaner solution; and,
dispersion - the break up of soil on the work surface and the scattering of it homogenously throughout the solution.

Alkaline cleaners are quite expensive as they are run at 70-85°C, resulting in high heating costs. Solvents can be used for precleaning. A solvent wipe will remove grease and solids effectively until the cloth and container become dirty, it will then only spread the dirt. A solvent dip is effective until contamination of the solution builds up. Furthermore, the use of some solvents can be a fire and health hazard. Vapour degreasing eliminates the problem of contamination, and effectively removes oil and grease, but solid soil tends to remain on the work.

Mechanical treatments such as sanding, grinding and abrasive blasting using shot, grit, alumina, glass beads and nut shells is efficient in removing all contamination and roughening the surface to give a mechanical key for adhesion, but the abrasive medium can easily become contaminated. Acid dips will remove oxide and rust.

Conversion coating consists of treating a metal in a solution which will convert the surface to a non-metallic, insoluble coating which will act as an inhibitive layer and provide a mechanical key for the organic top-coat. This improves the adhesion and corrosion resistance of organic coatings, whether they are solvent based or powder coatings.
Phosphating is used to provide a conversion coating on steel substrates. There are basically two types, zinc phosphate and iron phosphate with many other variations. Zinc phosphates have a fine grained crystal structure and give good corrosion resistance. If the structure is coarse some powders do not flow into the interstices but bridge across the crystals, which can lead to a degradation in mechanical adhesion. Iron phosphate is amorphous and gives better adhesion but poorer corrosion resistance. The phosphate bath consists of a very dilute aqueous solution of free phosphoric acid, (H_3PO_4); a primary metallic phosphate, ($Me(H_2PO_4)_2$), where Me is usually Zinc; and an accelerator. The accelerator is an inorganic oxidising compound which is normally a salt of Me, sodium or ammonia. They can be

chlorides, nitrites or nitrates. Phosphate coatings can be applied by spray or immersion in hot solutions.

Chromating can be used to provide a conversion coating on aluminium. The coating consists of an amorphous film of chromium compounds which are believed to be a mixture of soluble hexavalent chromium compounds and insoluble trivalent chromium compounds. Aluminium can also be phosphated. Various modifications to the above processes are available for pretreating aluminium.

Work has been done comparing the performance of various pretreatment schedules. Yearsley and Darkins, (72), describe a process known as Vaq-Fos, which provides simultaneous degreasing, descaling, surface cleaning, etching and phosphating of metals. The media contains the warm phosphating solution, a detergent and abrasive particles such as alumina, which is circulated by means of a pump and is bombarded onto the metal. They state that: "Trials on the pretreatment necessary to achieve good bonding and corrosion resistance of electrostatically sprayed epoxy powder have conclusively shown that pretreatments according to the process are best". Details of the trials undertaken are not given in the paper.

Lacey and Mauser, (63), studied 5 different pretreatments on cold rolled steel. These were a solvent scrubbed substrate; a 3-stage and 5-stage iron phosphate; a nitrite accelerated Zn phosphate; and a calcium modified Zinc phosphate process. There was no difference in adhesion between them, the solvent scrubbed substrate gave the best impact results with the calcium modified Zn phosphate the next best. Excellent results were reported for the calcium modified Zn phosphate after 572 hours exposure in a salt spray test, there being no significant paint loss.

Kelly and Burt, (60), also reported that the best overall corrosion resistance was obtained using a micro-crystalline calcium Zn phosphate pretreatment. Their studies included the following substrates: bare steel; 3-stage detergent iron phosphate; 5-stage iron phosphate; macro-crystalline Zn phosphate; and micro-crystalline calcium Zn phosphate.

Ashdown, (50), studied the following pretreatments on steel: tri-chloro-ethylene degrease; alkali phosphate solution by spray (Fe phosphate coating weight - 0.3 g/m^2); Zn phosphate solution by spray (1.3 and 2.5 g/m^2 coating weight); and Zn phosphate solution by dip (4 g/m^2 coating weight). The thicker coating of Zn phosphate applied by spraying gave very good appearance and adhesion results after a 2000 hour humidity test, whereas there was complete detachment of the epoxy powder coating on the tri-chloro-ethylene degreased steel after the same exposure. Ashdown also studied the effect of pretreatment on galvanised steel and aluminium. He studied the following aluminium pretreatments: tri-chloro-ethylene degrease; alkali phosphate solution by spray; acid chromate solution by dip; and acid chromate/phosphate solution by dip. He found the best humidity test results were obtained from the acid chromate and the acid chromate/phosphate treatment.

1.4 Powder deposition methods

A number of methods can be used to apply plastic powders,(76-87). Thermoplastics are usually applied by mechanical methods such as fluidised bed, flock gun and flame spraying. Electrostatic fluidised bed and electrostatic spraying are used to apply thin films of thermosetting polymers.

A fluidised bed consists of a container holding the powder through which a current of gas is passed. The gas levitates the powder so that it resembles a boiling liquid in appearance. The object to be coated is preheated to a temperature above the sintering range of the powder and then immersed in the fluidised bed. Disadvantages of this process are that there may be a size limitation on the object to be coated and uncontrollable coating thickness may be a problem. It has the advantage of there being no material wastage.

Flock gun spraying involves spraying the powder onto the preheated object. This technique overcomes the limitation on size but overspray and preheating present a problem.

Flame spraying works by feeding the powder into a fuel gas/oxygen flame at a controlled rate. The flame temperature is above the thermal degradation temperature of the polymer, but the time spent in the flame is not long enough for any degradation to take place. No preheating is required and the object size presents no problems. The uniformity of coating can be controlled but this depends upon the skill of the operator.

Electrostatic techniques require no preheating and thin coatings can be applied. The electrostatic fluidised bed consists of a charged particle cloud into which the object is placed, the fluidised bed acting as a powder reservoir. This technique first made the application of thin epoxy films possible but there is still a size limitation using this method. Electrostatic spraying overcomes this problem. Powder is passed into a gun in a stream of compressed air, where it passes a charged electrode. Each individual particle picks up an electrostatic charge and is attracted to the earthed object. Because of the mutual repulsion of each particle a uniform coating of self limiting thickness is built up on the work piece. The adhesion of the particle is strong enough to allow transfer to an oven where the coating is sintered and cured to give a thin continuous film. Some work is being done at Southampton University, and elsewhere, on the theoretical aspects of electrostatic charging of particles, their transfer to the work-piece and their adhesion prior to curing.

1.5 The curing stage

During stoving the electrostatically deposited particles firstly melt, and then flow to completely cover the substrate. Cross-linking reactions begin and the polymer starts to gel preventing any further flow over the substrate. At the end of the stoving cycle, the cross linking reactions are complete and the mechanical properties of the film are fully developed, (96).

Two techniques have been reported to study this process: the measurement of melt viscosities using the Weissenberg Rheogonometer; and the measurement of the kinetics and thermodynamics of cure using Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC). DSC measured the heat flux required to maintain an equal temperature in the sample and a reference. The kinetics of cure (reactivity), and the heat of cure can be studied using this technique. Information can also be gleaned about the glass transition and the onset of fusion.

Klaren, (94), has shown, by using DSC that increasing the heating rate from 20° C/minute to 80°C/minute moves the cure peak maxima, i.e. the curing temperature, up by 30° C for epoxy resins. He also used the Weissenberg Rheogonometer to measure melt viscosities, and found that, in practice, powder coatings which reach a lower melt viscosity during stoving gave films with better levelling. Higher heating rates increased the temperature at which the curing reactions start, resulting in a lower viscosity being reached during stoving, and better levelling of the coating.

In practice, therefore, thinner substrates will give better levelling than thicker ones. Gabriel, (88), confirms the work of Klaren. Using DSC, Burrows, (95), showed that increasing the heating rate from 8 to 32° C/minute moved the cure peak maxima from 200 to 230° C for a particular commercial epoxy powder coating.

Good flow is obtained in thermoplastic powders with a low molecular weight, (91), but the achievement of a good appearance, through good flow, is often in conflict with the attainment of good physical properties, (89). To get smooth finishes, low molecular weight resins, with a low Tg and having low melt viscosity are chosen but strong films are obtained from resins having a high molecular weight and high melt viscosity. Powders with a low Tg are not as stable as those having a high Tg.

To a certain extent, Nix and Dodge, (90), disagree with the work of Klaren. They have shown that poor levelling or orange peel is not always a result of high melt viscosity. Orange peel is probably caused by an agglomeration of powder particles on the surface and not by reduced flow due to high viscosity. They say clusters may be caused by low molecular weight species at the surface which may cause sticking of the particles to one another or electrostatic attraction of the particles to one another forming clusters which are not dispersed on spraying. They have also done some work on the effect of particle size on flow, smaller particle sizes being shown to give better flow than larger particles and particles having a wide size distribution being shown to flow better than those having a narrow one.

Freshwater, (92), discusses theoretically the effect of particle size and shape on powder coatings. He states that there is a need for research, both applied and fundamental into particle packing and its effect on:- the possible thickness of the coating; the incidence of porosity; the density of the coating; the number of point contacts; and the adhesion and cohesion of the film.

Brett, (93), used DSC to study the effect of state of cure on bond performance for an epoxy resin. The bond was made with aluminium, the samples being cured at various temperatures and the residual heat of reaction measured using DSC. They found that bond strength increased with degree of cure, bond failure being cohesive in the range 70-90% cure and adhesive in the range 90-100% cure.

1.6 Applications of powder coatings

Powder coatings have a wide variety of applications,(97-104). Thermoplastic powder coatings are typically used on domestic wirework, such as dishwasher baskets. Thermosetting powders applied by electrostatic spraying have been used for more critical applications. Many of the initial uses were indoor, for example tubular furniture, office equipment and furniture and casings for domestic electrical equipment. These are usually epoxy powder coatings, which are not normally used for outdoor applications because of their chalking tendencies. Outdoor uses now include car wheels, bicycle frames and mudguards (thermosetting polyester), and car trim and bumpers (textured nylon). Epoxy powder coatings are used for primers on car body shells in Japan and polyurethane powder coatings are widely used on bumpers, trim, light assemblies and mirrors. There are many other diverse uses of powder coatings, such as the coating of glass bottles to make them shatter proof and the use of coatings for electrical insulation.

CORROSION TESTING

CHAPTER 2

2.1 Corrosion Tests

2.1.1 Salt spray fog testing

Neutral salt spray fog testing (ASTM B 117-73 and BS 5466 part 1) is recommended for testing of ferrous and non-ferrous metals and also organic and inorganic coatings which can have a scratch or scribe line to measure corrosion spread.

The cabinet used for the test consisted of a fog chamber, a salt solution reservoir, a supply of suitably compressed air, an atomizing nozzle, specimen supports, provision for the heating of the chamber and the necessary means of control. The cabinet was made of perspex, a material that will not affect the corrosiveness of the fog or be corroded itself by the fog. The cabinet was designed in such a way that drops of solution that accumulate on the roof of the chamber do not fall onto the specimens or go back into the salt reservoir, they run to waste with the sprayed solution.

The specimens were supported on a perspex rack and were tilted at 30 degrees from the vertical. This rack allowed the solution to run away freely, the specimens to be separated so that there was no contact between them and it did not allow solution to drip from one specimen to another.

The spraying rate was measured by placing a 10 cm funnel in a measuring cylinder, positioning this in the cabinet near the specimens and measuring the amount of solution collected over the period of the test. To comply with the standard, this should be 1-2 mils per hour averaged over the period of the test.

The specimens were placed in the chamber just prior to bringing the cabinet up to the right temperature and switching on the air. The test duration was computed from the time these conditions were obtained. The solution used was $5^{\pm 1}$/parts by weight sodium chloride dissolved in 95 parts deionised water, the pH being 6.5 - 7.2 at 35°C. The temperature of the cabinet was 35 + 1.1 - 1.7° C.

The panels were exposed to the test for a period of 148 hours.

2.1.2 Static outdoor roof exposure

The site used for this test was an East facing balcony on the second floor of Aston University in Birmingham. The panels were secured to a frame, sloping at 45 degrees from the vertical, using polythene nuts and bolts, as shown in Figure 1. They were identified by painting numbers on the back of the panels and they were arranged randomly on the frame with the aid of random number tables. This precaution was taken to eliminate the effect that position on the frame may have on the corrosion performance. The panels were exposed from the beginning of July 1978 to April 1979, during a very severe winter and the period also experienced high rainfall. According to the Edgbaston Observatory in Birmingham, the period from July 1978 to March 1979 experienced rainfall of 663 mm compared to a mean of 566.5 mm calculated over a period of 85 years.

2.2 Production of corrosion panels

2.2.1 Pretreatments employed

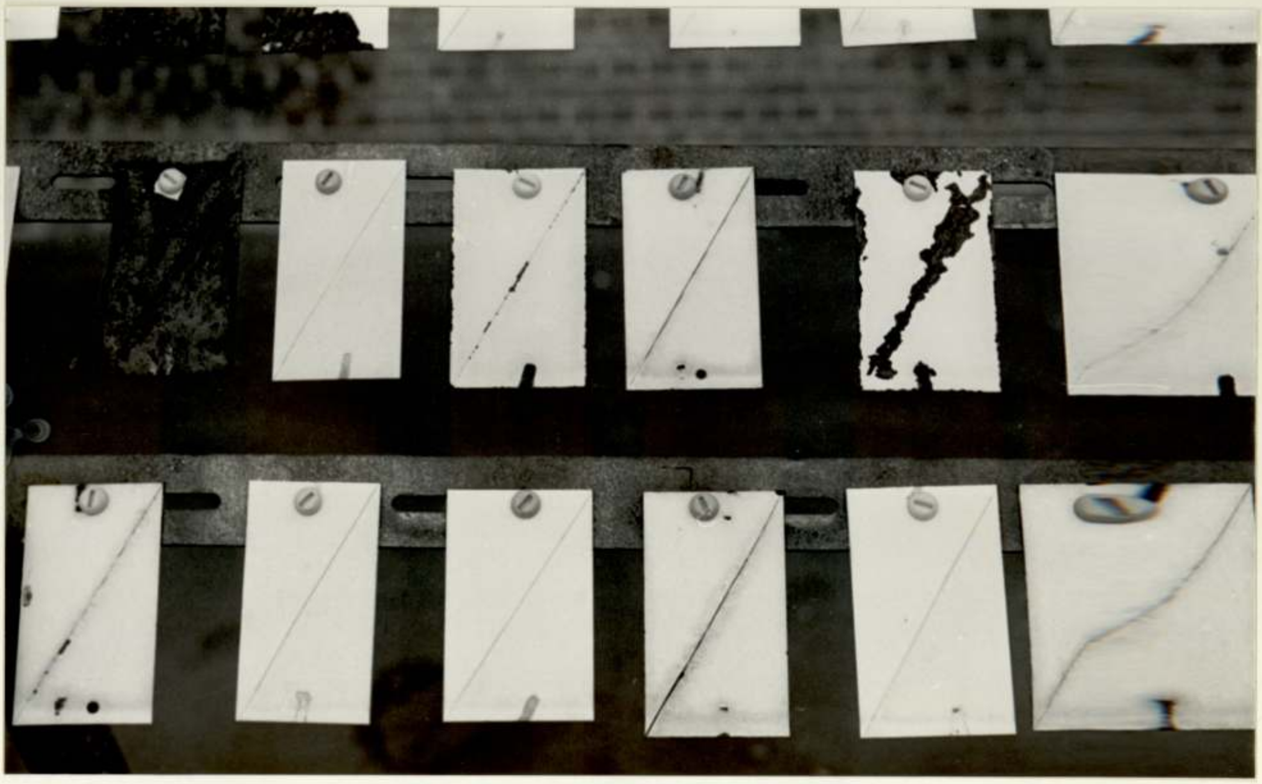
Two metals were used, hot rolled mild steel sheet and commercial purity aluminium sheet. These were cut into panels measuring 10 cm x 5 cm. The pretreatments applied to these panels are listed in Table 1.

Chromating and phosphating was carried out by using commercial solutions supplied by the manufacturer.

The chromating treatment forms an amorphous oxide-chromate coating on the surface of aluminium and aluminium alloys, which provides a good base for powder coatings. The iron phosphate treatment forms an amorphous coating and the zinc phosphate treatment forms a fine crystalline coating on ferrous surfaces. The making up, operation, testing and control of the solutions was carried out according to the manufacturers directions.

Chromating was carried out by immersing the aluminium panels, that had been degreased by dipping in acetone and wiping with cotton wool soaked in acetone, in the gently boiling solution for ten minutes. This was followed by rinsing firstly in running cold water and secondly in hot water at 75^{o} C for approximately 30 seconds. The work was then dried under a hot air dryer. This process produced an even coating which was light grey in colour. Two solutions, of differing strengths were used, one being made up according to the manufacturers instructions and found on analysis to

Figure 1 Static outdoor roof exposure site



be of slightly higher strength than expected. The other solution was deliberately made to a lower strength than that recommended.

TABLE 1

PRETREATMENTS APPLIED TO CORROSION PANELS

Mild Steel

(1) As received condition degreased by swabbing with cotton wool soaked in acetone.

(2) Grit blasting

(3) Zinc phosphating by immersion for 5 minutes at 65° C.

(4) Zinc phosphating by immersion for 2 minutes at 65° C.

(5) Iron phosphating by immersion for 5 minutes at 60° C.

(6) Iron phosphating by immersion for 2 minutes at 60° C.

Aluminium

(1) As received condition degreased by swabbing with cotton wool soaked in acetone

(2) Grit blasting

(3) Chromating by immersion for 10 minutes in a weak solution (gently boiling)

(4) Chromating by immersion for 10 minutes in a strong solution (gently boiling)

Before phosphating the steel panels were degreased in the same manner as the aluminium panels. Both the iron and the zinc phosphate coatings were applied by immersion in the solutions, for 2 and 5 minutes at 60 and 65° C respectively. This treatment was followed by rinsing under running cold water and drying under a hot air dryer. All of the panels were carefully wrapped in clean, dry tissue paper and stored in a sealed dessicator until they were coated.

The thicknesses of conversion coatings were measured after the panels had been produced. A sample was taken from each treatment and the panel weighed. The phosphate coated panels were immersed in a solution containing 150 g/l NaOH for 60 minutes, washed, dried and reweighed. The weight loss per unit area was calculated and this given as the coating weight. The coating weights for the chromated aluminium panels were assessed in a similar way, but the solution used to strip the coating consisted of 35 ml phosphoric acid, 20 g chromic acid and 965 ml distilled water. The coating weights for the different treatments are given in Table 2.

TABLE 2

CONVERSION COATING WEIGHTS

Treatment	Coating weight g/m^2
Zinc phosphate (5 mins @ 65^oC)	0.53
Zinc phosphate (2 mins @ 65^oC)	0.05
Iron phosphate (5 mins @ 60^oC)	0.38
Iron phosphate (2 mins @ 60^oC)	0.34
Chromating (strong solution)	0.68
Chromating (weak solution)	0.80

2.2.2 Powders and their application

Six different powders were used and these were a white polyester (acid glycidal), a white mixed polymer (polyester/ epoxy resin), a white matt epoxy, a white matt textured epoxy, a low-bake white epoxy powder and a white epoxy powder. The matt epoxy and the matt textured epoxy have the same resin, the only difference being that the matt textured epoxy powder contains an added flow restricting agent by the manufacturer.

The powders were applied by using an electrostatic spray gun in a polythene lined fume cupboard. Overspray was extracted using a fan and unlike commercial booths, no attempt was made to recycle it. An earthed bar was attached to the roof of the fume cupboard, from which the panels to be sprayed were hung. All the panels to be sprayed with one powder were coated before moving on to the next powder, which helped to limit contamination of one powder with another. Great care was taken in cleaning the booth and apparatus between powder changes.

The stoving schedules used were those recommended by the manufacturer and these are listed in Table 3. The panels were placed in an electrically heated oven set at the stoving temperature and the stoving time was measured from the time the oven reached this temperature after opening the door.

TABLE 3

RECOMMENDED STOVING SCHEDULES

Powder	Stoving schedule
Polyester	10 mins @ 200°C
Mixed polymer	15 mins @ 180°C
Matt epoxy	10 mins @ 200°C
Matt textured epoxy	10 mins @ 200°C
Low-bake epoxy	6 mins @ 160°C
Standard epoxy	15 mins @ 180°C

The thickness of the coating was assessed by measuring the thickness of the panel before coating and subtracting this from the thickness measured after curing the powder coating. These measurements were made by using a metric micrometer.

Six duplicate coated panels were produced for each powder and pretreatment. Diagonal scratches, completely penetrating the coating, were made on each panel by using a sharp scalpel blade and a steel rule. Three of the panels were subjected to salt spray fog testing and the other three to static outdoor roof exposure.

2.3 Powder coating gloss measurements

Spectral reflectivity measurements were made using a gloss meter. 100% reflectivity is recorded when the measurements are made on a perfect mirror and 0% is recorded when the surface is completely matt and reflects no light. Therefore surfaces of high gloss have a higher percentage reflectivity than surfaces of low gloss.

Gloss measurements were made of the powder coatings applied on degreased steel substrates only. The percentage reflectivity was highest for the mixed polymer and standard epoxy at 5.5%, 5 and 3% was recorded for the low-bake epoxy and polyester powder coatings respectively, and the matt and matt-textured epoxy powder coatings had the lowest figure at 0% and were therefore completely matt.

2.4 Potential-time measurements

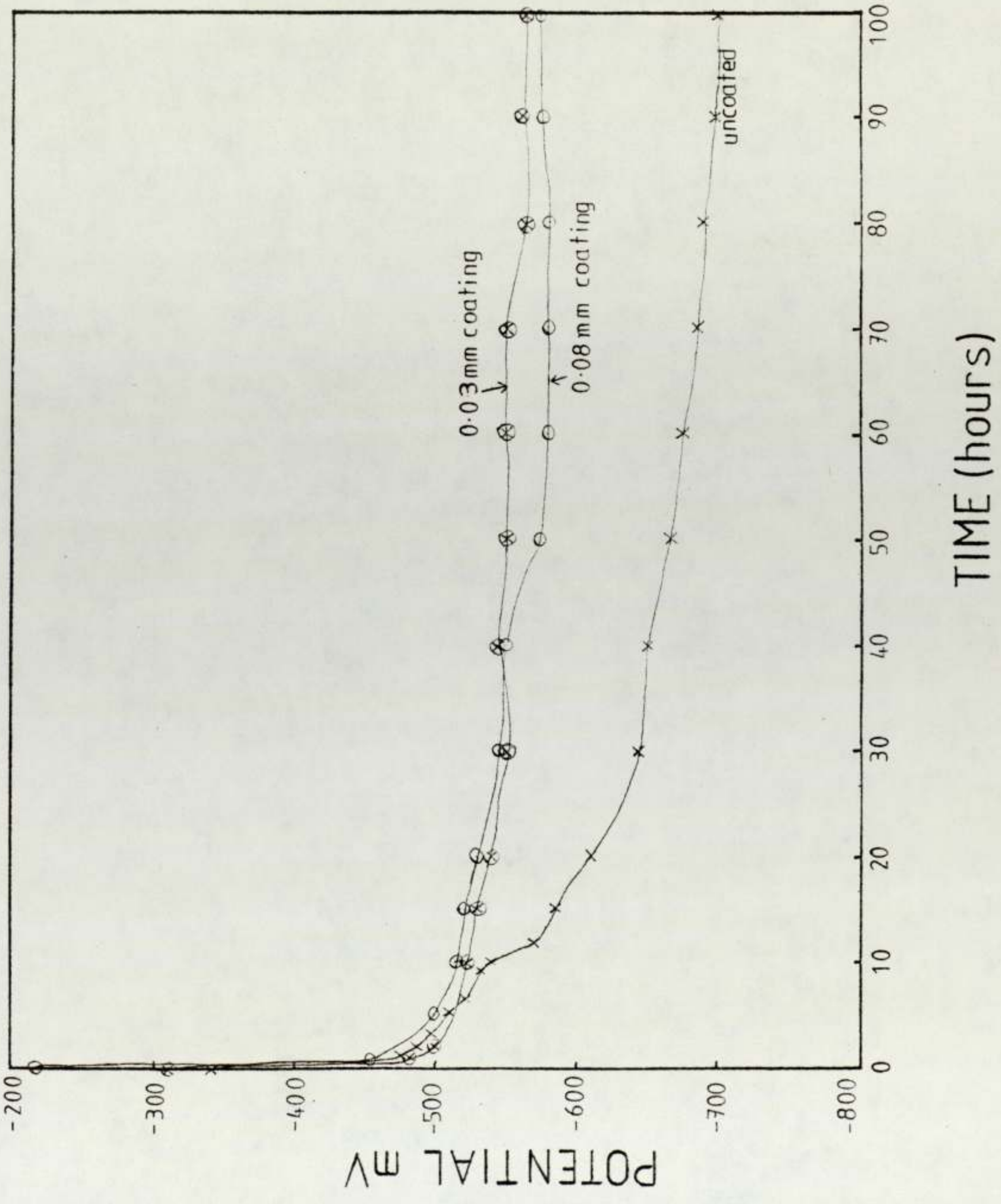
Potential-time measurements were made by using a flat bed pen recorder which gave a reading of potential against time. The progress of corrosion of the panel was measured by recording its potential with respect to a standard calomel electrode in a saline solution containing 50 g/l NaCl dissolved in deionised water at room temperature. The standard calomel electrode was placed very near to the surface of the panel and the solution was not stirred.

The panels used measured 10 x 3 cm and were coated with the powders to be studied. Thicknesses of the coating were assessed as described earlier. The backs and edges of the panels were coated with a stopping off lacquer, which was also used to define an area measuring 5 x 3 cm on the front of the panel.

Figure 2 gives the potential time measurement results for standard epoxy powder coatings on zinc phosphated mild steel. The zinc phosphated panels were cut from the thicker phosphated panels produced for the rest of the corrosion programme. Figure 2 also shows a curve for a bare zinc phosphated panel, i.e. one that had no standard epoxy coating topcoat. The other two curves in Figure 2 are for zinc phosphated panels covered with standard epoxy coatings of 0.03 and 0.08 mm thick.

FIGURE 2

Potential-time measurements for a standard epoxy powder coating on zinc phosphated mild steel



Figures 3 and 4 show the potential-time curves for standard epoxy, matt epoxy, matt-textured epoxy, low-bake epoxy, polyester and mixed polymer powder coatings on degreased mild steel. The test pieces were cut from standard panels, the polished sides of which were coated after degreasing by swabbing with cotton wool soaked in acetone. The thickness of the coating was 0.07 - 0.08 mm in all cases and the powders used were in a fresh condition. Figures 5 and 6 give potential time measurements for the same powders in a stale condition on degreased steel panels. The powders were rendered stale by leaving open to the atmosphere for at least 2 weeks.

FIGURE 3

Potential-time measurements for a standard, a matt-textured and a matt epoxy powder coating on degreased mild steel

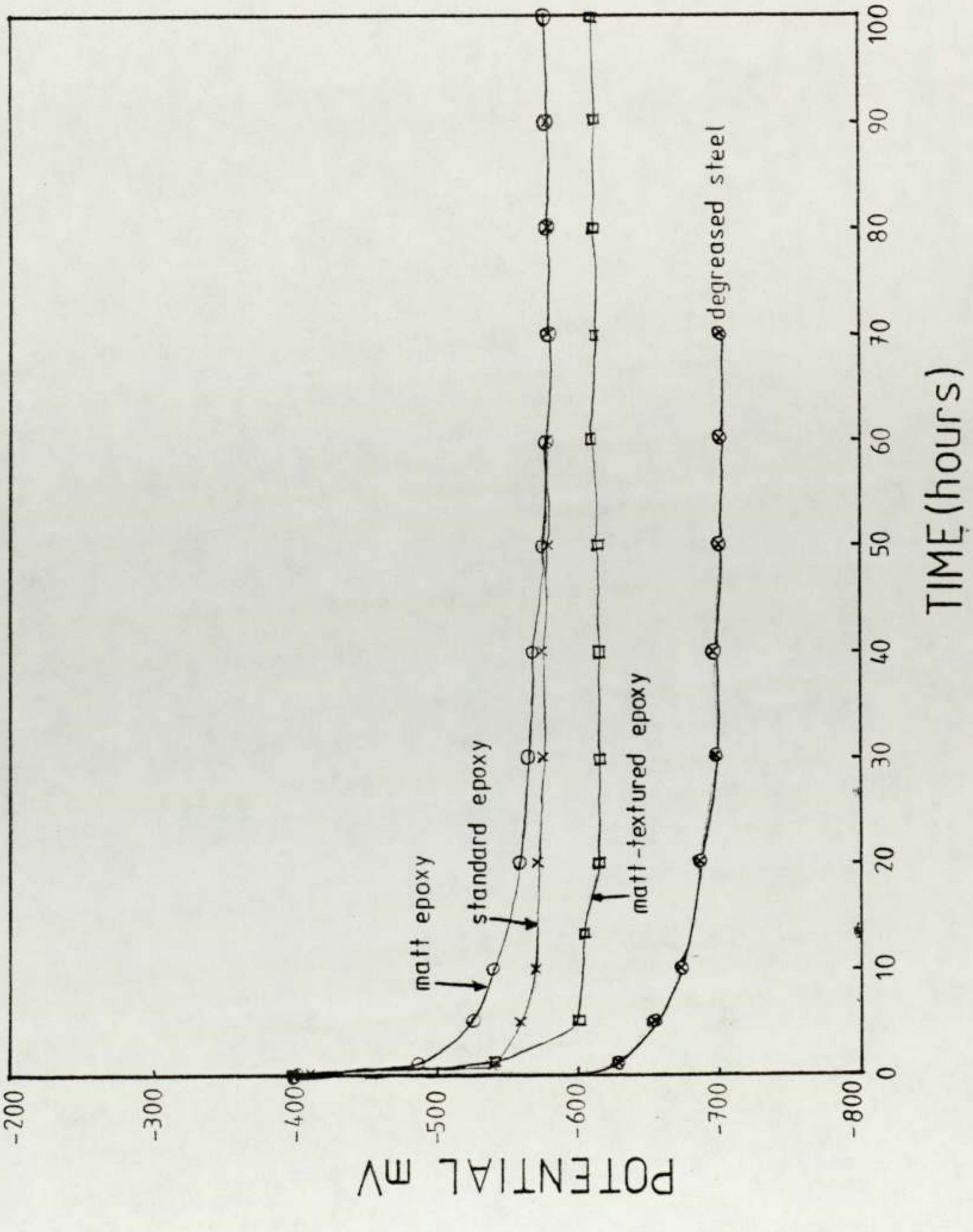


FIGURE 4

Potential-time measurements for a low-bake epoxy, a polyester and a mixed polymer powder coating on degreased mild steel

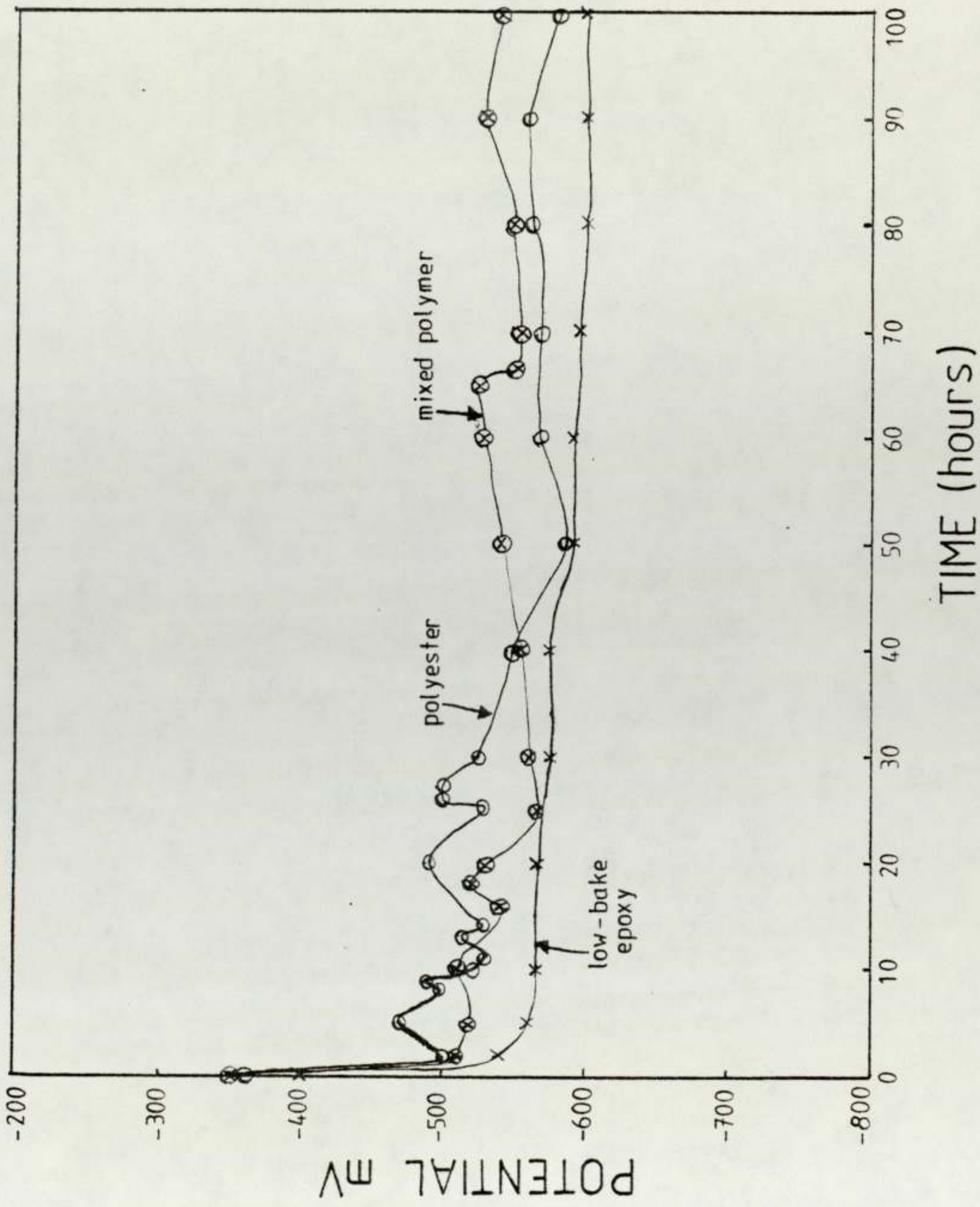


FIGURE 5

Potential-time measurements for a standard, a matt-textured and a matt epoxy powder coating on degreased mild steel (powder in a stale condition) .

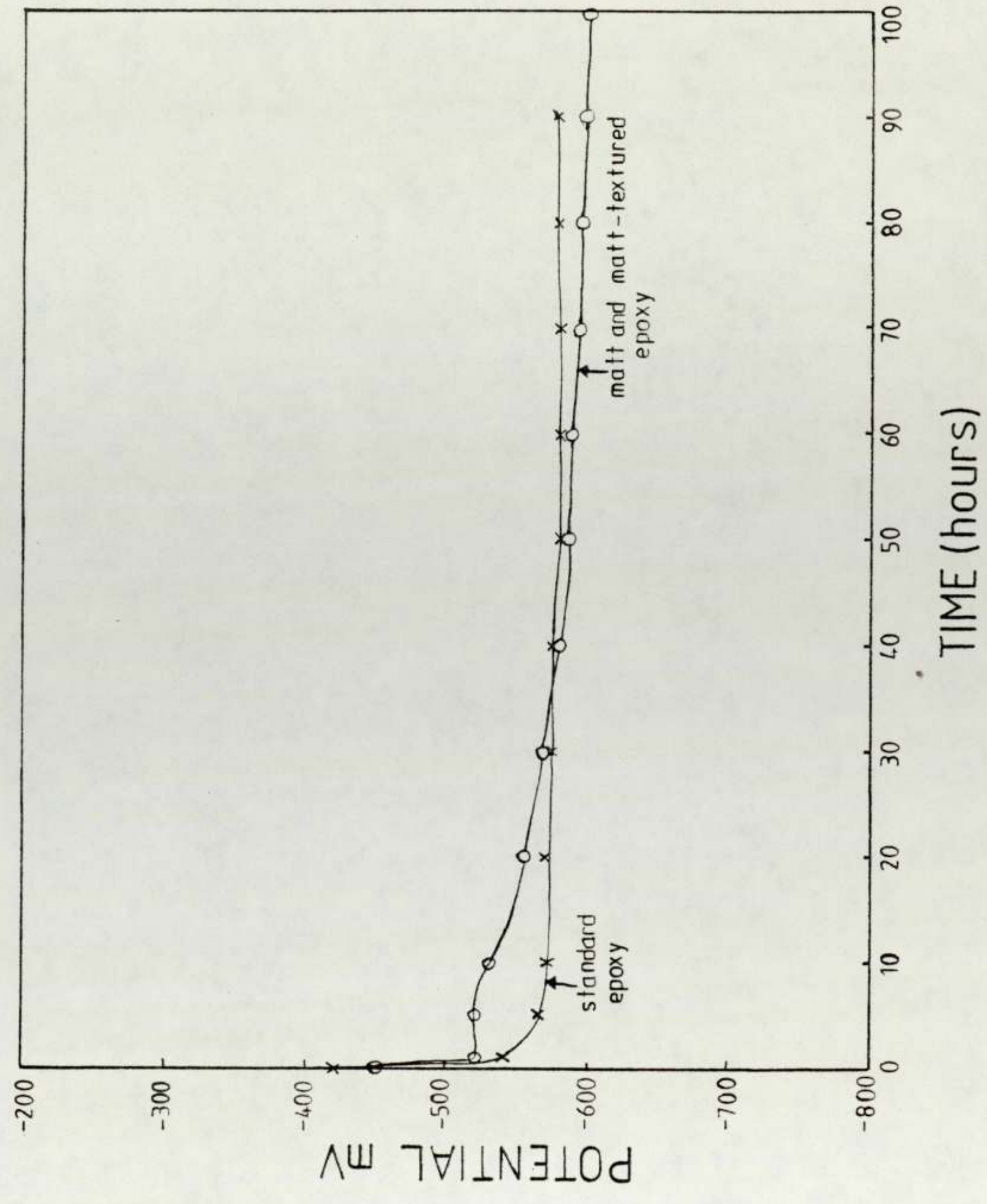
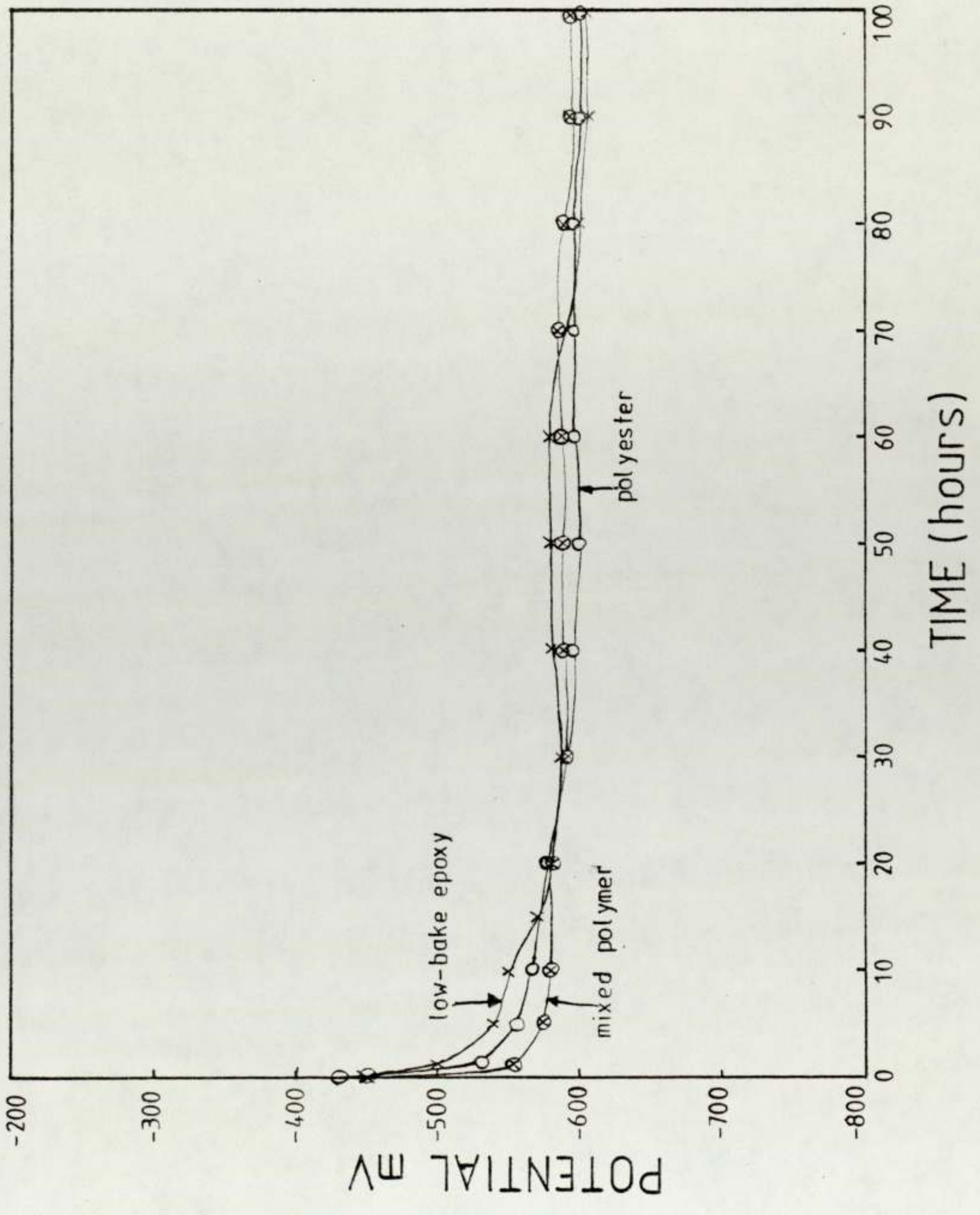


FIGURE 6

Potential-time measurements for a low-bake epoxy, a polyester and a mixed polymer powder coating on degreased mild steel (powder in a stale condition)



2.5 Corrosion results

Figures 7 - 12 show panels after exposure to neutral salt spray fog testing (ASTM B117-73) for 148 hours and Figures 13 - 18 show panels produced at the same time after static outdoor roof exposure. The panels subjected to salt spray testing were washed under running warm water and dried under a hot air dryer prior to photographing. The panels from the roof were not washed before a photographic record was made, because there was a marked difference in the amount of dirt retention on the different powder coatings. This can be seen on examination of Figures 13 - 18. It is surprising to note that the matt epoxy powder coatings show the least amount of dirt retention whilst the polyester powder coatings show the most. Also the mixed polymer powder coatings exhibit more dirt retention that the low-bake epoxy, standard epoxy and matt textured epoxy powder coatings.

The salt spray corrosion test results (Figures 7 - 12) infer that steel pretreatments have little effect on their corrosion resistance, except for the polyester and the matt epoxy powder coatings which show some improvement in corrosion protection on the zinc phosphated panel, given a long treatment time, over degreased as received steel. Static outdoor roof exposure (Figures 13 - 18) clearly shows that all of the pretreatments lead to an improvement in corrosion protection over degreased as received mild steel, and the best corrosion protection is afforded by zinc phosphating.

Powder coatings gave very good protection to aluminium substrates. Differences in performance cannot be gleaned by examining the panels subject to outdoor roof exposure. For aluminium substrates, salt spray testing appears to be the more severe test with the standard epoxy coatings on degreased aluminium providing very little corrosion protection.

Salt spray testing shows that low-bake epoxy and matt textured epoxy powder coatings give the worst corrosion protection. Although the resin system is the same the matt epoxy powder coatings provide better corrosion protection than the matt textured epoxy powder coatings. The best corrosion protection is obtained with mixed polymer powder coatings.

Comparisons are more difficult with the panels exposed to the static outdoor roof exposure test, as most of the products of corrosion have continually been washed away. Only the extent of the breakdown of the coating can be used as a measure of corrosion. Comparing the matt and the matt textured epoxy powder coatings it is quite clear that the matt textured epoxy powder coating shows some breakdown of the coating away from the scratch, proved by the presence of corrosion products showing through the coating. The low bake epoxy powder coatings have a similar appearance. The other coatings have broken down by corrosion starting at the scratch, the products of corrosion led to a stress being imposed on the immediately surrounding coating which broke down the adhesive bond leaving a larger area susceptible to corrosion attack. The extent of this form of breakdown is similar for the matt and matt textured epoxy powder coatings as can be seen by examining the as received steel panels. The polyester powder coatings suffer less from this form of breakdown and the low-bake epoxy powder coatings more than any other powder coating studied.

Figure 2 shows the potential time curves for zinc phosphated mild steel and for the same substrate coated with a standard epoxy powder coating. Figure 3 includes a curve for degreased mild steel and for the same substrate coated with a standard epoxy powder coating. After 30 hours the potential of the mild steel had dropped to -700 mV and was corroding, this being the equilibrium potential. It took 100 hours for the zinc phosphated steel to reach this potential and therefore the zinc phosphate coating is protective. The potential of the panels coated with powder coatings did not fall to this equilibrium potential during the period of the test, but the speed at which the potential dropped and the level to which it fell can be used as an indication of the corrosion protection properties of the coating. For instance, it is quite clear that a standard epoxy coating on zinc phosphated mild steel was more protective than on degreased mild steel.

Figure 3 also illustrates the potential time curves for matt and matt textured epoxy coatings. It can be seen that the matt epoxy is more protective than the matt textured epoxy at the same film thickness. Comparing Figure 3 with Figure 4 it can be seen that the corrosion protection properties of the low-bake and standard epoxy powder coatings are similar.

The potential-time curves for the polyester and the mixed polymer powder coatings are given in Figure 4. The shape of the curves for these coatings is different compared to the others. They both show a fluctuation in the potential of the underlying metal, indicating that there must be some form of breakdown of the coatings followed by either repair of the coating or inhibition of the corrosion reaction. The potential after 100 hours was higher for these than for any other coating, showing that these two coatings are more effective in preventing corrosion of the underlying metal than any other coating studied.

Figures 5 and 6 give the potential-time curves for the same powder coatings applied with the powders in a stale condition. There are some significant differences in the performance of these coatings compared to coatings applied from powders in a fresh condition. The curves for the standard and low-bake epoxy powder coatings are similar to those for the powders in a fresh condition. There has been some deterioration in the protection properties of matt epoxy powder coatings but some improvement for matt-textured epoxy coatings in the stale condition compared to coatings produced from fresh powders. In a stale condition the curves are practically identical for the matt and matt-textured epoxy powder coatings. The most marked difference in performance between fresh and stale powders can be seen in the polyester and mixed polymer powder coatings. In the stale condition, the fluctuation in potential did not occur and the potential after 100 hours fell to the same level as the low-bake epoxy powder coatings. For these powders it is clear that storage conditions of the powder are a very important factor in determining the corrosion protection proterties of the finished coating.

Figure 7 Corrosion panels after exposure to salt spray fog testing

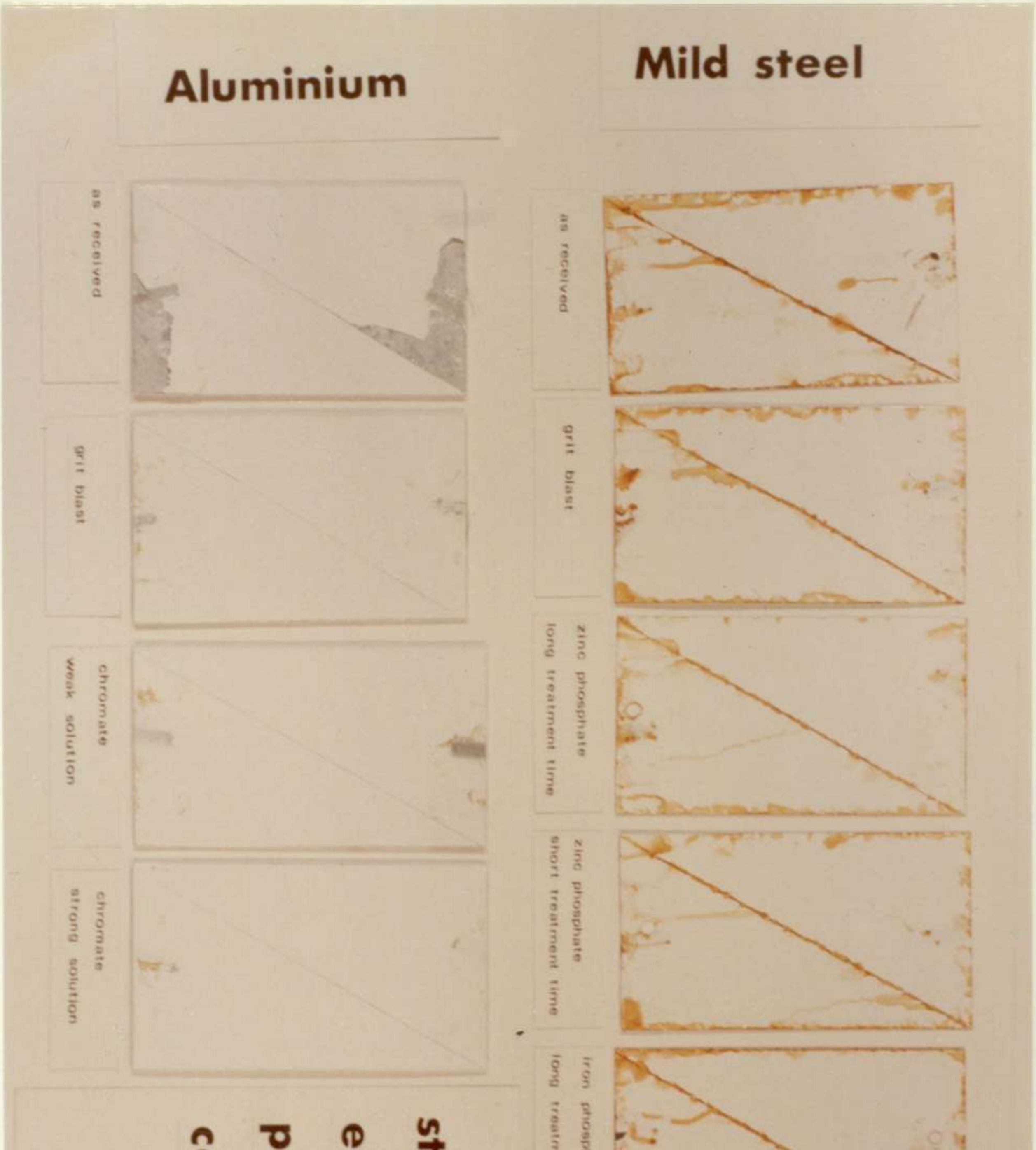


Figure 8 Corrosion panels after exposure to salt spray fog testing.

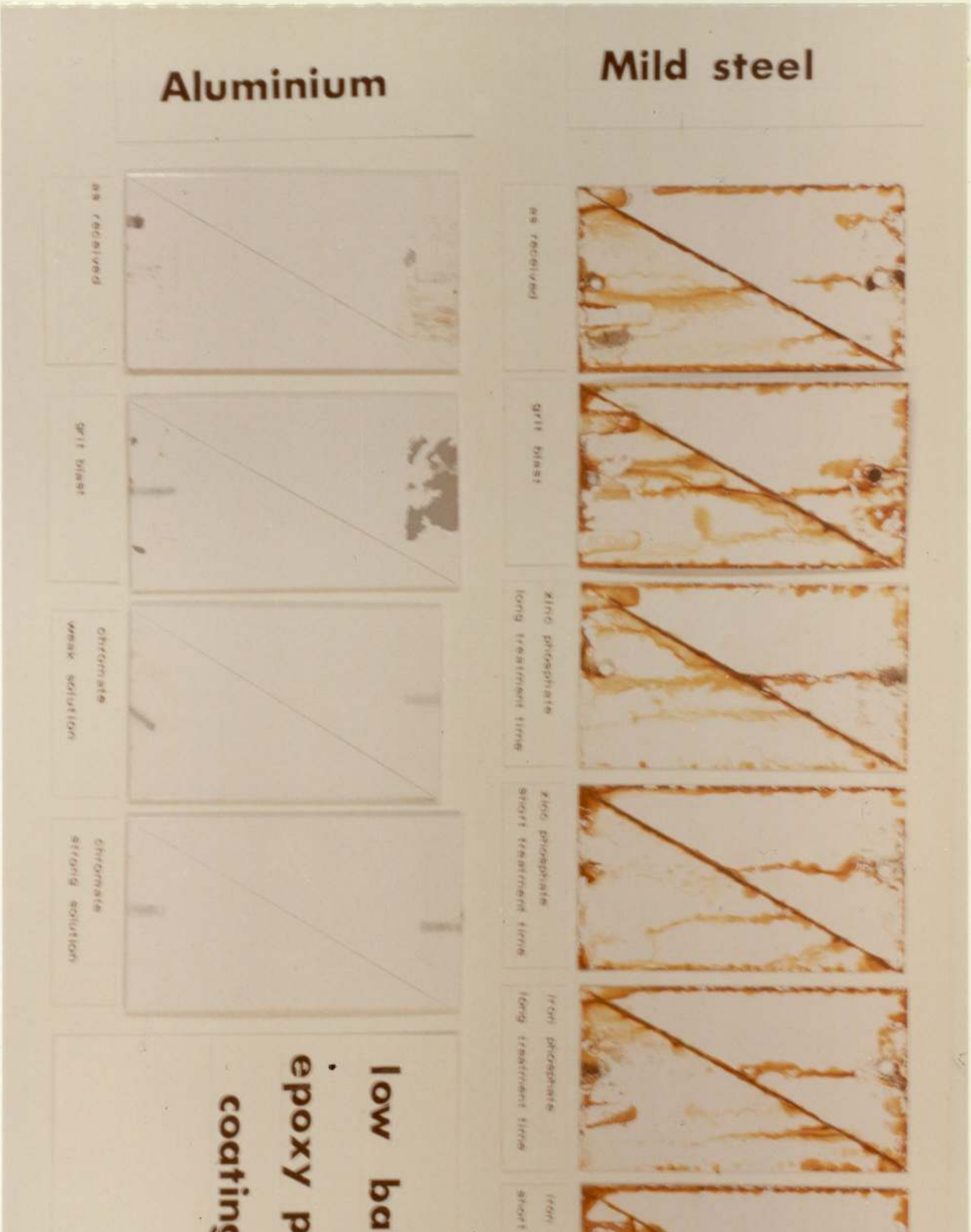


Figure 9. Corrosion panels after exposure to salt spray fog testing

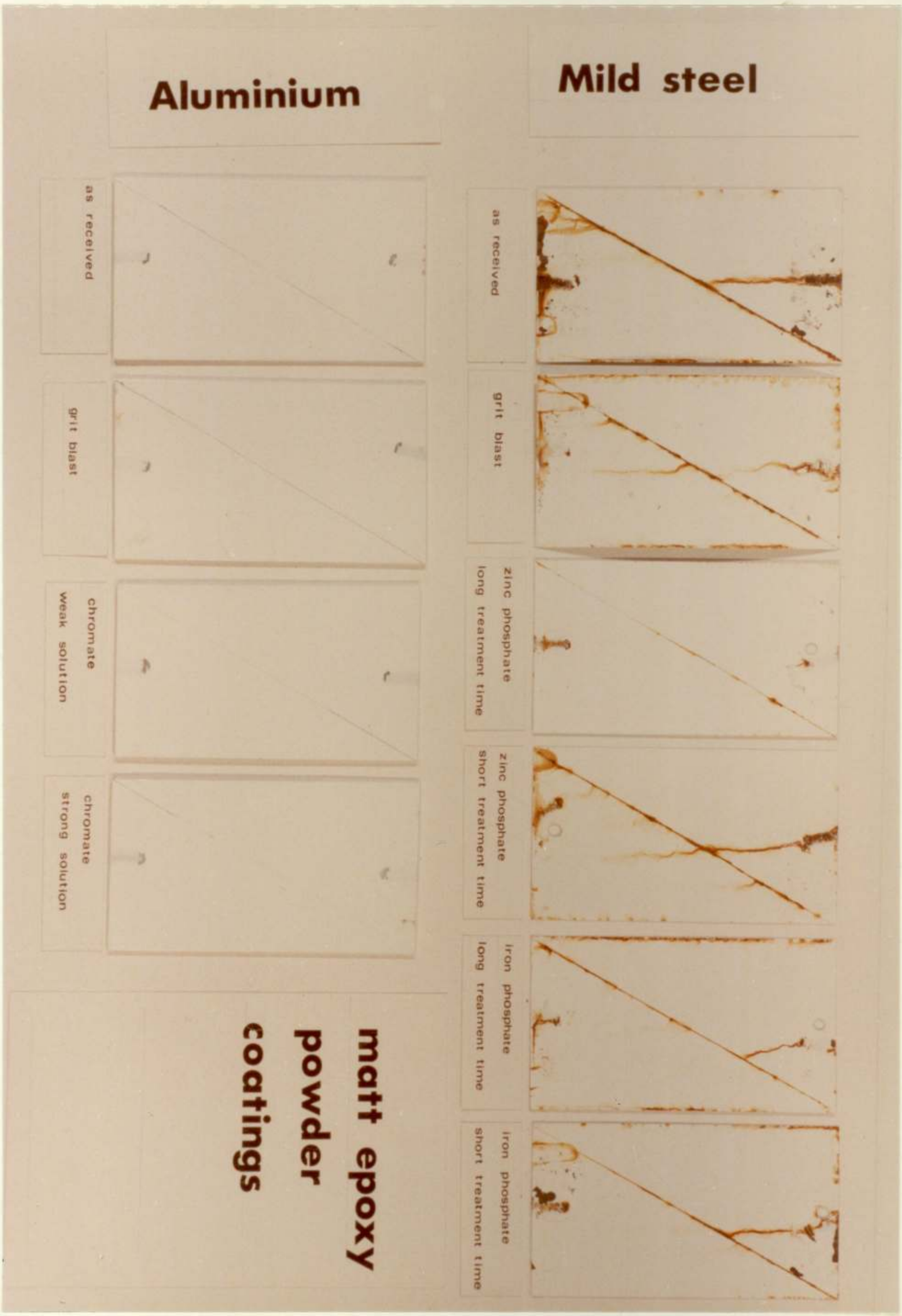


Figure 10 Corrosion panels after exposure to salt spray fog testing

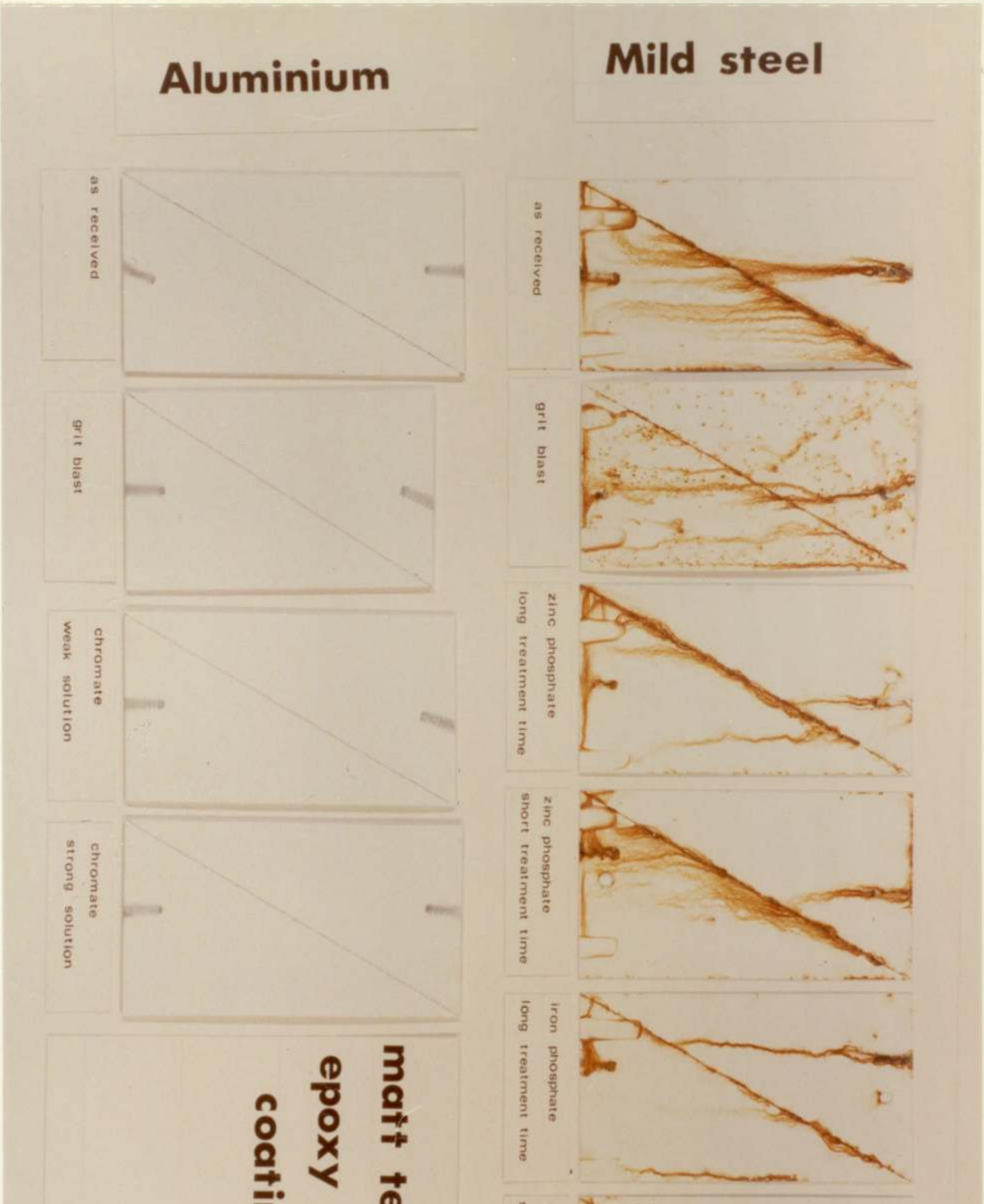


Figure 11 Corrosion panels after exposure to salt spray fog testing

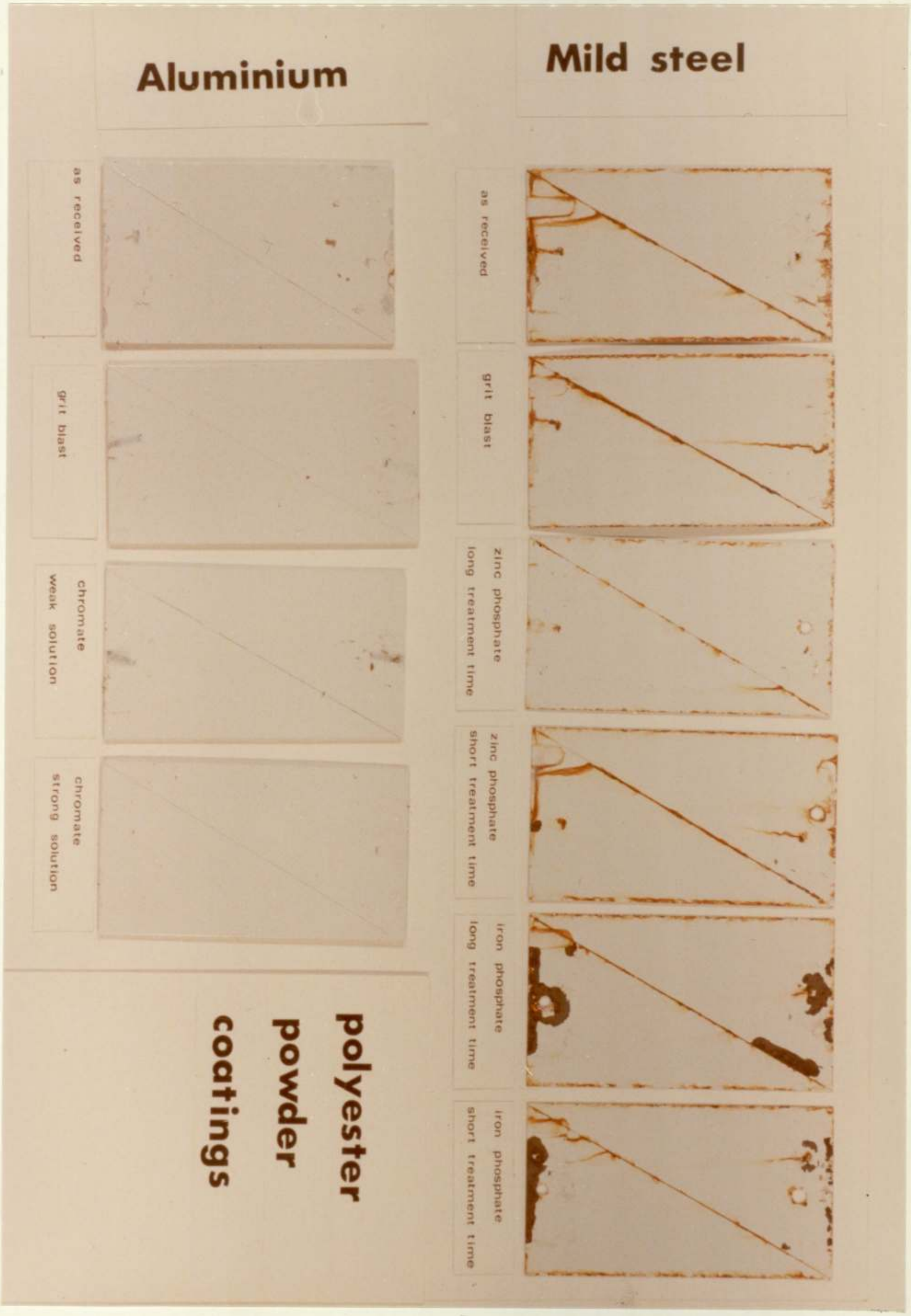


Figure 12 Corrosion panels after exposure to salt spray fog testing

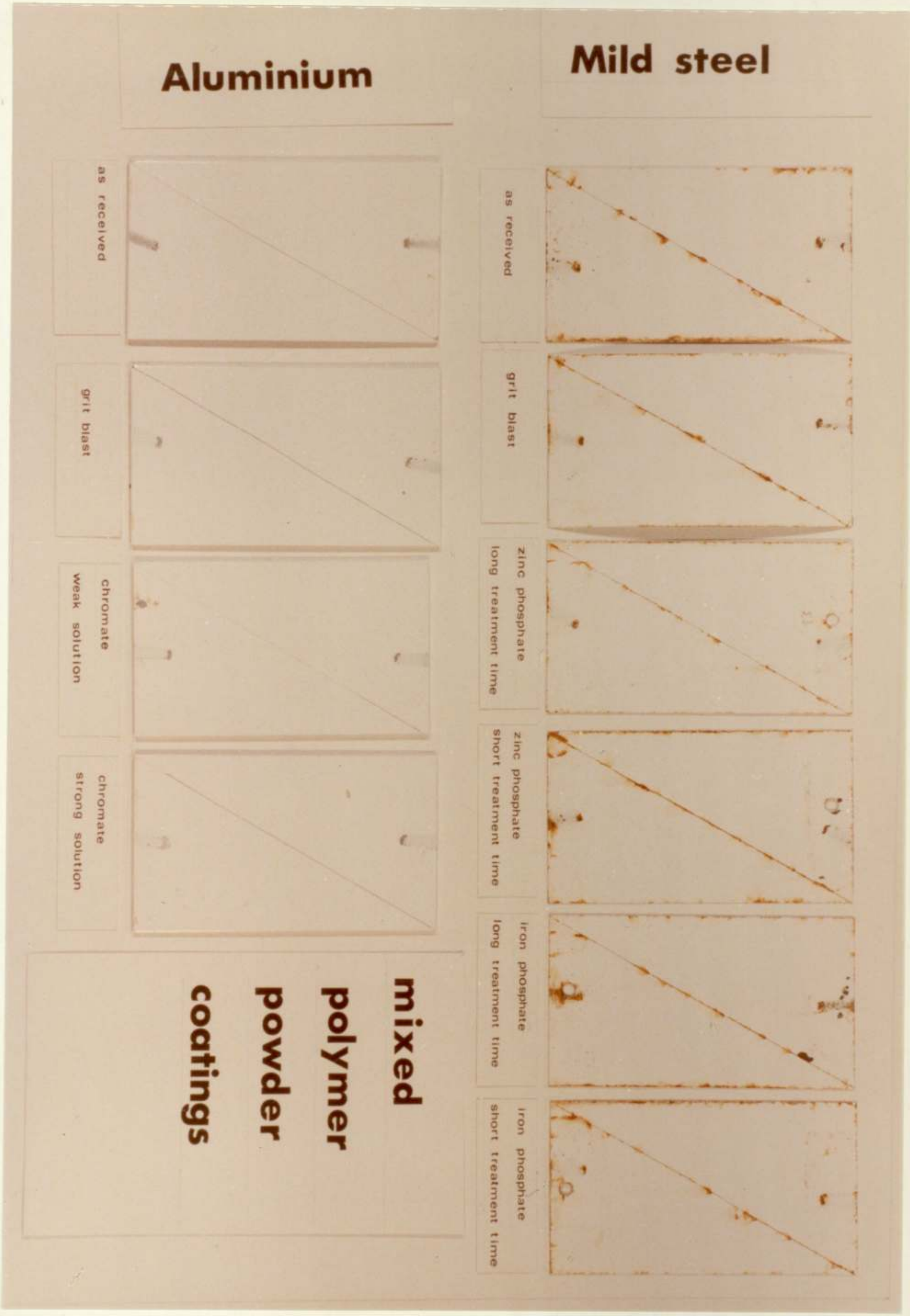


Figure 13 Corrosion panels after static outdoor roof exposure

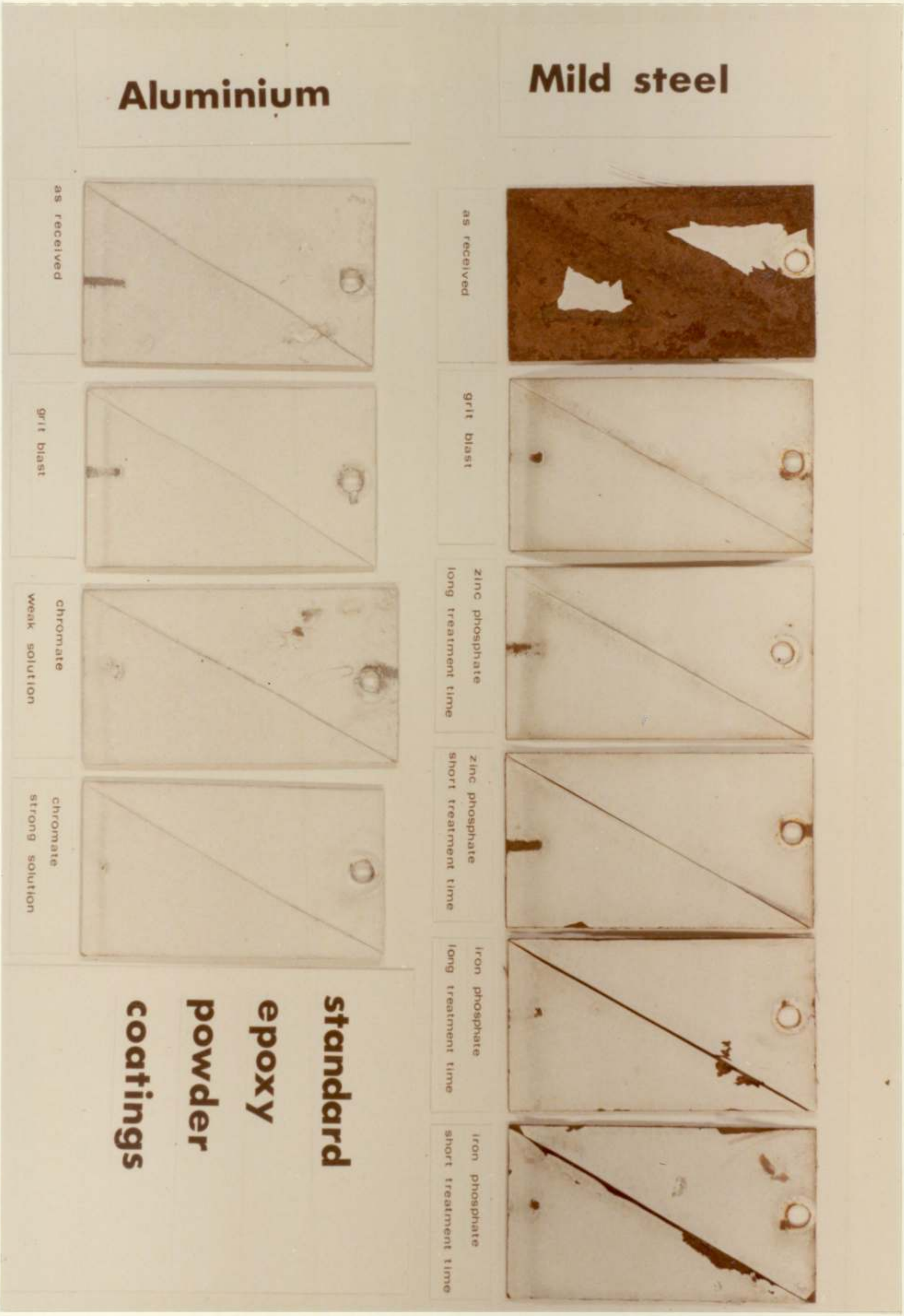


Figure 14 Corrosion panels after static outdoor roof exposure

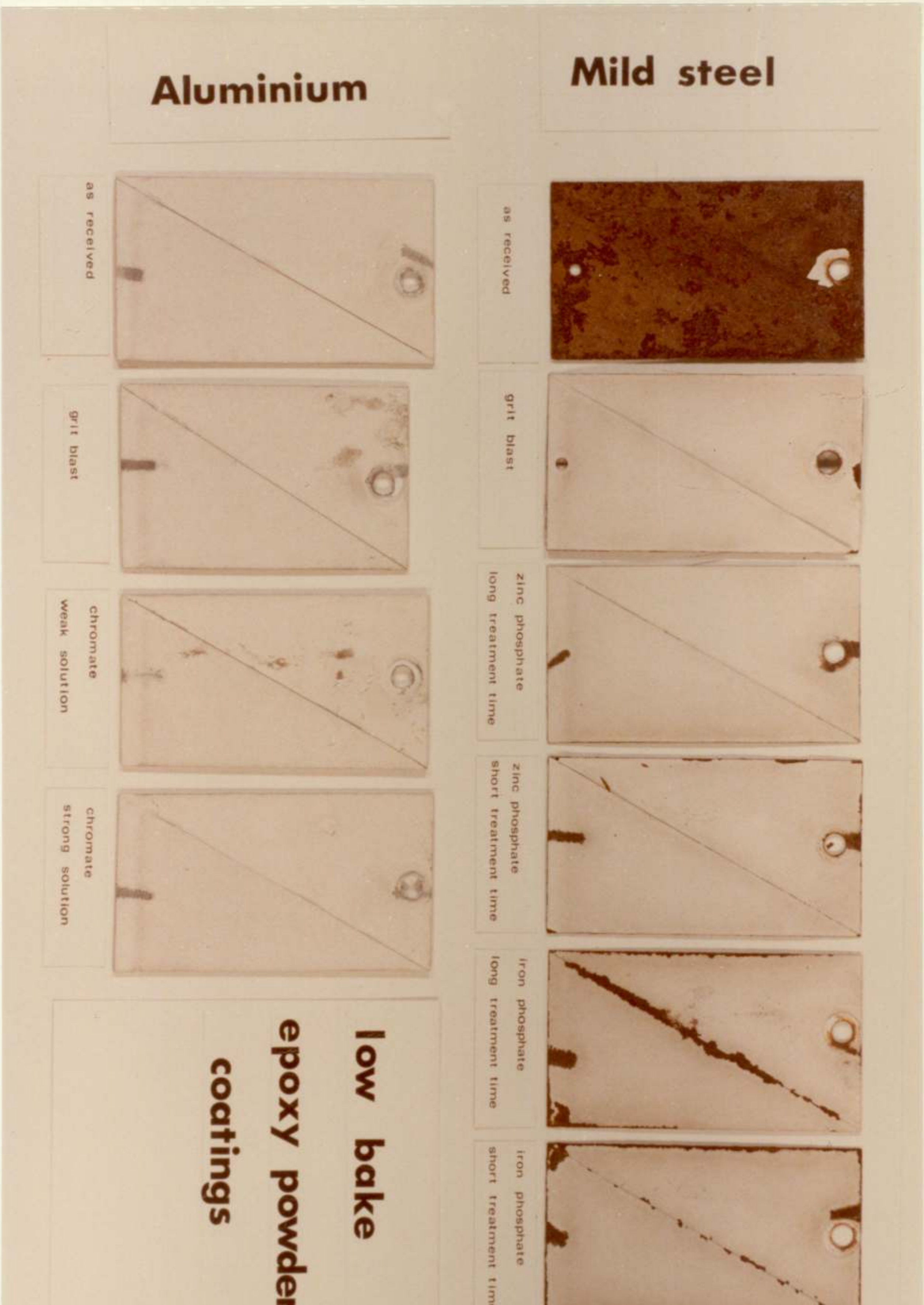


Figure 15 Corrosion panels after static outdoor roof exposure

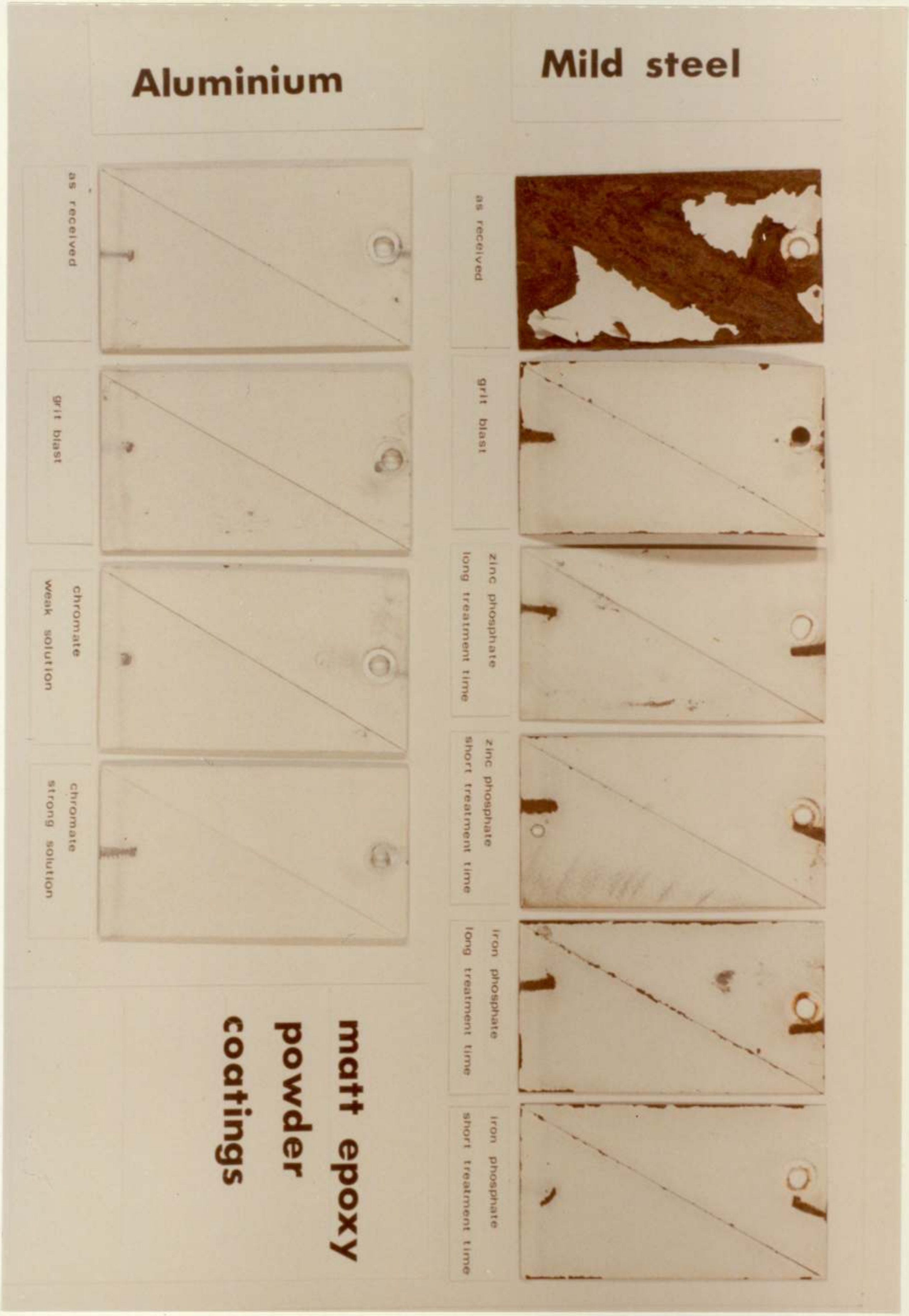


Figure 16 Corrosion panels after static outdoor roof exposure

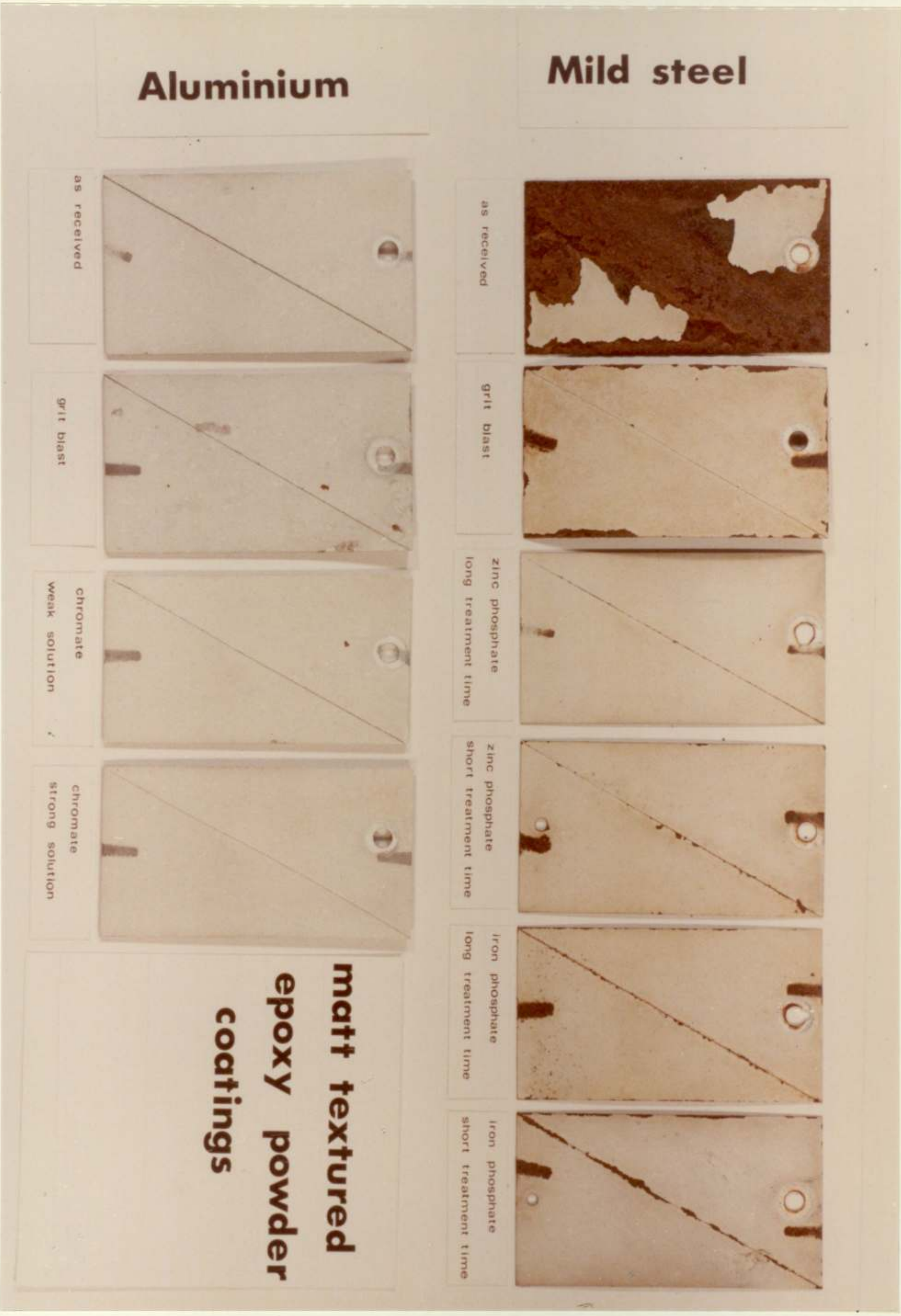


Figure 17 Corrosion panels after static outdoor roof exposure

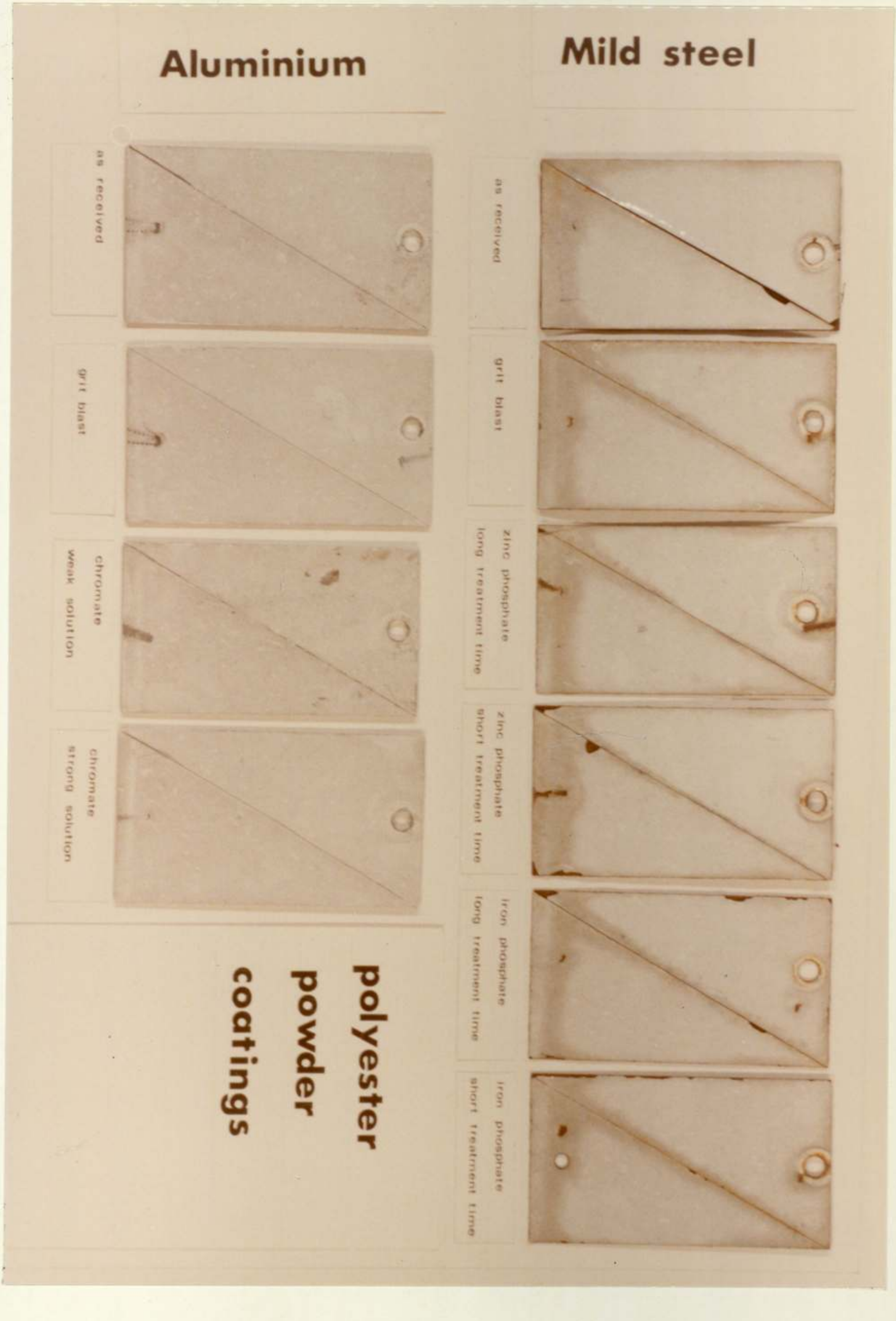
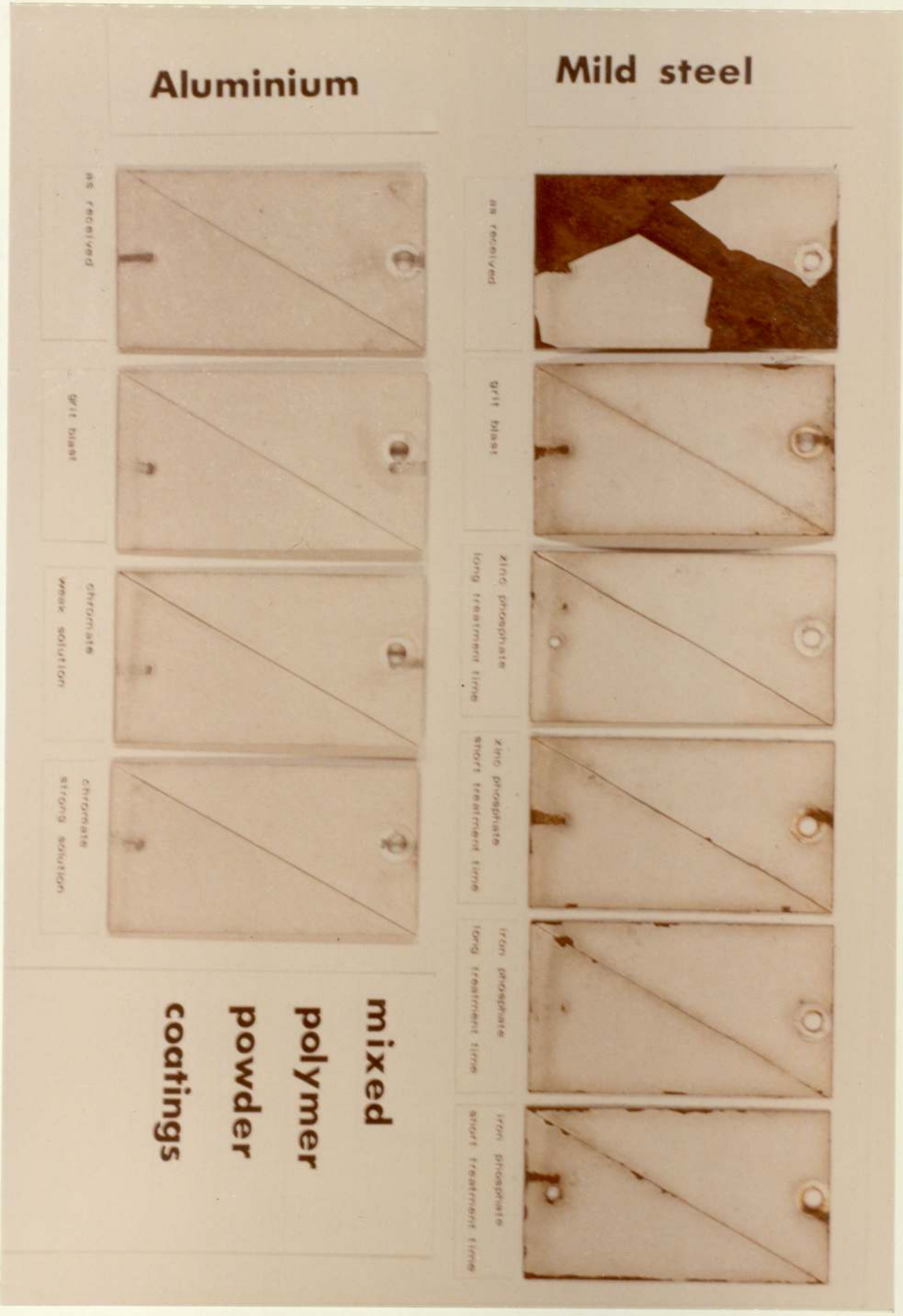


Figure 18 Corrosion panels after static outdoor roof exposure



HOT STAGE MICROSCOPY

CHAPTER 3

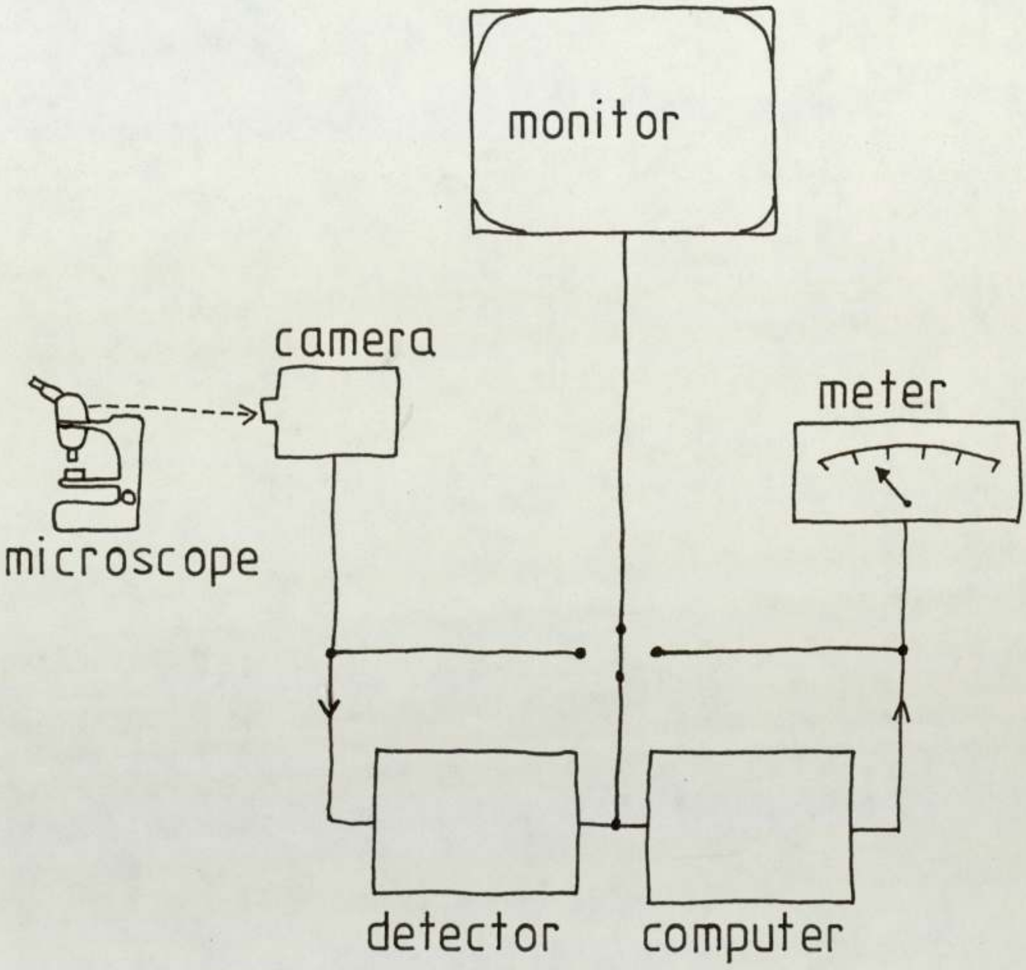
3.1 The Quantimet television microscope

When a powder coated article is placed in the curing oven, the particles melt and then flow over the surface and presumably into any voids on a micro-scale in the surface. This flow depends upon the viscosity and surface energy of the resin as well as the surface energy and topography of the metal. These two processes, i.e. melt and flow, have been studied using a hot stage microscope technique incorporating the Quantimet television microscope (QTM).

The QTM is conventionally used in metallurgical work to measure the area percentage of one phase in a structure, from a metallographically prepared specimen. There must be sufficient light contrast between phases to be able to do this. The progress of flow was studied by measuring the area occupied by powder on the substrate at different temperatures.

Figure 19 gives a breakdown of the QTM. It is a metallurgical microscope with a closed circuit television system and an image analysing circuit. In order for the detector in the image analysing circuit to operate correctly, there has to be sufficient light contrast between the features to be measured and the background. Either black or white features on a black or white background is ideal. A threshhold intensity setting is used to select the features to be measured, and the area selected can be seen on the television screen, which also appears as a direct % reading on a meter.

Figure 19 Breakdown of QTM

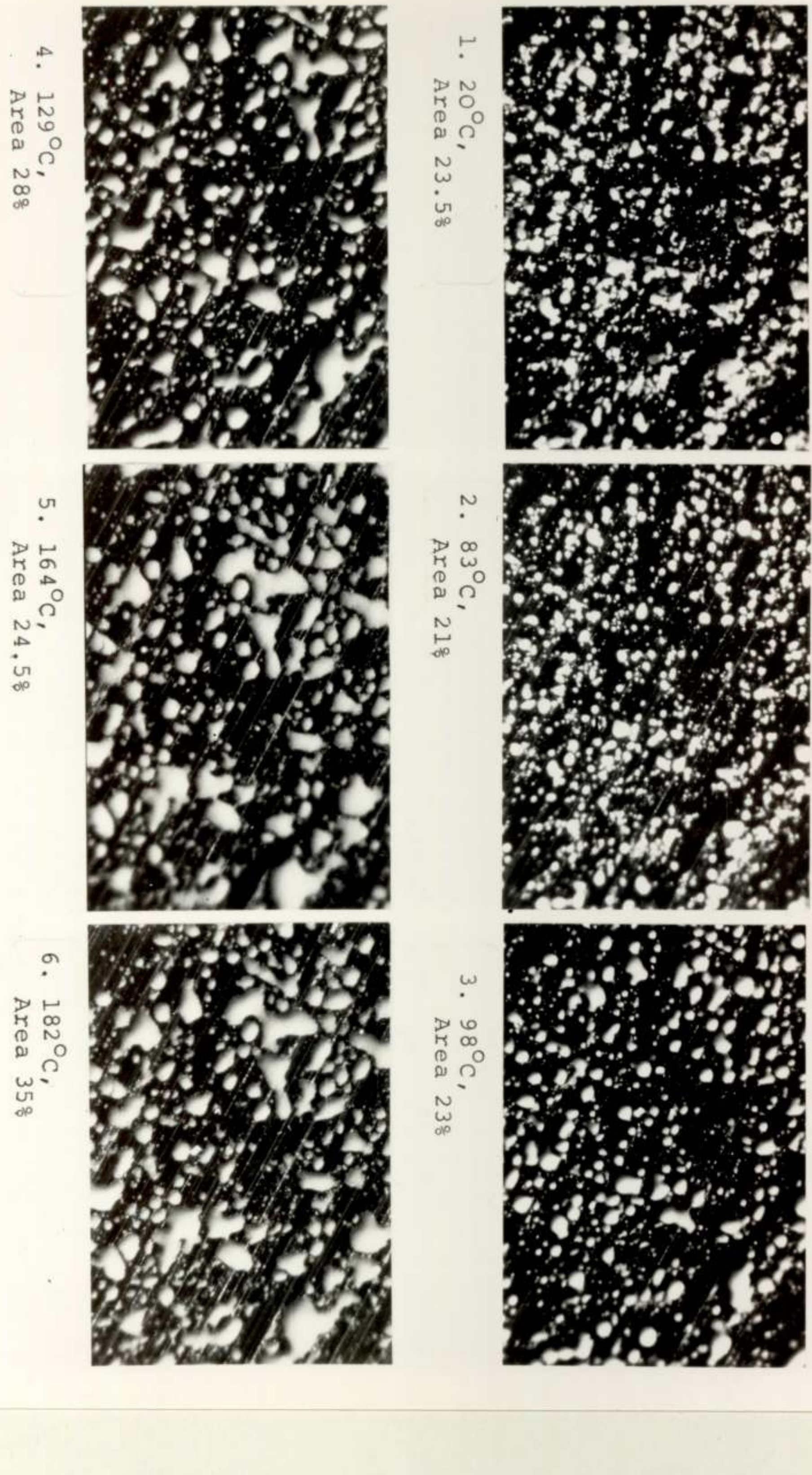


The QTM can be used with an epidioscope attachment which is used to measure features on photographs. At the onset of this work photographs were taken on a hot stage microscope which were later analysed on the QTM with the epidioscope.

The hot stage microscope was a metallurgical microscope with a resistance heater placed on the stage. The powders were sprinkled onto the test surface which was placed on the hot stage. A chromel/alumel thermocouple was welded onto the specimen and the heating rate was controlled and measured using a variable resistance and the X-Y plotter. A predetermined heating rate was maintained by drawing a line on the graph paper in the plotter, and following this set heating rate with a pen recorder. Oblique illumination was used by placing two lamps, one on either side of the specimen, at a distance of about 15 cms from it. This lighting system produced photographs of high contrast, but the contrast was not so good when the internal lighting system of the microscope alone was used. This produced an image where the powder particles tended to merge into the topographical features of the metal. A typical series of photographs produced using this technique are shown in Figure 20.

It was a logical step to modify the microscope on the QTM to serve as a hot stage instrument (Figure 21). This technique was an improvement, it cut out the photographic stage with the attendant saving in time and money. The

Figure 20 A series of photographs illustrating the flow of a powder with increasing temperature



1. 20°C, Area 23.5%

2. 83°C, Area 21%

3. 98°C, Area 23%

4. 129°C, Area 28%

5. 164°C, Area 24.5%

6. 182°C, Area 35%

Figure 21 Hot stage QTM

initial area covered by the powder could be measured, which meant that it could always be 20%, making it easier to compare results. The main advantage was that the threshold intensity setting had to be made only once at the beginning of the run, whereas with the previous technique it had to be adjusted for each photograph. This introduced a reproducibility error which was as much as 2.5% around the mean. This error was enough, in some cases, to mask important features on the flow curve such as the reduction in area effect due to the particles melting.

3.1.1 Experimental details

Temperature measurements were taken by welding a Chromel/Alumel thermocouple onto the test panel which measured 25 x 50 mm. A magnification of x80 was used throughout the work and a constant heating rate of 5°C per minute, except where otherwise stated, was employed. The powder was spread onto the panel, as evenly as possible, by using a brush after first sieving the powder through a 150 mesh (140 micron aperture) sieve. Care was taken to avoid contamination from one powder to the next.

3.2 The typical flow curve

Three of the four stages of cure, i.e. melt, flow and gel are shown on a typical flow curve for a thermosetting powder in Figure 22.

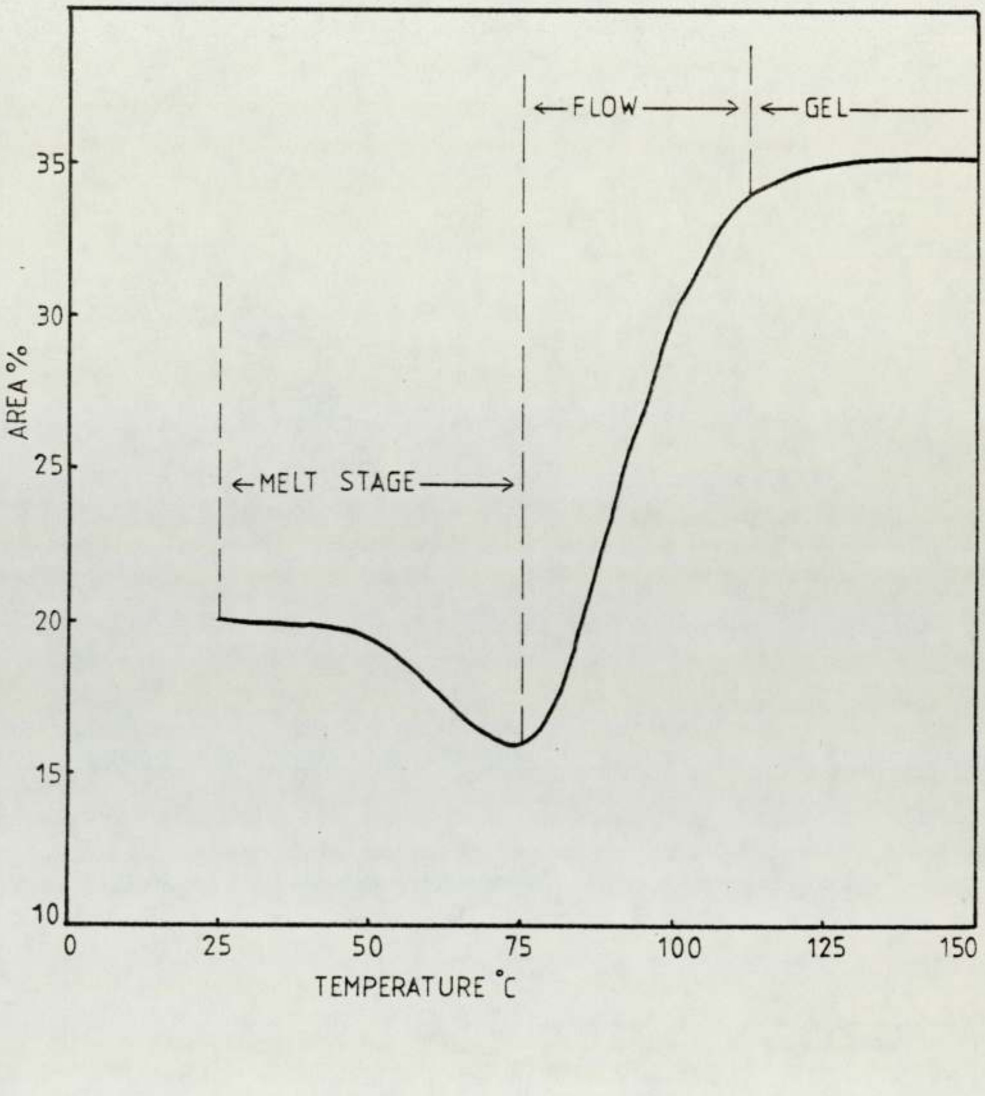
The melt stage of the curing cycle is accompanied by a decrease in area, which can be related to changes taking place in the powder particle. At room temperature the particles are rock shaped and they may contain some porosity, but as the particles melt, they assume a spherical shape, and occupy a minimum area on the metal surface.

The polymer viscosity is reduced as the temperature increases further and the globules spread and merge to wet the surface. This flow stage is accompanied by a sharp increase in area.

The gel stage results in there being little further increase in flow because the onset of cross-linking reactions causes an increase in polymer viscosity.

FIGURE 22

Idealised flow curve obtained using the hot stage Q.T.M. technique



3.3 The effect of powder type on flow

The powders studied were a standard epoxy, a low-bake epoxy, a matt epoxy, a matt-textured epoxy, a polyester and a mixed polymer. Only one substrate was used for this study, which was the polished side of a standard test panel that had been degreased in acetone.

The flow curves for these powders are shown in Figures 23 and 24.

The extent of the increase in area during flow depended on the powder type. All the gloss powders exhibited large increases in area whilst some of the matt ones gave very little increase. The matt-textured powder flows very little after the melt stage, whereas the matt powder flows significantly more. Both these powders contain the same resin, curing agent and pigments, the only significant difference being that the textured powder contains an added flow restricting agent to give the textured finish. The polyester and the mixed polymer powders gave coatings with high gloss and both showed a large increase in area due to flow. Gloss measurements indicated that the low-bake epoxy powder coating had lower gloss than the standard epoxy coating, and its flow is less, as shown in Figure 23.

FIGURE 23

Flow curves for standard, low-bake and matt epoxy powders

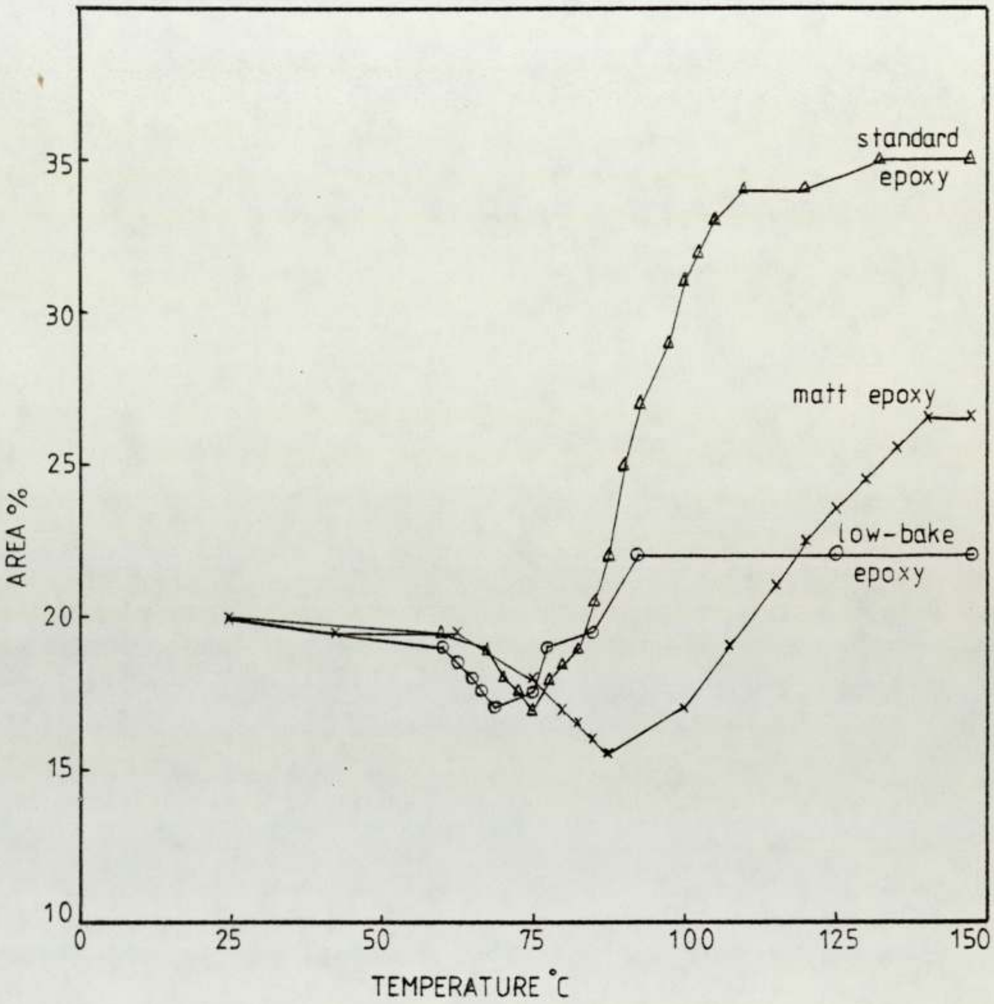
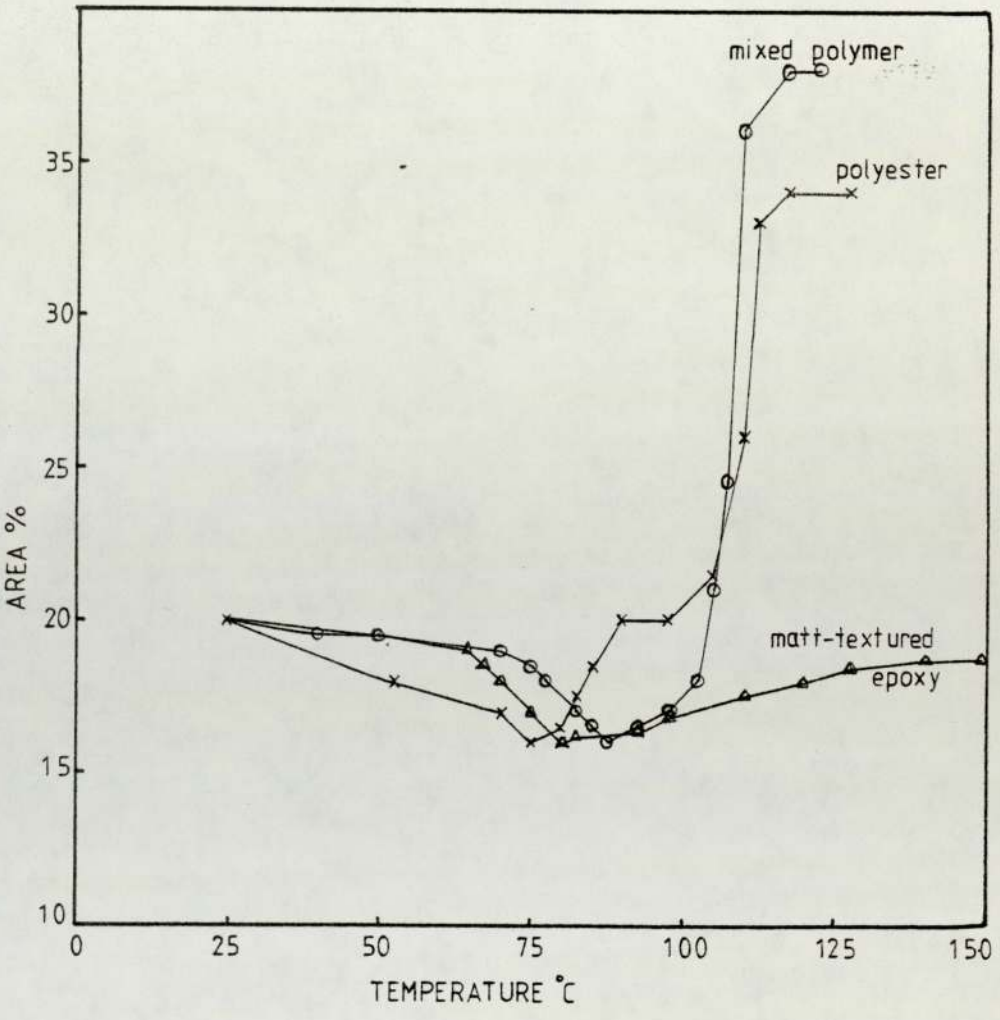


FIGURE 24

Flow curves for a matt-textured epoxy, a polyester and a mixed polymer powder



3.4 The effect of powder storage conditions on flow

To repress degradation of the powders, they were stored in sealed polythene bags, in sealed cans, and kept in a freezer. This action inhibited the uptake of moisture from the atmosphere, and prevented the occurrence of ambient temperature cross-linking reactions. For this study samples of the powders were exposed to the atmosphere for at least 2 weeks. Flow curves for the 6 powders in this 'stale' condition are given in Figures 25 and 26.

Except for the matt-textured and low-bake epoxy powders, the increase in area due to flow is less in the stale condition than in the fresh condition. By comparing Figures 23 and 24 with Figures 25 and 26 other differences between the fresh and stale powders can be gleaned. The melt temperature for the low-bake epoxy and the polyester is significantly lower in the fresh condition than in the stale condition. Also, the onset of gel temperatures for the mixed polymer, polyester and low-bake epoxy powders are significantly higher in the stale condition.

FIGURE 25

Flow curves for standard, low-bake and matt epoxy powders in a 'stale' condition

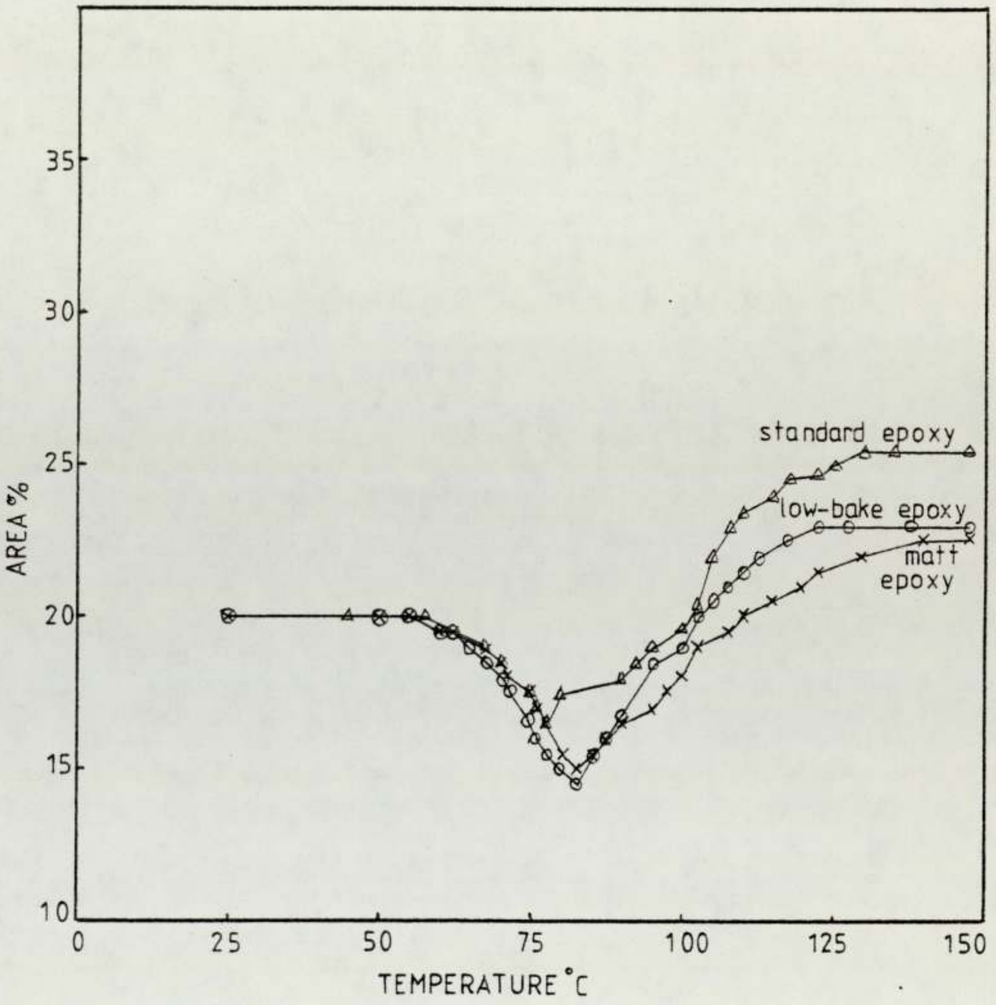
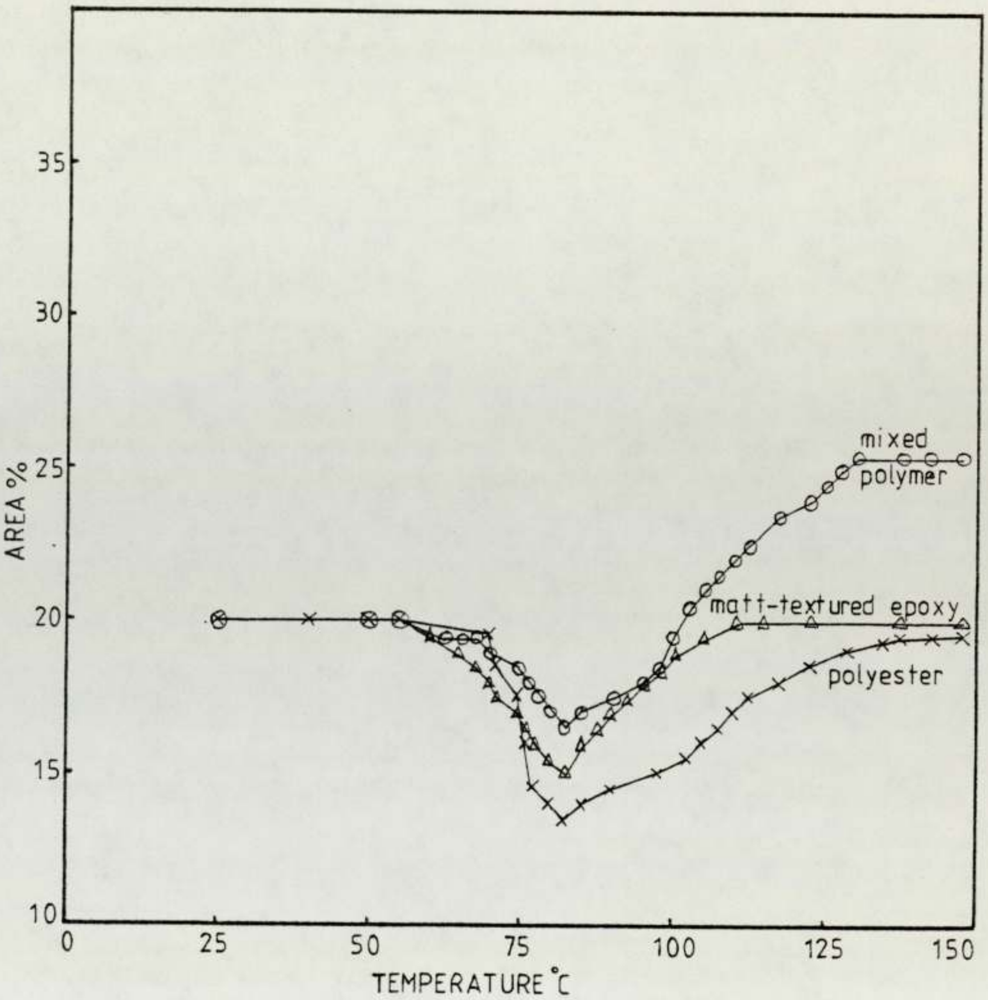


FIGURE 26

Flow curves for matt-textured epoxy, polyester and mixed polymer powders in a 'stale' condition

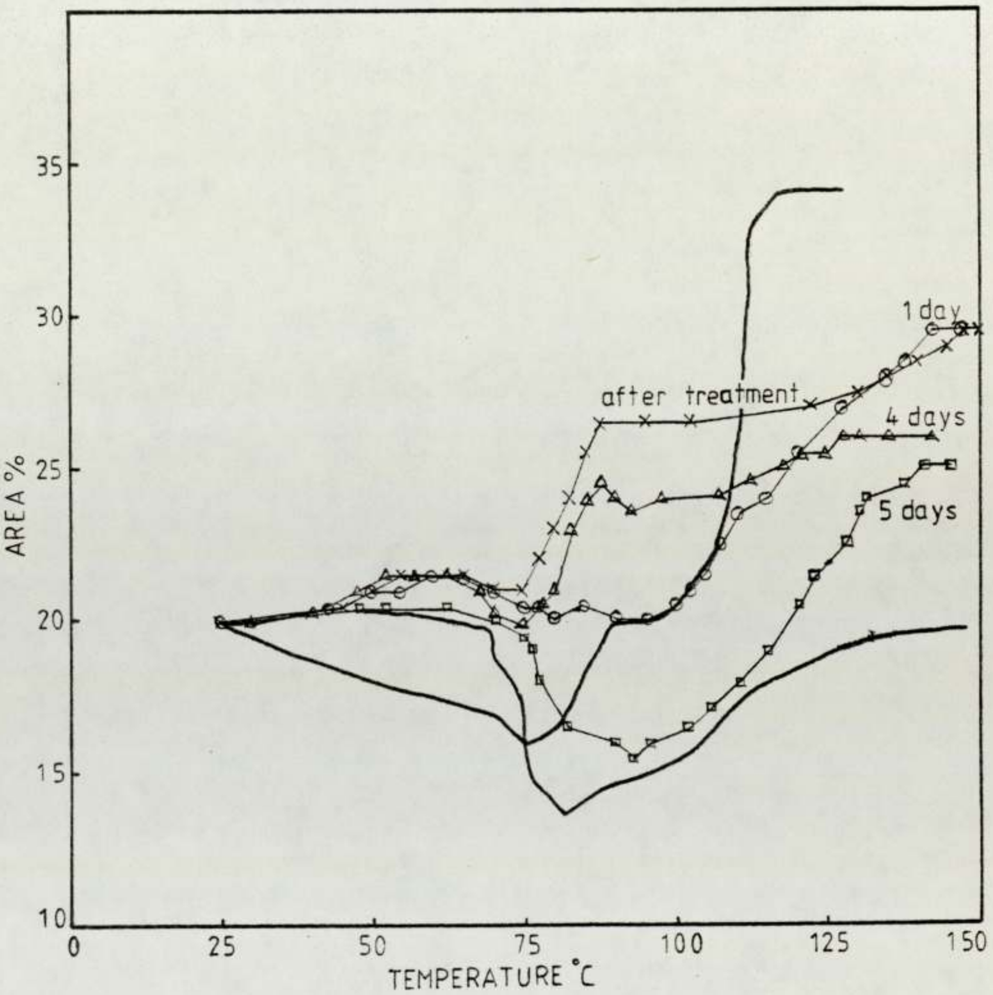


3.5 The effect of vacuum treatment on the flow of a stale powder

Figures 24 and 26 show that there is a considerable difference in the flow behaviour between 'fresh' and 'stale' polyester powder. It was thought that the uptake of moisture from the atmosphere may be an important contributary factor. To test this hypothesis polyester powder was treated in a vacuum at room temperature to remove its moisture content, which was found to be 0.5%. Immediately after treatment a flow curve on the standard steel test panel was recorded. The treated powder was left open to the atmosphere and flow curves were recorded at various time intervals. The results of this experiment are shown in Figure 27. For ease of comparison the flow curves for the fresh and stale condition are shown on the diagram by the thicker upper and lower curves respectively. It can be seen from this figure that vacuum treatment removes the reduction in area effect on melting, which only returns after 5 days exposure to the atmosphere. Although vacuum treatment results in an increase in flow of the stale powder, flow is not as high as in the fresh condition. Moisture uptake is only one factor inhibiting the flow of stale powders.

FIGURE 27

Flow curves for polyester powder in a 'stale' condition after vacuum treatment



3.6 The effect of metal surface on flow

Various surface treatments were applied to steel and aluminium, and these are listed in Table 4. The flow curves recorded for the standard epoxy powder on these substrates are illustrated in Figures 28-32.

There was a significant difference in the flow behaviour of the standard epoxy powder on the various substrates. On all of the aluminium and phosphated steel substrates, the flow on the grit blast surfaces was considerably less than for the other pretreatments. There was no such difference between the as received and grit blast steel surfaces. Grit blast and as received mild steel were both quite rough surfaces, whereas the grit blast aluminium was very rough compared to the as received aluminium. The differences in flow behaviour on aluminium and steel appeared to be due to the surface condition and not to the chemical differences between the two metals. This can be seen by comparing the similarity of flow on fresh metallographically polished samples of the two metals, Figures 28 and 29. There was a difference in the flow characteristics on the as received mild steel and aluminium which cannot be explained by surface topography alone. The as received aluminium was smoother than the as received mild steel, but there was still less flow on the former. This may have been due to the nature of the oxide film on aluminium. Chromating had the effect of increasing the flow of the powder on aluminium, the effect being greater with more concentrated solutions. This may be due to the change in the chemical nature of the surface.

TABLE 4

SURFACE TREATMENTS APPLIED TO STEEL AND ALUMINIUM SUBSTRATED

Substrate	Surface condition	Surface Treatment
Steel	Metallographically polished	Washed with alcohol
Steel	As received	Degreased with acetone
Steel	Grit Blast	Degreased with acetone
Steel	As received	Degreased with acetone plus commercial zinc phosphate treatment
Steel	Grit blast	Degreased with acetone plus commercial zinc phosphate treatment
Steel	As received	Degreased with acetone plus commercial iron phosphate treatment
Steel	Grit blast	Degreased with acetone plus commercial iron phosphate treatment
Aluminium	Metallographically polished	Washed with alcohol
Aluminium	As received	Degreased with acetone
Aluminium	Grit blast	Degreased with acetone
Aluminium	As received	Degreased with acetone plus commercial chromate treatment
Aluminium	Grit blast	Degreased with acetone plus commercial chromate treatment

FIGURE 28

Flow curves for a standard epoxy powder on aluminium

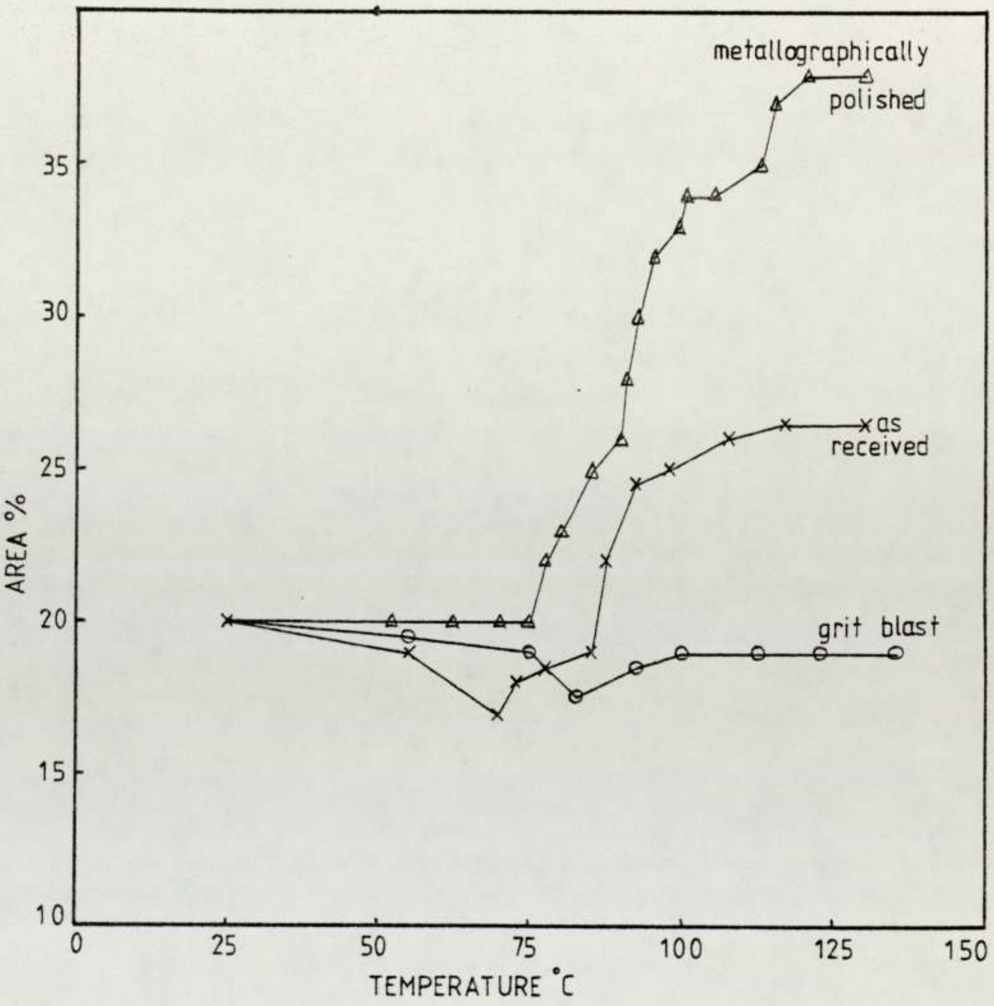


FIGURE 29

Flow curves for a standard epoxy powder on mild steel

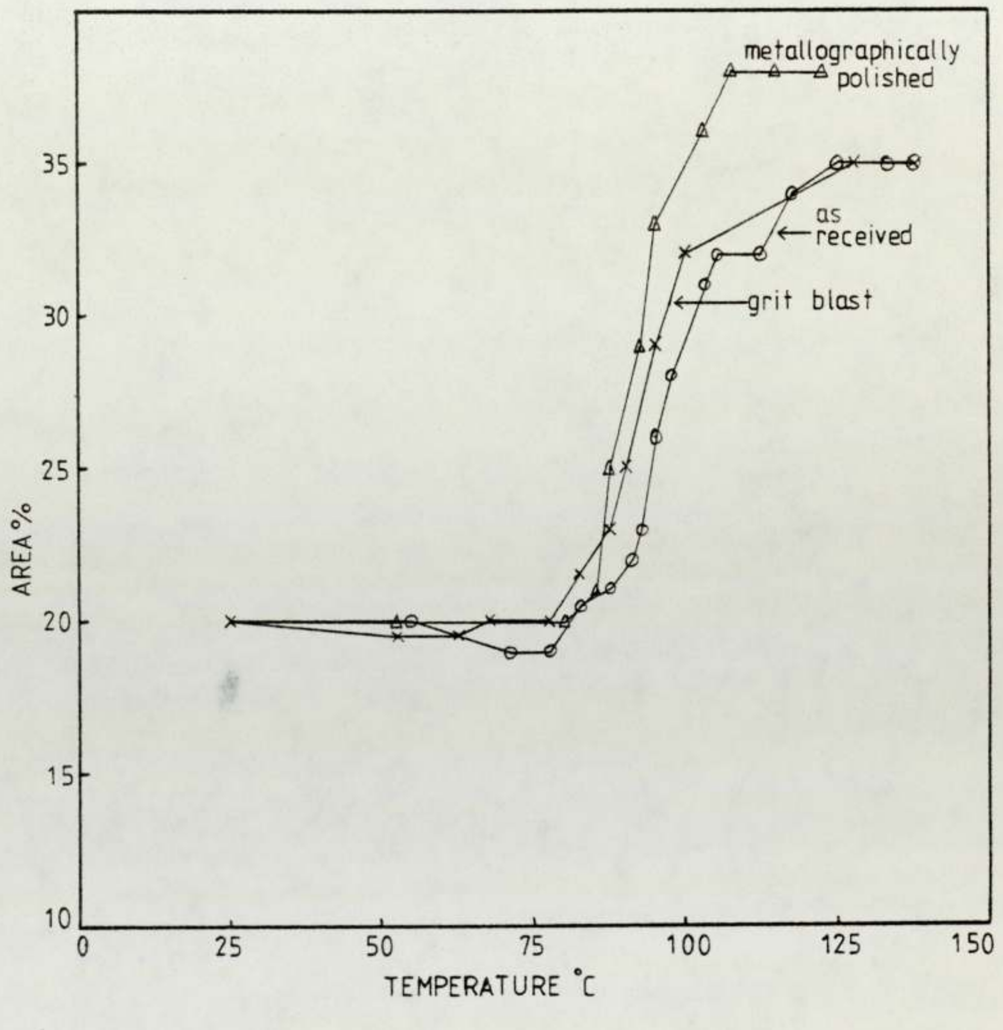


FIGURE 30

Flow curves for a standard epoxy powder on mild steel subjected to commercial iron phosphate treatment

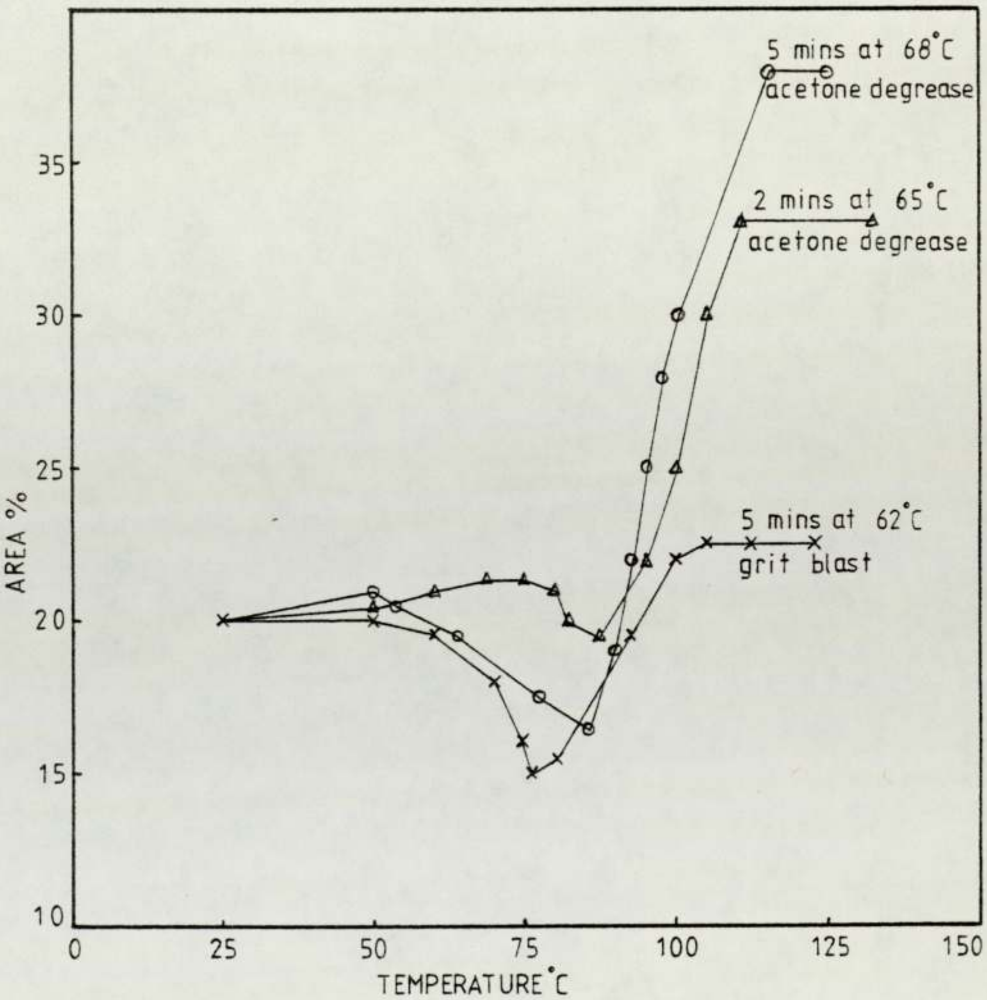


FIGURE 31

Flow curves for a standard epoxy powder on mild steel subjected to commercial zinc phosphate treatment

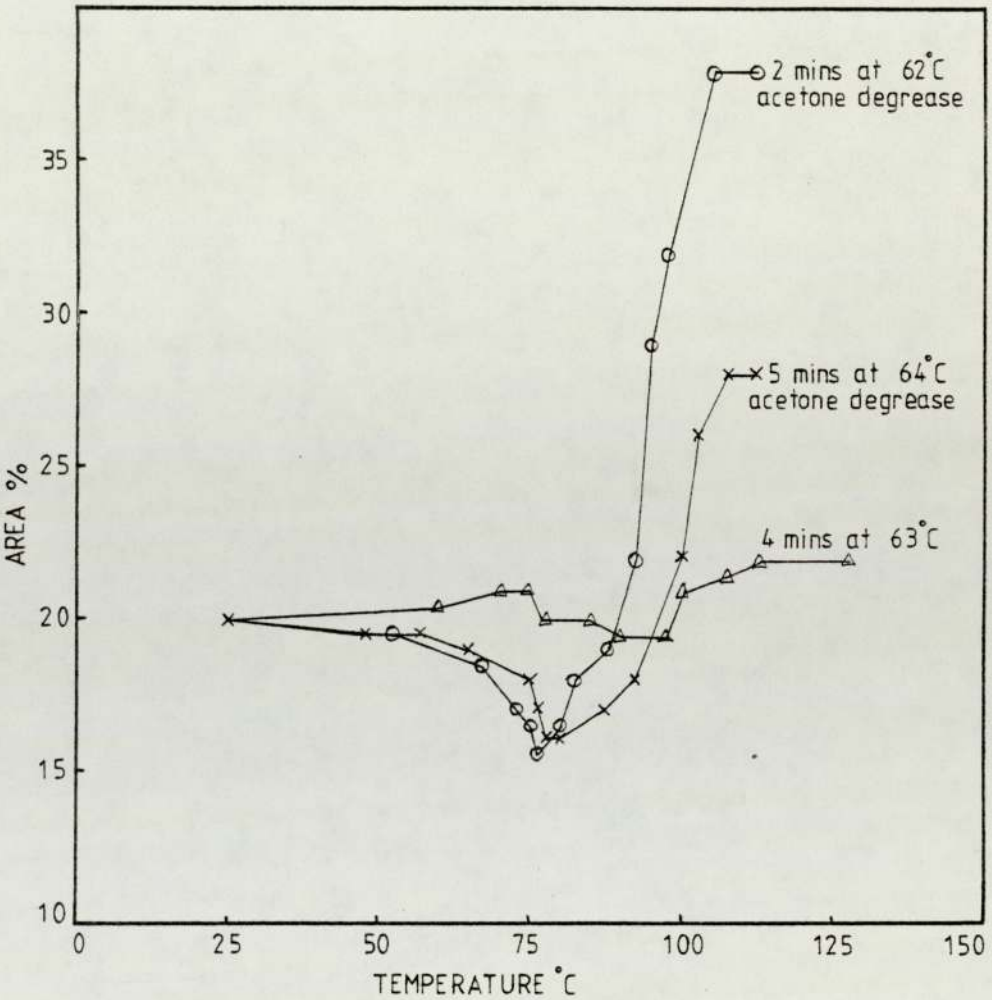
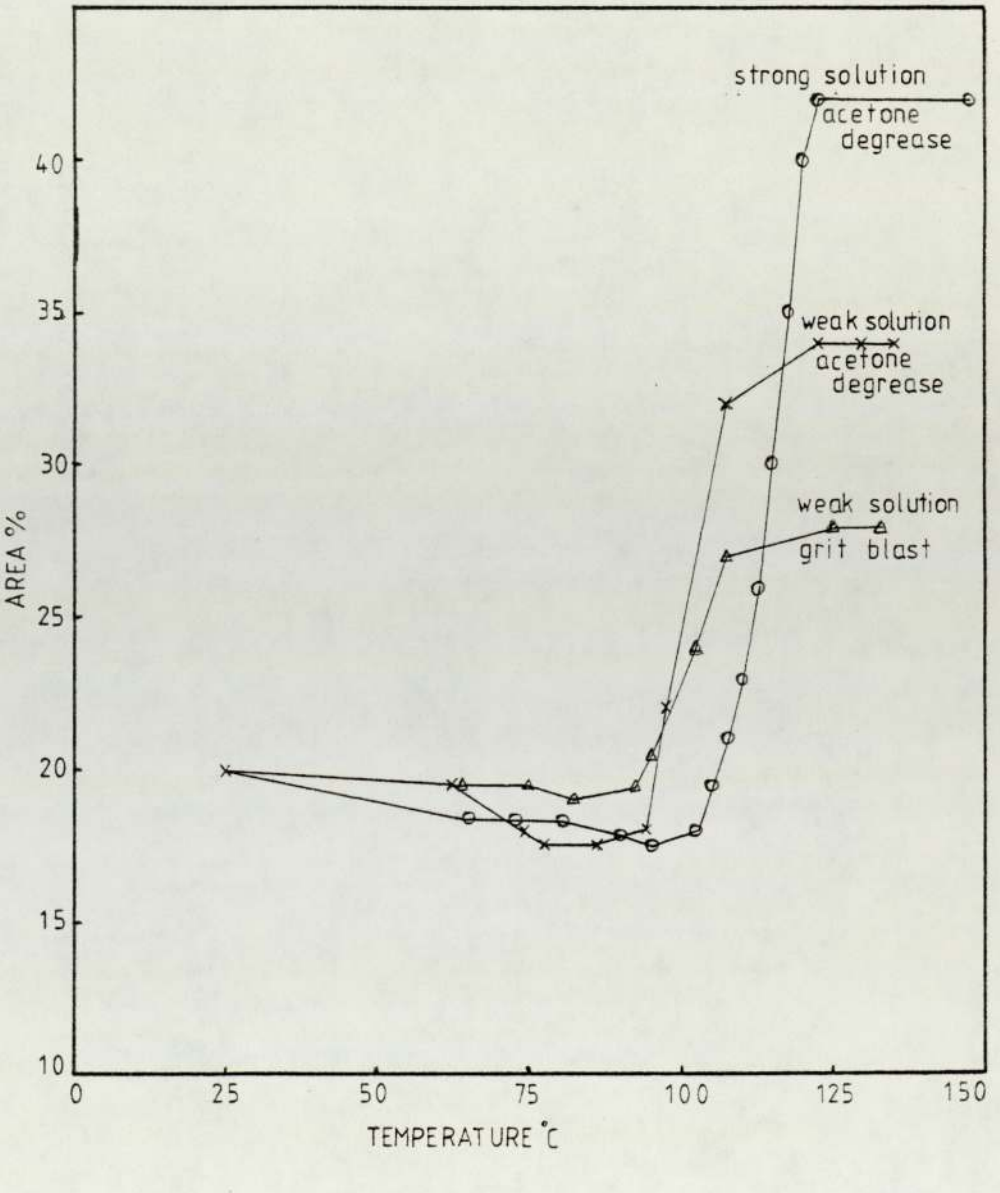


FIGURE 32

Flow curves for a standard epoxy powder on aluminium subjected to a commercial chromate treatment



DIFFERENTIAL THERMAL ANALYSIS STUDIES

CHAPTER 4

4.1 Description of differential thermal analysis

Since the introduction of commercial differential thermal analysers in the 1950's there have been numerous publications describing the use of thermal methods in the laboratory. Pope and Judd (113), give a good account of the history, techniques and applications of differential thermal analysis (DTA). DTA is a technique which involves heating the test sample and an inert reference sample under identical conditions and measuring any temperature difference between them, either against time or against a fixed temperature. Any physical or chemical changes occurring in the test sample which give rise to evolution of heat lead to a temporary increase in temperature of the sample with respect to the reference, and conversely changes leading to absorption of heat cause the temperature of the sample to drop with respect to the reference. DTA produces a curve of the temperature difference between the sample and a reference (ΔT), versus a fixed temperature (t). Processes causing the evolution of heat are shown as an exothermic peak, and those absorbing heat as an endothermic trough on this curve. The heat of reaction can be obtained by measuring the area above or beneath the curve.

The thermal behaviour of a wide range of materials can be readily evaluated by means of DTA. The DTA curve may give information on physical changes occurring in the material such as melting and freezing, crystalline and glass transitions; and on chemical changes such as curing, decomposition and degradation reactions. A hypothetical DTA curve for a thermosetting powder coating material is shown in Figure 33 which illustrates the endothermic glass transition and moisture evaporation, and the exothermic curing reaction peak.

Thermal analysis studies of powder coating materials have been reported in the literature using differential scanning calorimetry (94). Although the field of application of DTA and differential scanning calorimetry (DSC) is practically identical the two techniques are distinctly different. The difference may be elucidated by reference to Figure 34. DSC records the energy necessary to maintain zero temperature difference between the sample and the reference, either against time or temperature. In DSC the sample and reference have two separate heaters, and therefore as the temperature is kept the same the energy input to the sample will be either higher or lower than the reference depending upon whether endothermic or exothermic changes are taking place. DTA uses a single heater and thermocouples are used to measure the temperature difference between the sample and the reference.

FIGURE 33

A hypothetical DTA trace

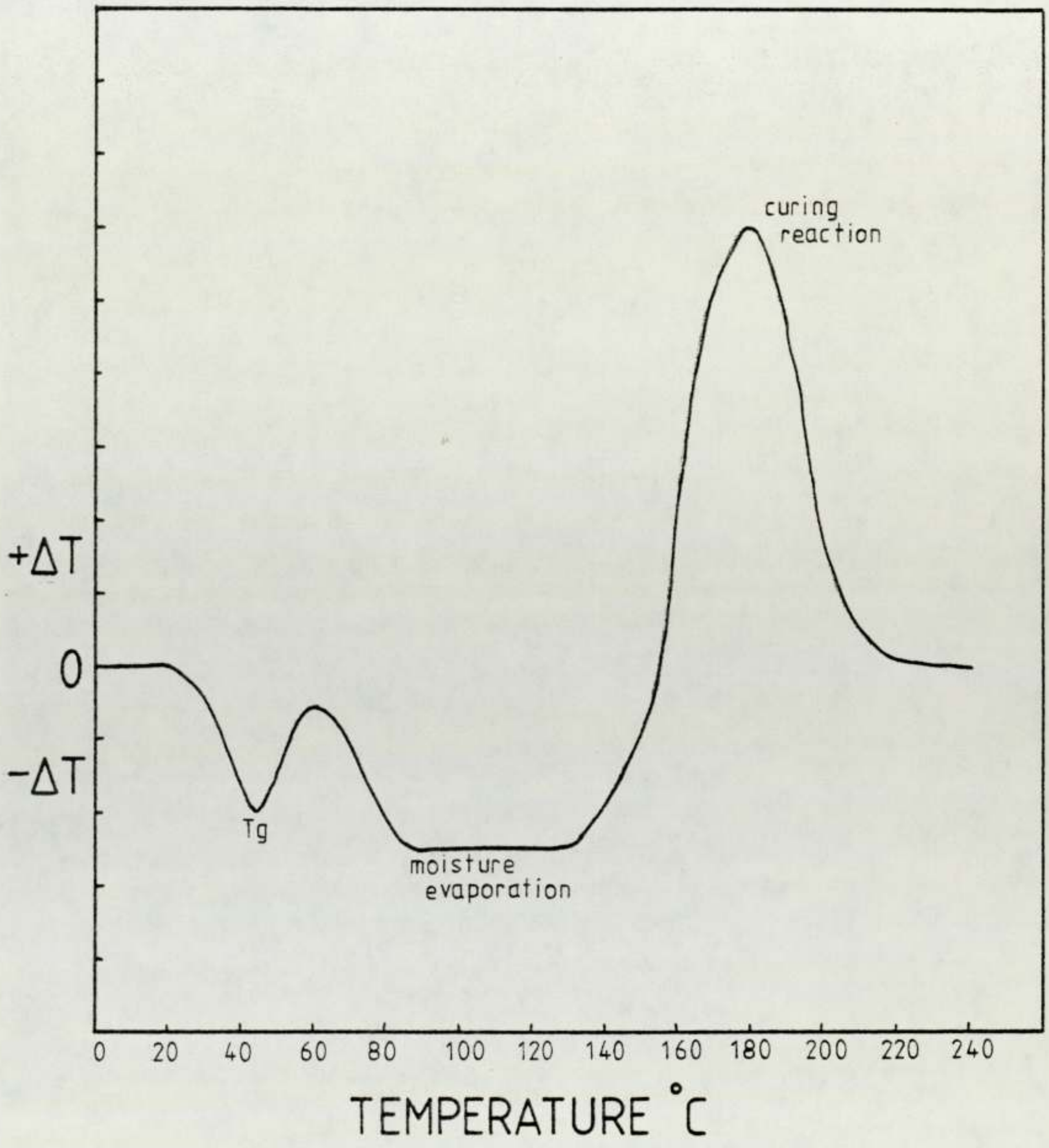
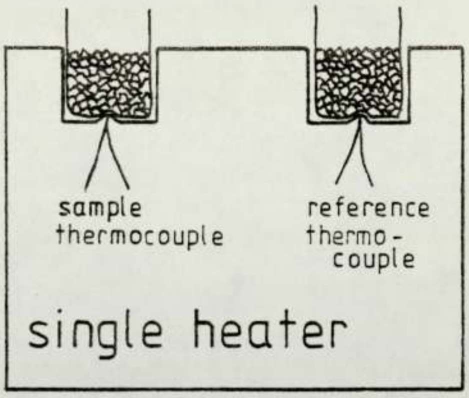


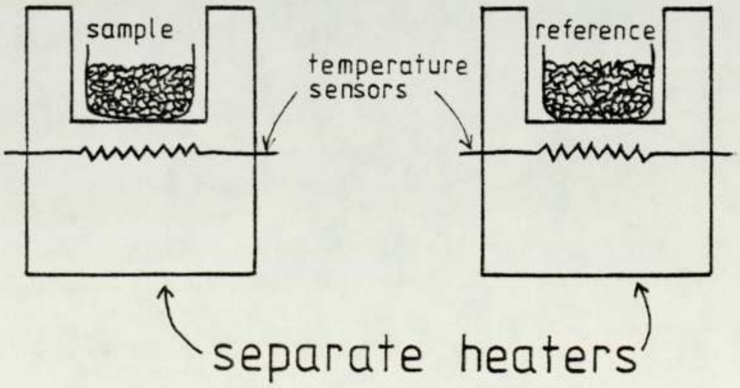
FIGURE 34

Fundamental differences between DTA and DSC

(a) DTA



(b) DSC



4.2 Experimental details

The sample and reference are placed in crucibles which are housed in a ceramic specimen holder assembly in such a way that the hot junction of a thermocouple sits in a dimple in the base of the crucible. The whole assembly is surrounded by an electrically heated furnace, which can be controlled, to give heating rates of up to 20°C per minute, by means of a separate temperature programming unit. The temperature of the reference, (t), is plotted against time on an adjoining twin pen recorder which simultaneously records the temperature difference between the sample and the reference, (ΔT).

Long quartz crucibles, (10 cm long), were used to prevent frothing of the material onto the ceramic specimen holder. If this is contaminated, it has to be thoroughly cleaned, otherwise inconsistent results are produced. An inert material is used as a reference, and in this study powdered alumina was used. At frequent intervals runs were carried out using alumina as the sample as well as the reference, to check the sensitivity of the apparatus. In this case there should be no thermal difference between the sample and the reference, and a straight line graph should be produced. Except in one case, where the specimen holder had become contaminated with some powder, straight lines were produced.

The DTA was used in two separate studies; firstly to study the effect of partial curing on the properties of a powder coating; and secondly, to investigate the effect of storage conditions on the powder.

4.2.1 The effect of partial curing

It was thought that incomplete curing may have an effect on the mechanical and corrosion resistant properties of the coating.

Six coated steel test panels were produced that has been cured for 3, 6, 9, 12, 15 and 20 minutes at 180°C. Standard epoxy powders on acetone degreased steel substrates were used for this study. Samples for differential thermal analysis were scraped from the panels which were subsequently used for corrosion and adhesion testing.

The degree of cure was assessed by measuring the heat of reaction for the uncured powder and comparing this to the heats of reaction for the scrapings, which were of course only partially cured. Subtracting the heat of reaction for the partially cured from the heat of reaction for the uncured sample, gave an indication of how far the reaction proceeded during the curing cycle. It was assumed that no curing reactions had occurred in the uncured sample.

The heat of reaction was assessed by measuring the area under the peak using the Quantimet television microscope as an epidioscope and dividing this by the sample weight. The heat of reaction is given in arbitrary units but never the less this serves as a comparison for degree of cure. These results together with adhesion and corrosion spread results are given in Table 5.

The coated panels were subjected to a salt spray corrosion test (ASTM B117-73) for 120 hours, followed by adhesion testing according to the modifed cross-hatch method described in Chapter 5. Corrosion spread measurements were made after stripping off the coating with a scalpel blade after immersion in acetone.

By studying the results in Table 5 it can be seen that a standard epoxy powder coating is fully cured after 6-9 minutes at 180°C. The mode of adhesion failure is markedly different for partially cured films compared to fully cured films. Partially cured films fail by the coating coming away in small flakes, whereas the fully cured films pull off in a continuous strip. Curing for times necessary to give 100% cure leads to a reduction in adhesion. Corrosion spread measurements are similar for all panels, but filiform corrosion becomes an important mechanism for corrosion for those coatings that are completely cured.

TABLE 5

THE EFFECTS OF PARTIAL CURING ON A STANDARD EPOXY POWDER COATING

Sample treatment	Heat of reaction (arbitrary units)	% cure	% Adhesion	Corrosion spread (mm)	
				Min	Max
No cure	47.62	0	-	-	-
3 mins @ 180°C	45.13	5.2	75 (flaky)	2	7
6 " " "	19.26	59.6	75 (flaky)	2	6
9 " " "	0	100	75 (continuous)	3	7 *
12 " " "	0	100	2	3	6 *
15 " " "	0	100	0	2	4 *
20 " " "	0	100	24	2	5 *

* Also some filiform corrosion running up to 16 mm from the scratch line.

4.2.2 DTA studies on the effect of storage conditions

At the beginning of the study it was thought that the degradation of stored thermosetting powders could be brought about by two factors. Firstly, storing at room temperature may enable some cross-linking reactions to take place, and secondly improper sealing of storage containers may allow the uptake of moisture from the atmosphere.

Stale powders do not flow readily, which may give rise to problems during application, such as the clogging of feeding channels for electrostatic deposition. Work described in the previous chapter has shown that the way molten particles spread over the surface during stoving, may be inhibited in powders that have been stored in unsealed containers at room temperature.

Six different powders were chosen for this study; a standard epoxy, a matt-textured epoxy, a matt epoxy, a low-bake epoxy, a polyester and a mixed polymer. The powders were studied in two conditions:-

a) Stored in sealed polythene bags in a sealed can in a freezer since they were received from the manufacturer.

b) Stored at room temperature, and open to the atmosphere for 2 weeks.

Sample weights were between 0.12 and 0.14 g, and constant heating rates of 5, 10, and 15° C per minute were used.

The DTA curves for these powders at a heating rate of 5°C per minute are shown in Figures 35-40. For the matt textured epoxy powder it was found that the curing reaction peak temperature at 5°C per minute is 170°C, and at heating rates of 10 and 15°C per minute it is increased to 185 and 195°C respectively.

All of the epoxy powders show very distinct exothermic curing peaks (Figures 35-38), whilst the polyester and the mixed polymer powders give less distinct peaks (Figures 39 and 40). All of the powders show a smaller peak for the powder in the stale condition, which is probably due to cross-linking reactions having started at room temperature in the stale powders. Moisture evaporation can be seen to have taken place for some of the powders in the stale condition. This is more obvious for the matt-textured, matt and low-bake epoxy powders (Figures 36, 37 and 38), than for the standard epoxy powder (Figure 35) and is not seen in the polyester powder in the stale condition (Figure 39). It can be concluded from this that some powders absorb moisture from the atmosphere when they are stored in unsealed containers at room temperature. The most important conclusion that can be drawn after examination of Figures 35 - 40 is that the heat of curing is smaller for the stale powders and that this is due to ambient temperature cross-linking reactions taking place.

FIGURE 35

DTA traces for a standard epoxy powder

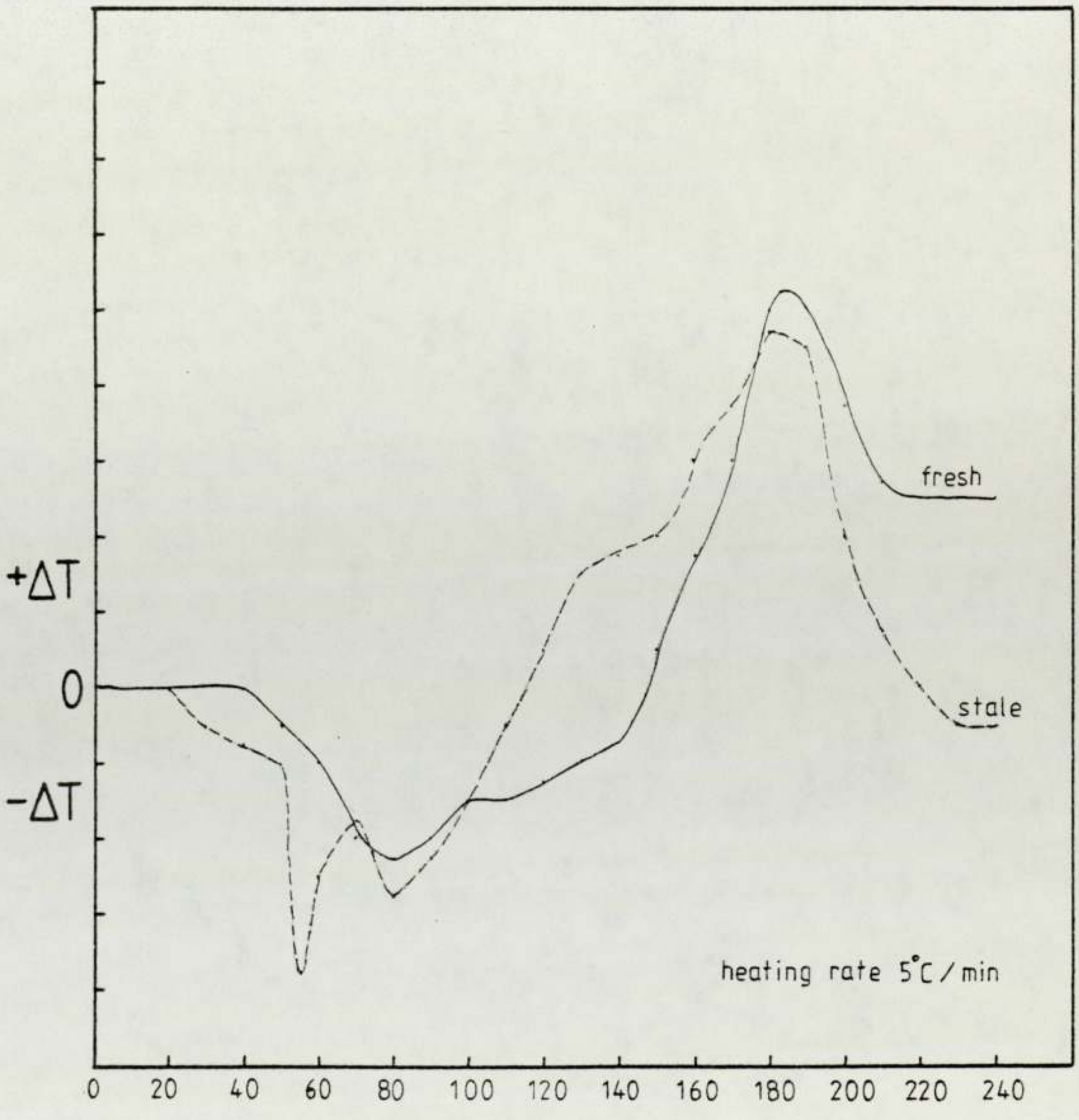


FIGURE 36

DTA traces for a matt-textured epoxy powder

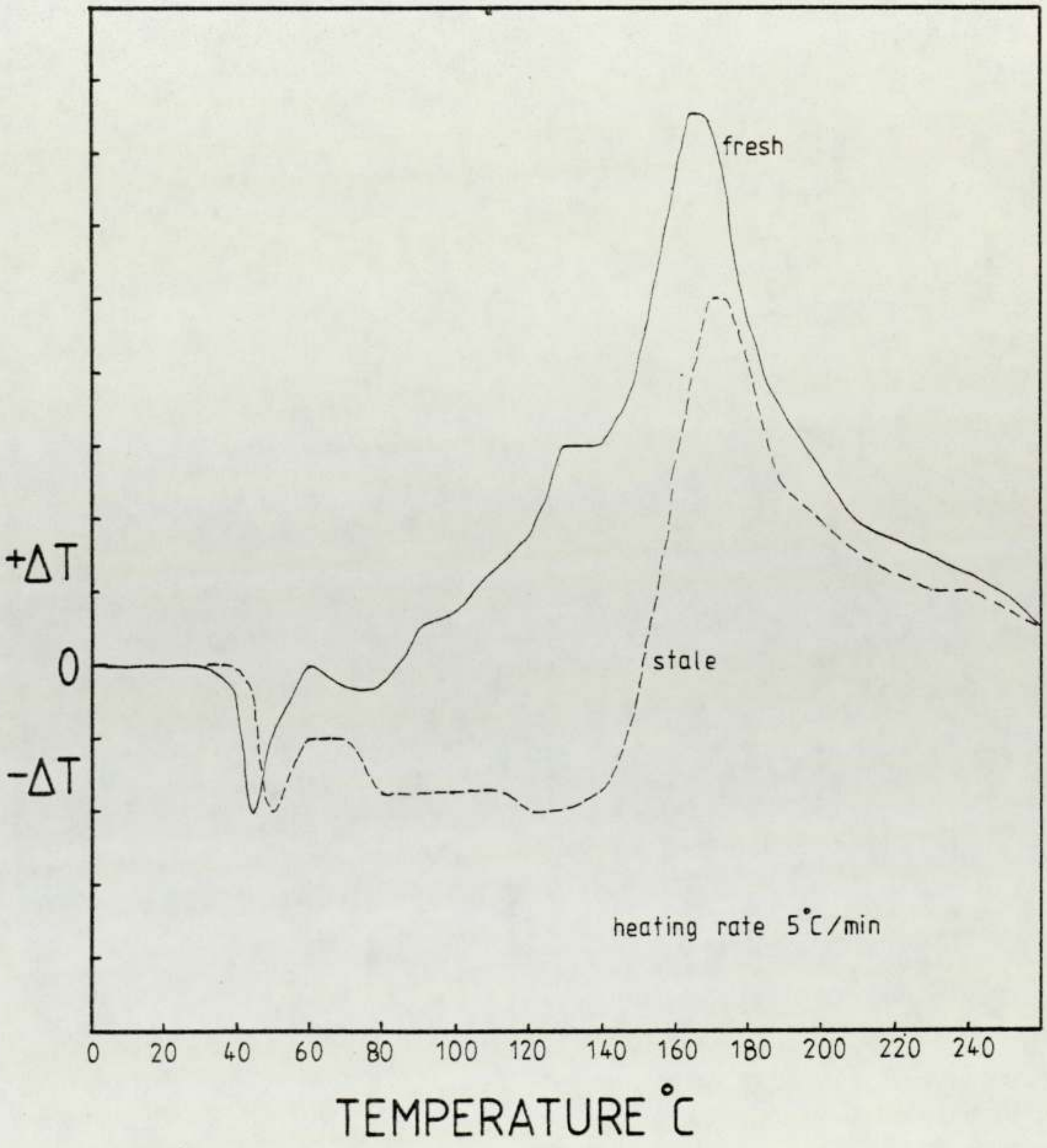


FIGURE 37

DTA traces for a matt epoxy powder

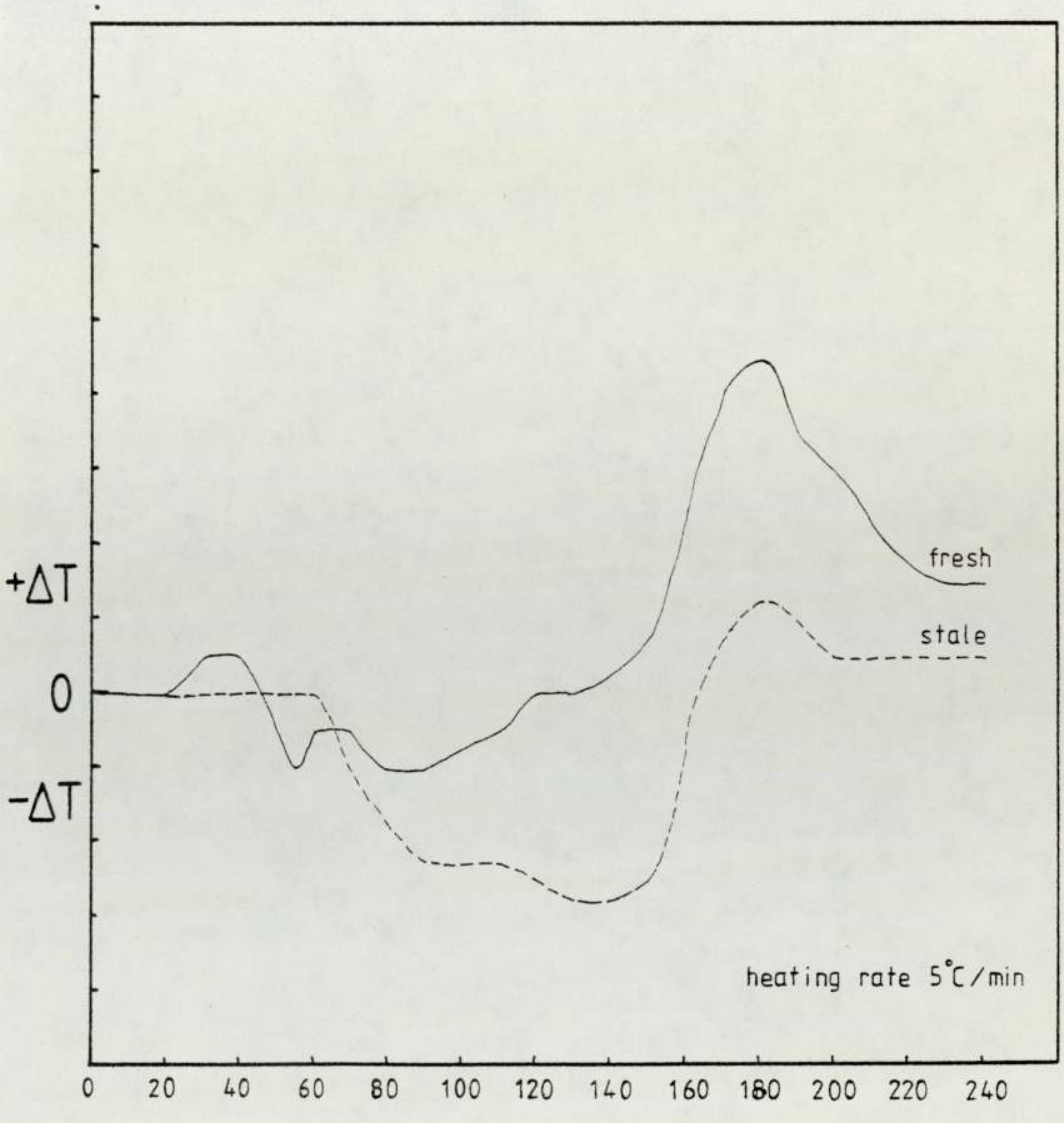


FIGURE 38

DTA traces for a low-bake epoxy powder

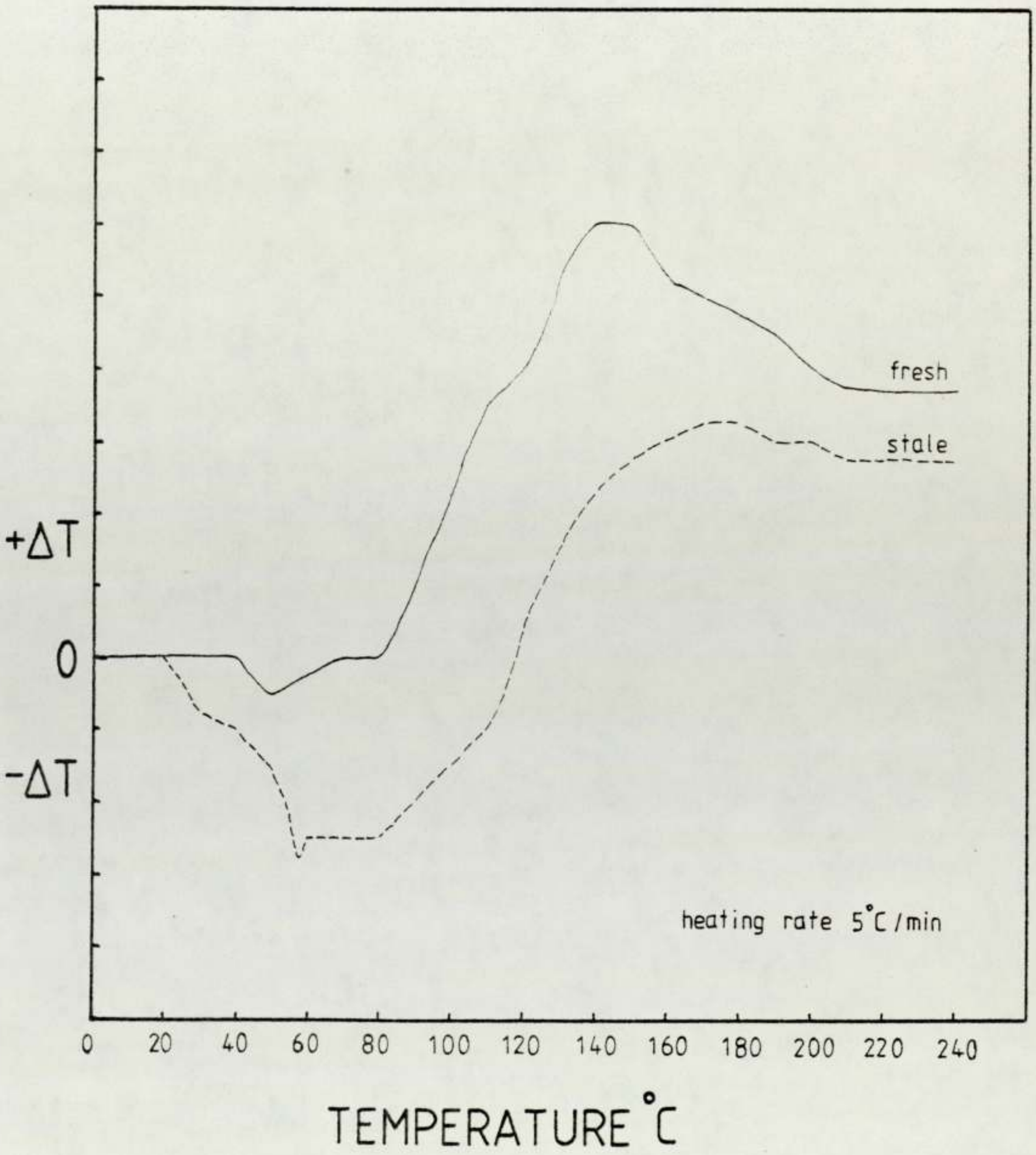


FIGURE 39

DTA traces for a polyester powder

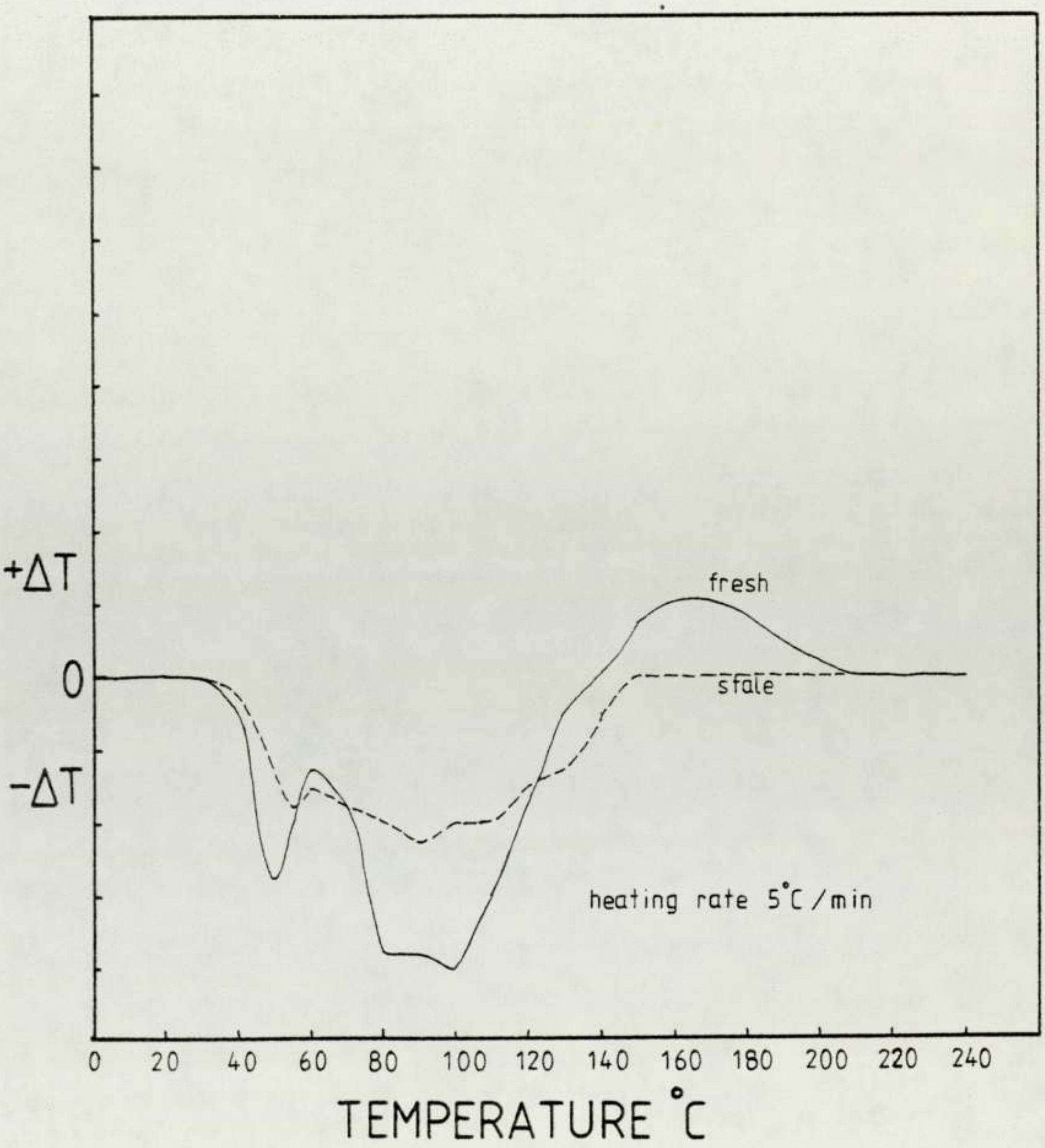
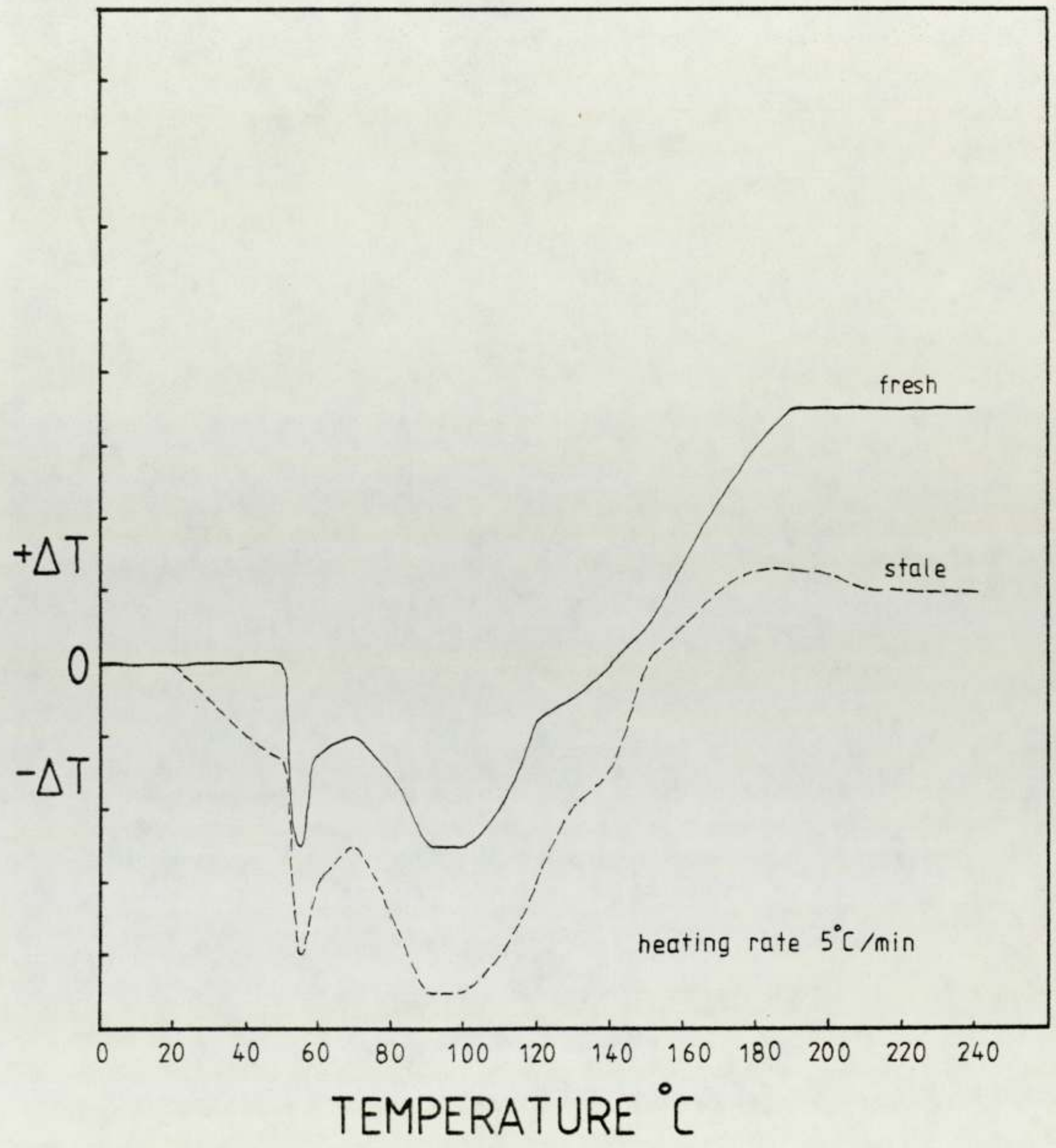


FIGURE 40

DTA traces for a mixed polymer powder



ADHESION OF POWDER COATINGS

CHAPTER 5

5.1 Theory of adhesion

There are three major factors which govern the level of adhesion of powder coatings to metal substrates. These are the nature of the chemical bond between the two, the degree of mechanical keying and internal stresses formed within the coating.

The chemical bond will depend upon the chemical nature of the resin in the powder coating and also upon the pretreatment that the metal substrate has received.

The degree of mechanical keying will be influenced by the topography of the metal and the extent to which the polymer flows into the surface during the melt and flow stage of the curing cycle.

Internal stresses may be induced during cure, or factors such as thermal stresses may arise while the coating is in use.

Bullett, (105), has discussed the role that internal stresses play in determining the adhesion of paint films. With conventional solvent paints, tensile stresses will develop in the coating, and at the interface, because of the shrinkage that occurs during solvent loss and later because of the chemical processes that occur in the film.

These stresses will exist in powder coating films but will not be so high because solvent loss shrinkage has been eliminated. The extent to which such stresses build up at the interface depends upon the stress/strain characteristics of the polymer. For example, a highly plasticised film will be less susceptible to this type of adhesion failure than one which contains little plasticiser.

Bullett also states that the stresses, that build up due to differential expansion and contraction between the coating and the substrate on heating and cooling, can in some cases be high enough to exceed adhesion forces. In any case, this could be a significant factor if the coating is subjected to thermal cycling, as a fatigue type of interface failure may occur. It will be seen later that thermal cycling forms the basis of an adhesion test.

Bullett also discusses the effects of water, which may cause swelling of the coating and leaching out of soluble components of the coating with a resultant shrinkage on drying.

Gaynes, (106), and Gignoux, (107), discuss the role of mechanical adhesion by roughening the surface by grit blasting. As well as producing a chemically clean surface, sand blasting improves adhesion in two other ways. It provides mechanical anchorage and it increases the area over which adhesion forces can act.

McGill, (108), gives a very good account of the factors governing mechanical adhesion. He suggests that the shape of pits in the surface is important. Penetration of a fluid into surface pits depends upon their radii of curvature, but if they are small, deep or of irregular shape it may be difficult for viscous liquids to flow into them. The improvement in performance brought about by sand blasting may partly be due to replacing sharp edged or deep pits by shallow open structures which can more easily be filled with a viscous fluid.

McGill, (108), and Lewis et al, (109), have reviewed the theory of wetting. Good film adhesion depends upon the ability of the coating fluid to thoroughly wet the surface, and this will depend upon the surface free energies of the components of the system as well as the viscosity of the coating liquid. Metals and metal oxides have high surface energy values (500-5000 ergs cm^{-2}), compared to materials such as waxes, most polymers, and most organic solids (less than 100 ergs cm^{-2}). Because most organic liquids have a low surface energy they would spread freely on high surface energy solids as this would result in a lowering of the total energy of the system. Conversely, it is more usual for there to be non-spreading when organic liquids are put onto low surface energy solids, because their surface energies are similar and there would be no lowering of the energy of the system. A metal with a greasy and/or dusty surface will behave as a low surface energy solid, and wetting will not take place, resulting in a poor adhesive bond. In order to get good adhesion, the metal surface must be free of contaminants which lower the surface free energy of the metal. Improper wetting leads to the formation of a weak layer at the interface due to pockets of air between the two materials. This interfacial porosity has the effect of reducing the surface area over which adhesive forces act.

The strength of the chemical bond will depend upon polar attractions between the metal surface and the coating. Lewis et al, (109), state that most metals have -OH groups on their surface and one would expect adhesion to be best with those coatings which are capable of chemical reactions with such groups. They state that epoxy and polyurethane paints can chemically react with any group having an active hydrogen and this is the reason why they exhibit excellent adhesion to metals. Chemical adhesion, therefore, is very much dependent on the chemical nature of the resin in the coating material. The chemical nature of the metal surface will also be very important. A surface free of dust, grease and excessive amounts of scale is more likely to allow these polar interactions to take place. Consequently, a clean surface is essential for good chemical adhesion. Chemical conversion coating processes such as phosphating of steel and chromating of aluminium, do not improve initial adhesion performance, although better adhesion results will be seen after exposure to a corrosive environment because there will be less corrosion undercutting of the organic film.

Kut, (110), has published results which show that optimum initial adhesion performance is obtained after degreasing mild steel (free of rust and scalc) with trichloroethylene only, compared to other pretreatments such as alkali degreasing, abrasive blasting and zinc phosphating.

5.2 Adhesion tests

Adhesion tests suitable for powder coatings fall into two categories, destructive and non-destructive.

Davies and Whittaker, (111), review tests suitable for measuring adhesion of metal coatings to metals, although some of these are suitable for powder coatings. Lewis et al, (109), describe test methods applicable to organic coatings. The tests described are numerous, emphasising the fact that there is not a good universally acceptable test for measuring adhesion.

Some of the destructive tests will be described here. Scratch tests involve making a series of cuts through the paint with a knife or diamond cone and assessing for adhesive failure either before or after pulling off weakly bonded areas with pressure sensitive tape. A test of this type is described in an ASTM standard D 3359-76(112).

Another test consists of dropping standardised steel balls onto the test panel from a standard height, which may result in adhesion failure of the coating. Similar tests are elongation tests, which can consist either of bending the test panel around a cone, or, as in the Erichsen test, the coated panel is deep drawn into a cup or cylinder, the degree of adhesion being measured by the amount of elongation a specimen will endure before adhesive failure.

Other tests are more quantitative and usually based on measuring the force required to remove the coating from the substrate. The coating may be removed by peeling, chiselling off with a knife, ultracentrifuge, applying alternate stresses as in fatigue testing and many others.

Thermal cycling tests are based on stresses building up at the interface due to differential expansion and contraction between the coating and the basis metal. Failure may occur after a certain number of cycles and this is taken as a measure of adhesion.

Ultrasonics can either be applied as a destructive or a non-destructive test. As a destructive test low frequency energy is used to induce stresses at the interface sufficient to detach the coating. As a non-destructive test it is purely qualitative and is similar to the technique used for testing defects in castings. The technique merely detects flaws at the interface. X-rays can be used in a similar way.

Although other workers have used the Ultracentrifuge to measure adhesion of uncured powders after electrostatic deposition, calculations have revealed that the speeds required to detach cured powder coatings from their substrates would be far too high to be practically applicable.

5.3 Limitations of adhesion tests

The main problem is that none of the tests are really quantitative, i.e. they do not measure the bond strength between the coating and the basis metal.

The peel test may appear to be quantitative, but in order to perform the test on powder coatings, the cohesive strength of the film has to be increased in some way. If was found in initial trials with peel testing that the adhesive bond was much higher than the cohesive strength of the powder coating, that is, failure always occurred in the coating. Reinforcement of the coating, by increasing the thickness or incorporating strips of aluminium foil may or may not affect the adhesive bond. Similar problems are encountered with other mechanical type adhesion tests.

The cross-hatch adhesion test, (112), is the only one that most closely resembles a standard accepted test for powder coatings. This test involves making an X-cut in the film using a scalpel blade, applying pressure sensitive tape and assessing adhesion qualitatively on a 0-5 scale. Another method described in the standard, is to make a series of 6 or 11 cuts, and then another series at right angles to the first. Adhesion is again assessed after applying pressure sensitive tape. Even if reproduction of results in one laboratory can be achieved by using this technique, it is unlikely that results can be compared from one laboratory to another. It is probably only a suitable test for putting adhesion results in a "pecking" order.

5.4 Cross-hatch adhesion testing

A number of modifications were made to the ASTM standard method to make the test more reproducible and suitable for testing powder coatings and these are described below.

The test used in this work consisted of making a series of 6 cuts, 4 mm apart, and then another series at 60 degrees to the first. Pressure sensitive tape was applied and the area of coating remaining was assessed. This percentage area was given as a measure of adhesion, e.g. if no coating was removed the adhesion would be 100%. When coated panels were tested they all exhibited 100% adhesion. For this reason tests were carried out on corroded panels. Some differences between different coatings put onto various substrates could then be seen when the excellent level of adhesion had been reduced somewhat during exposure to a corrosive medium.

Good reproducibility of results could not be achieved by making the cuts with a scalpel blade. Tests on the same panel gave results varying from 44 to 86%. This problem of reproducibility was overcome by making fine cuts using a horizontal milling machine.

Results obtained using this technique, on panels sprayed with different powders on various substrates, after exposure to the salt-spray corrosion test (ASTM B117-73), are given in Table 6.

TABLE 6

CROSS-HATCH ADHESION TEST RESULTS

	Polyester	Standard Epoxy	Low-bake Epoxy	Mixed Polymer	Matt Epoxy	Matt-textured Epoxy
Degreased as received steel	100%	100%	98%	80%	98%	100%
Grit-blast steel	88%	100%	100%	100%	100%	100%
Zn Phosphate thick coating	100%	100%	100%	100%	100%	100%
Zn Phosphate thin coating	100%	100%	100%	100%	100%	100%
Fe Phosphate thick coating	76%	100%	92%	100%	99%	99%
Fe Phosphate thin coating	100%	100%	100%	98%	99%	99%
Degreased As received aluminium	94%	0%	72%	88%	98%	94%
Grit-blast aluminium	100%	100%	100%	90%	100%	100%
Chromated Al (weak solution)	88%	100%	88%	85%	80%	100%
Chromated Al (Strong solution)	100%	100%	100%	85%	100%	100%

5.5 Thermal cycling test

This test was carried out on strips cut from the panels used for cross-hatch adhesion testing. One cycle was taken as immersion in ice and water at $0^{o}C$ followed by 30 seconds in boiling water at $100^{o}C$. The number of cycles to failure was taken as a measure of adhesion. A maximum of 15 cycles were carried out.

The results of this test are shown in Table 7.

TABLE 7

THERMAL CYCLING TEST RESULTS

The code used in this table to denote the surface condition of the underlying metal is as follows:-

a-degreased as received steel; b-grit-blast steel;
c-Zn Phosphate thick coating; d-Zn Phosphate thin coating;
e-Fe Phosphate thick coating; f-Fe Phosphate thin coating;
g-degreased as received aluminium; h-grit-blast aluminium;
i-Chromated Al (weak solution); j-Chromated Al (strong solution).

POLYESTER

	Onset of detachment	Condition after 15 cycles	Other comments
a	-	No detachment	-
b	-	" "	-
c	-	" "	-
d	-	" "	-
e	After 1 cycle	Detachment not complete	Continuous detachment up to 13 cycles
f	" "	" " "	" "
g	" "	No further detachment	-
h	-	No detachment	-
i	-	" "	-
j	-	" "	-

TABLE 7 (CONTINUED)

STANDARD EPOXY

	Onset of detachment	Condition after 15 cycles	Other comments
a	After 11 cycles	No further detachment	-
b	-	No detachment	-
c	-	" "	-
d	After 7 cycles	Detachment not complete	Further detachment up to 9 cycles
e	" "	No further detachment	-
f	After 8 cycles	" " "	-
g	After 1 cycle	Complete detachment	Complete detachment after 3 cycles
h	-	No detachment	-
i	-	" "	-
j	After 8 cycles	No further detachment	-

LOW-BAKE EPOXY

	Onset of detachment	Condition after 15 cycles	Other comments
a	After 1 cycle	Detachment not complete	Further detachment up to 6 cycles
b	-	No detachment	-
c	-	" "	-
d	-	" "	-
e	After 2 cycles	Detachment not complete	Further detachment up to 7 cycles
f	" "	" " "	Further detachment up to 10 cycles
g	After 1 cycle	Complete detachment	Complete detachment after 10 cycles
h	-	No detachment	-
i	-	" "	-
j	-	" "	-

TABLE 7 (CONTINUED)

MIXED POLYMER

	Onset of detachment	Condition after 15 cycles	Other comments
a	After 1 cycle	Detachment not complete	Further detachment up to 13 cycles
b	After 7 cycles	Detachment not complete	" " "
c	After 5 cycles	No further detachment	-
d	After 1 cycle	" " "	-
e	" "	Detachment not complete	Further detachment up to 11 cycles
f	" "	" " "	Further detachment up to 15 cycles
g	" "	No further detachment	-
h	-	No detachment	-
i	After 1 cycle	No further detachment	-
j	" "	" " "	-

MATT EPOXY

	Onset of detachment	Condition after 15 cycles	Other comments
a	After 1 cycle	Detachment not complete	Further detachment up to 6 cycles
b	After 12 cycles	No further detachment	-
c	-	No detachment	-
d	-	" "	-
e	After 1 cycle	Detachment not complete	Further detachment up to 15 cycles
f	" "	Detachment not complete	" " "
g	" "	" " "	Further detachment up to 3 cycles
h	-	No detachment	-
i	After 1 cycle	No further detachment	-
j	-	No detachment	-

TABLE 7 (CONTINUED)

MATT TEXTURED EPOXY

	Onset of detachment	Condition after 15 cycles	Other comments
a	After 6 cycles	Detachment not complete	-
b	-	No detachment	-
c	-	" "	-
d	-	" "	-
e	After 1 cycle	Detachment not complete	Further detachment up to 15 cycles
f	" "	" " "	" "
g	" "	" " "	" "
h	-	No detachment	-
i	-	" "	-
j	-	" "	-

5.6 Discussion of adhesion results

Examination of Tables 6 and 7 indicate that adhesion of the coatings is generally very good. Firstly, looking at the aluminium substrates, it is obvious that degreasing alone does not lead to good adhesion of the powder coating, whereas the situation is greatly improved by either grit blasting or chromating in a strong solution.

Degreasing of steel substrates results in better adhesion than just degreasing aluminium. Adhesion is enhanced by grit blasting and this is more apparent after inspection of the thermal cycling test results (Table 2). There is no improvement after iron phosphating, whereas zinc phosphating results in excellent adhesion, with 100% adhesion for all coatings. Looking at the individual coatings, polyester and matt-textured epoxy powder coatings gave the best overall adhesion performance. The cross-hatch adhesion test results on the standard epoxy powder coating are excellent except for the degreased aluminium substrate which failed completely at 0% adhesion. The results of thermal cycling tests are not so good for the standard epoxy powder coating.

On drawing conclusions from these adhesion results it must be remembered that the tests were made after a corrosion test. Obviously the results will depend upon the corrosion protection properties of the system, and therefore the resistance of the coating to corrosion undercutting and the attendant diminution of adhesion, as well as the inherent adhesion of the coating to the substrate.

SCANNING ELECTRON MICROSCOPE STUDIES

CHAPTER 6

6.1 Description of scanning electron microscope (SEM)

Scanning electron microscopy is a very well known technique used for the study of surfaces of bulk materials. Its application is very broad and includes the study of fracture surfaces and biological materials as well as being used as a quality control technique for the manufacture of integrated circuits. For the study of surface coatings, the SEM has proved to be a very relevant technique.

Basically scanning electron microscopy employs a beam of electrons which scan the surface of the specimen in a two dimensional raster. When the electrons hit the surface of the specimen they are emitted in numerous ways. Most of the electrons are absorbed by the material and constitute the specimen current. High energy back scattered electrons or low energy secondary electrons emitted from the surface layers are detected and produce an image close to that seen by the human eye. X-ray analysis is possible on the SEM as electrons from the electron beam interact with those in the specimen, displacing them from their shells and causing the emission of x-rays which have a wavelength characteristic of the elements in the specimen..

The SEM displays certain characteristics which make it a very desirable instrument of research. Enormous depth of field enables the study of three dimensional objects at very high magnification to be carried out.

The SEM has been used to study various facets of powder coatings.

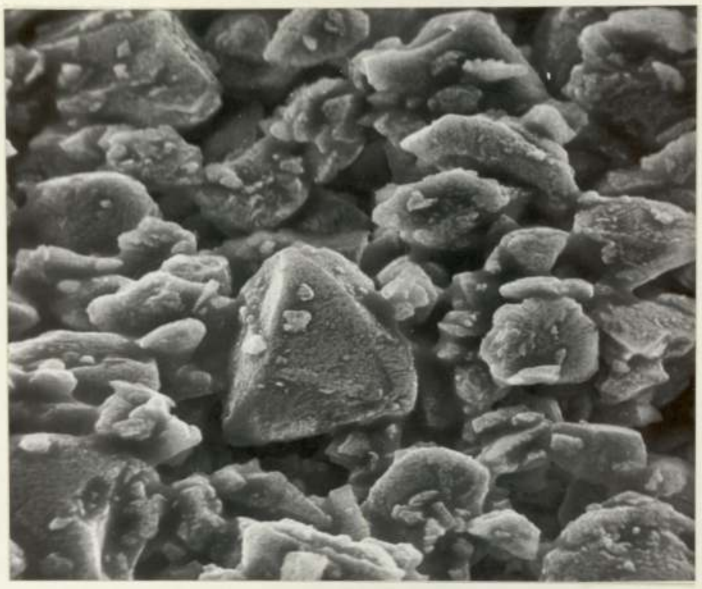
6.2 Powder particles

Back-scattered electron images of polyester, low-bake epoxy, standard epoxy and matt epoxy powder particles at a magnification of x1000 (x1k) can be seen in Figures 41 and 42. The specimens were produced by sprinkling the sieved powders with a brush onto an aluminium stub, the surface of which was covered with double sided sellotape. The samples were then coated with a thin layer of carbon, using a vacuum deposition technique used for the production of replicas for transmission electron microscopy. This rendere the surface of the particles electronically conductive.

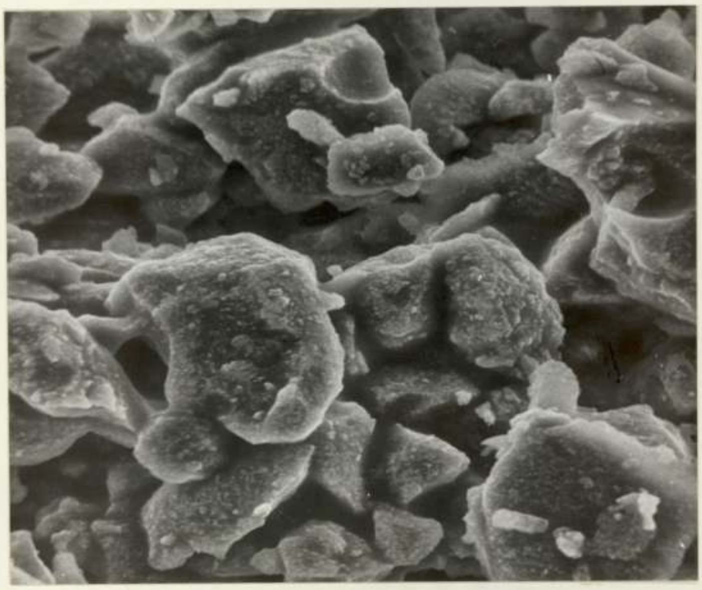
Examination of Figures 41 and 42 reveals that all of the powders have angular and rock shaped particles which can be related to the manufacturing technique, which involved crushing the melt mixed constituents in a mill followed by classification to give the desired particle size range. Examination of Figures 41 and 42 reveals the particle size distribution of all the powders to be similar.

Coulter counter analysis confirmed that the particle size distribution of the powders studied were similar. Basically the Coulter counter measures the electrical resistance of a fluid passing through a fine orifice. When a particle dispersed in the fluid passes through the orifice the electrical resistance changes to an extent dependent upon the volume of the particle, which can be related to the particle diameter if the particle approximates to a spherical shape. The Coulter counter records the number of particles passing and measures their volume. Obviously, the technique only gives accurate results if the particles

Figure 41 SEM photographs of polyester and standard epoxy powders



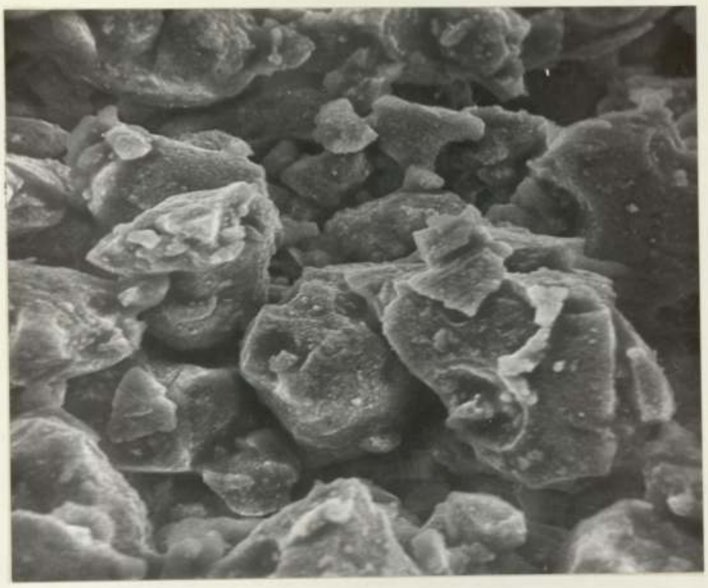
polyester



standard epoxy

magnification ×1k

Figure 42 SEM photographs of matt and low-bake epoxy powders



matt

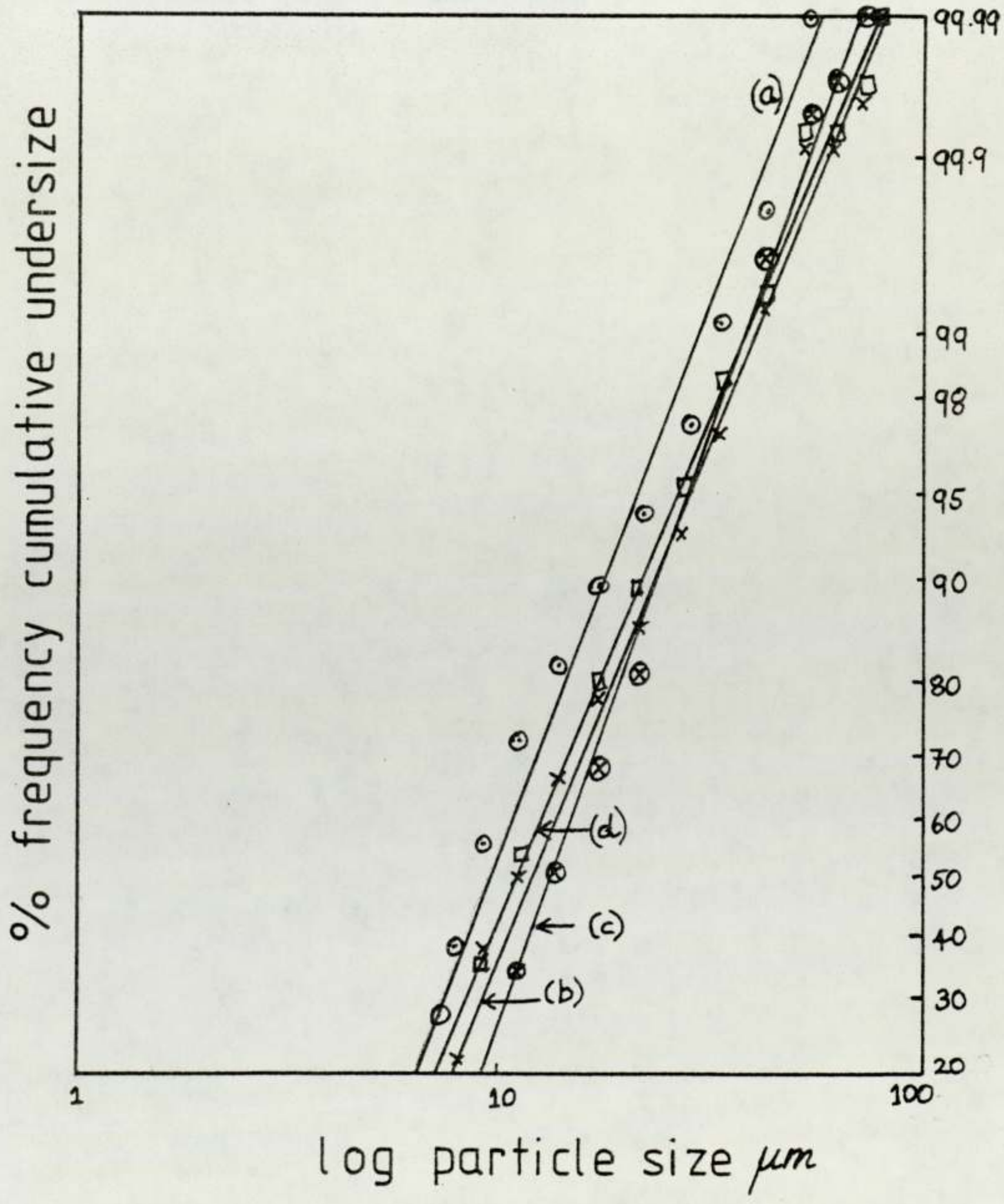
low-bake

magnification × 1k

are thoroughly dispersed in the saline fluid and are not in an agglomerated form. This was achieved by placing an ultrasonic probe in the fluid containing the powder and a drop of teepol until the powder was fully dispersed. This was checked by microscopic examination of a smear on a glass slide. Because it was difficult to compare the distributions by examining histograms, the results were plotted on logarithm-probability paper to give a straight line plot for each distribution. These are given in Figure 43. The median particle size can be read from the graph as the particle size where 50% of the particles are oversize. The slope of the graph represents the particle size distribution, a steep slope for a narrow size distribution and a less steep slope for a wider size distribution.

FIGURE 43

Particle size distributions for a) polyester, b) low-bake epoxy, c) standard epoxy and d) matt epoxy powders



6.3 Metal substrates

Small samples, approximately 5 x 5 mm, were cut from the metal surfaces to be studied, and attached to aluminium stubs with the aid of double sided sellotape. The surfaces were coated with carbon, to render them conductive, in the same way as the powders were coated. The images produced were from back scattered electrons.

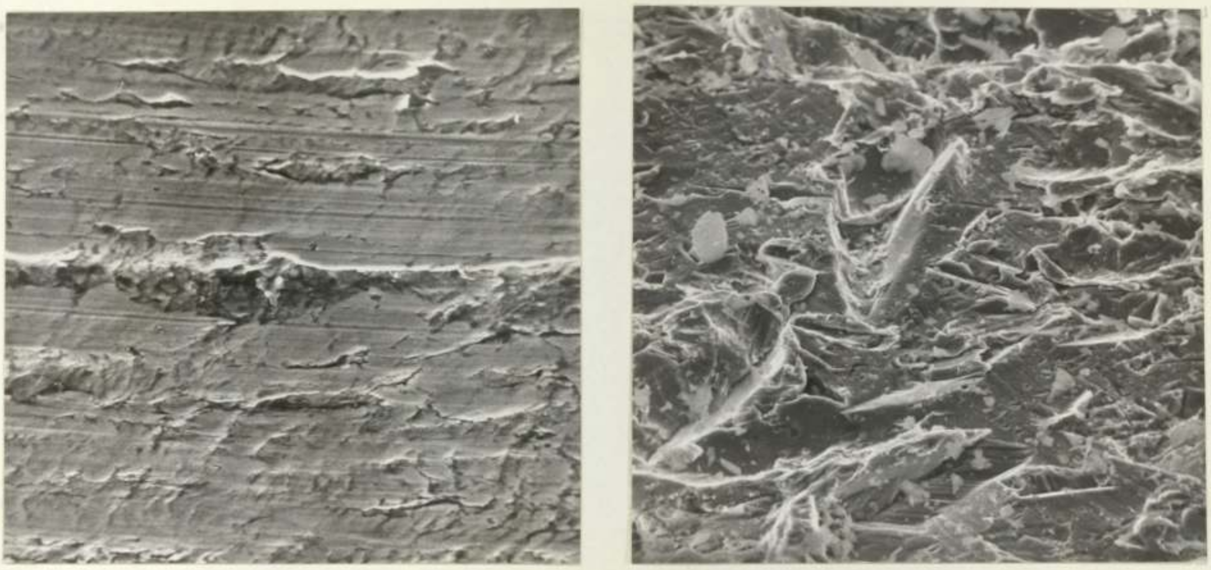
Figure 44 shows the surface of mild steel and aluminium in the as received and grit blast condition, at magnifications of x1.25 and x1.3k. From Figure 44 it can be seen that grit blasting leads to a roughening of the surface with the production of angular pits. Also the surface of as received aluminium is smoother than the surface of the as received mild steel.

Figure 45 shows Zn phosphate crystals on the surface of the sample immersed in the phosphating solution for 5 minutes, at magnifications of x600 and x650. X-ray analysis was carried out on this sample, and the traces for the crystals and the rest of the surface are shown in Figures 46 and 47 respectively. The trace for the crystals shows a large phosphorous and zinc peak which are only very small peaks for the remainder of the substrate. Phosphate crystals were not seen on any of the other phosphated coatings and the x-ray trace for the iron phosphate coating given a long immersion time is given in Figure 48, which only shows a small phosphorus peak.

X-ray traces for the chromated coatings are given in Figures 49 and 50. The chromium peak is larger for the chromate coating produced from a weak solution than that produced from the stronger solution. Table 2 in Chapter 2 shows that the weak solution produced the greater coating weight.

Figure 44 SEM photographs of mild steel and aluminium in the as received and grit blast conditions

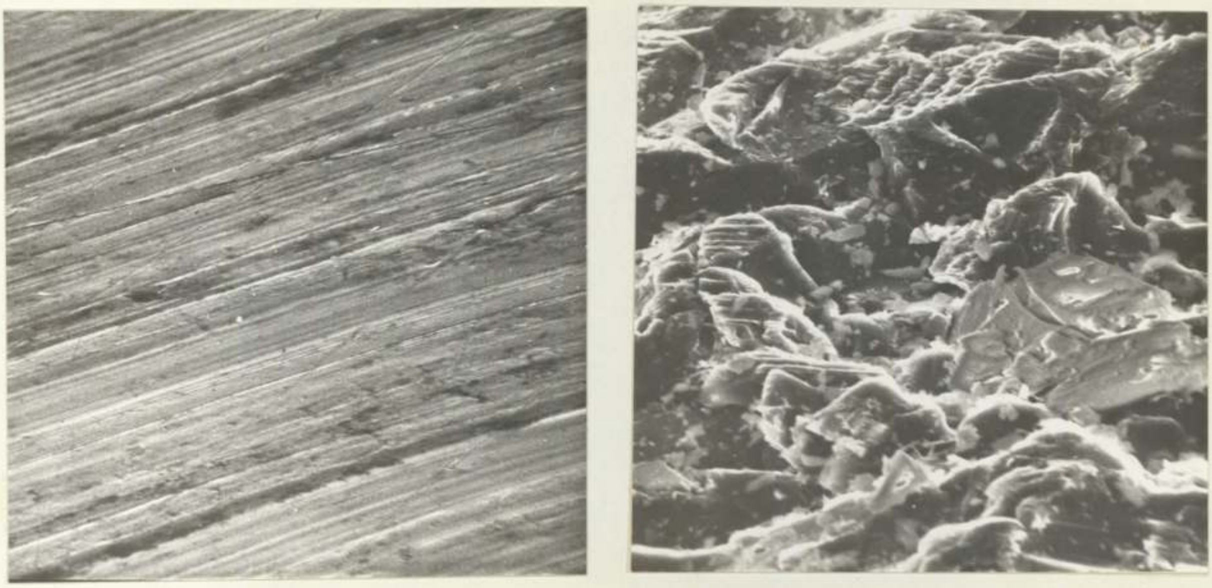
MILD STEEL



as received

grit blast

ALUMINIUM

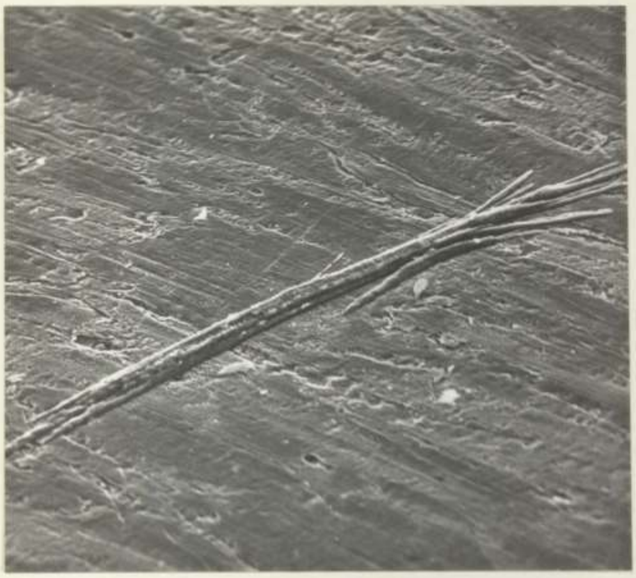


as received

grit blast

magnification ×1·25 k

Figure 45 SEM photographs showing zinc phosphate crystals



magnification × 650

magnification × 600

Figure 46 X-ray trace for zinc phosphate crystals

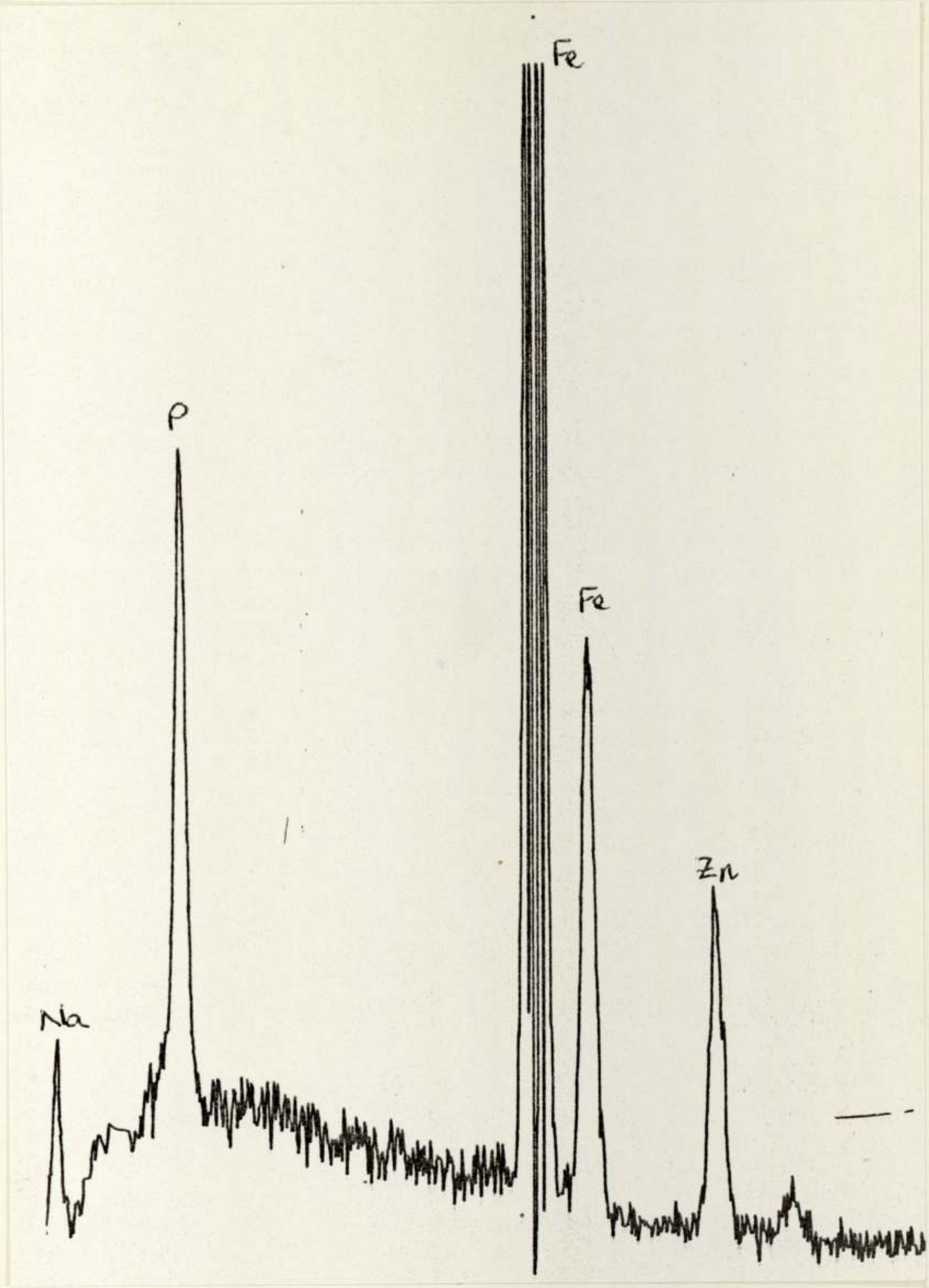


Figure 47 X-ray trace for the remainder of the zinc phosphated steel surface

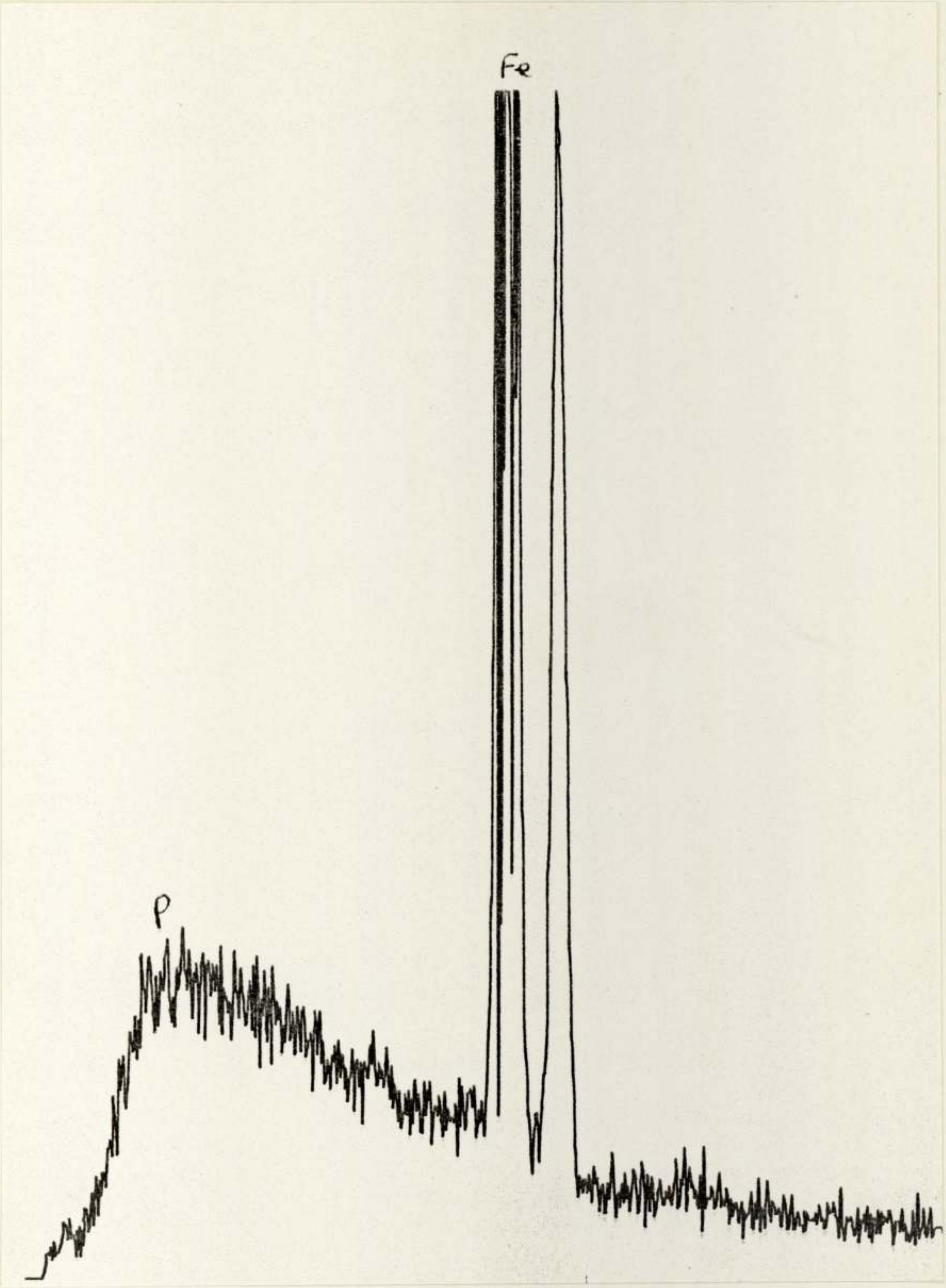


Figure 48 X-ray trace for iron phosphated steel

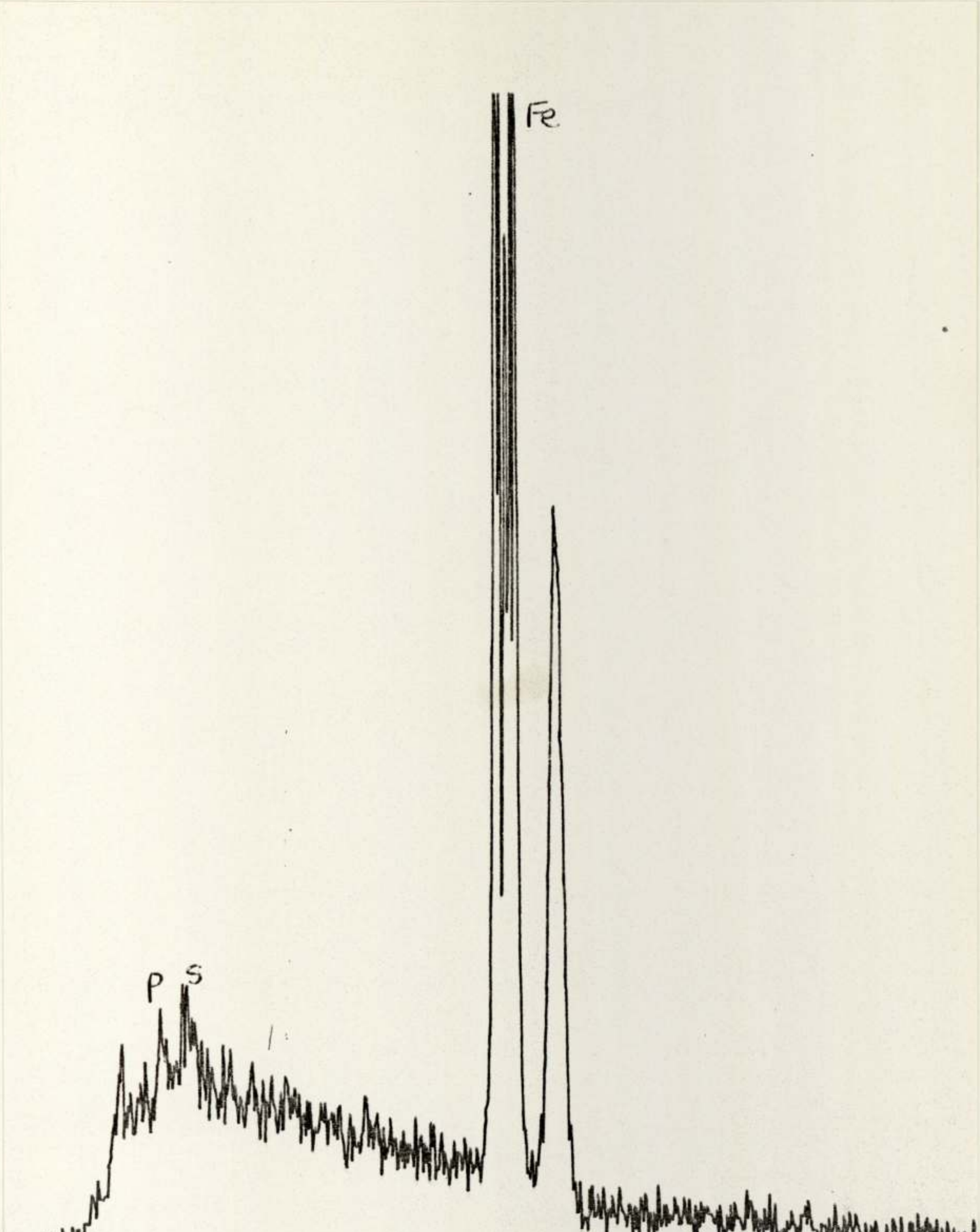


Figure 49 X-ray trace for aluminium treated in weak chromating solution

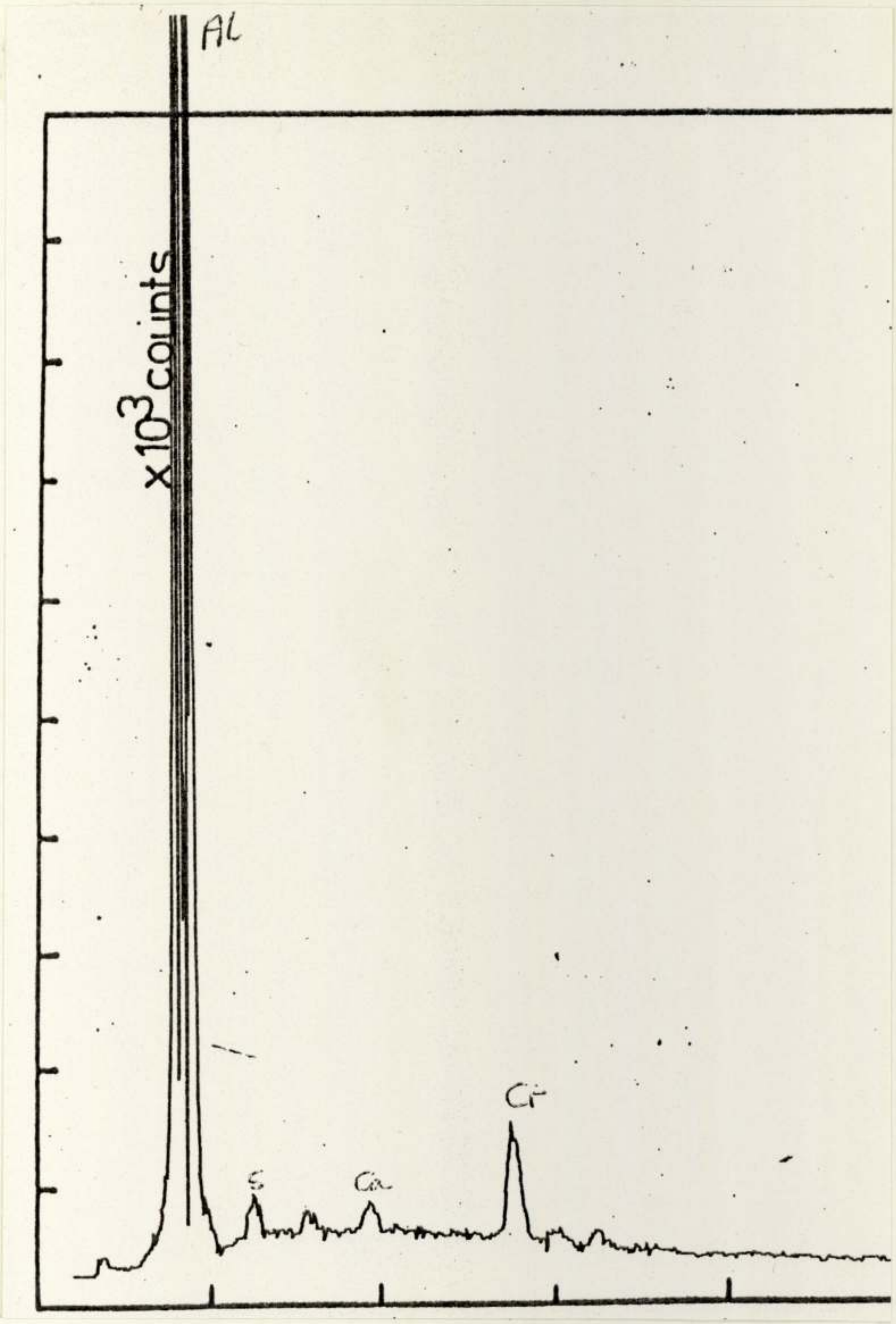
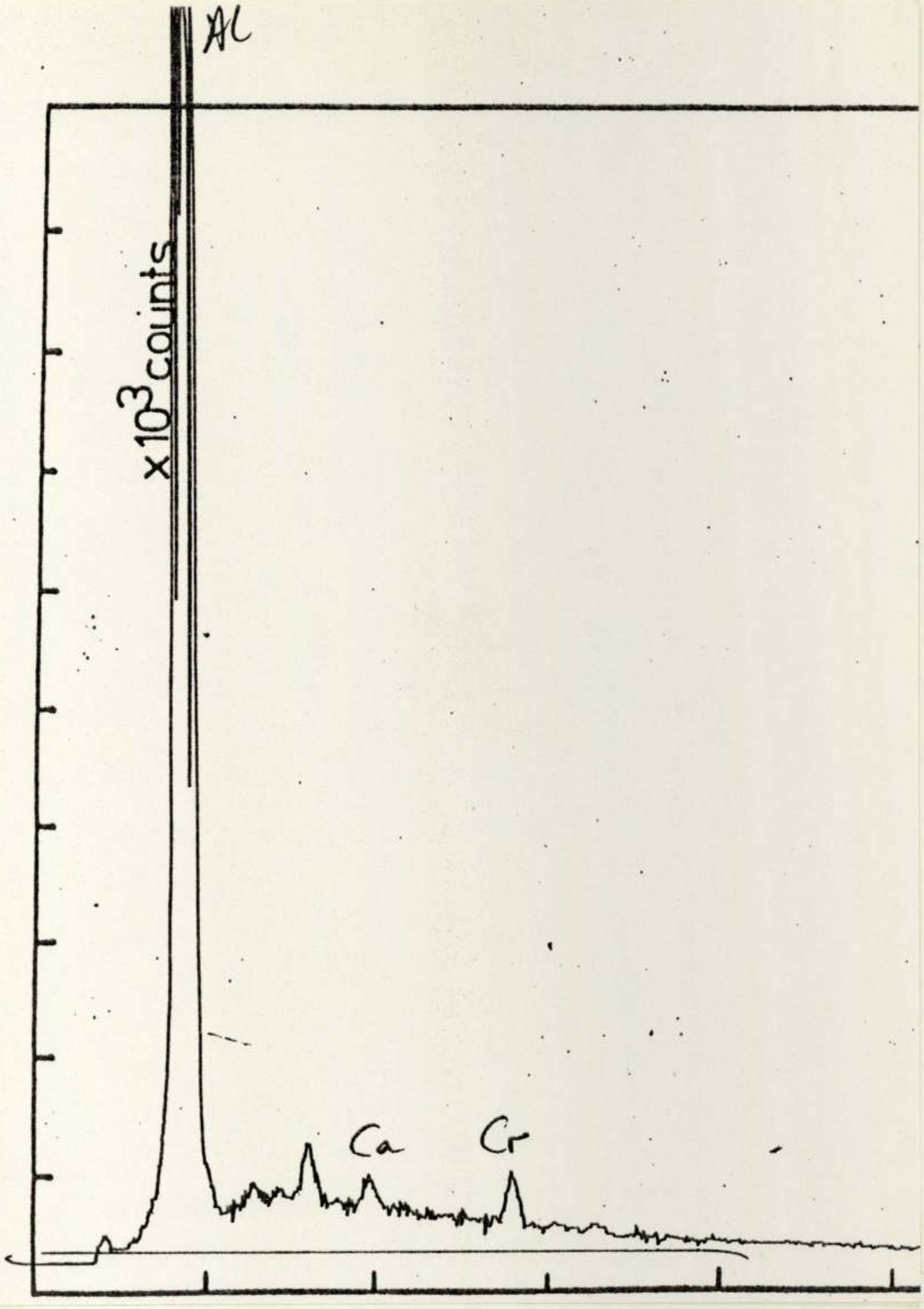


Figure 50 X-ray trace for aluminium treated in strong chromating solution



6.4 Powder coating surfaces

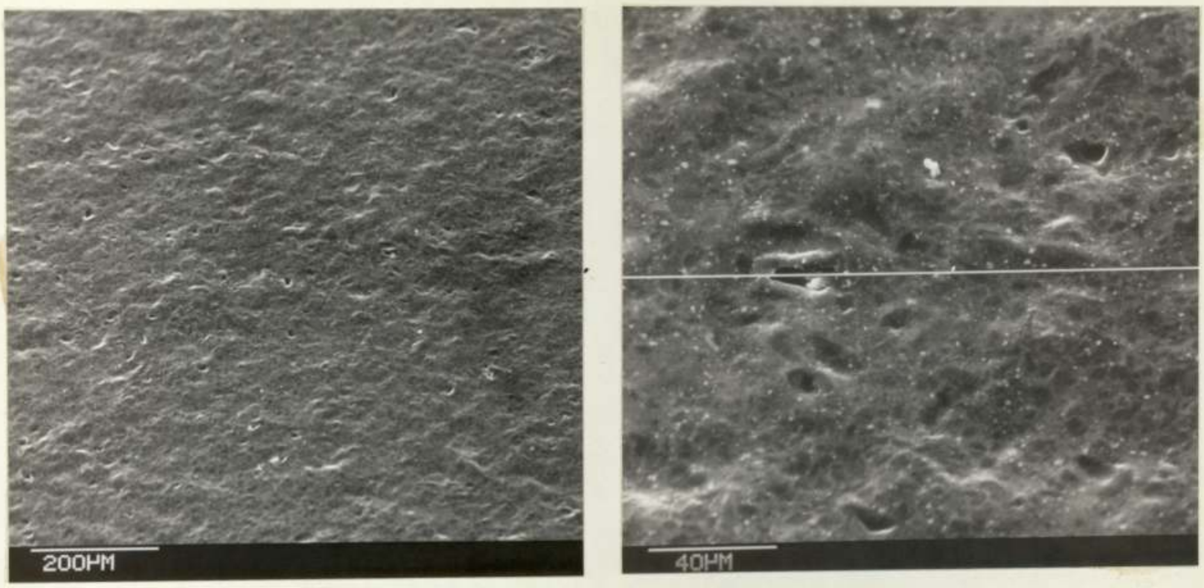
Coatings were put onto degreased steel in the normal way and after curing samples were taken for mounting on the aluminium stubs. The specimens were produced in the same way as for the metal substrates and were coated with carbon as before. Images were produced from back-scattered electrons.

Photographs of the matt and matt textured epoxy coatings are shown in Figure 51, at magnifications of x100 and x500. Although the surfaces of both coatings are rough, the roughness is on a more macro scale for the matt-textured epoxy coating. The photographs of both coatings at higher magnification show pores of up to 10 μm in diameter. The matt-textured epoxy coating has depressions in the surface which greatly reduce the thickness of the coating at these points.

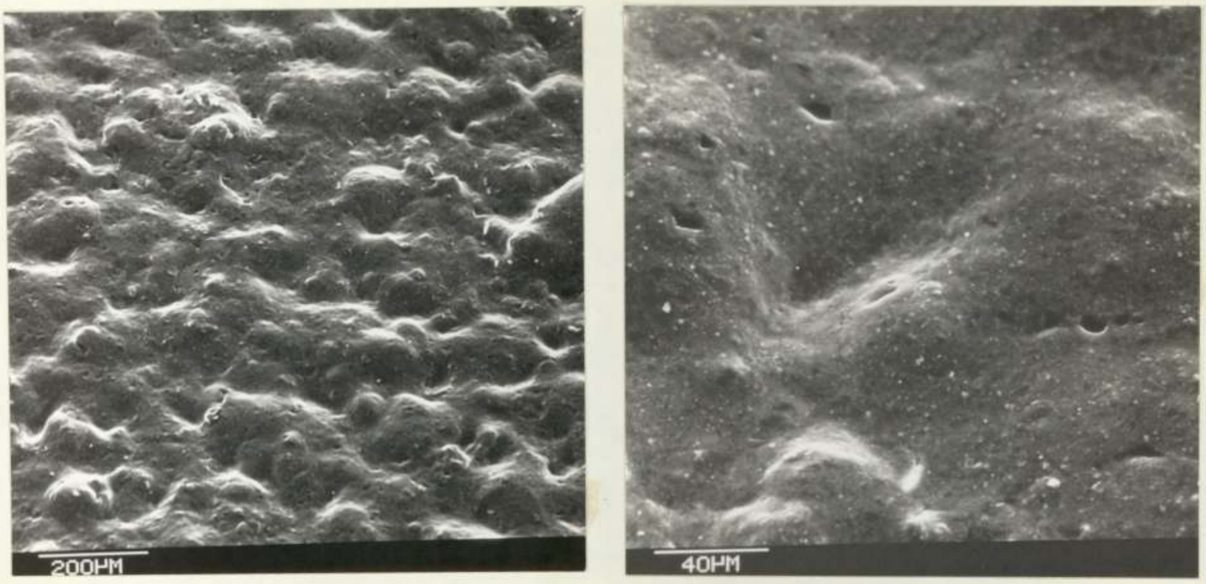
Low-bake epoxy, standard epoxy, polyester and mixed polymer coatings were also examined on the SEM. The surfaces were very smooth and all of the coatings had some pores of up to 10 μm in diameter.

Figure 51 SEM photographs of the surface of matt and matt-textured epoxy powder coatings

MATT



MATT-TEXTURED



6.5 Interfacial porosity

Attempts were made to examine the interface between the coating and the metal substrate, all of which revealed few positive results.

The first attempt involved producing a fracture surface of shot blast steel coated with a low-bake epoxy powder coating. A brittle fracture was induced by immersing the sample in liquid nitrogen immediately followed by fracturing with the aid of a vice and hammer. The specimen was produced in the usual way and back scattered images were produced. No interfacial porosity could be seen using this technique, (Figure 52).

A second attempt consisted of examining a section of a polyester powder coating which was produced by peeling away part of the coating from the substrate which was degreased, as received steel, (Figure 52). Although detachment of the coating from the substrate can be seen at the interface, it may be due to the stresses imposed on the coating during peeling rather than to interfacial porosity. Porosity can be seen in the section of the coating, especially towards the surface of the coating.

Figure 52 SEM photographs of cross-sections of powder coatings

peeled section

fracture surface

magnification × 1 k

DISCUSSION

CHAPTER 7

7.1 Corrosion resistance

7.1.1 Theory

The mechanisms of the protective action of wet paint coatings has been well documented (114, 115, 116, 117) and it may be possible to apply these theories to powder coatings. In 1952 Mayne (114) discussed the protective action of paints on steel substrates. The reactions for the corrosion of a steel surface are given:

Anodic : $4Fe \rightarrow 4Fe^{2+} + 8e$

Cathodic : $4O_2 + 4H_2O + 8e \rightarrow 8OH^-$

The reactions are spacially separated and a current flow between the cathodic and anodic areas occurs in the metal. To inhibit corrosion the flow of current needs to be stopped by either suppressing the cathodic or anodic reactions or by inserting a large resistance in the circuit which impedes the movement of ions away from the corroding surface.

Cathodic reaction inhibition involves preventing the meeting of electrons, water and oxygen. For a paint film to do this it must be impervious to electrons, otherwise the reactions will be merely transferred from the metal surface to the surface of the film. The film must also be impermeable to either water or oxygen and therefore the paint must act as a barrier to the transport of water or oxygen and electrons.

Experiments have shown that paint films are so permeable to oxygen and water that they cannot function in this way.

The anodic reaction can be inhibited in one or two ways. Firstly cathodic protection involves making the potential of the iron more negative, which happens if the paint is pigmented with a less noble metal such as zinc and if the pigment particles are in contact with each other. Zinc dust dispersed in the paint fulfils these conditions. Secondly, anodic passivation occurs when steel becomes covered with a protective film of an iron compound which is impervious to ions. This type of film forms when certain inhibitive materials are present in the paint film, or in the case of red lead paints may be soaps formed by reaction between a basic pigment and linseed oil.

Some organic coatings give excellent protection from corrosion even though they contain no pigments and no soluble inhibitive salts. Examples of such coatings are clear varnishes which have a high electrolytic resistance impeding the movement of ions. Later published work by Mayne (115) and Kendig and Leidheiser (116) have given experimental work which conclusively shows that the electrical properties of an organic coating are very important in determining the corrosion protection properties of the coating.

The corrosion protection properties of an organic coating will depend upon the extent to which the coating itself degrades during use. Mayne (114) stated that painted steel remains good for a long period if it is kept sheltered from heavy rain and if the atmosphere is not heavily polluted. During rainy periods coatings will take up water, the electrical resistance of the coating will fall and a corrosion current will flow. The electrical resistance of a paint film may also be reduced by oxidation which is likely to occur in strong sunlight.

7.1.2 Comparison of paints with powder coatings

There is no evidence in this work on which to make comparisons of corrosion protection properties between powder coatings and wet paint systems. To make fair comparisons one would need to use a paint with an identical resin system and pigments to the powder coating and this was not available. There is no evidence in the literature of such a comparison being made, although many comparisons have been made on ecological and economic grounds and these have been cited in Chapter 1.

Mayne's theory suggests that paint coatings protect the underlying steel by a combination of anodic inhibition and the electrical resistance of the coating preventing the movement of ions. From potential time measurement evidence it can be seen that polyester and mixed polymer powder coatings applied from powders in the fresh condition protect the underlying steel in the same manner as paints protect the substrate. Steel protected by these coatings exhibits a rise and fall in the potential as a protective passive film is formed and subsequently broken down (Chapter 2 Figure 6). These results would indicate that with these coatings anodic passivation is occurring as well as protection due to the electrical resistance of the coating. Polyester and mixed polymer powders in the stale condition do not protect by anodic passivation but by virtue of the electrical resistance of the coating and the protection afforded is then similar to that provided by epoxy powders. This conclusion was drawn from the fact that the potential of these powder coatings shows a steady decrease in potential with time and the corrosion protection of epoxy powder coatings is not radically altered when the powders are stale. As the steel pretreatments were the same in each case (degreased with acetone), it is clear that there must be something in polyester and mixed polymer coatings applied from fresh powders that causes anodic inhibition. It is unlikely that the pigment, TiO_2, would provide such inhibition and if it did why should it not provide inhibition when the powder is in the stale condition? It is more likely that the coating contains a soluble substance which leaches out and acts as an inhibitor. Differential thermal analysis shows that in the stale condition the powders contain some moisture and exhibit smaller exothermic curing peaks indicating that the cross linking reactions have been occurring at room temperature (Chapter 4). In the case of polyester and mixed polymer powder coatings the action of soluble inhibitive materials is impaired when the powders are in the stale condition. These materials may become 'locked' in the structure of the powder during ambient temperature curing and are not liberated when the powder is cured on the substrate.

7.1.3 The effect of pretreatment

Good corrosion protection is provided by powder coatings that adhere well to the substrate. The best corrosion protection is provided when the substrate is either grit blast or zinc phosphated (Chapter 2), and these pretreatments lead to excellent adhesion of the coating to the substrate (Chapter 5). Grit blasting produces a greater surface area over which adhesive forces can act and also provides a mechanical key for the coating. Zinc phosphating also produces a rough surface as crystals of zinc phosphate are present on the surface, and therefore this pretreatment may be effective in a similar manner to grit blasting. However, zinc phosphating also produces a layer of zinc phosphate crystals on the surface which provide a corrosion inhibiting layer. It's behaviour in this way can be seen by examining the potential time measurement results (Chapter 2, Figure 2) which show that zinc phosphating alone is effective in supressing the corrosion of the underlying steel. Therefore, it is likely that zinc phosphate is effective in two ways. Firstly, it provides a good mechanical key for the powder coating and secondly, it produces an inhibitive layer between the steel and the powder coating.

The coating weights of zinc and iron phosphate produced for this study (Chapter 2, Table 2) were very low compared to those produced by other workers. Rudolf and Hansen (68) examined zinc phosphated cold rolled steel using scanning electron microscopy and the coatings were produced by immersion and also by spraying the solution. A continuous zinc phosphate crystal layer was formed after 3 minutes immersion and after 10 minutes the coating weight was 4.5 g/m^2 compared to 0.5 g/m^2 after 5 minutes immersion in this study. They also show S.E.M. photographs of zinc phosphate crystals which are very similar in size and shape to those produced in this study (Chapter 6, Figure 45), but they cover the entire surface. S.E.M. photographs of zinc phosphate coatings on steel are also given by Kuehner (75). Again the crystals are of a similar size and shape and cover the entire surface, whereas, those found in this study did not completely cover the surface. Ashdown (50) in his study on the effect of preparation of metal surfaces on the performance of powder coatings quotes zinc phosphate coating weights of 1.3 and 2.5 g/m^2 by spraying the solution and 4 g/m^2 by immersion in the solution. It is clear that the zinc phosphate coatings produced in this study were thinner than those normally encountered and corrosion protection properties of powder coatings may be considerably enhanced on these thicker zinc phosphate coatings. However, Jenkins (59) found that the adhesion of powder coatings was impaired when applied onto thick phosphate coatings. It was found in this study that adhesion was enhanced by the zinc phosphating pretreatment and corrosion protection was better than just degreasing in acetone. The use of thin phosphate coatings may be a useful compromise by providing good but not excellent corrosion protection and at the same time giving improved adhesion of the powder coating to the substrate.

7.2 The powder particle

The manufacturing technique greatly influences the powder particle size and shape. For instance, spray drying techniques produce spherical shaped particles of uniform size with enclosed porosity (35), whereas melt mixed powders have angular, rock-shaped particles that also contain some porosity (Chapter 6, Figures 41 and 42). Zorll (118), also published S.E.M. photographs of melt mixed powder particles of similar shape but porosity could not be resolved, whereas, Nix and Dodge (90) observed voids 0.5 - 5 microns in diameter in transparent red acrylic powder particles. Particle size and shape is important in two ways, firstly, it influences the way dry powders flow through a funnel, i.e. spherical powders with a uniform particle size flow more freely and free flow is important for electrostatic deposition techniques where the powders have to be transported along a tube to the spraying gun. Secondly, it influences the manner in which the particles pack together on the metal surface. Crowley (35) has observed that the unfused powder coating is 3-7 times the thickness of the final fused film and the powder particles are very loosely packed containing many voids. Even when uniform spheres are packed in cubical array there are 48% voids and this is reduced to 26% when they are packed in a tetrahedral pattern. When optimum packing is obtained using spheres of different sizes, there are still 15% voids present.

Freshwater (92) stated that the nature of particle packing is likely to influence the coating in a number of ways. It may affect the possible thickness of the coating, the incidence of porosity and possibly the adhesion and cohesion of the film.

S-E.M. photographs of a cross section (Chapter 6, Figure 52) and of the surface of a fused powder coating (Figure 51) show there to be some pores present up to 10 microns in diameter. Some of these pores are spherical in shape whilst others are triangular and they mostly occur towards the surface of the film. The pore shape may have some bearing on the origin of pores in powder coatings. Zoril (118) has published S.E.M. photographs of fused powder coatings that have been detached from the substrate. They show approximately 50% pores in the lower film region, which are spherical in shape. As no photograph magnification was quoted it is impossible to give the pore size. This compares to porosity of approximately 15% in the upper regions of matt-textured epoxy powder coatings produced for this study and the incidence of porosity was lower in the other powder coatings studied.

Pores in powder coatings can originate from three possible sources. Firstly the pores may originate from pores in the powder particle, secondly, they may be gaseous products of curing that have failed to escape whilst the film was molten and of low viscosity and thirdly, they may be from voids in the unfused film that have not been filled by flow of the molten particles. All of these mechanisms could produce pores of the size observed, the first and second producing spherical shaped pores and the third angular shaped pores. Spherical pores, as observed by Zorll, could therefore be formed only by the first two mechanisms and a high percentage of porosity would only be expected if either the viscosity of the powder was that high that it did not allow the escape of gases, or if the powder coating had been improperly cured. It would be expected that if the viscosity was high the coating would also contain angular pores produced by the third mechanism. As the pores were solely spherical in shape, it can be concluded that the interfacial porosity observed by Zorll was the result of an improper curing schedule.

7.3 Curing of powder coatings

The hot stage microscopy technique gave an indication (Chapter 3) of the flow characteristics of the different powders studied. Flow has an effect on the levelling of the coating as can be seen by studying the matt and matt textured epoxy powders. These are the only two powders with identical resin and pigment systems and therefore the only two on which direct comparisons can be made. The matt-textured epoxy powder contains an added flow restricting agent, which has the result of reducing flow of the molten particles, (Chapter 3, Figure 24). This poor levelling produces a decorative, textured finish with a thickness that varies across the surface as can be seen from the S.E.M. photographs, (Chapter 6, Figure 51). The flow of the matt epoxy powder is still low but higher than the matt-textured epoxy powder (Chapter 3, Figure 23) and this results in a smoother surface finish (Chapter 6, Figure 51). Some correlation can be made between the flow of these powders and the corrosion protection properties of the coatings produced from them. Although corrosion spread is similar after static outdoor roof exposure (Chapter 2, Figures 17 and 18), general corrosion through the coating is higher for the matt-textured epoxy powder coating. This is because although the thicknesses of the coatings are nominally the same, the roughness of the matt-textured epoxy coating results in there being many areas on the panel where the coating is a lot thinner. Also, powders with poor flow are likely to produce coatings containing more porosity than those with good flow. These two factors reduced thickness and more porosity, will reduce the overall electrical resistance of the coating and therefore reduce its corrosion protection performance. Correlations of this sort, between flow and corrosion protection properties of the coating, are difficult to make for the other powder coatings studied because the resins and pigments are different and these will also have a bearing on the corrosion performance. However, generally it can be seen that the two powders exhibiting the best flow properties, polyester and mixed polymer, (Chapter 3, Figure 24) also provide the best corrosion protection (Chapter 2, Figures 4, 15 and 16).

Flow of the standard epoxy, mixed polymer and polyester powders is greatly reduced when the powders are in a stale condition, whereas the low-bake, matt and matt-textured epoxy powders are not affected in this way by poor storage conditions, (Chapter 3, Figures 23-26). This reduced flow results in poorer corrosion protection by polyester and mixed polymer powder coatings applied from powders in the stale condition. Flow can be increased by vacuum treating stale polyester powders to remove moisture (Chapter 3, Figure 27) but flow does not return to its original high level and it deteriorates again as the powder picks up moisture from the atmosphere. Moisture is clearly one of the factors rendering a powder 'stale' but obviously the most important is the irreversible ambient temperature cross-linking reaction. Ambient temperature cross linking probably acts by increasing the viscosity of the molten particles and therefore restricting their flow during curing. Nix and Dodge (90) have examined the flow behaviour of individual particles and clusters of particles, and have observed that agglomerates flow more slowly than individual particles. They state that the poor flow of clusters results in orange peel and that they are probably caused by low molecular weight species at the surface causing the particles to stick to one another. Adsorbed moisture at the surface could behave in this manner and cause the particles to stick together to form agglomerates exhibiting poor flow characteristics. Vacuum treatment would result in the breakdown of these clusters and the return of better flow characteristics.

Partial curing of powder coatings results in the films failing in a flaky manner on adhesion testing (Chapter 4, Table 5) and the failure is continuous when the coating is fully cured. Partially cured coatings probably contain a lot of porosity which undermines the cohesion of the film. Cross hatch adhesion testing, however, shows that partially cured films adhere better than fully cured films. This result is surprising and it could be related to internal stresses present in the fully cured film that are absent in the partially cured coating. The effects of internal stresses on the adhesion of powder coatings has been discussed in Chapter 5. During curing, shrinkage occurs and tensile stresses build up in the coating and at the interface which reduce the adhesion of coating to the substrate.

Corrosion spread measurements on panels subjected to salt spray testing indicate that corrosion performance is hardly deteriorated by improper curing. This situation would probably be very different during long term service as the mechanical properties of the coating would be very important in determining it's corrosion protection properties, as flaking of the coating would result in exposed metal corroding.

CONCLUSIONS

Corrosion resistant properties of powder coatings are to a large extent influenced by the pretreatment given to the underlying metal. Grit blasting is effective by providing mechanical anchorage for the powder coating. Zinc phosphating of steel is more effective than grit blasting by providing a corrosion inhibiting layer of zinc phosphate crystals as well as giving mechanical anchorage to the coating. These pretreatments result in good adhesion of the coating to the substrate and there is a strong correlation between good adhesion and good corrosion protection.

The corrosion protection afforded by powder coatings depends upon the powder type. Polyester and mixed polymer powder coatings provide more corrosion protection than any of the epoxy types studied, with standard, low-bake and matt epoxy giving a similar degree of protection which is more than that given by matt-textured epoxy powder coatings.

Poor storage conditions, i.e. those that allow the powder access to a moist, warm environment, adversely affect the powder by impairing the dry flow characteristics of powders in such a way that tubes used during electrostatic application may become blocked with powder. Also, the corrosion protection properties of polyester and mixed polymer powder coatings are adversely affected when they are applied from powders stored under poor conditions compared to coatings produced from fresh powders, but epoxy powder coatings are not affected in this way. Differential thermal analysis studies have revealed significant differences between powders stored in sealed containers inside a freezer and powders left open to the atmosphere at room temperature for at least two weeks. Powders stored at room temperature contain moisture and exhibit a smaller exothermic curing peak than those stored at sub-ambient temperature, indicating that storage at room temperature allows some cross-linking to take place. Ideal storage involves keeping the powder in a well sealed container such as a sealed polythene bag inside a sealed can and keeping the storage temperature well below the ambient temperature, ideally at refrigerator temperatures. Powders stored under these conditions behave in a similar manner to fresh ones. The attainment of ideal storage conditions is obviously more important for polyester and mixed polymer powders although it would add considerably to the cost of the final coating.

There is not a good, universally accepted, quantitative adhesion test for powder coatings. Problems arise when trying to develop one because after effective pretreatment the adhesive bond between the coating and substrate is stronger than the coating and this condition precludes any mechanical test being applied. A good adhesion test was not developed during this study.

For a powder coating to have optimum mechanical properties it must be properly cured. Improper curing results in the film flaking away from the substrate during adhesion testing.

Properly cured coatings fail by peeling off in a continuous strip indicating that the cohesion of the film is fully developed only after 100% cure.

A hot stage microscope technique has been developed to measure the melt and flow characteristics of powder coatings, by measuring the area covered by powder or molten globules on the substrate at various temperatures. The increase in area covered, after melting, indicates the extent to which the powder flows. It has been found that, generally, powders that exhibit a high degree of flow produce coatings that have a higher gloss and better corrosion protection properties than those that show a smaller amount of flow. The technique also revealed that stale polyester powder flows less than fresh polyester and that the performance in the fresh condition can partially be revived by vacuum treatment to remove adsorbed water but the poor flow characteristics gradually return after exposure to the atmosphere.

Scanning electron microscopy revealed that powder coatings contain porosity which is not interconnecting. The percentage porosity in the coatings produced for this study is not as high as that observed in powder coatings by other workers.

This work has attempted to highlight the factors that effect the corrosion protection properties of powder coatings and has gone some way towards elucidating the subject. However, future work along similar lines, could lead to a greater understanding of the mechanisms by which powder coatings protect and possibly lead to the optimisation of powder coating systems. Suggestions for future work will now be outlined.

SUGGESTIONS FOR FUTURE WORK

1. The work carried out in this study should be extended to encompass other powder coating systems in common usage, such as acrylics and polyurethanes.

2. More extensive work should be carried out to study the effects of pretreatments on powder coatings. This especially applies to zinc phosphate pretreatments where the operating variables are known to effect the quality of zinc phosphate coating produced. These operating parameters should be studied to find out the conditions for optimum performance of the powder coating.

3. A study should be made comparing the properties of a powder coating with a similar wet paint system. Comparisons should be made primarily on corrosion protection properties and secondly on other features that may effect this such as adhesion and the incidence of porosity.

4. More work should be carried out on adhesion tests that could be carried out on powder coatings that have been freshly produced, i.e. tests that would not involve firstly having to undermine the adhesion of the coating. Such a test would probably not involve mechanically stripping the coating from the substrate. The development of this test should be preceded by a more fundamental study of the nature of the bond between powder coatings and their substrates.

5. Further work on the incidence of porosity in powder coatings should be carried out. The emphasis should be on the origins of porosity with scanning electron microscopy studies being made in conjunction with hot stage microscopy to see if there is any correlation between flow and the incidence of porosity.

REFERENCES

1. R.K. Anderson and D.N. Hunder, Plating, 1974, 61, 662.

2. Metals and Materials, 1976, May, 31.

3. Ault and Wiborg, unpublished paper 1976.

4. G.E. Bond and J.N. Ralston, Industrial Finishing, 1973, 25, No.305, 4.

5. J.G. Bullivant, Plating, 1972, 59, 827.

6. M. Cowley, I.E.E. Conference publication No. 133 - Electrical Methods of Machining, Forming and Coating, 18-20th November 1975.

7. B. Feinberg, Manufacturing engineering and management, 1975, June, 32.

8. R.D. Hardy, S.M.E. Technical paper FC.74-189.

9. G. Hesterman, Product Finishing, 1976, January, 16.

10. A. Lemmens, Proceedings of the International Symposium on powder coatings, 13-15th February, 1968.

11. T. Parmley, Europlastics monthly, 1974, February/March, 59.

12. W.R. Pascoe, Plating, 1973, 60, 590.

13. D. Payne, Industrial Finishing and Surface Coatings, 1973, 25, No.299, 42.

14. M.V. Rothschild, Plating, 1973, 60, 1146

15. D.R. Savage, S.M.E. Technical paper FC.74-656.

16. R.C. Harrington, Encyclopedia of polymer science and technology, Supp. Vol. 1, Published by Interscience publishers, New York, 1976, 544.

17. P.G. de Lange, Interfinish 1976, 9th World Congress on Metal Finishing, Amsterdam.

18. D.R. Savage, Metal Finishing, 1974, January, 44.

19. Warren St. John, Mechanical Engineering, 1974, February, 23.

20. A. Taft, Industrial finishing and surface coatings, 1972, 24, No. 294, 26.

21. J. Teresko, Proceedings of powder coating conference, November 17th 1972, Cleveland, Ohio.

22. T. Tobin, Proceedings: 3rd North American Conference on Powder Coating, April 1974, Toronto, Canada.

23. J.D. Toff, I.E.E. Conference publication No. 133 - Electrical methods of machining, forming and coating, 18-20th November 1975.

24. J.R. Weschler, Proceedings of powder coating conference, November 17, 1972, Cleveland, Ohio.

25. E.R. Westmore, The Production Engineer, 1973, September, 303.

26. International Pinchin Johnson publication.

27. J.W. Hagan and O.W. Smith, Materials protection and performance, 1973, 12, No. 9, 31.

28. W.A. Wallman and R.K. Hong, Proceedings of powder coating conference, November 17th, 1972, Cleveland, Ohio.

29. Leon E. Wolinski, Polymers, paint and colour journal, 1973, 929.

30. Pigment and resin technology, 1976, September, 10.

31. Industrial finishing and surface coatings, 1976, April, 22.

32. Industrial finishing, 1975, October, 9.

33. B. Belina, Proceedings: 3rd North American Conference on powder coatings, April 1974, Toronto, Canada.

34. J.K. Christensen, S.M.E. Technical paper FC.72-941.

35. J.D. Crowley et al, Journal of paint technology, 1972, 44, No. 571, 56.

36. E.W. Drew, Product Finishing, 1975, August, 18.

37. K.E. Guiles, Proceedings of powder coating conference, November 17th, 1972, Cleveland, Ohio.

38. N.H. Gulpen and A.J. Van der Werff, Journal of paint technology, 1975, 47, No. 608, 81.

39. R.C. Harrington, Proceedings: 3rd North American Conference on powder coating, April 1974, Toronto, Canada.

40. S. Kut, Product Finishing, 1974, November, 25.

41. S. Kut, Transaction of the Institute of Metal Finishing, 1973, 51, 191.

42. R.E. Pike,
Part I - Metal Finishing, 1974, 72, March, 52.
Part II - " " " " April "

43. A.P. Rolfe, Metals Australia, 1974, June, 143.

44. R.D. Taft et al, S.M.E. Technical paper FC.72-942.

45. D. Thiemann, Proceedings: 3rd North American Conference on powder coating, April 1974, Toronto, Canada.

46. S.T. Harris, Book - The Technology of Powder Coatings, Portcullis Press, London 1976.

47. R. Stanfield, Industrial Finishing, 1976, 28, No. 339, 6.

48. J.R. Weber, Proceedings of the International Symposium on Powder Coatings, 13-15th February 1968.

49. A.S.M. metals handbook, 8th edition, 1964, 2, 531.

50. R.A. Ashdown, Product Finishing, 1974, November, 33.

51. G.E. Brumbaugh, S.M.E. Technical paper FC.74-541.

52. G.E. Brumbaugh, Proceedings of the Powder Coating Conference, November 17th 1972, Cleveland, Ohio.

53. G.E. Brumbaugh, S.M.E. Technical paper FC.74-657.

54. G.E. Brumbaugh, S.M.E. Technical paper FC.74-943.

55. A.V. Corbit, Anti-Corrosion Methods and Materials, 1972, 19, No. 11, 3.

56. V. Cupr and J.B. Pelikan, Henry Brutcher translation No. 6605, Translated from Metalloberflasche, A65, 19, 187.

57. C.B. Doherty, Materials Performance, 1974, November, 12.

58. D. James, Industrial finishing and surface coating, 1975, 27, No. 324, 5.

59. D.G. Jenkins, University of Aston final year B.Sc. thesis, January 1976.

60. R.A. Kelly and J.A. Burt, Metal Finishing, 1973, January, 49.

61. R.A. Kelly and J.A. Burt, Automotive Industries, 1974, November, 41.

62. A.J. Koch and F.R. Jones, Product Finishing, 1975, December, 6.

63. R.M. Lacey and J.I. Mauser, Electroplating and Metal Finishing, 1974, April, 30.

64. G. Lorin, Book - Phosphating of Metals, Finishing Publications Ltd., 1974.

65. P. Lowe, Proceedings of the International Symposium on Powder Coatings, 13-15th February 1968.

66. W. Machu, Industrie Chemique Belge, 1963, No. 3, 227.

67. P. Morris, Industrial Finishing, 1976, 28, No. 339, 4.

68. G. Rudolph and H. Hansen, Transactions of the Institute of Metal Finishing, 1972, 50, pt. 2, 33.

69. H. Stein, Industrial Finishing, 1972, 24, No. 294, 32.

70. E. Wagner, Henry Brutcher translation No. 3507, translation from Mitteilungen Forschungs - Gesellschaft Blech verarbeitung, 1954, No. 7, 79.

71. A Williams, Proceedings of the International Symposium on powder coatings, 13-15th February, 1968.

72. I.H.A. Yearsley and P.D. Darkins, Transactions of the Institute of Metal Finishing, 1973, 51, 173.

73. Materials in design engineering, 1964, May, 101.

74. W.G. Willows, Proceedings of the International Symposium on Powder Coatings, 13-15th February 1968.

75. M.A. Kuehner, Industrial Finishing, 1972, 48, No. 2, 18.

76. D.R. Savage, Proceedings: Powder coating conference, November 17th 1972, Cleveland, Ohio.

77. G.F. Hardy, Journal of Paint Technology, 1974, 46, No. 599, 73.

78. J.A. Cross, I.E.E. Conference publication No. 133 - Electrical methods of machining, forming and coating, 18-20th November 1975.

79. A.W. Bright, Proceedings of the International Symposium on Powder Coatings, 13-15th February 1968.

80. A.W. Bright and R.P. Corbett, I.E.E. Conference publication No. 133 - Electrical methods of machining, forming and coating, 18-20th November, 1975.

81. J.D. Toff, I.E.E. Conference publication No. 133 - Electrical methods of machining, forming and coating, 18-20th November, 1975.

82. J. Szasz, Industrial Finishing, 1970, 22, No. 270, 4.

83. W.J. Richardson, Surfacing Journal, 1974, July, 10.

84. J.A. Cross, Industrial finishing and surface coatings, 1975, April, 4.

85. J.D. Toff, Product finishing, 1976, 29, No. 3, 14.

86. M.J. Drury, Product finishing, 1974, 27, No. 11, 37.

87. M. Cowley, Product finishing, 1975, 28, No. 5, 22.

88. S. Gabriel, Journal of the Oil and Colour Chemists Association, 1976, 59, 52.

89. M.J. Hannon et al, Journal of Coatings Technology, 1976, 48, No. 621, 42.

90. V.G. Nix and J.S. Dodge, Journal of Paint Technology, 1973, 45, No. 586, 59.

91. O.W. Smith and J.V. Koleoske, Journal of Paint Technology, 1973, 45, No. 582, 60.

92. D.C. Freshwater, Proceedings of the International Symposium on Powder Coatings, 13-15th February 1968.

93. C.L. Brett, Journal of Applied Polymer Science, 1976, 20, 1431.

94. A. Ghijsels and C.H.J. Klaren, Proceedings XIIth FATIPEC Kongress 1974, Garmisch-Partenkirchen, 12-18th May 1974.

95. I.D. Burrows, University of Aston final year B.Sc. thesis, January 1975.

96. J.F. Williams, Materials protection and performance, 1974, 10, No. 9, 15.

97. British Plastics and Rubber, 1976, June, 20.

98. Industrial Finishing, 1975, October, 11.

99. J.R. Clifton, Materials Performance, 1976, May, 15.

100. G.E. Barrett, Product Finishing, 1974, April, 17.

101. A.C. Green, Product Finishing, 1975, May, 13.

102. E. Hall, The Engineer, 1974, March, 47.

103. R.B. Zimmerli, Metal Progress, 1974, September, 101.

104. W.H.B. Pritchard, Polymers, Paint and Colour Journal, 1978, March, 173.

105. T.R. Bullet, Recent advances in adhesion, American Chemical Society Symposium, Washington, D.C., September 1971.

106. N.I. Gaynes, Metal Finishing, 1975, 73, Nos. 6, 7 and 8, 39, 41, 40.

107. M. Gignoux, Proceedings of the International Symposium on Powder Coatings, 13-15th February, 1968.

108. W.J. McGill, Journal of the Oil and Colour Chemists Association, 1977, 60, 121.

109. A.F. Lewis and Lloyd J. Forrestal, Book - Adhesion of Coatings, Chapter 3, Vol. 2, Pt. I (Dekker N.Y. 1969)

110. S. Kut, Metal Finishing, 1973, 71, Nos. 6, 7 and 8, 41, 41, 48.

111. D. Davies and J.A. Whittaker, Metallurgical Review No. 112, Metals and Materials, 1967, 12.

112. ASTM Standard D.3359-76, Standard Method for Measuring Adhesion by Tape Test.

113. M.I. Pope and M.D. Judd, Book - Differential Thermal Analysis, Printed by Heyden & Son Ltd., 1977.

114. J.E.O. Mayne, Research (London), 1952, 5, 278.

115. J.E.O. Mayne, British Corrosion Journal, 1970, 5, 106.

116. M.W. Kendig and H. Leidheiser, Journal of the Electrochemical Society, 1976, 123, No. 7, 982.

117. J. Boxall and J.A. Von Fraunhofer, Transactions of the Institute of Metal Finishing, 1976, 54, 112.

118. U. Zorll, Progress in organic coatings, 1976, 4, No. 2, 79.

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