Mechanical Factors in the Adhesion of Polyethylene to Aluminium

D. E. PACKHAM,* K. BRIGHT† and B. W. MALPASS† *Van Leer (U.K.)*
Limited, Passfield Research Laboratories, Liphook, Hampshire,
United Kingdom

Synopsis

The adhesion of low-density polyethylene to porous anodic films on aluminum was studied using the 180° peel test. Relative values of bond strengths, obtained by using polymer with and without antioxidant and by forming the bond in air or in vacuo, indicated that good adhesion could be obtained, despite previous evidence to the contrary, in conditions where oxidation of the polyethylene was suppressed. The relation between peel strength and anodic film thickness and film-forming voltage implied that the polyethylene entered pores in the film during bond formation. This was supported by the change of the category of the adhesion to one dependent upon polymer oxidation when the pores in the anodic film were sealed prior to bond formation. It is suggested that the mechanism of adhesion to porous anodic films on aluminum involves keying of the polymer into the pores in the film.

INTRODUCTION

Many previous workers have studied the adhesion of polyethylene to metals. While some have emphasized the deleterious effect of weak boundary layers in the polymer on bond strength[1-5] and others have studied the action of adhesion promotors of various kinds,[6,7] a large number have demonstrated a connection between polymer oxidation and good adhesion.[8-12] Thus, Bright and Malpass[12] showed that the oxidation of polyethylene was catalyzed by iron, and so its adhesion when sintered onto steel was good. The adhesion, however, could be reduced practically to zero either by sintering the polymer in vacuo or by sintering in air with antioxidant present in the polymer.

These earlier results have been discussed in the context of the adsorption and rheological theories of adhesion. Thus, oxidation may improve adhesion by introducing polar groups into the polymer, or the increased bond strength might be a consequence of increased strength of the surface layers caused by crosslinking which would accompany oxidation. Here, as in

* Present address: School of Materials Science, The University, Bath, United Kingdom.

† Present address: Formica International Ltd., 84-86, Regent Street, London, W. 1, England.

most cases of adhesion, the contribution of mechanical effects has not been considered significant.[13]

Adhesion to Aluminum

The present authors, like earlier workers,[14] found that while adhesion to degreased aluminum was low, prior treatment of the aluminum with hot sodium dichromate–sulfuric acid solution produced a much stronger adhesive bond. In view of previous work discussed above, it seemed likely that the enhanced adhesion was a consequence of adsorbed chromium causing oxidation of the polymer. The chromium(III) might have acted catalytically or, in the case of chromium(VI), as an oxidizing agent. A tracer study,[15] however, indicated that the quantity of chromium adsorbed in the procedure used amounted to a small fraction of a monolayer. This explanation was then considered less likely.

It has been suggested[16] that the sulfuric acid–dichromate treatment produces an oxide on aluminum similar to that formed by anodic oxidation in a pore-producing electrolyte. For this reason, adhesion to aluminum-bearing porous anodic oxide films was investigated.

Structure of Porous Anodic Films on Aluminum

When aluminum is anodized in an electrolyte with appreciable power to dissolve alumina, a duplex film is produced with a barrier layer next to the base metal and a much thicker porous layer on the outside.[17] Keller, Hunter, and Robinson[18] produced films by anodizing at constant voltage in sulfuric, phosphoric, chromic, and oxalic acids and studied the pore structure. The porous layer consisted of hexagonal prismatic oxide cells each containing a pore circular (or possibly star-shaped) in cross section extending from the outer surface to the barrier layer (Fig. 1). Keller et al.[18] found that the cell size increased linearly with voltage, but that the
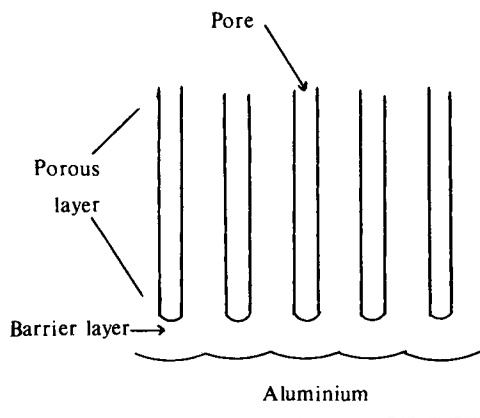

Fig. 1. Cell and pore structure of porous anodic films on aluminum.

pore diameter remained constant for a given electrolyte, concentration, and temperature. Thus, the porosity, i.e., the percentage of the cell cross-sectional area occupied by the pore, decreased with forming voltage.

The model proposed by Keller et al.,[18] although not without its opponents,[17,19,20] has received general support in most of its features by a number of subsequent workers.[21-23] O'Sullivan and Wood[24] have recently published a detailed electron-microscopic study of porous alumina films which differs from that of Keller et al. in claiming that pore diameter as well as cell size is proportional to forming voltage. This means that the porosity of the film is independent of forming voltage. In another recent paper,[25] a linear (but not proportional) relationship was observed between forming voltage and pore diameter by indirect means. This gives the same type of relationship between porosity and forming voltage as that of Keller et al.[18]

The total thickness of a porous anodic film is a function of the quantity of electricity used to produce it. The empirical equation,[26]

$$\text{thickness } (\mu m) = \frac{\text{current density } (amp/ft^2) \times \text{time } (min)}{30} \tag{1}$$

shows that the thickness is somewhat less than that predicted by Faraday's laws because of dissolution of the oxide in the electrolyte.[17]

Porous anodic films can readily absorb a dye. This ability can be lost and the corrosion resistance of the anodic film improved by "sealing," for example, by immersion in boiling water.[17] For effective sealing with hot water, both the type and concentration of the impurities and the pH have to be carefully controlled.[27] The mechanism of sealing involves blocking of the pore mouths by processes such as hydration of the oxide, followed by narrowing and gradual elimination of the rest of the pore.[28,29]

EXPERIMENTAL

Materials

Aluminum. SI 0 (B.S. 1470) 20 s.w.g. sheet. Impurities permitted: silicon, copper, and iron not greater than 0.01%.

Polyethylene. Alkathene P109 low-density polyethylene powder from I.C.I. The manufacturers quote a density of 0.92 g/cm^3 and melt flow index at 190° of 10 g/10 min (load 2.16 kgf). Infrared analysis showed 22 methyl and 14 ethyl groups per 1000 carbon atoms. No antioxidant was present.

Antioxidant. 2,6-Ditertiary-butyl p-cresol.

Polyethylene containing antioxidant was prepared by soaking a weighed quantity of polymer in a solution containing a known amount of antioxidant in dichloromethane. The solvent was removed under vacuum.

Procedure

Anodizing and Sealing

The aluminum was cut into sheets 6 in. × 4 in. and degreased in trichloroethylene vapor.

The electrolytes used for anodizing were 4% w/w phosphoric acid (prepared from acid of S.G.1.75) at 24°, and 15% w/w sulfuric acid (prepared from acid of S.G.1.84) at 10°, except for the comparison of sealed and unsealed films (Table II) when the temperature was 18°C.

The anodizing current was derived from a laboratory rectifier unit. The procedure employed as to place the specimen in a stirred, thermostatically controlled bath and to switch on the circuit with the potentiometer on the rectifier unit set to zero. The potentiometer was turned to increase the voltage to the require value over about 5 sec. This voltage was maintained throughout the anodizing by adjusting the potentiometer if necessary. At the end of the anodizing period, the anode was quickly removed from the bath, rinsed thoroughly with deionized water and, unless it was to be sealed, with acetone, dried in air at 30°C, and stored over silica gel.

The specimens to be sealed were placed in a large volume of boiling deionized water for a period equal to the anodizing time. They were then rinsed with acetone, dried at 30°C in air, and stored over silica gel. The pH of the sealing water remained close to neutral after sealing.

Tests on Anodized Samples

Thickness. For thicker films (above 10 μm), thickness values were obtained on a number of samples by determining the weight loss on stripping the anodic film in hot phosphoric acid–chromic acid solution assuming a density of 2.5 g/cm^2 for the anodic film.[26] Values found agreed well with those obtained from eq. (1) which could, therefore, be used to give a reliable value of thickness.

The stripping method was not sufficiently sensitive to be applied to the thinner films produced. Here, the thickness was obtained by bending the sample into a U which has the effect of stretching the base metal and crack the oxide normal to its surface.[28] The thickness was then measured directly in a scanning electron microscope.

Measurement of Pore Volume. The method described by Odier[30] was used. The weight gain on immersion in an aqueous solution of 5 g/l. Alizarin Green at 60° was taken as being proportional to the pore volume of the anodic film.

Test for Sealing. A drop of aqueous Alizarin Green solution (ca. 20 g/l.) was placed on the specimen and left for 5 min. The color could not be removed from an unsealed specimen by rinsing with water or with the use of scouring powder. The dye washed off sealed specimens leaving no green stain. Similar tests to this have commonly been employed.[26,27]

Preparation of Bonds

The 6 in. × 4 in. panels were heated in an oven at 200°C for 10 min and removed. A layer of polyethylene powder about $^1/_2$ in. thick was sprinkled

over the surface. After 1 min, the excess polymer which had not adhered was tapped off and the panels were returned to the oven for 20 min. At the end of this sinter time, the panels were removed from the oven and allowed to cool in air. This procedure produced a coating of polymer between 0.8 mm and 1.0 mm thick. Variation within these limits has been shown to have no significant effect on 180° peel strength.[31]

For sintering in vacuo, a modified procedure had to be used. A layer of polymer was placed on the cold panels which were then placed in a vacuum oven. The oven was flushed twice with oxygen-free nitrogen and evacuated with a rotary oil pump. The heating elements were switched on, and, after about 1 hr when the temperature was ca. 200°, the heat was switched off. The oven took about 2 hr to cool to room temperature when the specimens were removed. All the vacuum-sintered specimens discussed in this paper were prepared simultaneously.

Test of Adhesion

Lines 2 cm apart were scored through the polymer to the substrate. These 2-cm strips were peeled[31] at a peel angle of 180° on an Instron testing machine with a cross-head speed of 50 cm/min. Thus, four peels of nearly 6 in. in length were obtained from each panel.

DISCUSSION AND RESULTS

The anodizing solutions used in this work were sulfuric and phosphoric acids as neither would be expected to oxidize polyethylene. The conditions used were those of Keller, Hunter, and Robinson[18] so that use could be made of the quantitative results they obtained. Their estimates of pore diameter were 120 Å for sulfuric acid-formed films and 330 Å for those formed in phosphoric acid.

The effect on peel strength of process variables associated with the method of bond formation and testing has been reported elsewhere,[15,31] and the values used in this work have been chosen to minimize variation from these sources.

Effect of Antioxidant and Vacuum Sintering

The need for polymer oxidation in the adhesion of polyethylene to steel has been demonstrated by preventing oxidation, either by sintering the polymer in vacuo or by using polymer containing antioxidant. Table I shows the results (preliminarily reported earlier[32]) of applying this technique to adhesion to anodized aluminum and to other substrates. As expected, the adhesion to steel falls to almost zero as the concentration of antioxidant is increased and vacuum sintering also yields a low peel strength. The results for adhesion to aluminum etched in both sodium hydroxide solution and the sulfuric acid–sodium dichromate solution show a similar pattern. In contrast, the adhesion to anodized aluminum (a) is good when the bond is formed in vacuo and (b) does not show the catastrophic drop when polymer containing antioxidant is used. These results imply that

TABLE I
Adhesion to Anodized Aluminum Compared with Other Substrates

Metal	Treatment after degreasing	Antioxidant added to polythene	Sintered in air or vacuum	No. of peels	Peel strength,[a] kgf/cm	
Aluminum	etched in H_2SO_4/$Na_2Cr_2O_7$ at 63°C for 10 min	None	air	8	2.08 ± 0.21	12.2%
		480 ppm	air	8	1.09 ± 0.11	11.6%
		5000 ppm	air	8	0.29 ± 0.06	25.8%
		none	vacuum	4	0.21 ± 0.04	13.5%
Aluminum	etched in 10% NaOH at 40°C for 30 sec	none	air	4	2.58 ± 0.19	4.6%
		480 ppm	air	8	0.51 ± 0.08	18.6%
		5000 ppm	air	8	0.11 ± 0.02	31.1%
		none	vacuum	4	0.18 ± 0.04	14.5%
Steel	etched in 50% HCl for 30 sec at room temperature	none	air	4	3.01 ± 0.11	2.3%
		5 ppm	air	4	1.86 ± 0.22	7.5%
		540 ppm	air	4	0.41 ± 0.07	10.3%
		none	vacuum	4	0.75 ± 0.25	21.2%
Aluminum	anodized in 15% w/w H_2SO_4 at 20 V for 60 min at 10°C	none	air	4	1.97 ± 0.19	6.0%
		480 ppm	air	4	2.88 ± 0.33	7.3%
		5000 ppm	air	4	2.72 ± 0.27	6.3%
		none	vacuum		approx. 3.0	
Aluminum	anodized in 15% w/w H_2SO_4 at 10 V for 60 min at 10°C	none	air	4	0.75 ± 0.09	7.6%
		480 ppm	air	4	1.03 ± 0.06	3.9%
		none	vacuum	4	1.49 ± 0.27	11.4%
Aluminum	anodized in 4% w/w H_3PO_4 at 20 V for 60 min at 24°C	none	air	4	1.49 ± 0.18	7.5%
		480 ppm	air	4	1.18 ± 0.05	2.5%
		none	vacuum	4	1.33 ± 0.09	4.5%
Aluminum	anodized in 4% w/w H_3PO_4 at 10 V for 60 min at 24°C	none	air	4	2.50 ± 0.15	3.7%
		480 ppm	air	4	1.51 ± 0.06	2.9%
		none	vacuum	4	1.54 ± 0.18	7.5%

[a] With 95% confidence limits and percentage coefficient of variation.

adhesion to porous anodic films is by some mechanism independent of polymer oxidation. It was thought that the mechanism might involve penetration of polymer into the pore of the anodic film, so a series of experiments was carried out to test this point.

Variation of Anodic Film Thickness

The effect of thickness on adhesion was studied for anodic films formed under four sets of conditions: in sulfuric acid at 10 V and 20 V and in phosphoric acid at 10 V and 20 V. Different thicknesses were produced by altering the anodizing time. Figure 2 shows the results for the 20 V sulphuric acid films. A rise in adhesion with anodic film thickness can be seen. Also plotted in Figure 2 are values proportional to the pore volume per unit area for similar films obtained by the method of Odier.[30] The similarity in the shape of the two curves in Figure 2 is noteworthy.

Figure 3 shows the results for the films produced by the other anodizing conditions; a similar trend is apparent. The films were too thin for reliable results to be obtained for pore volume by the gravimetric method of Odier. It is interesting to note that Keller et al.[18] give the porosities, i.e., percentage of cross-sectional area of the cell occupied by the pore, for the films shown in Figure 3 as follows: 10 V phosphoric, 30%; 20 V phosphoric, 16%; and 10 V sulfuric, 12%; which are in the same order as the peel strength for a standard film thickness.

Variation in Forming Voltage

According to Keller et al.,[18] films produced by anodizing at constant current density for the same time but at difference forming voltage would be expected to have different porosities. Variation in voltage produces changes in current density. However, it was found that by working with phosphoric acid in the range of 10 V to 24 V, the current density changes were small. Figure 4 shows that peel strength fell with anodizing voltage
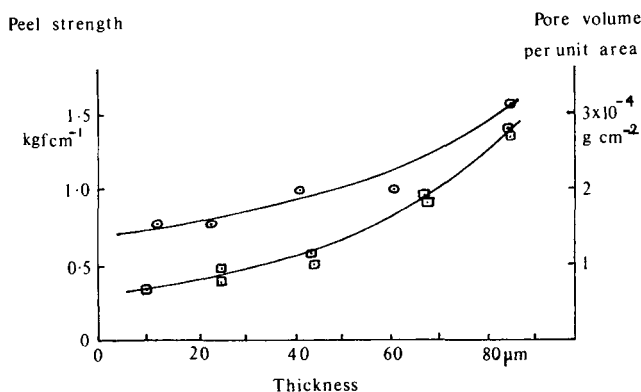

Fig. 2. Effect of thickness of anodic films formed in sulfuric acid at 20 V on pore volume per unit area (□) and peel strength (○).

for two series of samples, one anodized for 30 min, the other for 60 min. The current density varied from 0.09 to 0.13 A/dm² in the first series and from 0.11 to 0.14 A/dm² in the second. The tendency was for higher current densities which would produce thicker films to occur at higher voltages. However, Figure 4 shows that the adhesion to these films was less. Porosity values from Keller et al.[18] are also plotted in Figure 4. Adhesion falls with voltage in a manner expected of porosity.

Sealed and Unsealed Films

Anodic films formed in sulfuric acid at 16.5 V and 18°C for 30 min were used for comparison of adhesion to sealed and unsealed films. As Hoar and Wood[33] have produced evidence that once an anodized specimen has been allowed to dry out, subsequent sealing is less complete, specimens were placed in the sealing bath while still wet. A sealing time equal to the anodizing time is usually considered adequate,[26] so specimens were sealed for 30 min. The sealing test indicated that this was satisfactory and, moreover, that subsequent heating in air at 200°C for 10 min (the preheating time) and for a further 20 min (the sintering time) did not destroy the sealing.

The results in Table II show that there was a considerable decrease in adhesion to sealed specimens when polymer containing antioxidant is used. This is characteristic of adhesion to the nonanodized substrates in Table I. This decrease in adhesion was not observed for the unsealed substrate. It is thought that the high adhesion of the polyethylene with 5000 ppm antioxidant to the unsealed substrate might be due to improved flow properties of the modified polymer. Measurements with a Daven-
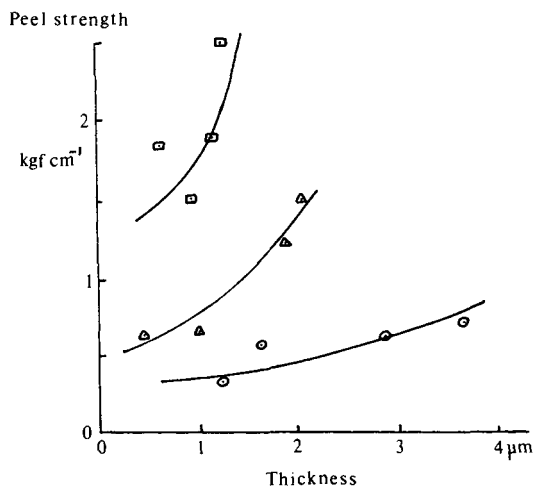
Fig. 3. Effect of thickness of anodic films on peel strength. Anodizing voltages and electrolytes are: (□) phosphoric acid, 10 V; (△) phosphoric acid, 20 V; (○) sulfuric acid, 10 V.
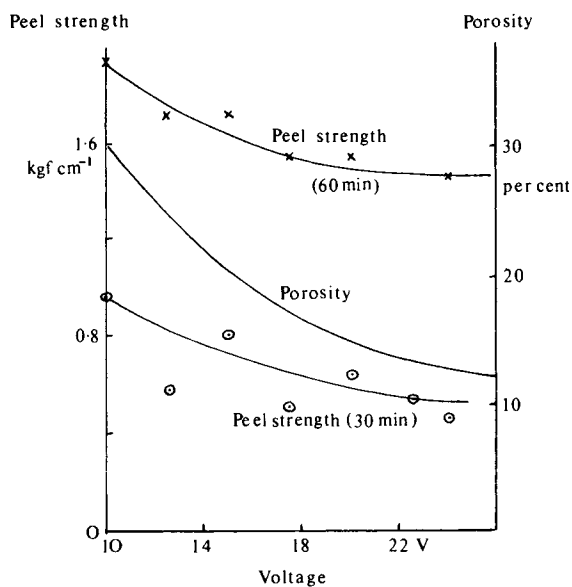
Fig. 4. Variation in peel strength and porosity[18] with anodizing voltage for films formed in phosphoric acid at approximately constant current density. Anodizing times: ($\times$) 60 min.; ($\odot$) 30 min.

TABLE II
Adhesion to sealed and Unsealed Anodic Films

Antioxidant added to polyethylene	No. of peels	Peel strength,[a] kgf/cm
unsealed		
None	8	1.54 ± 0.08 6.4%
5000 ppm	4	6.61 ± 0.78 7.5%
sealed		
None	6	3.84 ± 0.15 4.3%
5000 ppm	4	2.39 ± 0.42 11.2%

[a] With 95% confidence limits and percentage coefficient of variation.

port Melt Indexer Model III indicated that at 200° the MFI of the unmodified polymer was 15 g/10 min (2.16 kgf load) but that with polymers containing antioxidant was 18 g/10 min.

CONCLUSIONS

Thus, it has been shown that the adhesion of polyethylene to porous anodic films on aluminum is independent of oxidation of the polymer. It increases with thickness and porosity of the film. If the pores are sealed, however, oxidation of the polymer is required for good adhesion. In view

of the findings of O'Sullivan and Wood,[24] some doubt must be entertained about the interpretation of the porosity variation given in Figure 4; but even without these results, the inference of the rest of the work is that the polymer adheres by a mechanism involving penetration of the polymer into pores on the substrate. Direct evidence of this penetration has been obtained by examining the polymer surface involved in the scanning electron microscope[32] and will be published in detail elsewhere.[34]

It seems, therefore, that adhesion of polyethylene to high-energy substrates may fall into two extreme categories: (a) dependent on polymer oxidation and (b) for porous substrates independent of polymer oxidation. Most cases involve some combination of the two.

Adhesion in the first category—exemplified by that to steel—can be interpreted in terms of the adsorption or rheological theories. Introduction of polar groups into the polymer could cause stronger adsorption onto the substrate. Alternatively, it could be that oxidizing conditions cause reaction in the surface of the polymer eliminating weak surface layers.

Adhesion to porous anodic films on aluminum falls into the second category. Here, adhesion depends on penetration of polymer into pores in the substrate, and mechanical keying in some form contributes to the bond. Such a mechanism has not previously been emphasized in this context.

When it is suggested that mechanical effects are significant, it is not claimed that keying is exclusively responsible for the bonding, for wherever the polymer and substrate come into contact, dispersion forces at least will contribute to the adhesion between them.

Several possible explanations of the effect of mechanical keying can be made. When polyethylene is peeled from a relatively smooth surface, the stress is transmitted to the interfacial region of the polymer which has often been claimed to be weaker than the bulk. If the polymer is keyed into pores in the substrate, most of the stress might be borne by the polymer in the region of the mouth of the pores rather than at the interface. The load then would be borne partly by the core of "bulk" polymer within the mouth of each pore. Another somewhat similar explanation can be given in terms of the ease with which molecules of different sizes could enter a small pore. Small molecules, such as low molecular weight polymer and additives, would enter the pores more readily so a fractionation effect might be observed. This would mean that the strength of the polymer just outside the pores would be greater than just above a fairly smooth surface.

The structure of the porous oxide on anodized aluminum is unusual. This work raises the question of whether there are other oxide structures where mechanical effects are significant in adhesion. Indeed, preliminary results indicate that such factors may contribute to adhesion to certain thick oxide films on copper.

References

1. J. J. Bickerman and C. R. Huang, *Trans. Soc. Rheol.*, **3**, 5 (1959).
2. J. J. Bickerman, *J. Appl. Polym. Sci.*, **2**, 216 (1959).
3. J. J. Bickerman and D. W. Marshall, *J. Appl. Polym. Sci.*, **7**, 1031 (1963).
4. J. M. Sykes and T. P. Hoar, *J. Polym. Sci. A1*, **7**, 1385 (1969).
5. J. P. Tordella, *J. Appl. Polym. Sci.*, **14**, 1627 (1970).
6. C. L. Gray, W. L. MacCarthy, and T. F. McLaughlin, *Mod. Packaging*, **34**(10), 143 (1961).
7. G. G. Vincent, *J. Appl. Polym. Sci.*, **11**, 1553 (1967).
8. H. A. Arbit, E. E. Greisser, and W. A. Haine, *Tappi*, **40**, 161 (1957).
9. F. J. Bockhoff, E. T. McDonel, and J. E. Rutzler, *Ind. Eng. Chem.* **50**, 904 (1958).
10. A. A. Berlin, S. F. Bulachera, and Y. L. Morozov, *Plast. Massy.*, **10**, 3 (1962).
11. F. K. Borisova, A. V. Kiselev, A. Y. Korolev, V. I. Lygin, and I. N. Solomonova, *Koll. Zhur.*, **28**, 792 (1966).
12. K. Bright and B. W. Malpass, *Eur. Polym. J.*, **4**, 431 (1968).
13. G. Salomon, in *Adhesion and Adhesives*, 2nd ed., Vol. 1, R. Houwink and G. Salomon, Eds. Elsevier, Amsterdam, 1965, p. 6.
14. K. H. Pohl and A. T. Spencer, *Mod. Plast.*, **41**(7), 119 (1964).
15. D. E. Packham, Ph.D. Thesis, City University, London, 1970.
16. D. D. Eley and R. Rudham, *Adhesion Fundamentals and Practice* (Ministry of Technology) Maclaren, London, 1969, p. 91.
17. J. W. Diggle, T. C. Downie, and C. W. Goulding, *Chem. Rev.*, **69**, 365 (1969).
18. F. Keller, M. S. Hunter, and D. L. Robinson, *J. Electrochem. Soc.*, **100**, 411 (1953).
19. J. F. Murphy and C. E. Michelson, *Proc. Conf. Anodising Aluminium*, Nottingham, Aluminum Development Assoc., London, 1961, p. 83.
20. J. F. Murphy, *Proc. Symp. Anodizing Aluminium*, Birmingham, 1967, p. 3
21. C. J. L. Booker, J. L. Wood, and A. Walsh, *Brit. J. Appl. Phys.*, **8**, 347 (1957).
22. M. Paganelli, *Alluminio*, **27**(1), 3 (1958).
23. G. Paolini, M. Masoero, F. Sacchi, and M. Paganelli, *J. Electrochem. Soc.*, **112**, 32 (1965).
24. J. P. O'Sullivan and G. C. Wood, *Proc. Roy. Soc.*, **A317**, 511 (1970).
25. A. Dekker and A. Middlehoek, *J. Electrochem. Soc.*, **117**, 440 (1970).
26. Aluminium Federation Information Bulletin 14, Aluminum Federation, London, 1966.
27. H. Richard, *Proc. Conf. Anodising Aluminium*, Nottingham, Aluminum Development Assoc., London, 1961 p. 181.
28. J. P. O'Sullivan and G. C. Wood, *Trans. Inst. Metal Finishing*, **47**, 142 (1969).
29. J. P. O'Sullivan, J. A. Hockey, and G. C. Wood, *Trans. Faraday Soc.*, **65**, 535 (1969).
30. J. Odier, *Metaux Corrosion-Usure*, **20**, 113 (1945).
31. D. E. Packham, *Aspects of Adhesion*, **6**, 127 (1971).
32. K. Bright, B. W. Malpass, and D. E. Packham, *Nature*, **223**, 1360 (1969).
33. T. P. Hoar and G. C. Wood, *Electrochim. Acta*, **7**, 333 (1962).
34. B. W. Malpass, D. E. Packham, and K. Bright, *J. Appl. Polym. Sci.*, **18**, 3249 (1974).