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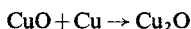
Adhesion of Polyethylene to Copper: Reactions between Copper Oxides and the Polymer

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In order to get good adhesion between polyethylene and copper previous workers have oxidised the metal in an alkaline solution to give a matt black oxide layer. It was thought that the good adhesion was a consequence of copper (II) oxide in this layer oxidising the polymer and being reduced to copper (I) oxide in the process. In this paper, changes in oxide composition during bonding by melt coating at 200°C were followed by coulometric reduction supported by x-ray and electron diffraction. It is shown that for coating times required to get good adhesion, the changes of composition of the oxide film are not the result of interaction with the polymer. The change from the higher to lower oxide is probably due to reaction with the base metal:

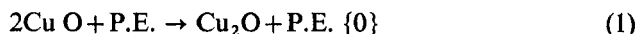


INTRODUCTION

Many studies of the adhesion of polyethylene to metals have found good adhesion is associated with conditions where the polymer can oxidise. Thus oxidation of the polymer directly with permanganate or chromic acid¹⁻³ or catalytically, for example by a steel substrate, lead to good adhesion.⁴⁻⁶ Prevention of oxidation either by applying the polymer in an inert atmosphere or by incorporating antioxidant in it has been shown to lead to a poor bond.^{2,4,7}

Adhesion of polyethylene to copper is generally poor. Bright and Malpass⁴ ascribed this to the copper's inhibiting oxidation of the polymer. Much higher adhesion, however, can be obtained with copper if the metal is oxidised prior to bonding to give a thick matt black surface oxide.⁸⁻¹¹ This

may be produced by either a proprietary solution "Ebonol C"⁸ or solution such as sodium chlorite, sodium hydroxide and trisodium phosphate, which is claimed to be similar in effect.¹⁰⁻¹² Baker and Spencer^{8,9} studied the adhesion of polyethylene to Ebonol C-treated copper by analysing the oxide on the copper by coulometric reduction before and after coating with polyethylene. After bonding they found less copper (II) oxide and more copper (I) oxide in the film (Table I). They claimed that their results showed that the copper (II) oxide oxidised the polyethylene, accounting for the good adhesion:



This explanation has been generally accepted.¹³⁻¹⁵

TABLE I

Composition of Ebonol C formed films on copper found by Baker and Spencer⁹ before and after bonding to polyethylene

Alloy	Initial film composition (mC/cm ²)			Final film composition (mC/cm ²)		
	Cu ₂ O	CuO	Total	Cu ₂ O	CuO	Total
BeCu	101	358	459	260	155	415
Cu	146	2198	2344	1285	1022	2484 ^a
BeCu	141	1455	1596	1333	167	1502

^a Probably 2307.

The discovery of polyethylene to metal adhesion where the substrate topography, rather than polymer oxidation, played a critical role^{16,17} led to the present work which re-examined the adhesion to copper with the matt black oxide films. A thorough examination of the changes in oxide composition during the bonding procedure was made using coulometric reduction supported by x-ray and electron diffraction. Changes in the state of oxidation of the polymer during the bonding were studied by reflection infra-red spectroscopy.

EXPERIMENTAL DETAILS

The copper used was deoxidised sheet, 1.2 mm thick (B.S. 1172). Low density polyethylene from I.C.I. Ltd., was employed: Alkathene 190400 (density 0.916 g/cm³, m.f.i. 20). It was stated by the manufacturer to be additive-free.

Copper: chemical polishing

Panels of copper measuring 10 cm × 15 cm were washed with dilute hydrochloric acid to remove oxide followed by a wash with distilled water and acetone. The panels were degreased in trichloroethane vapour for 10 minutes and in the boiling liquid for a further 10 minutes. They were next chemically polished by immersion for 10 minutes at room temperature in a solution consisting of:

60 ml orthophosphoric acid (S.G. 1.75)
10 ml nitric acid (S G. 1.42)
30 ml acetic anhydride
8 ml distilled water

They were then washed with distilled water followed by acetone.

Copper: formation of matt black oxide films

The chlorite formed films were prepared by immersing the chemically polished copper in a solution containing

3 g/l sodium chlorite
10 g/l tri-sodium orthophosphate
5 g/l sodium hydroxide

The solution was maintained at 90°C. Various oxidation times were used, 20 minutes being the most common.

X-ray and electron diffraction of the oxides

Electron diffraction patterns of the oxides on the copper surface were obtained using a reflection-diffraction stage in a Jeol JEM 6A transmission electron microscope. Complementary x-ray diffraction results were obtained on some of the oxide scraped from the surface of the copper using a Debye-Scherrer powder camera.

Coating with polyethylene

The copper panels were put in an oven at 200°C which was immediately filled with nitrogen and left for 10 minutes. They were removed and one side was covered with polyethylene powder. After 2 minutes any excess powder was tipped off and the panels returned to the oven now containing air for (usually) 20 minutes coating time. The panels were then removed from the oven and allowed to cool in air.

Peel tests

The polyethylene was scored with a sharp blade to enable 2 cm strips to be peeled on an Instron testing machine in the 180° mode at a peeling rate of 250 mm/min.

Infra-red spectroscopy

Some coatings were removed by immersing the laminate in dilute hydrochloric acid to dissolve the oxide. Infra-red spectra of the surface region were recorded on a Hilger and Watts Infracan mk. II H900 spectrophotometer using a Wiltec internal reflection A.T.R. attachment and a KRS 5 crystal. The "carbonyl index" was obtained for some of the spectra by comparing the absorption in the 1720 cm^{-1} carbonyl region with that at the 1471 cm^{-1} CH_2 absorption as an internal standard.

Coulometric reduction

The coulometric reduction technique, developed by Evans and Miley,¹⁸ measures the quantity of electricity required for the galvanostatic cathodic reduction of a defined area of oxide on the surface of a metal. Idealised

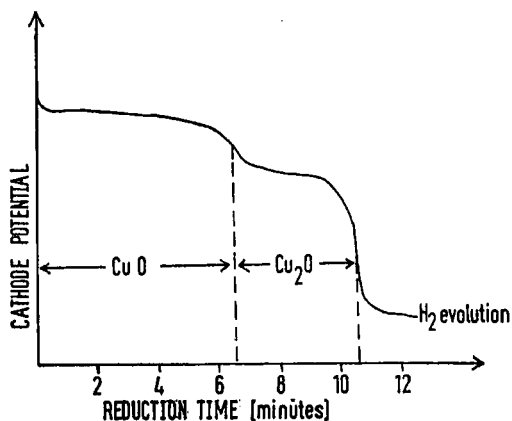


FIGURE 1 Typical coulometric reduction trace for a mixed oxide film.

results for copper shown as a plot of cathode potential against time are given in Figure 1. As the potential remains essentially constant while a particular cathode process, such as the reduction of copper (II) oxide to copper, occurs the reduction time for that process is easily obtained. Using the known value of the current the "thickness" of each oxide in mC cm^{-2} can be calculated. If a density for the oxide is assumed the average thickness can be expressed in units such as μm .

In order to obtain accurate results, Campbell and Thomas¹⁹ showed that it was necessary to exclude oxygen which tends to be reduced at the cathode along with the oxide. Care is also needed in choice of electrolyte. Ammonium chloride, previously used, has been shown to dissolve copper oxides in the absence of a current, and so gives low values for thickness. The conditions

chosen for this work were based on the studies of Bouillon *et al.*²⁰ and Rönnquist.²¹ The apparatus developed is shown in Figure 2.

The electrolyte, 0.1 M sodium hydroxide, was boiled and cooled in a stream of oxygen-free nitrogen, and then forced into the reduction cell which had previously been flushed out with nitrogen. The cathode of the cell was the oxidised copper sheet clamped against a rubber O ring which enabled

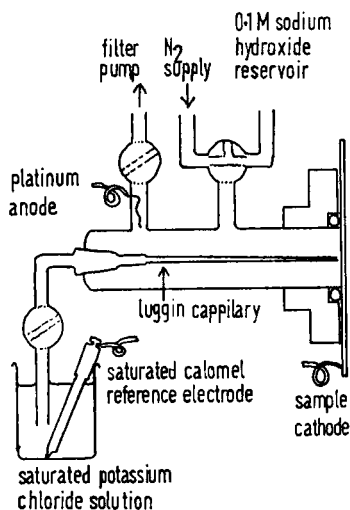


FIGURE 2 The coulometric reduction apparatus for identification and quantitative estimation of oxides on copper.

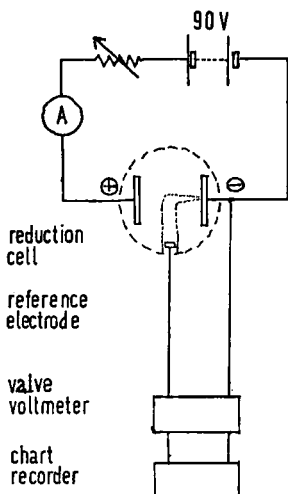


FIGURE 3 The electrical circuit for the coulometric reduction apparatus.

a circular area of 6.16 cm^2 of the oxide to be reduced leaving the rest of the sheet for other tests. The circuit used, Figure 3, provided a consistent current by passing the applied potential through a large resistance R . The cathode potential was measured via a Luggin capillary and saturated calomel electrode connected to a valve voltmeter and recorder.

The form of the results were as shown in Figure 1. The ascription of the rest potentials to the oxides shown was confirmed by x-ray and electron diffraction. The quantitative accuracy of the method was confirmed by chemical dissolution of the oxide from the copper in oxygen-free dilute hydrochloric acid and estimating the copper in solution by atomic absorption spectroscopy. In some of the work it was necessary to assay the oxide under the polyethylene after coating. To do this the polymer was removed by Soxhlet extraction with xylene in a nitrogen atmosphere. The surface remaining was hydrophobic, perhaps due to undissolved polymer gel, and this prevented complete electrolytic reduction of the oxide. This difficulty was overcome either by vacuum deposition of about 300 \AA of gold on the surface to give good electrical contact or, more simply, by adding a non-ionic surfactant to the electrolyte.

Thus, with these refinements, the coulometric reduction technique was capable of reliable qualitative and quantitative analysis of the oxides on copper both before and after coating with polyethylene.

RESULTS AND DISCUSSION

The changes in oxide composition were studied to see what information these might give on the adhesion. Good adhesion between the polyethylene and the matt black films can be obtained with a coating time of 20 minutes, following 10 minutes preheating of the copper panel. The results of heating for up to 30 minutes at the bonding temperature (200°C) will therefore be discussed before considering changes occurring at longer times.

Table II shows results for chlorite-formed films with 20 minutes coating time. Before heating, the oxide was entirely copper (II) oxide. After the coating sequence, there is a loss of the higher oxide and a gain of a similar amount (when expressed in mC cm^{-2}) of copper (I) oxide. These results then are similar to those of Baker and Spencer (Table I). However, in the present work measurements were also made on the reverse side of the copper sheet and somewhat similar changes occur there!

As it appeared that the changes in oxide composition during coating were not necessarily a consequence of the presence of the polymer, some sheets with chlorite-formed films were heated for 30 minutes in nitrogen and others for 20 minutes in air then the oxide changes noted (Table III and IV). The results for the inert atmosphere are similar to the results for the coated side

in Table II, i.e. n coulombs of higher oxide have been converted to n coulombs of the lower oxide. When heated in air the change is similar except that rather more copper (I) oxide is formed.

It seems that two reactions are occurring. First, in the inert atmosphere n

TABLE II

Composition of chlorite-formed films on copper before and after coating with polyethylene at 200°C in air for 20 minutes. Each result is the mean of 10 reductions. 95% confidence limits are given

Side of copper sheet	Oxide composition mC/cm ²				
	Initial CuO	Final CuO	Loss CuO	Final Cu ₂ O	Final total
Coated side	176±4	146±4	30	30±1	176
Reverse side	176±4	143±4	33	43±3	186

TABLE III

Changes in composition of chlorite-formed films on copper brought about by heating for 30 minutes in nitrogen at 200°C

	Oxide composition mC/cm ²				
	Initial CuO	Final CuO	Loss CuO	Final Cu ₂ O	Final total
	50	40	10	12	52
	168	87	81	80	167
	173	117	56	48	165
	194	154	40	42	196
	215	186	29	35	221
	220	173	47	53	226

coulombs of CuO are changed to n coulombs of Cu₂O. If CuO was reduced by metallic copper such a change would be observed:



This reaction seems to be thermodynamically feasible with a free energy change at 500 K of about -18 kJ mol^{-1} . However, it has been pointed out that for metal-metal oxide reactions, the strain and interface components of the total free energy can become significant, but are difficult to assess.²² There is some support for the reaction to be found in the literature.^{23,24}

The second reaction, occurring in addition to (2) in the presence of air, is the oxidation of metallic copper well known to occur at 200°C:



Thus for normal coating times the oxide changes occurring (Table II) are satisfactorily explained without postulating reaction between copper (II) oxide and the polymer according to Eq. (1). Indeed, Eq. (1) requires n coulombs of copper (II) oxide to be changed to $n/2$ coulombs of copper (I) oxide which is incompatible both with the results of Table II and Baker and Spencer's own results (Table I).

An alternative explanation, logically possible although chemically unlikely, of the results in Table II is that copper (II) oxide is reduced by reaction (1) and *exactly* the necessary additional copper (I) oxide is produced by reaction

TABLE IV

Changes in composition of chlorite-formed films on copper brought about by heating for 20 minutes in air at 200°C

Oxide composition mC/cm ²				
Initial CuO	Final CuO	Loss CuO	Final Cu ₂ O	Final total
125	97	28	40	137
129	112	17	37	149
168	155	13	38	193
214	190	24	43	233
217	168	49	53	221
249	192	57	72	264
320	274	46	54	328
362	294	68	72	370

(3). To test this possibility copper with a copper (I) oxide film was coated with polyethylene and the oxide was assayed before and after coating. The results in Table V make it clear that unstabilised polyethylene effectively prevents oxygen from reacting with the copper by reaction (3).

For longer coating times the situation is more complex. Beyond about 20 minutes the adhesion deteriorates somewhat, Figure 4, and most of the copper (II) oxide is reduced, Table VI. Less copper (I) oxide is formed than Eq. (2), or indeed Eq. (1), requires. With a coating time as long as 40 minutes the polymer is visibly degraded: it has a brownish tinge. The infra-red spectrum, Figure 5, shows that oxidation, as measured by the appearance of carbonyl group absorption, is insignificant until a coating time of more than 20 minutes. After this oxidation increases rapidly. It is interesting to note an

abrupt change in density, which has been associated with degradation,²⁵ also occurs after 20 minutes heating at 200°C, Figure 6. It seems reasonable to conclude for the long coating times that some reduction of oxides of copper occurs by products of degradation of the polymer.

TABLE V

Changes in composition of copper (I) oxide films on copper after coating with polyethylene at 200°C in air for 20 minutes. The number of reductions for each set of conditions is shown in brackets and 95% confidence limits are given

Pretreatment of copper	Oxide Composition mC/cm ²		
	Initial Cu ₂ O	Final Cu ₂ O	
		Coated side	Reverse side
Chemically polished	8.5±1.3 (6)	8.8±1.5 (9)	24.6±2.7 (7)
Oxidised 200°C 20 min air	23.8±3.5 (5)	23.4±3.3 (4)	27.3±4.1 (6)

TABLE VI

Composition of chlorite-formed films on copper before and after applying polyethylene at 200°C in air for various coating times

Coating time (minutes)	Oxide composition mC/cm ²								
	Initial CuO	Coated side				Reverse side			
		Final CuO	Loss CuO	Final Cu ₂ O	Final total	Final CuO	Loss CuO	Final Cu ₂ O	Final total
20	176	146	30	29	175	141	35	38	179
40	192	0	192	83	83	150	42	60	210
60	178	0	178	62	62	152	26	53	205

CONCLUSIONS

The good adhesion of polyethylene to the matt black oxide films formed in "Ebonol C" or alkaline chlorite solution, which can be obtained with modest coating times at elevated temperatures, does not depend as previously supposed, upon the copper (II) oxide oxidising the polymer. Changes which

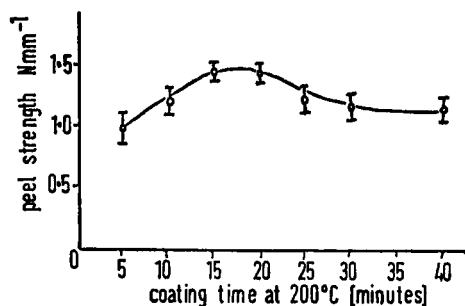


FIGURE 4 Effect of coating time on the peel strength of low density polyethylene applied at 200°C to copper with a chlorite-formed film produced by 20 minutes oxidation. Bars represent 95% confidence limits.

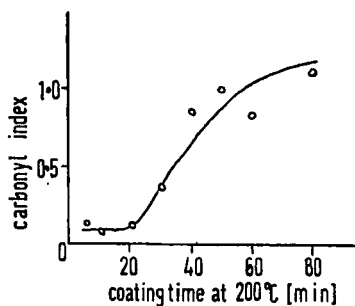


FIGURE 5 Adhesion of polyethylene to chlorite-formed films on copper. Variation with coating time at 200°C of carbonyl index of the region of polymer adjacent to the substrate.

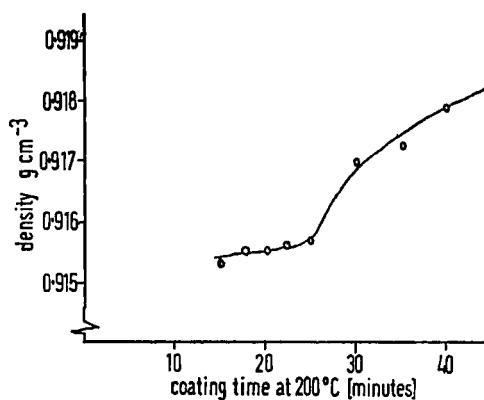
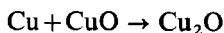


FIGURE 6 Adhesion of polyethylene to chlorite formed films on copper. Variation of the density of the polymer with coating time at 200°C.

occur in the oxide composition do not involve reaction with the polymer and are a consequence of the tendency of copper (II) oxide to change to the thermodynamically more stable copper (I) oxide at 200°C which probably occurs by reaction with metallic copper,



Indeed the infra-red spectrum of interfacial regions of the polymer show that little oxidation has occurred. The carbonyl index is less than 0.15 which should be compared with a value of about 0.35 for polyethylene applied to steel in similar experimental conditions. This suggests that adhesion to these matt black oxide films may provide another example of good adhesion of polyethylene to metals in the absence of polymer oxidation. Such adhesion was found to be associated with an unusual substrate topography.^{16,17} The possibility that the surface topography exerts a critical role in adhesion to the matt black oxide films on copper is examined in detail elsewhere.²³

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