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High-resolution SEM studies of chromate conversion coatings

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Scanning electron microscope studies have shown that chromate paint pretreatment of aluminium resulted in the deposition of a film comprising layers of spherical-shaped particles. On alkali-etched substrates the particle size varied from between 60 nm to less than 10 nm. The larger particles tended to occur either in some of the larger pits on the surface or in the vicinity of intermetallic particles. Uniformly sized 50 to 60 nm particles were deposited on the surface of a polished substrate. Penetration of organic resins into the particulate surfaces may contribute towards the good paint and lacquer adhesion resulting from the pretreatment process.

1. Introduction

Although a wide range of factors influence the adhesion of organic coatings to metal surfaces [1], in a number of instances the microtopography of the substrate has been established as a major factor [1–3]. Substrates with good adhesive properties are often covered with whisker-like fibres which protrude into the coating to increase mechanical keying [4], produce fibre-reinforced interfaces [5], or act as local stress-raisers so that tearing of the organic coating occurs with extensive energy dissipation. In this context, the type of pretreatment employed is unimportant; e.g. it has been demonstrated both for hot water treatment of aluminium prior to polyethylene lamination [2] and for phosphoric acid anodizing [5] the processes only become effective after the onset of fibre growth.

Pretreatment is a major step in the coil-coating of aluminium and is required to ensure that adhesion of the paint or lacquer to the metal is sufficient to give adequate service life and withstand the wide range of forming operations that may be carried out. Although the importance of pretreatment is recognised, relatively little is known concerning the factors controlling adhesion of the paint or lacquer. As a result the causes of occasional failures during service life of a painted or lacquered product are not always understood [6].

One of the commonest forms of pretreatment is chromate conversion [7], where metal is immersed in a solution of chromic and hydrofluoric acid with or without a ferricyanide accelerator, and as a result a film is formed comprising mainly hydrated chromium oxide particles, coated with an adsorbed monolayer of the accelerator [8, 9]. Although the bulk structure of the film has been established, direct observation of the microstructure of the surface has not been made. Chromate/phosphate pretreatments have been modified so that they produce very large particles which can be seen in the scanning electron microscope [10]. However, the microstructure of the particles was not observed and it is this which may be far more important in determining the adhesive properties of the surface.

The major problem in studying microstructures of conversion coatings in the SEM is the contribution to the image of electrons from subsurface features and the relatively low yield of secondary electrons from the surface of a film of low atomic number and fine topographical detail. A number of methods can be used to overcome these problems, including low loss, backscattered electron microscopy [11], sputter-coating the surface with high secondary electron emitters, and the use of featureless substrates [12]. Because all of the previous studies have been carried out using normal secondary electron microscopy, the latter two methods were selected for the study of chromate pretreatments to be described here.

2. Experimental procedure

All samples for analysis were prepared in the laboratory by the immersion of coupons of commercial-purity rolled aluminium in standard commercial Alocrom 1200E solutions (ICI, Slough) at 35° C for periods of 6 sec, 12 sec or 1 min. Prior to pretreatment the metal was cleaned by immersion in Ridolene 34 alkali cleaner (ICI, Slough) at a temperature of 60° C for 30 sec. The samples were also desmutted by immersion in 25 vol % nitric acid at room temperature for a period of 30 sec. Samples were thoroughly rinsed in tap water between each operation and rinsed in deionized water following pretreatment. Electropolished surfaces were pretreated without further cleaning.

Platinum coating of the pretreated samples was carried out in an Ion Tech. sputter coater [13]. Samples were coated for 20 min with the platinum target being irradiated by an 8 keV, 5 mA argon ion beam. To ensure uniformity of coating the sample was rotated continually throughout the deposition process. Under similar conditions, platinum has been found to deposit at a rate of approximately 0.5 nm min^{-1} [13].

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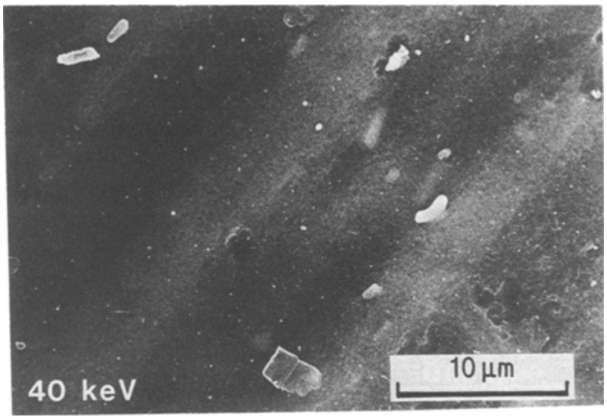


Figure 1 Relatively featureless low-magnification SEM image of 0.13 μm chromate film.

2.1. SEM examination

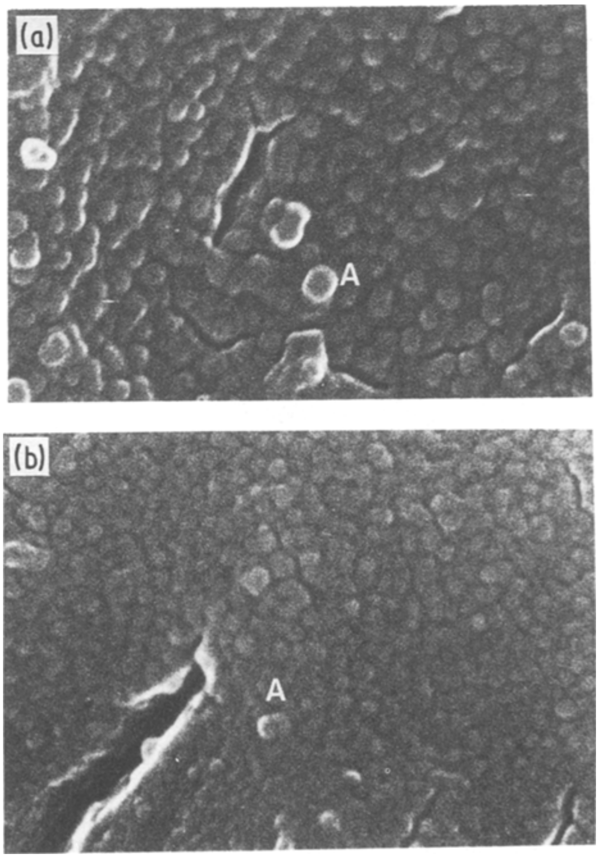
Secondary electron microscopy was carried out on the upper stage of an ISI DS 130 scanning electron microscope. Apart from the increased resolution derived from the reduced spherical and chromatic aberration, use of this stage results in images containing a much higher contribution from secondary electrons emitted directly from the sample [14]. The enhanced contribution of secondary electrons arises as a result of the location of the sample within the magnetic field of the objective lens and the detector above the lens. Consequently secondary electrons emitted from the surface are constrained to spiral around the lines of force of the lens from sample to detector. A range of primary beam energies was used in the SEM investigation, depending on the surface sensitivity and resolution required.

Film thickness determinations were carried out using the energy-dispersive spectrometer (EDS) system in the lower stage of the microscope. Calibration curves for film thickness against chromium and aluminium intensity ratios have already been published [12].

3. Results

Pretreatment for 6 sec at 35° C resulted in a film of 0.13 μm average thickness. When viewed at low magnification (Fig. 1) the platinum-coated surface of the film appears relatively featureless. At higher magnifications, however, the detailed structure can clearly be seen (Fig. 2) as an array of circular particles extending over the full area of the surface investigated. Particle diameters observed vary from approximately 50 to 60 nm down to approximately 10 nm where they were difficult to resolve in the microscope. Variations in particle size may reflect the variations in local conditions that occur during the deposition of the chromate film on the metal surface, so it is clear that a more detailed study of particle size with respect to location may lead to an improved understanding of the film forming process. In this context it is of interest to note the large particles observed in a circular area resembling the large alkaline etch pits that can occur in regions close to intermetallic particles (Fig. 3). Although particle sizes in individual areas are relatively constant, isolated larger particles were also observed, randomly distributed over all the areas studied (Fig. 2). Variation in contrast across individual large particles (Fig. 2a) indicates that they are spherical in shape rather than rod-like, and this is consistent with the spherical nature of particles in chromium hydroxide gels [15].

Particles were observed on the surface regardless of the primary beam energy used in the microscope (Fig. 4). Despite the enhancement of the surface secondary electron emission which resulted in the observation of surface structure, when the beam energy was reduced to 5 keV the pitted interface between the film and substrate (Fig. 4) was visible. Observation of the interface is due to electrons backscattered from the interface forming secondary electrons as they pass from the sample into the vacuum, and it results in micrographs showing an apparently undulating surface (Figs 4b and c) with the undulations following



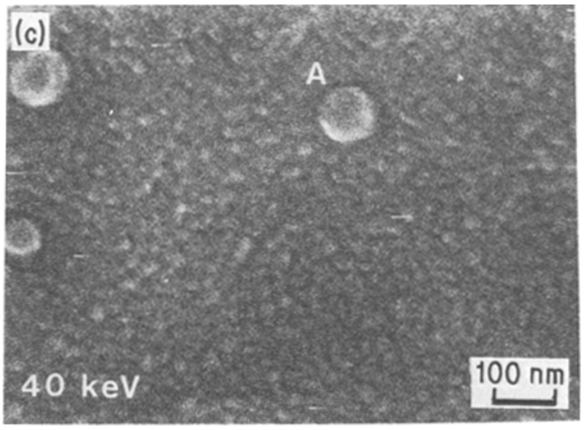


Figure 2 High-resolution SEM images of 0.13 μm film (platinum-coated): (a) largest particles found, (b) intermediate-sized particles, (c) smallest particles found. (A) larger particles randomly distributed across all areas of the surface.

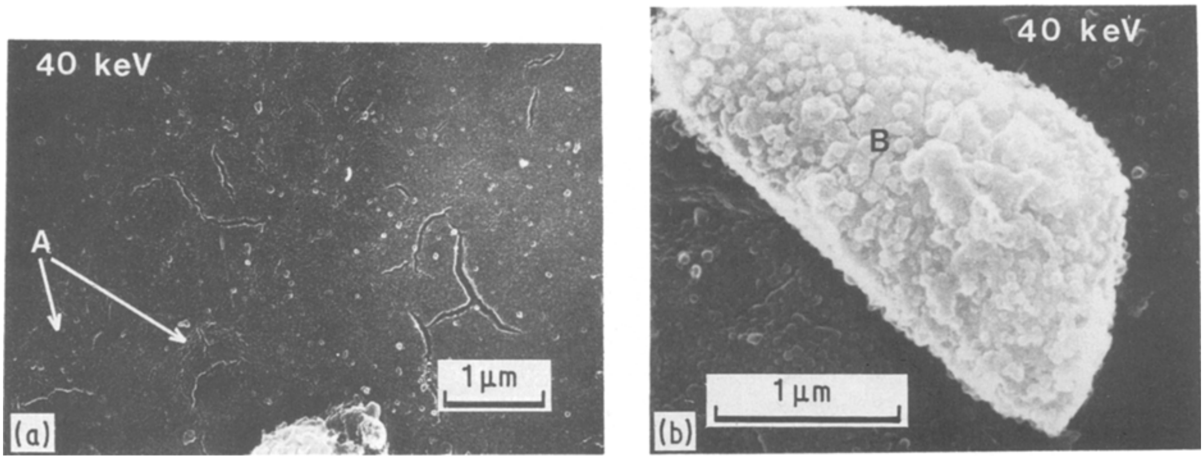


Figure 3 (a, b) Larger particles observed on the surface of 0.13 μm film. (A) Larger particles within features resembling large etch pits, (B) intermetallic particle covered with large irregular-shaped particles.

the original pitted topography. Reduction of the primary beam energy to 2 keV decreases the escape depth of the backscattered electrons to the extent that the interfacial image is no longer visible in the secondary electron micrographs (Fig. 4a). Particles observed in the micrographs obtained at a lower primary beam energy were not so sharply resolved as those found at higher voltages but were observed with sharper contrast. Differences of this kind reflect the poorer resolution and lower background signals obtained with the use of lower primary beam energies in the microscope. Particles of platinum deposited during sputter-coating are of a size below that which can be resolved (typically 1 nm) by the scanning electron microscope even at the magnifications used in the current experiments.

A particulate surface structure was also observed on an uncoated pretreated and electropolished substrate (Fig. 5). Particles observed across this surface were of more uniform size than those found in the film on the alkali-etched surface. In addition, a layer-like structure can be seen close to faults within the film. A total of three layers can be seen in the micrograph (Fig. 5b). A layer structure confirms that the films comprise spherically shaped particles and not cylindrical particles extending through the film to the metal surface. Uniformity of particle size on a surface with absence of significant topography again shows that a relationship between topography and particle size may exist.

The film on the electropolished surface was also covered with a high density of small cracks similar to those observed on thicker films [6] (Figs 5a and b) but much shorter in length and greater in number. In addition the cracks have not combined to form the familiar mud-cracking patterns observed on thicker films. Cracks of this nature extending through the film may be the origin of faults or channels observed in transmission electron micrographs of similar films and thought to be responsible for the transmission of reactive species to the metal surface that results in the continuation of film growth [16].

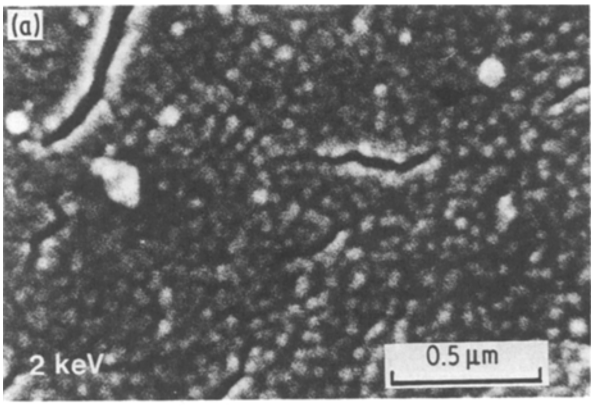
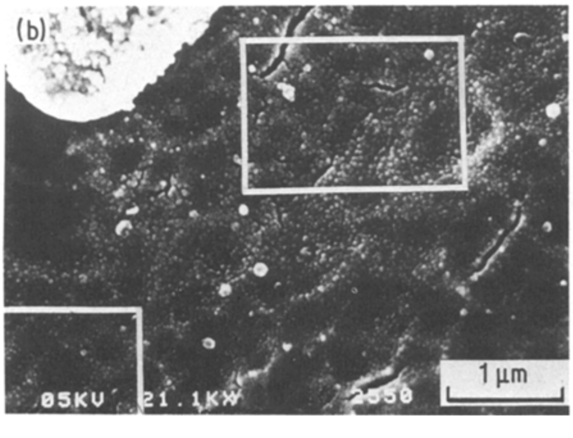
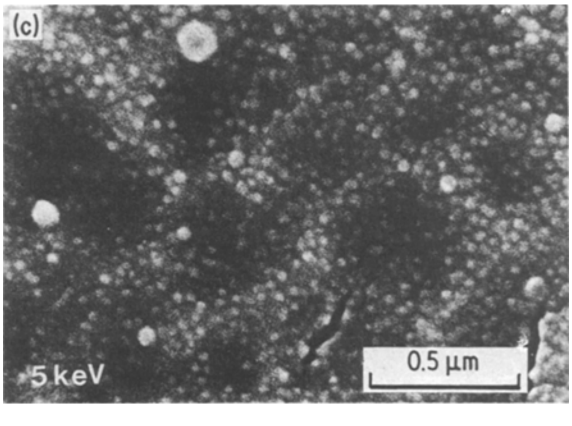


Figure 4 Subsurface imaging effects in SEM micrographs of 0.13 μm film (platinum-coated): (a) 2 keV micrograph showing total absence of pitted interfacial image, (b) lower magnification 5 keV image showing pitted topography and areas studied at higher magnification in (a) and (c), (c) 5 keV micrograph clearly showing pitted interfacial topography.





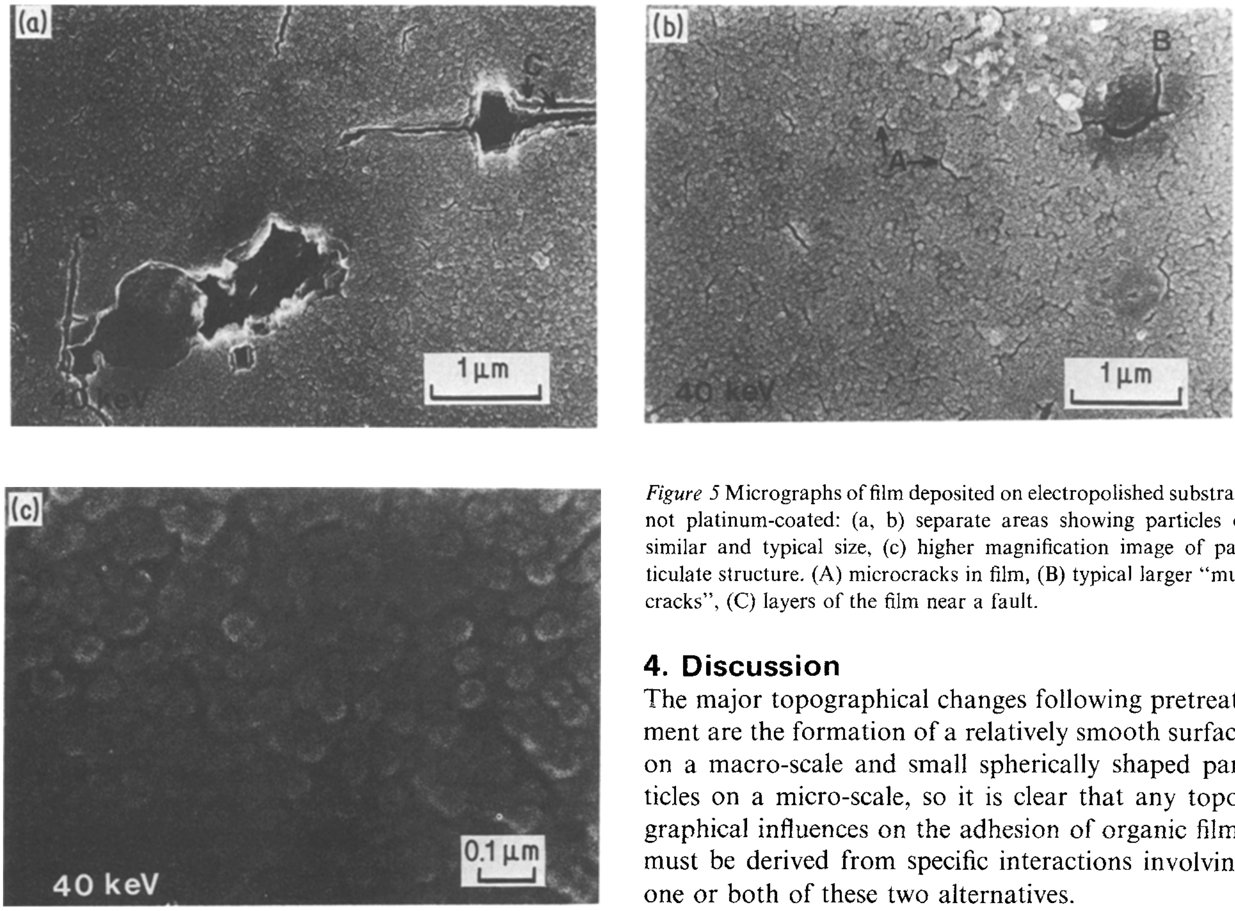


Figure 5 Micrographs of film deposited on electropolished substrate not platinum-coated: (a, b) separate areas showing particles of similar and typical size, (c) higher magnification image of particulate structure. (A) microcracks in film, (B) typical larger "mud cracks", (C) layers of the film near a fault.

Interfacial imaging effects are reduced as the film thickness increases, provided that no additional variations in the chemistry or structure of the film occur as a result of the longer pretreatment times required [12]. As a result, with certain thicker films it again becomes possible to observe the film structure without initially platinum coating (Fig. 6a and b) despite the fact that the film was formed on an alkali-etched substrate. Like the surface of the thinner film formed on the same substrate, the surface structure comprises an array of uniformly sized particles with some larger particles randomly distributed across it. However, particles are not always observed so readily. On a second sample it was necessary to both platinum-coat it and to use the highest spatial resolution obtainable from a higher primary beam energy, 40 keV, in order to resolve the surface structure of an array of very fine particles, of a size which even under these conditions was difficult to resolve (Fig. 6c). More clearly resolved were the layers of particles that can be seen close to an edge of a crack formed during drying of the freshly precipitated film. Particles observed within the cracks of both samples studied (Figs 6b and c) are of similar size to those observed on the surface of the film not coated with platinum. However, particulate structure of this kind was not observed generally within the cracks, so this may reflect the influence of a subsurface feature (an intermetallic particle or a deep pit) on particle size.

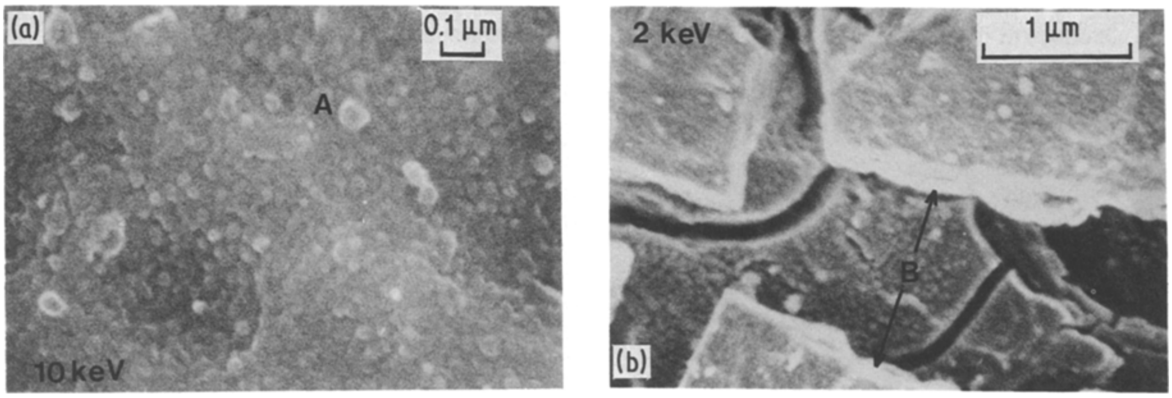
In summary, spherically shaped particles were found on all the pretreated surfaces. The sizes of these particles varied on each sample studied, and on films formed on alkali-etched surfaces the sizes also varied across the surface.

4. Discussion

The major topographical changes following pretreatment are the formation of a relatively smooth surface on a macro-scale and small spherically shaped particles on a micro-scale, so it is clear that any topographical influences on the adhesion of organic films must be derived from specific interactions involving one or both of these two alternatives.

The mud-cracking found on thicker films may influence mechanical keying of organic coatings to the pretreated surface. However, there is little practical evidence to suggest that the adhesion of coatings to thicker films is superior to that found on thinner films, so this is likely to be a minor effect.

Although pretreatment did not result in surfaces covered with a network of filaments similar to those found following phosphoric acid anodizing [3] or boiling water treatment of aluminium [2] a similar mechanism of adhesion promotion could occur. However, instead of the surfaces being locked together via filaments of alumina penetrating into the coating, locking would occur via filaments of the organic coating formed by penetration of the coating between the particles on the surface. Although the particles appear as discrete spheres in the micrographs it is probable that they are close-packed in the pretreatment film, and either the contact region was not observed in micrographs or the surface particles had dehydrated in the vacuum. However, spaces between contacting groups of three particles will be present and could provide the locations for film penetration to occur. Studies of organic lacquers on porous anodized surfaces [17] have shown that lacquer molecules can penetrate deep into the anodic films to provide keying of the film to the surface. However, baking of samples was required before penetration occurred. The dimensions of the pores in anodic films are 15 to 30 nm, comparable in size to the 10 to 15 nm spaces between particles. Cross-sectional studies of microtomed sections similar to those described for adhesives and paints on anodic films [17, 18] would be useful in establishing whether penetration of coatings into the film does occur.



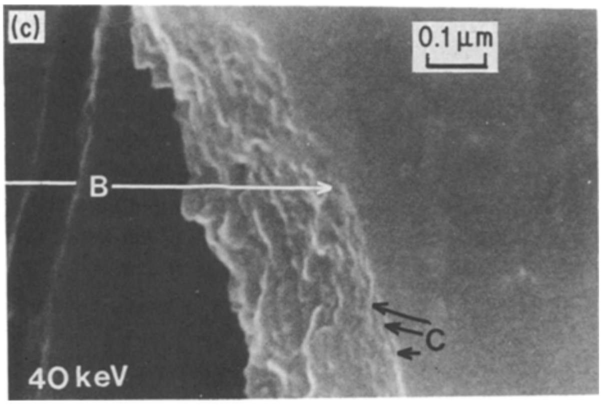


Figure 6 Micrographs of thicker films deposited on normal alkali-etched substrate (film thickness ca. 1.5 µm): (a) particulate structure of film surface observed on non-platinum-coated surface, (b) similar-sized particles observed in cracks of film shown in (a), (c) another sample of 1.5 µm film (platinum-coated) with very fine surface particles and larger particles within cracks. (A) Larger particles randomly distributed across surface, (B) width of larger "mud cracks" in films, (c) layer structure.

A porous pretreated surface could also influence the adhesion of organic coatings by an alternative mechanism. During the curing or setting of organic coatings, low molecular weight material can diffuse to surfaces or interfaces and as a result a weak interfacial layer is formed. Surface fibres are believed to penetrate through the layer and both strengthen it [3] and allow bonding to occur between the surface and the higher molecular weight regions of the polymer. On chromate-pretreated surfaces the spaces between the particles could act as a sink for the low molecular weight material, and as a result bonding would again occur between the pretreated surface and the higher molecular weight regions of the bulk of the coating.

Perhaps the most important feature of both chromate pretreatment and phosphoric acid anodizing, however, is that both result in surfaces with exceptionally high degrees of micro-roughness so that both will be very efficiently wetted by organic coatings. As a result there will be a high degree of contact between the coating and the surface and a high probability of interfacial bond formation. Clearly the larger the number of interfacial bonds the greater the adhesion of the coating to the surface. Also the more bonds that must be broken before loss of paint or lacquer adhesion will occur, the longer the service life of the product.

References

1. A. J. KINLOCH, *J. Mater. Sci.* **15** (1981) 2141.
2. R. BAINBRIDGE, D. LEWIS and J. M. SYKES, *Int. J. Adhesion Adhesives* **2** (1982) 175.
3. J. D. VENABLES, D. K. MACNAMARA, J. M. CHEN, T. S. SUN and R. L. HOPPING, *Appl. Surf. Sci.* **3** (1979) 88.
4. T. T. WANY and H. N. VIZIRANI, *J. Adhesion* **4** (1972) 353.
5. J. S. AHEARN, T. S. SUN, J. D. VENABLES, C. FROEDE and R. HOPPING, *Met. Soc. A* (1982) 125.
6. J. A. TREVERTON, *Met. Soc.* **275** (1981) 64.
7. N. J. NEWHARD, *Met. Finish.* **6** (1972) 49.
8. J. A. TREVERTON and N. C. DAVIES, *Surf. Interface. Anal.* **3** (1981) 194.
9. J. A. TREVERTON and M. P. AMOR, *Trans. Inst. Met. Finishing* **60** (1984) 92.
10. D. J. ARROWSMITH, J. K. DENNIS and P. R. SLIWINSKI, *ibid.* **62** (1984) 117.
11. O. C. WELLS, A. BOYDE, E. LIFSHIP and A. REZUNOWICH, "Scanning electron microscopy" (McGraw-Hill, New York, 1974) 139–159, 160–179.
12. J. A. TREVERTON and M. P. AMOR, *J. Microsc.* **140** (1985) 383.
13. A. C. EVANS and J. FRANKS, *Scanning* **4** (1984) 169.
14. H. KAWAMOTO, S. YAMAZAKI, A. ISHIKAWA and R. BUCHANAN, *Scanning Electron Microsc.* **15** (1984) 22.
15. G. POPE, E. MATIZEVIC and C. PATEL, *J. Colloid Interface Sci.* **80** (1981) 74.
16. R. C. FURNEAUX, G. E. THOMPSON and G. S. WOOD, *Corros. Sci.* **19** (1979) 63.
17. K. OMATA, K. MAEDA, T. ODA and Y. OTAKA, *Aluminium* **57** (1981) 811.
18. W. BROCKMANN, O. D. HENNEMANN and H. KOLLEK, *Organic Coatings Appl. Polym. Sci. Proc. (ACS)* **37** (1982) 165.

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