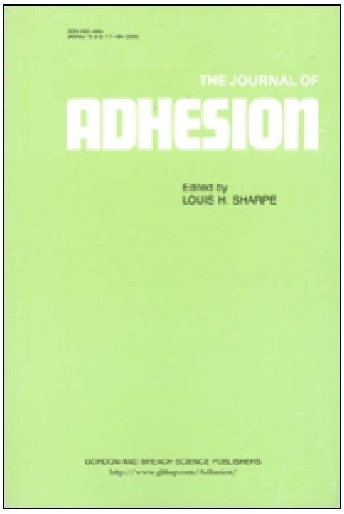

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Adhesion of Polyethylene to Copper: Importance of Substrate Topography

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In order to get good adhesion between polyethylene and copper previous workers have oxidized the metal in alkaline solution to give a matt black oxide film. In this paper it is shown that the good adhesion obtained is associated with the very rough, fibrous nature of the matt black oxide film. Adhesion rises as the layer develops on the copper. If the fibres are damaged to alter the topography without changing the chemical nature of the substrate, the adhesion falls markedly. If the chemical nature of the oxide film is changed by electrolytic reduction, with minimum change in topography, the adhesion is still substantial. Adhesion to these matt black oxide films is still good if oxidation of the polymer is suppressed either by incorporation of stabilizers or by coating in a nitrogen atmosphere. This further points to the importance of topography in adhesion to these surfaces.

INTRODUCTION

Good adhesion of polyethylene to copper may be obtained if, prior to bonding, the copper surface is oxidized to give a matt black oxide. It was previously considered that the origin of the good adhesion was oxidation of the polymer by copper(II) oxide in the film. Although consistent with much work linking good adhesion of polyethylene to metals with polymer oxidation, this explanation was shown in the previous paper[1] to be invalid. A more detailed study was therefore undertaken of adhesion to matt black oxide films formed on copper either in proprietary "Ebonol C" or in an alkaline chlorite solution. The effect of film thickness and topography on adhesion and of the coating atmosphere and stabilizing additives in the polymer were considered.

EXPERIMENTAL DETAILS

Polyethylene

Two grades of low density polyethylene were used, both stated by the manufacturer (I.C.I. Ltd.) to be additive free:

Alkathene 190400, density 0.916 g/cm^3, m.f.i. 20,
Alkathene P109, density 0.92 g/cm^3, m.f.i. 10.

For some of the experiments additives were incorporated. The polymer powder was soaked in a solution of antioxidant (2,6-di-tert-butyl-paracresol) in methylene chloride and the solvent was allowed to evaporate. Oxanilide was similarly incorporated from benzene solution.

Copper

Deoxidized sheet, 1.2 mm thick (B.S. 1172) was chemically polished[1] and matt black oxide films were prepared either by oxidation at 90°C in a solution of 180 g/l of "Ebonol C" obtained from Enthone Inc. (*Ebonol C—formed films*) or by oxidation in alkaline chlorite-phosphate solution as previously[1] described (*Chlorite formed films*). The thickness of the oxide film was measured by coulometric reduction.[1]

Steel

10 × 15 cm mild steel panels were prepared for bonding by degreasing in trichloroethane followed by etching for 30 seconds at room temperature in 6M hydrochloric acid and rinsing with water and acetone.

Coating with polyethylene

The copper or steel panels were melt coated with the polymer at 200°C in air as described previously.[1] Some coatings were applied in a nitrogen atmosphere. This involved placing the panels covered with polymer powder in the oven at room temperature. After repeated evacuation of the oven and flushing with nitrogen, the panels were heated in a nitrogen atmosphere to 180°C and the oven switched off and allowed to cool to room temperature before admitting air.

Peel tests

The adhesion was measured by a 180° peel test conducted at a peel rate of 250 mm/min.[1]

RESULTS AND DISCUSSION

Thickness of oxide and adhesion

Both types of matt black oxide film increased in average thickness linearly with the time the copper panel was immersed in the oxidizing solution (Figure 1). For a given oxidation time the Ebonol C formed films were considerably thicker. When the films were coated with polyethylene and the peel strength subsequently measured, the adhesion was found to increase for the first 10 minutes oxidation of the copper and then to level out (Figure 2).

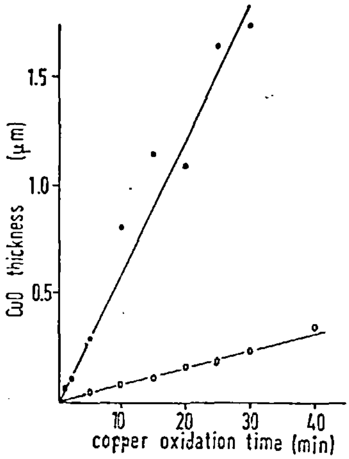


FIGURE 1 Growth of oxide on copper immersed in alkaline chlorite solution [O] and "Ebonol C" solution [●].

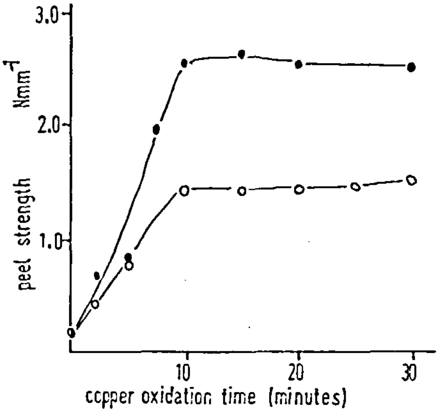
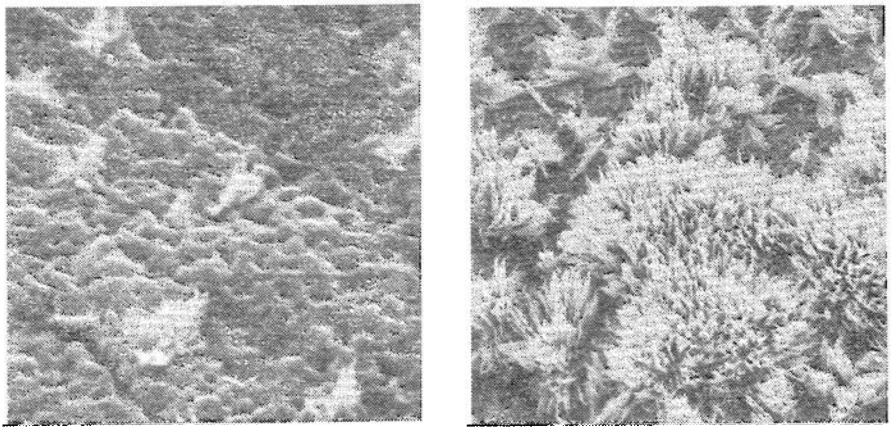


FIGURE 2 Peel strength of polyethylene (190400) to chlorite formed films [O] and Ebonol C formed films [●] on copper. Each point represents the mean of four values.

This plateau value was about 1.4 N/mm for the chlorite formed films, but higher (2.6 N/mm) for the Ebonol C formed films. The low adhesion to Ebonol C formed films produced by short oxidation times is clearly not a simple consequence of average oxide thickness.



(a) (b)

FIGURE 3 Scanning electron micrograph of the surface of copper oxidized at 90°C in "Ebonol C" solution for (a) 4 minutes and (b) 10 minutes. (Base of micrograph represents 20 μm.)

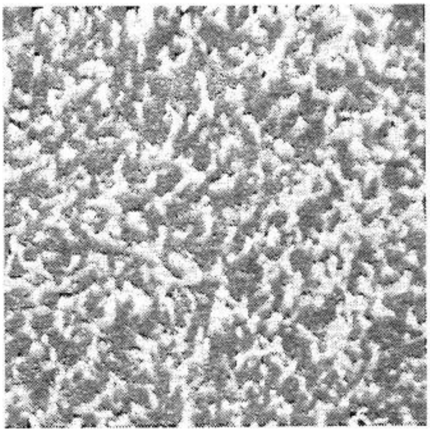


FIGURE 4 Scanning electron micrograph of the surface of copper oxidized at 90°C in alkaline chlorite solution for 30 minutes. (Base of micrograph represents 5 μm.)

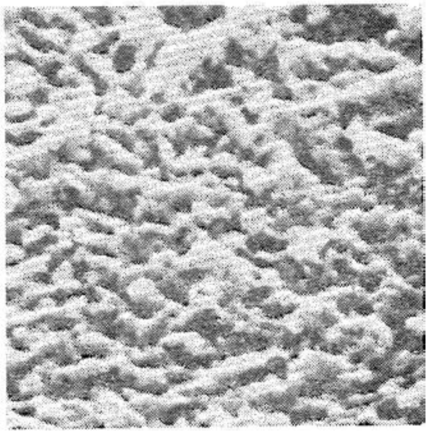


FIGURE 5 Scanning electron micrograph of the surface of polyethylene removed from alkaline chlorite oxidized copper by dissolving the oxide in hydrochloric acid. (Base of micrograph represents 5 μm.)

There is much evidence[2-6] to suggest that copper(II) oxide (but not copper(I) oxide) can grow in whisker mode and moreover Vazirani[7] has shown that Ebonol C formed films can adopt this form, so the topography of the films produced in this work was examined in the scanning electron microscope. Figure 3 shows the Ebonol C films. After 4 minutes oxidation oxide whiskers have begun to grow on a rough surface. This gave a peel strength of about 0.8 N/mm. By 10 minutes oxidation a beautiful "floral" array of whiskers had developed, covering almost the whole surface, and the peel strength had increased to 2.6 N/mm. A similar parallel development of topography and adhesion was found for the chlorite-formed films, although in detail the topography is different. At longer oxidation times these films consist of a continuous array of nodular fibres (Figure 4).

During melt coating the polymer conformed well to the topography of the matt black oxide film. This was shown by dissolving the substrate in hydrochloric acid and examining the polymer surface in the scanning electron microscope. Figure 5 shows a polyethylene surface removed in this way from a substrate similar to that of Figure 4.

Topography and adhesion

The fibrous nature of the matt black oxides suggests that, as with anodized aluminium,[8] topography rather than any specific chemical interaction such as polymer oxidation may be the significant factor leading to good adhesion. In order to test this idea topography was changed without altering the chemical nature of the surface, and, in a second experiment, the surface chemical composition was changed with minimum alteration to topography. First then, adopting a technique used by Bair *et al.*,[9] the matt black oxide films were buffed with filter paper until shiny to damage the oxide fibres. When coated with polymer and tested in the usual way the adhesion was found to be much poorer (Table I).

TABLE I

Adhesion of polyethylene (190400) to matt black oxide films on copper. Effect of damaging the oxide surface on the peel strength

Treatment of copper	Original oxide		Damaged oxide	
	Peel strength N mm^{-1}	No. of peels	Peel strength N mm^{-1}	No. of peels
20 minutes in alkaline chlorite	1.63±0.06	7	0.47±0.11	8
20 minutes in Ebonol C	2.52±0.15	3	0.87±0.11	3

(95% confidence limits are indicated)

In order to change the chemical nature of the substrate without substantially altering the topography copper sheets were oxidized in the alkaline chlorite solution and the oxide was then reduced to copper by making the sheet cathode in decimolar sodium hydroxide electrolyte. The sheets were removed from the electrolyte with the current still flowing and were rinsed with distilled water. On exposure to the atmosphere the newly formed copper would be expected to oxidize superficially to copper(I) oxide. This was confirmed by coulometric reduction.[1]

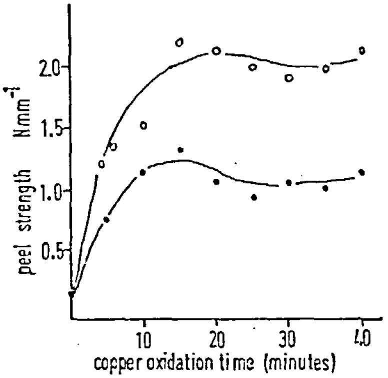


FIGURE 6 Adhesion of polyethylene (P109) to copper. Treatment of copper: top curve 20 minute chlorite formed film, bottom curve 20 minute chlorite formed film subsequently reduced to copper. (Each point represents the mean of at least four values.)

The peel strength of polyethylene, which had been applied to this reduced oxide, is compared in Figure 6 with that of the original matt black oxide. For oxidation times greater than ten minutes or so adhesion to the reduced oxide was good, around 1.1 N/mm. This should be compared with a value of about 0.17 N/mm for the same polymer to chemically polished copper with an atmospherically formed copper(I) oxide film. Adhesion to the reduced oxide was lower than that to the unreduced oxide. Although in the scanning electron microscope, the two surfaces are not very different in appearance, it is quite likely that during the electrolytic reduction, atmospheric oxidation and additional rinsing and manipulation, the reduced oxide had become damaged to some extent, accounting for the lower adhesion.

Polymer oxidation and adhesion

Finally the effect of suppressing any possible oxidation of the polymer was investigated. A phenolic antioxidant (2-6-di-tert-butyl-paracresol) was incorporated at different concentrations into samples of polyethylene which were then applied in the melt to various substrates. Table II shows the peel strengths. For steel where the adhesion is strongly oxidation dependent, the adhesion falls to a low value, even with a low concentration of antioxidant. By contrast the copper surfaces with fibrous topography all maintain good adhesion even in the presence of 5000 p.p.m. antioxidant. The adhesion to the "Ebonol C" formed film and, to a lesser extent, to the chlorite-formed film falls somewhat when antioxidant is introduced. This may imply that oxidation plays some part, although not an essential part, in the adhesion. The source of this oxidation may be adsorbed chlorite not completely removed in the rinsing after growing the oxide film.

TABLE II

Effect of concentration of antioxidant in polyethylene (190400) on adhesion to various substrates

Substrate	Concentration of antioxidant p.p.m.	Peel strength N mm^{-1}	No. of peels
Mild steel	None	2.13±0.12	34
	500	0.14±0.03	4
	1000	0.12±0.05	4
	2000	0.28±0.10	4
	5000	0.49±0.13	4
Chlorite-formed films on copper	None	1.47±0.06	8
	500	1.21±0.09	8
	1000	1.17±0.03	8
	2000	1.44±0.07	8
	3000	1.45±0.06	8
Reduced chlorite-formed films on copper	None	1.03±0.03	11
	500	0.99±0.05	8
	1000	0.93±0.03	4
	2000	0.96±0.10	4
	5000	1.03±0.03	4
"Ebonol C" formed films on copper	None	3.25±0.10	8
	500	2.63±0.20	8
	2000	2.22±0.15	4
	5000	2.54±0.14	4

(95% confidence limits are indicated)

Under some circumstances in the presence of copper phenolic antioxidants are found to be ineffective. Their stabilizing power can be re-established by using them in conjunction with a copper complexing agent such as oxanilide.[10,11] Some tests were performed using polyethylene containing both phenolic antioxidant and oxanilide. The results shown in Table III lead to the same conclusions as those of Table II: good adhesion to the fibrous surfaces occurs even when the polymer is strongly stabilized against oxidation.

TABLE III

Effect of antioxidant and complexing agent on the adhesion of polyethylene (190400) to chlorite formed films on copper

Substrate	Additives in polymer	Peel strength N mm^{-1}	No. of peels
Chlorite-formed films	None	1.56±0.11	6
	2500 p.p.m. oxanilide+ 2500 p.p.m. anti-oxidant	1.01±0.04	8
Reduced chlorite-formed films	None	1.09±0.04	8
	2500 p.p.m. oxanilide+ 2500 p.p.m. anti-oxidant	0.98±0.05	8

(95% confidence limits are indicated)

Further evidence supporting the independence of good adhesion and polymer oxidation was obtained by coating the substrate in a nitrogen atmosphere instead of in air. Coating in nitrogen required a different procedure from that usually employed. Table IV shows results for polymer applied in nitrogen and in air *using the same schedule of coating time and temperature.* With both atmospheres similar adhesion is obtained.

TABLE IV

Effect of coating atmosphere on the adhesion of polyethylene (190400) to chlorite-formed films on copper

Substrate	Coating atmosphere	Peel strength N mm^{-1}	No. of peels
Chlorite-formed films	Air	1.29±0.11	8
	Nitrogen	0.94±0.11	10
Reduced chlorite-formed films	Air	1.07±0.09	8
	Nitrogen	0.94±0.19	10

(95% confidence limits are indicated)

CONCLUSIONS

In a previous paper[1] it was shown that copper(II) oxide did not oxidize polyethylene during bonding to the matt black oxide films on copper and that little oxidation of the polymer at the interface with the substrate took place. In this paper it is shown that the good adhesion to the chemically formed copper(II) oxide is due to the oxide's adopting a whisker form. Adhesion builds up as the fibrous topography develops. If the fibres are physically damaged adhesion is seriously reduced. If the chemical nature of the substrate is changed without drastic alteration of the topography, the adhesion is still good.

The results of Bair *et al.*,[9] who studied the adhesion of polyethylene to Ebonol C formed films, are consistent with this overall picture. They found that lowering the temperature of bond formation to about 100°C considerably lowered the peel strength, and plausibly ascribed this to stress concentrations produced by a relatively large number of air bubbles trapped at the polymer substrate interface.

As pointed out earlier, in connection with adhesion to porous anodic films on aluminium,[8] 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. The results reported here show that adhesion to the matt black oxide films on copper (and to the surface formed when they are electrolytically reduced) fall mainly into the second category. The good adhesion is a consequence of the rough, fibrous topography and so such substrates are suitable for bonding with polyolefins heavily stabilized against oxidation. The question as to whether such oxidation-independent adhesion may be obtained with a range of high energy substrates, and a more detailed consideration of the mechanism of adhesion are discussed elsewhere.[12]

Acknowledgements

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