

The effect of pulsed reverse current on the polarization behaviour of acid copper plating solutions containing organic additives

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The polarization behaviour of acid copper solutions containing polyethers, sulphopropyl sulphides and chloride ions was studied using both direct and pulsed reverse current. The effect of these additives on the rest potentials of copper foils immersed in the electrolyte was also studied. Polyethers were found to have an inhibiting effect on the deposition of copper whereas the sulphopropyl sulphides produced a stimulating (i.e. depolarizing) effect. Chloride ion concentration was found to have an influence on the adsorption characteristics of the polyether. The use of pulsed reverse current in solutions containing both polyether and sulphopropyl sulphide was found to inhibit the adsorption/diffusion of the sulphopropyl sulphide at the cathode surface. Thus at higher current densities, above 2 A dm^{-2} , the inhibiting effect of the polyether produced a shift in the cathodic polarization potential to more negative values as compared with an equivalent current density using direct current. At lower current densities, below 2 A dm^{-2} , the depolarization effect of the sulphopropyl sulphide was still effective. This effect of pulsed current on additive containing solutions can improve dramatically the metal distribution in low current density areas on plated items. This was illustrated by plating Hull cell panels using both pulsed and direct current.

1. Introduction

The use of pulsed reverse current on acid copper solutions has been shown in practical applications in the printed circuit industry to produce an increase in the 'hole throwing power' of acid copper solutions containing organic additives. The purpose of this study was to determine the main reasons for this observed effect. This was achieved by examining the effects of organic addition agents which are used normally in commercial formulations as brighteners. The effect of these additives on the throwing power of the electrolytes was assessed by comparing the slopes of potential/current density curves. Generally, the higher the rate of change of potential with current density, the better the throwing power because this tends to shift the current density distribution from a primary to a secondary distribution.

Commercial brightener systems almost invariably contain a synergistic combination of addition agents consisting of

(i) A polyether which may be polyethylene glycol, polypropylene glycol, block or random co-polymers of propylene and ethylene oxide or a polyether surfactant having one or more hydrophobic groups. This component acts as a grain refiner but does not give bright deposits by itself.

(ii) A sulphopropyl sulphide or disulphide. Examples of these would be mercaptopropane sulphonic acid or its disulphide. The combination of a polyether

and a sulphopropyl sulphide will give bright deposits but no appreciable levelling.

In addition to these basic brightener components, other organics may be present which act as levellers or have additional brightening properties. These brightener systems are the subject of several patents [1–5]. For the purpose of this study, a simple brightener system consisting of mercaptopropane sulphonic acid or its disulphide in combination with a random copolymer of polyethylene oxide and polypropylene oxide (25%) of various molecular weights was used. This enabled an understanding of the cause of the increase in throwing power obtained with pulsed reverse current to be achieved.

2. Experimental procedure

2.1. Preparation of the electrolyte

The same basic electrolyte was used for all of the tests; its formulation was as follows: copper sulphate (pentahydrate), 75 g l^{-1} ; sulphuric acid (98%), 114 ml l^{-1} ; chloride ion (as Cl^-), 60 p.p.m. The chloride ion concentration was subject to alteration when the effect of this was studied.

2.2. Pulse parameters

To limit the number of variables, pulse parameters were held constant for all the tests. The program used

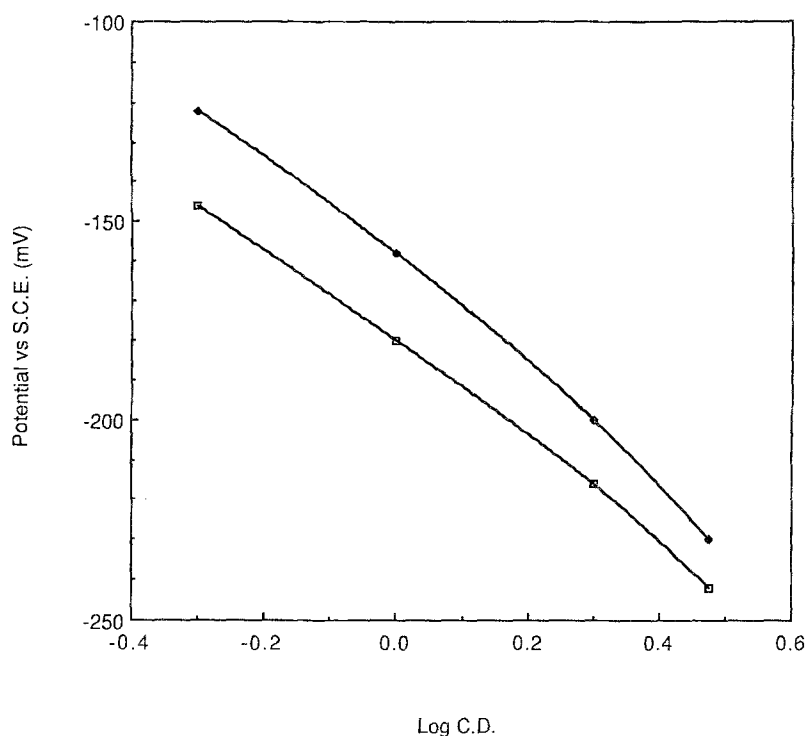


Fig. 1. Effect of pulsed reverse (◆) and direct current (◻) on the base electrolyte.

was one that had been found effective in practice and consisted of the following: cathodic pulse time, 10 ms; anodic pulse time, 0.5 ms; anodic/cathodic current density ratio, 3:1.

2.3. Polarization studies

Polarization studies using a rectangular cell of fixed geometry were carried out using both direct and pulsed current. Cathode potential was determined using a salt bridge positioned so that it was approximately 1 mm from the centre of the cathode surface in conjunction with a saturated calomel electrode. The potential was measured using a Solartron digital voltmeter. In the case of pulsed current, the figure obtained represented the average potential of the cathode. Vigorous air agitation was used in the cell in order to minimise the effects of concentration polarization and to be as close as possible to commercial practice.

Steady-state cathode potentials were recorded at current densities of 0.5, 1, 2 and 3 A dm⁻² and a temperature of 22°C for a number of different additive combinations; 3 A dm⁻² was chosen as the maximum current density to avoid concentration polarization masking polarization effects produced by the additives themselves. In all cases, rest potentials when no current was passing were also recorded. To confirm that changes in the polarization slope did in fact produce changes in metal distribution, Hull cell tests were carried out and thickness measurements performed at various distances along the panel.

2.4. Rest potential studies

Before current was applied the potential of the copper substrate immersed in the electrolyte was measured

with and without additives. This then allowed the calculation of exchange current densities by Tafel extrapolation to the rest potential.

3. Results and discussion

3.1. Results of polarization studies

Results of the polarization studies are given in the form of Tafel plots, i.e. potential against log of the current density in A dm⁻². If ideal Tafel behaviour is obeyed, these plots would all be straight lines.

3.1.1. Effect of direct and pulsed reverse current on the base electrolyte. It can be seen from the results shown in Fig. 1 that with both pulsed and direct current, the electrolyte followed Tafel behaviour reasonably closely over the current density range studied. The slopes of the lines were also very similar. Thus from a polarization point of view, the use of pulsed reverse current with an electrolyte without additives would not be expected to improve throwing power.

3.1.2. Effect of direct and pulsed reverse current on electrolytes containing single additives. The effect of single additives on the polarization characteristics of the electrolytes at a chloride concentration of 60 p.p.m. was studied. The effect of adding (i) 75 p.p.m. polyether (Oxilube 50 000, referred to as Ox); (ii) 40 p.p.m. mercaptopropane sulphonic acid-sodium salt (referred to as MPS); (iii) 40 p.p.m. bis(3-sulphopropyl)disulphide-disodium salt (referred to as SSP) — was studied using direct and pulsed reverse current: results are shown in Figs 2 and 3. The concentrations used were chosen because these are typical of the concentrations used in commercial brightener systems. (Oxilube is a trade mark of Shell Chemicals

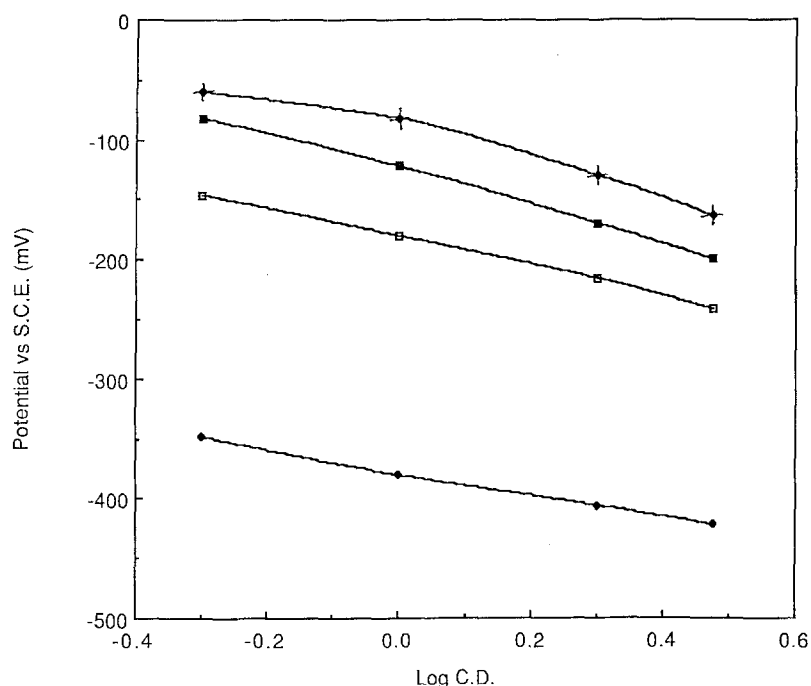


Fig. 2. Effect of single additives on the polarization behaviour of an acid copper electrolyte using direct current: □ no additions, ◆ Oxilube, ■ MPS, ▲ SSP.

Ltd. It is a random co-polymer of ethylene and propylene oxides containing 25% propylene oxide by weight. The average molecular weight is 50 000 except where stated.)

It can be seen from the results shown in Fig. 2 that the Oxilube shifted the potential at which the deposition took place to more negative values. The two sulphopropyl sulphides used in the experiment shifted the potential of deposition to less negative values. It is probable therefore that they had some catalytic effect on deposition. As in Fig. 1, the slopes of all the lines are similar indicating that these additives would have little effect on the throwing power.

It can be seen from the results shown in Fig. 3 that the trends observed with pulsed current are the same as for direct current in that the polyether still produced

a large shift to more negative values in the deposition potential at a given current density while the sulphur compounds produced a shift to less negative potentials owing to their catalytic effect. Again the slopes of the lines are not significantly different, thus the addition of single additives would not lead to an increase in throwing power by using pulsed reverse current.

3.1.3. Effect of direct and pulsed reverse current on electrolytes containing sulphopropyl sulphides and polyether in combination. The effects of direct and pulsed reverse current were then examined using two additives in combination. These measurements were taken at several different chloride levels. The results of these measurements are shown in Figs 4, 5, 6 and 7.

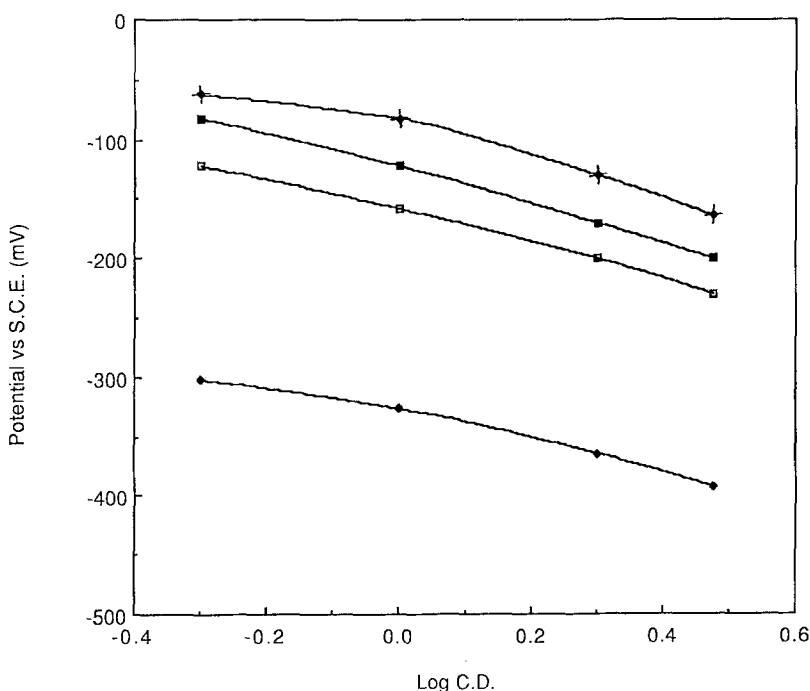


Fig. 3. Effect of single additives on the polarization behaviour of an acid copper electrolyte using pulsed reverse current: □ no additions, ◆ Oxilube, ■ MPS, ▲ SSP.

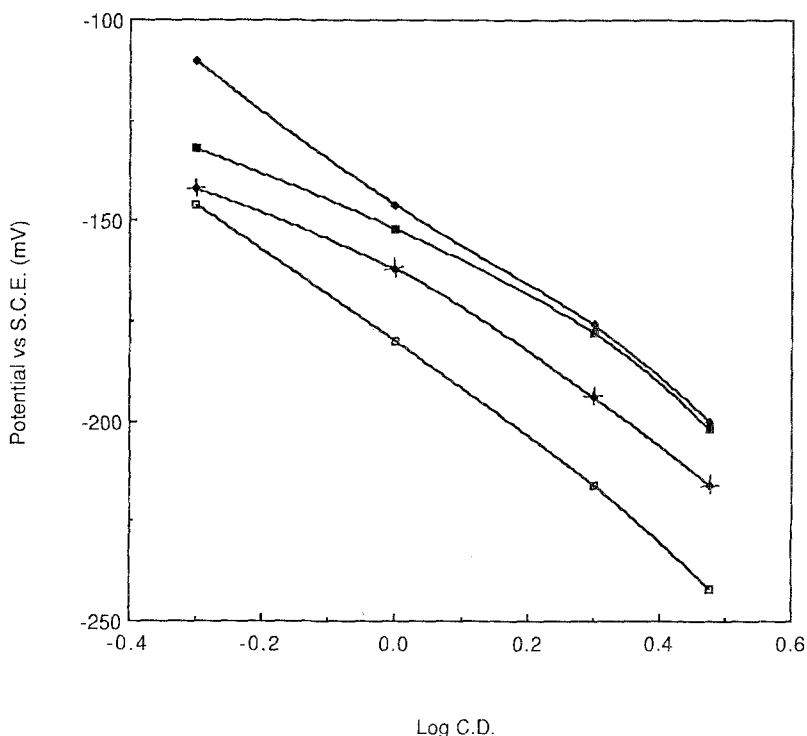


Fig. 4. Effect of varying chloride concentration on an electrolyte containing MPS (40 p.p.m.) and Oxilube 50 000 (75 p.p.m.) using direct current: \square no additions, \blacklozenge 60 p.p.m. Cl^- , \blacksquare 100 p.p.m. Cl^- , \blacktriangle 200 p.p.m. Cl^- .

Figure 4 indicates that with direct current, there would be little effect on the throwing power when the additives are combined. Additions of chloride produced a shift in deposition potential to more negative values, which suggested that chloride influences the adsorbability of the polyether. However, deposition potentials with the combined additives were still less negative than when no additives were present which suggested that the sulphopropyl sulphide was preferentially adsorbed.

Figure 5 shows the effect of chloride concentration on the polarization behaviour of an electrolyte containing 40 p.p.m. of SSP and 75 p.p.m. of Oxilube 50 000 using direct current.

It can be seen from these results that this additive behaved similarly to MPS. Again, raising the chloride level raised the deposition potential but did not change the slope of the polarization curve.

The effect of pulsed reverse current on the polarization behaviour was then examined using the same additive concentrations as described for Figs 4 and 5. Figures 6 and 7 show the results obtained with MPS and SSP, respectively. It can be seen from these figures that the use of pulsed reverse current had a large effect on the polarization slope and that similar effects were obtained with MPS and SSP. Significant deviation from Tafel behaviour occurred when pulsed reverse current was applied to these solutions. It appeared

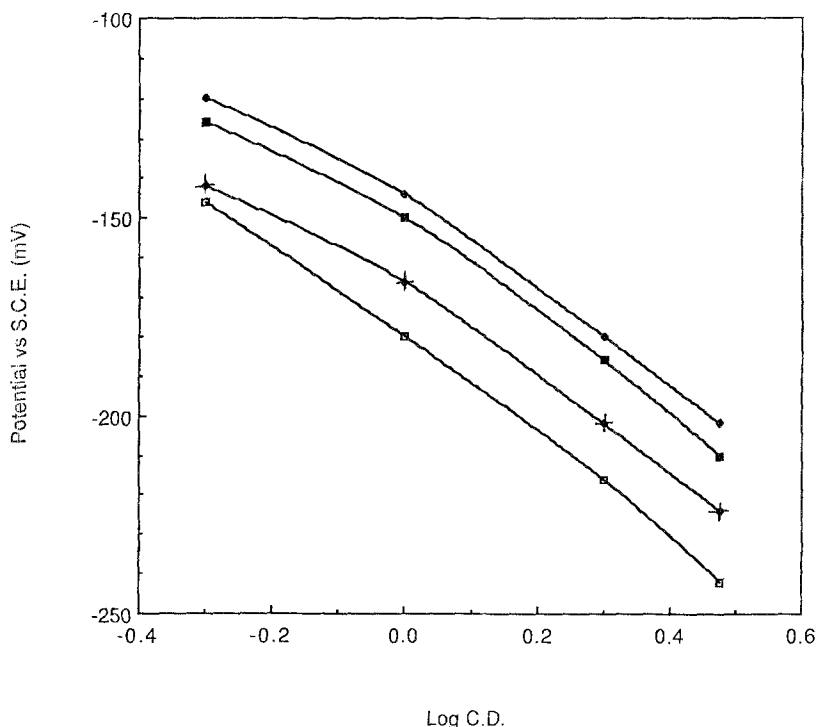


Fig. 5. Effect of varying chloride concentration on an electrolyte containing SSP (40 p.p.m.) and Oxilube 50 000 (75 p.p.m.) using direct current: symbols same as in Fig. 4.

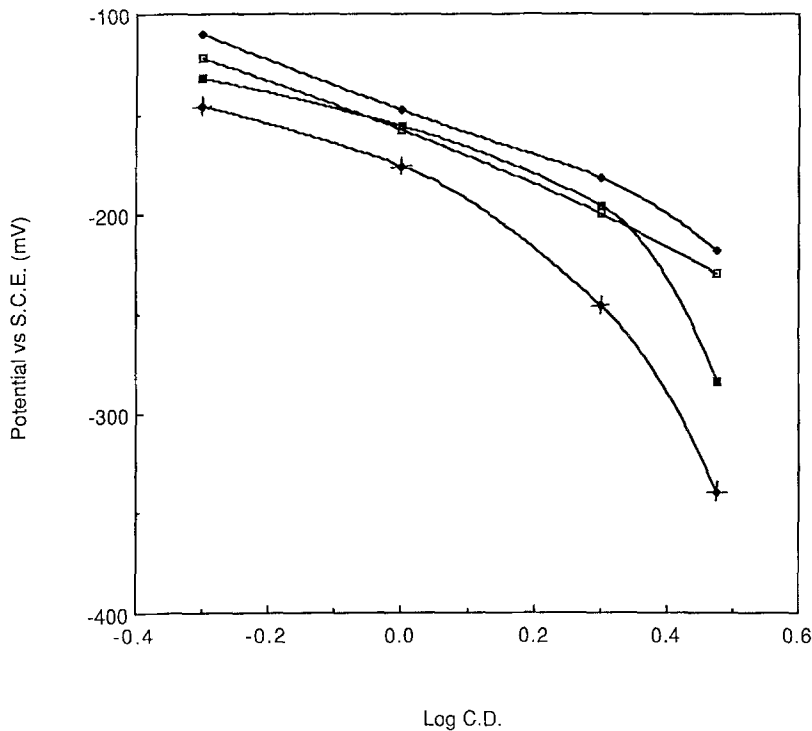


Fig. 6. Effect of varying chloride concentration on an electrolyte containing MPS (40 p.p.m.) and Oxilube 50000 (75 p.p.m.) using pulsed reverse current: symbols same as in Fig. 4.

that at higher current densities, polarization of the cathode surface occurred which in turn meant that low current density areas were depolarized. This would encourage the deposition of metal at low current density and so should give better metal distribution. Chloride concentrations of 100 to 200 p.p.m. were necessary for this effect to be maximized.

3.1.4. Effect of varying polyether concentration using direct current. The effect of the polarization characteristics of concentrations of Oxilube 50000 ranging from 0.75 to 75 p.p.m. was studied using direct current. These results are shown in Fig. 8.

It can be seen from the results illustrated in this figure that even very small additions of the polyether had an appreciable effect on the deposition potentials recorded. The effect of polyether concentration increased rapidly up to a concentration of 37.5 p.p.m. and above this concentration, there was little effect on the deposition potential. This suggested that around this concentration, there was sufficient polymer present in the solution to reach adsorption equilibrium. Thus, the optimum concentration of polyether was probably between 30 and 75 p.p.m. Concentrations up to 750 p.p.m. appeared to produce essentially the same results as 75 p.p.m.

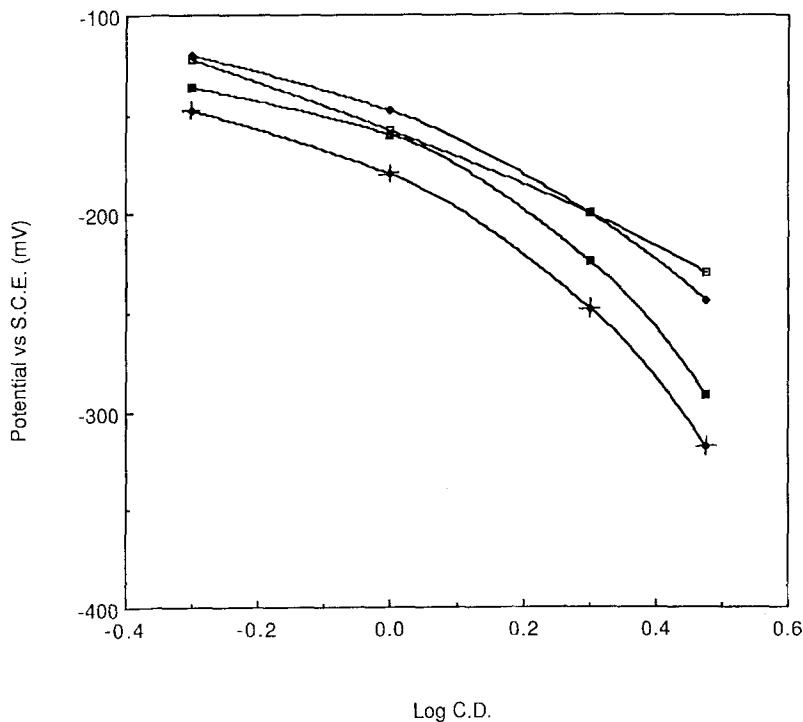


Fig. 7. Effect of varying chloride concentration on an electrolyte containing SSP (40 p.p.m.) and Oxilube 50000 (75 p.p.m.) using pulsed reverse current: symbols same as in Fig. 4.

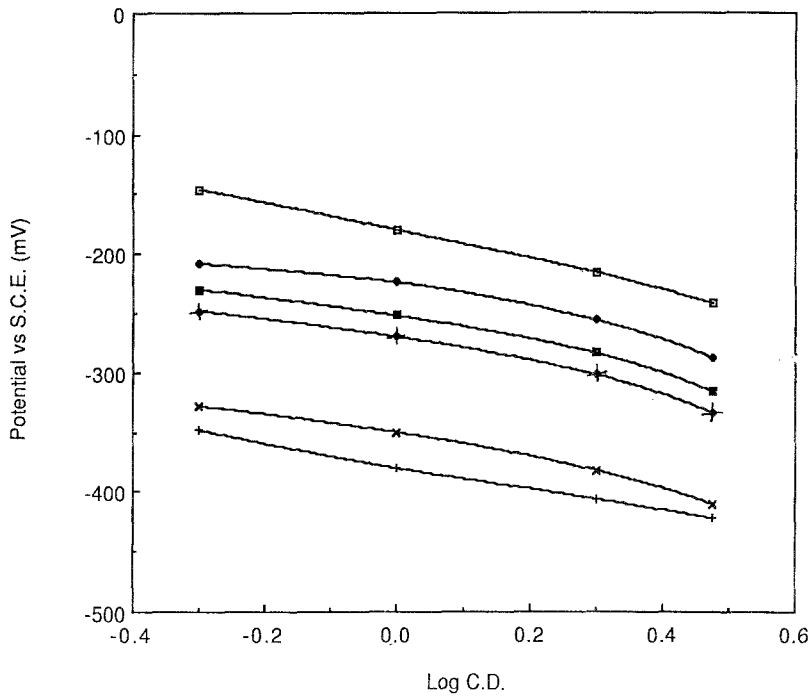


Fig. 8. Effect of varying Oxilube concentration at a chloride concentration of 100 p.p.m. using direct current: \square no additions, \blacklozenge 0.75, \blacksquare 3.75, \blacklozenge 7.5, \times 37.5, $+$ 75 p.p.m.

3.1.5. *Effect of direct and pulsed reverse current on an electrolyte containing polyether plus varying concentration of MPS.* Using an electrolyte containing 100 p.p.m. of chloride ion and 75 p.p.m. of Oxilube 50 000, the effect of varying the concentration of MPS using both direct and pulsed reverse current was studied. The results are shown in Figs 9 and 10.

It can be seen from Fig. 9 that over the whole concentration range studied, varying the MPS concentration had little effect on the polarization curves although, at concentrations of 40 p.p.m. and above, there was slightly more depolarization at higher current densities than at lower concentrations.

The effects of varying the concentration of MPS with pulsed reverse current can clearly be seen in Fig. 10. At the lowest concentrations, pulsed current

reduced the depolarizing effect of the MPS throughout the current density range. At concentrations of 10 to 40 p.p.m., the depolarizing effect was reduced at progressively higher current densities until at 100 p.p.m., the depolarizing effect of the MPS appeared not to be affected. Thus it was concluded that the most effective concentration range for MPS was between 10 to 40 p.p.m.

3.1.6. *Effect of polyether molecular weight on the polarization characteristics with direct current and pulsed reverse current.* The Oxilube which was used for the tests is available in several molecular weight ranges. The effect of changing the molecular weight of the Oxilube was investigated and the results are shown in Figs 11, 12 and 13.

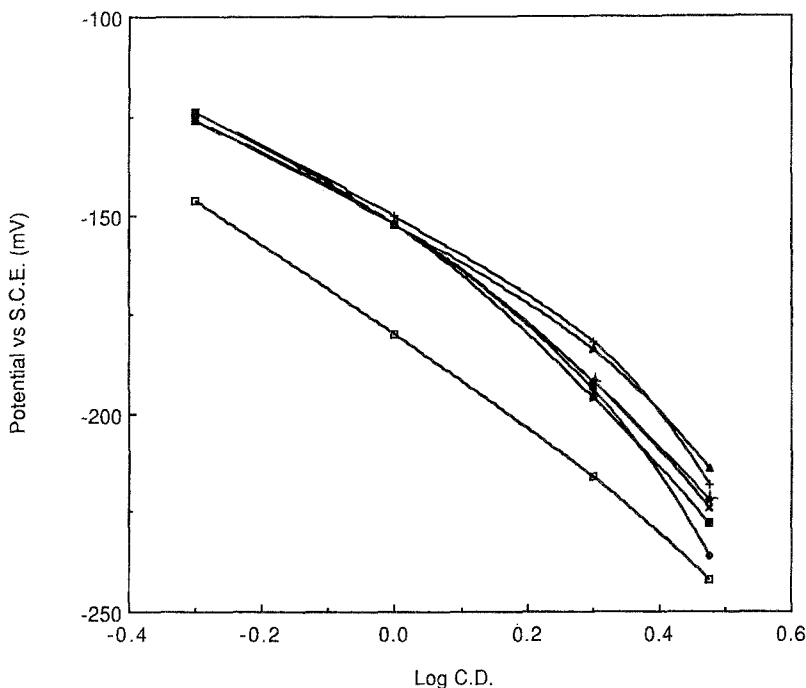


Fig. 9. Effect of varying MPS concentration in an electrolyte containing 75 p.p.m. of Oxilube 50 000 and 100 p.p.m. of chloride ion using direct current: \square no addition, \blacklozenge 1, \blacksquare 5, \blacklozenge 10, \times 20, $+$ 40, \blacktriangle 100 p.p.m. MPS.

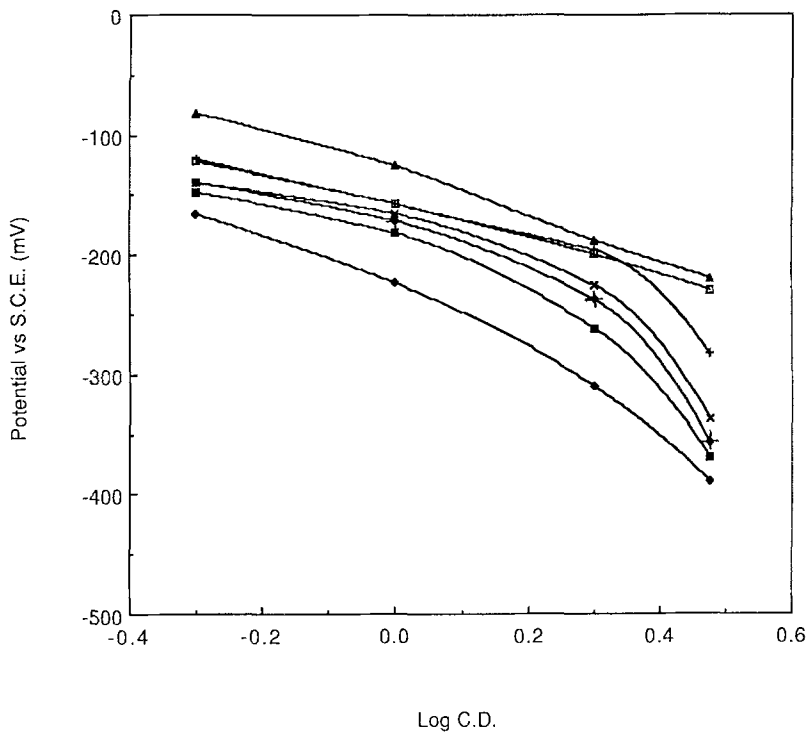


Fig. 10. Effect of varying MPS concentration in an electrolyte containing 75 p.p.m. of Oxilube 50 000 and 100 p.p.m. of chloride ion using pulsed reverse current: symbols same as in Fig. 9.

Three polymers having molecular weights of 18 000, 50 000 and 92 000 were examined at a concentration of 75 p.p.m. These additives were examined singly using direct current and in conjunction with 20 p.p.m. of MPS with both direct and pulsed reverse current.

It can be seen from Fig. 11 that the molecular weight of 50 000 produced the highest deposition potentials. It may be expected that at higher molecular weights, the surface coverage would increase which would cause a rise in the deposition potential. However, beyond a certain molecular weight, steric factors may prevent adequate coverage. This was observed with the high molecular weight (92 000) polymer. It

was also noted that deposits from the electrolyte with the 92 000 molecular weight polymer gave very uneven nodular deposits.

It can be seen from the results shown in Fig. 12 that using direct current for a solution containing 20 p.p.m. of MPS, the electrolyte containing the polymer with a molecular weight of 50 000 gave the most negative deposition potentials and also produced a slope which was slightly greater than using higher or lower molecular weights.

Figure 13 illustrates the results obtained using an electrolyte containing 20 p.p.m. MPS with the three different molecular weight ranges using pulsed reverse

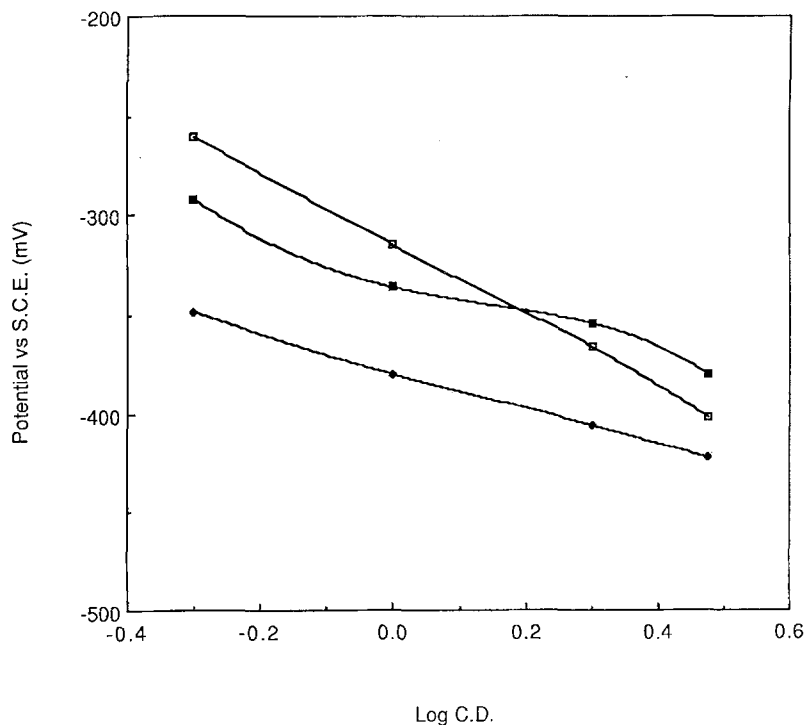


Fig. 11. Effect of varying molecular weight on the polarization characteristics of an electrolyte containing polyether using direct current: □ Ox 18, ◆ Ox 50, ■ Ox 92.

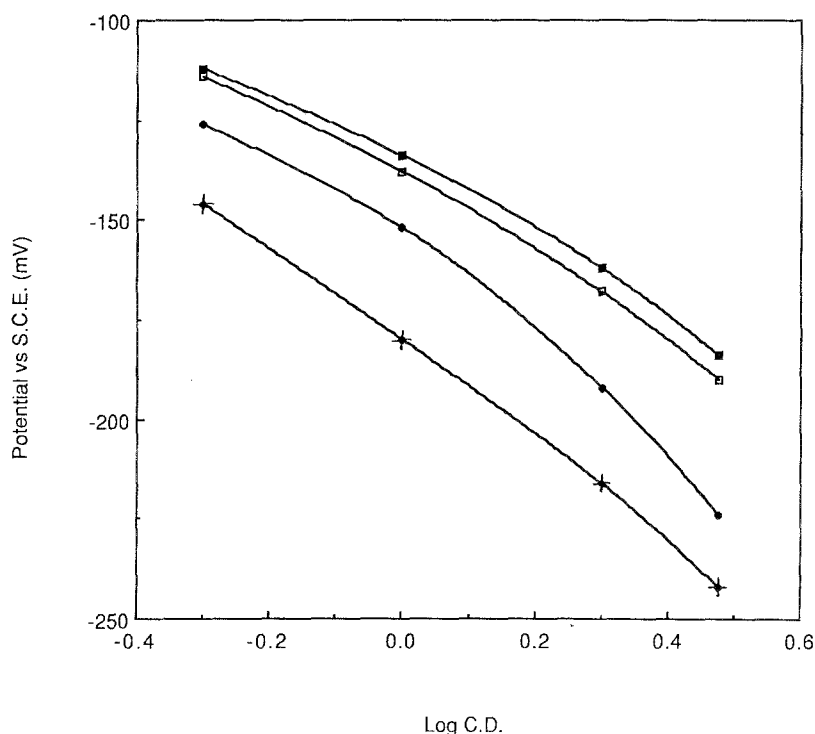


Fig. 12. Effect of varying molecular weight of polyether on the polarization characteristics of an electrolyte containing MPS (20 p.p.m.) and polyether using direct current: \square Ox 18 20 p.p.m., \blacklozenge Ox 50 20 p.p.m., \blacksquare Ox 92 20 p.p.m., \times no additions.

current. It can be seen from these results that the greatest effect on the polarization slopes was obtained with the 50 000 molecular weight polymer. This indicated that from the viewpoint of improving throwing power, the 50 000 molecular weight polymer was the most suitable of the three molecular weights studied.

3.2. Results of rest potential studies

The results in Table 1 illustrate that the addition of Oxilube to the electrolyte caused the rest potential to become more negative up to a concentration of 7.5 p.p.m. The exchange current densities, which were

calculated by Tafel extrapolation, also showed a decrease with increasing polymer concentration.

The effect on the rest potential of additions of MPS and SSP are shown in Table 2.

It can be seen from these results that the addition of both MPS and SSP caused the rest potential to move to less negative values. Calculation of exchange current densities showed an increase. This was due to the catalytic effect of these compounds on the reduction and oxidation of copper.

Table 3 shows the effect of the combined additives (sulphopropyl sulphides + polyether) on the rest potentials and exchange current densities.

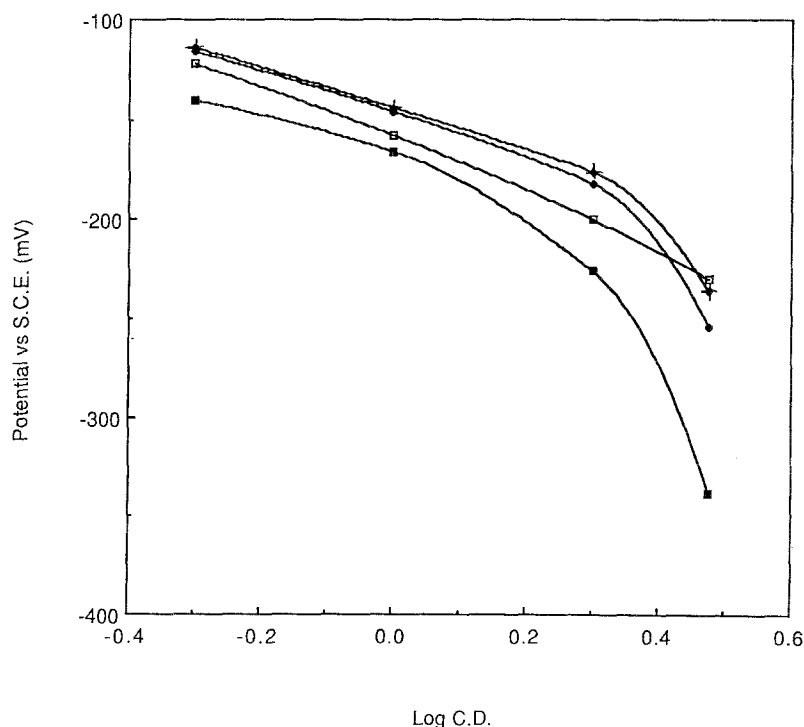


Fig. 13. Effect of varying molecular weight of polyether on the polarization characteristics of an electrolyte containing MPS (20 p.p.m.) and polyether using pulsed reverse current: \square no additions, \blacklozenge Ox 18 20 p.p.m., \blacksquare Ox 50 20 p.p.m., \times Ox 92 20 p.p.m.

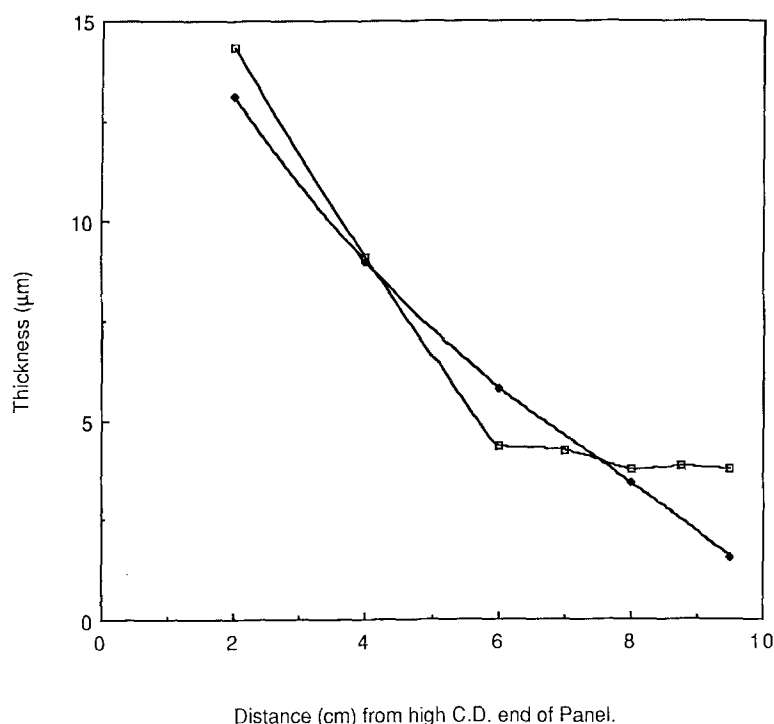


Fig. 14. Effect of pulsed reverse current on the metal distribution on a Hull cell panel from an electrolyte containing 40 p.p.m. MPS, 75 p.p.m. of Oxilube and 100 p.p.m. of chloride. Conditions 2 A, 10 min, 22°C: □ pulsed reversed current, ◆ direct current.

In combination, the additives produced an increase in the exchange current density as compared to an electrolyte with no additives.

To summarize the results of the polarization studies, it appeared from the data obtained that electrolytes containing both polyether and sulphopropyl sulphides, in the presence of chloride ion, could give a much better throwing power at low current densities with pulsed current than with direct current. To test this hypothesis, Hull cell panels were plated at 2 A cell current using both pulsed and direct current. In the case of pulsed reverse current, 2 A was the time averaged overall current. Thickness distribution profiles of the panels were measured using a coulometric method and the results are shown in Fig. 14.

It can be seen from the thickness distribution displayed in this figure that a very different metal distribution was obtained by the use of pulsed reverse current with the electrolyte containing additives especially at low current densities where much more metal was deposited than when direct current was used. Thus it may be expected that on items such as printed circuit boards, an improvement in the 'hole throwing power' would result.

Table 1. Effect of additions of polyether on the rest potentials and exchange current densities (100 p.p.m. Cl^-)

Additions (p.p.m. Ox 50 000)	Rest potential (mV)	Exchange current density ($10^{-4} A cm^{-2}$)
0	-38	6.96
0.75	-78	2.95
3.25	-92	2.91
7.5	-100	2.36
32.5	-100	0.35
75	-100	0.13

3.3. Factors affecting the incorporation of organic additives in acid copper solutions

The mechanisms of incorporation of organic additives into nickel deposits have been discussed in some detail by Edwards [6]. He identified two general cases for the incorporation of additives where this is controlled solely by diffusion and where a combination of adsorption and diffusion occurs. Diffusion alone is rarely encountered and only occurs if irreversible adsorption occurs at the cathode surface. Usually the incorporation of organic additives is controlled by an adsorption/diffusion mechanism. Research into the adsorption characteristics of polyethers and sulphopropyl sulphides from acid copper electrolytes has indicated that in the case of these additives, the rate of incorporation at the cathode is negligible and so the surface effect of these additives is controlled entirely by adsorption. Current theories concerning the effect of these organic compounds at the cathode are as follows.

3.3.1. Adsorption of polyether molecules. The adsorption behaviour of polypropylene glycol has been studied using differential capacitance methods by Stoichev *et al.* [7, 8]. The results obtained showed that,

Table 2. Effect of sulphopropyl sulphides on rest potentials and exchange current densities (60 p.p.m. Cl^-)

Additions	Rest potential (mV)	Exchange current density ($10^{-4} A cm^{-2}$)
No additions	-38	6.96
40 p.p.m. MPS	-18	19.6
40 p.p.m. SSP	-18	27.6

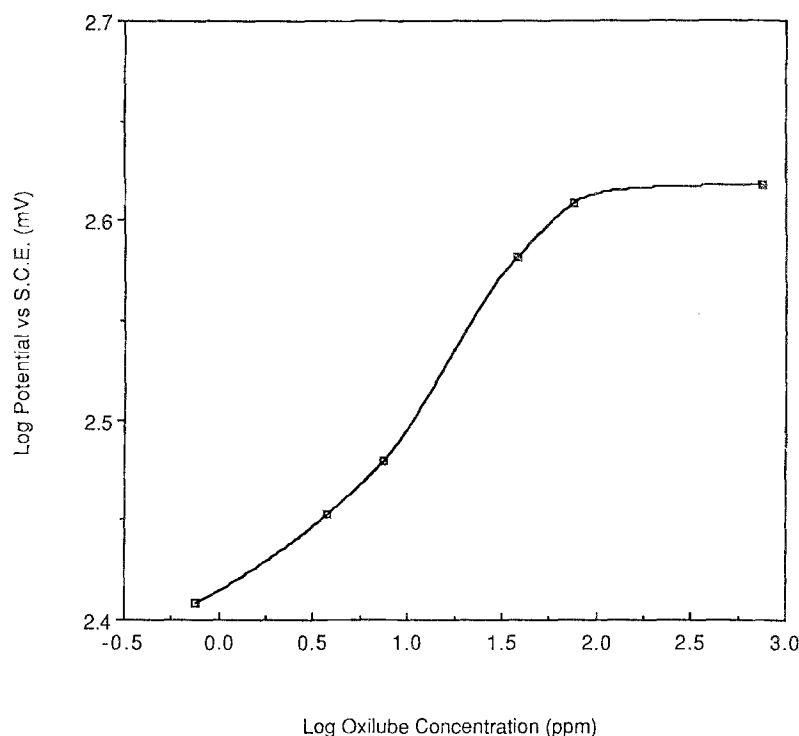


Fig. 15. Effect of polyether concentration on the deposition potential of copper at 2 A dm^{-2} , 22°C .

in a support electrolyte consisting of $1 \text{ N H}_2\text{SO}_4$, the polypropylene glycol was very weakly adsorbed. However, as the results in Fig. 2 in this paper show, the presence of a polyether in an acid copper electrolyte has a very strong influence on the deposition potentials, which are shifted to more negative values by up to 200 mV. An explanation for this was provided by Yokoi *et al.* [9] who suggested that the polyether molecules can form complexes with cuprous ions and be adsorbed on the surface as a cationic polyelectrolyte. In the absence of chloride ions, the cuprous ions are adsorbed on the cathode surface and reduced to copper metal with little shift in deposition potential. It was proposed by Yokoi *et al.* [9] that chloride ions could become specifically adsorbed on the cathode and interact with the chelated cuprous ions effectively binding the polyether molecule to the cathode surface. This process would shift the deposition potential to more negative values since incoming copper ions would have to pass the barrier of adsorbed polyether. This explains the influence of chloride ions on the adsorption behaviour of the polyether which can be observed in the results section. Also, because the polyether is bound to the surface via a bond between chelated cuprous ions and adsorbed

chloride ions, it is unlikely to become incorporated into the deposit. Thus the surface coverage is likely to be governed solely by adsorption and so diffusion can be ignored. This explains the ability of the polyether to suppress deposition over a wide range of potentials. Above a certain molecular weight, steric factors may prevent uniform surface coverage by the polyether. This was observed when using the highest molecular weight polymer (Oxilube 92 000). In this case, nodular deposits were formed because of this factor, because deposition would be likely to occur at a higher rate in areas where the polymer was not adsorbed. A log/log plot of potential against Oxilube concentration (see Fig. 15) indicated that at a temperature of 22°C , maximum surface coverage was obtained at a concentration of around 75 p.p.m. since no appreciable change in deposition potential was obtained at higher concentrations.

3.3.2. Adsorption of the sulphopropyl sulphide. The adsorption of an organic disulphide (composition unspecified) on a copper surface has been studied by Stoichev *et al.* [7, 8]. It was found that, in a solution of $1 \text{ N H}_2\text{SO}_4$, the disulphide was strongly adsorbed on the copper surface. An interesting finding from this work was that the degree of adsorption had an inverse relationship with concentration. It was proposed that this was caused by the anionic nature of the disulphide causing mutual repulsion thus preventing increased adsorption with increasing concentration. This observation provides an explanation for the results observed in Fig. 9 in this present paper where a concentration of 1 p.p.m. of the added MPS in the presence of polyether produced almost the same effect on the deposition potentials as 100 p.p.m. In an electrolyte containing polyether molecules, the effect of adding a sulphopropyl sulphide is to cause the deposi-

Table 3. Effect of combined additives on the rest potentials and exchange current densities (60 p.p.m. Cl^-)

Additions	Rest potential (mV)	Exchange current density ($10^{-4} \text{ A cm}^{-2}$)
No additions	-38	6.96
75 p.p.m. Ox + 40 p.p.m. MPS	-34	10.6
75 p.p.m. Ox + 40 p.p.m. SSP	-36	8.7

tion potentials to shift to around the same values as for a polyether free system. This may be due to either preferential adsorption on the surface and exclusion of the polymer layer, or by specific adsorption on the surface and catalysis of copper deposition. The fact that the polyether and sulphopropyl sulphide work synergistically together in brightener formulations suggests that the latter case is the more likely. This is further supported by the proposed mechanism of adsorption of the polyether by cuprous ions interacting with specifically adsorbed chloride ions. Because the chloride ions are small, they are not likely to be displaced by the added sulphopropyl anions. The actual mechanism of catalysis has not yet been established but it is probable that the catalysis mechanism is a fully reversible process because the system appears to be almost totally under adsorption control. If the catalysis mechanism were irreversible, the sulphopropyl sulphide would be consumed at the cathode surface and diffusion control would take over at high current densities. Some evidence for the adsorption control of the sulphopropyl sulphide is provided in Fig. 9 where at a concentration of only 1 p.p.m., if consumption of the MPS were an appreciable factor, it would be expected that diffusion limitations would begin to be apparent at the higher current densities and the deposition potential would shift to more negative values. Further evidence for adsorption control is provided by experimental results which show that the consumption of these addition agents is very low and the sulphur content of the copper deposited from electrolytes containing these additives is almost undetectable. This was confirmed by producing a foil of copper from an electrolyte containing 40 p.p.m. of MPS and 75 p.p.m. of Oxilube 50 000 with 100 p.p.m. Cl^- . The foil was analysed for sulphur using proton induced X-ray emission analysis which can detect levels of sulphur down to 0.01%. No sulphur was detected in the deposit using this method. Finally, it has been reported by Kardos [10] that levelling can be induced in copper deposited from an acid electrolyte containing only polyether and chloride if the article to be plated is first immersed in a solution containing a sulphopropyl sulphide. This 'surface catalysed levelling' is thought to be due to the catalytic effect of the sulphopropyl sulphide and was found to persist for over 30 min of plating. Thus it was concluded that the sulphopropyl sulphide was not consumed but remained adsorbed on the surface of the growing deposit.

3.3.3. Adsorption of chloride ions. In an additive free system, when chloride ions are added to the base electrolyte, a depolarization effect occurs. This has been reported by Stoichev and Rashov [11]. The depolarization effect was reported to increase in a linear fashion with increasing chloride concentration and the addition of 100 p.p.m. of chloride to an additive free electrolyte resulted in a depolarization of approximately 25 mV. In the presence of polyether, however, this depolarization effect is overridden by

the increased polarization effect of the polyether when in combination with chloride ions.

3.4. Effect of pulsed reverse current on the adsorption of organic additives

The use of pulsed reverse current would not be expected to increase the throwing power of an acid copper electrolyte without additives because whenever any form of modulated current is used for metal deposition, a higher cathodic current density needs to be applied to maintain the same average rate of deposition as obtained by an equivalent direct current. This higher current density applied during the pulse lowers the electrode resistance of the cathode for a given average current density and so would be expected to produce a deterioration in throwing power.

Thus the observed changes in the polarization characteristics of electrolytes containing additives are responsible for the effect of increased throwing power at low current densities observed in Fig. 14, and in the practical applications of plating 'through holes'. From the experimental data obtained in this study, it appears that the adsorption of the polyether was not much affected by the application of pulsed reverse current but in the case of the sulphopropyl sulphide, progressive desorption tended to occur as the average current density was increased. This shifted the deposition potentials to more negative values owing to the polarization effect of the polyether. Thus low current density areas were depolarized relative to high current density areas and consequently, a more uniform deposition was observed. A possible explanation for the effect of pulsed reverse current on the adsorption behaviour of the additives used in the study is as follows.

3.4.1. Effect of pulsed reverse current on the adsorption of polyethers. As discussed previously, the polyether molecules are not specifically adsorbed on the copper surface but form complex polycations with cuprous ions and are bound to the cathode surface by specifically adsorbed chloride ions. During the anodic pulse, oxidation of copper from the cathode surface occurs. As the anodic pulses are relatively short, much of this copper will probably be oxidized to copper (I). Because of the ability of the polyether layer to chelate this species, it may be expected that the polyether layer would trap much of the copper (I) formed during the anodic pulse. This process would not be expected to cause desorption since the polyether layer would remain attached via chloride ions. During the following cathodic pulse, the concentration of cuprous ions built up during the anodic pulse would be reduced again to copper metal. The net effect of this would be that the adsorption of the polyether would be relatively unaffected by the use of pulsed reverse current.

3.4.2. Effect of pulsed reverse current on the adsorption of sulphopropyl sulphides. Unlike the adsorption of the polyether, it is likely that the sulphopropyl sulphides

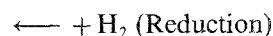
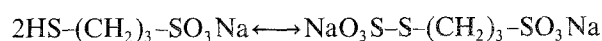
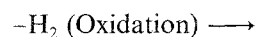
are adsorbed specifically. The active sulphide or disulphide group has a high affinity for copper and differential capacitance measurements have shown that these species are adsorbed strongly on copper surfaces immersed in a sulphuric acid (1N) electrolyte [7, 8]. These species also have a strong catalytic effect on the deposition of copper. The mechanism of catalysis has not been fully established, but probably involves the active sulphide or disulphide groups. Because reduction and oxidation are reversible, and the catalyst presumably lowers the activation energy for this process, it is quite probable that both oxidation and reduction of copper are catalysed by sulphopropyl sulphides. Thus during the anodic pulse, copper would be preferentially oxidized from the copper atoms in the lattice attached to the sulphopropyl sulphide molecules. This would tend to cause a copper ion to be removed from the surface in association with a sulphopropyl sulphide molecule. During the cathodic pulse, this desorption process would tend to be reversed and if the cathodic pulse were long enough, the catalytic effect of the sulphopropyl sulphide would be re-established. The speed at which the catalytic effect of the sulphopropyl sulphide molecule is reestablished depends upon the rate of resorption and this in turn depends upon the bulk solution concentration of the sulphopropyl sulphide. This explains the results observed in Fig. 10. At a concentration of 1 p.p.m. MPS, the rate of resorption was so low that even the lowest applied pulsed reverse current densities had a significant effect on the deposition potentials and at an average current density of 3 A dm^{-2} , the potential was almost the same as for an electrolyte with no MPS added. As the concentration of MPS was increased, the current density at which the effect of the desorption of MPS was evident also increased. This was due to an increased rate of resorption. Finally, at a concentration of 100 p.p.m. MPS, the rate of resorption was sufficiently high to prevent the polarization effect being observed in the current density range studied.

3.4.3. Effect of levellers. As mentioned at the beginning of this paper, commercial brightener formulations usually contain a levelling agent in addition to polyethers and sulphopropyl sulphides. These levelling agents can have widely different chemical structures. Pheno-safranin dyes are popular as levelling agents and their adsorption and effect on cathodic polarization has been studied by Stoichev *et al.* [7]. Levellers usually function by means of a mechanism of diffusion controlled inhibition and so act as polarizing agents. Thus if pulsed reverse current is to be applied to commercial brightener systems, the effect of the levelling agents cannot be ignored. Stoichev *et al.* [7] and also Mirkova *et al.* [12] found that a complex three-way synergism exists between the leveller, the polyether and the disulphide. This complicated adsorption situation means that the behaviour of these electrolytes under conditions of pulsed reverse current cannot be predicted easily. Consequently, the

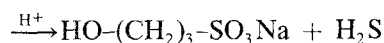
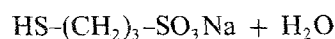
use of pulsed reverse current does not lead to an improvement in distribution of copper on the walls of holes in printed circuit boards in all cases.

3.5. Chemical stability of the additives used in acid copper electrolytes

3.5.1. Sulphopropyl sulphides. The two sulphopropyl sulphides used in the experiments had the following structures: $\text{HS}-(\text{CH}_2)_3-\text{SO}_3\text{Na}$, mercaptopropanesulphonic acid Na salt (MPS); $\text{NaO}_3\text{S}-(\text{CH}_2)_3-\text{S}-\text{S}-(\text{CH}_2)_3-\text{SO}_3\text{Na}$, bis(3-sulphopropyl)disulphide Na salt (SSP). The SSP is the disulphide of the MPS and the two species are interchangeable by oxidation and reduction in the following manner:

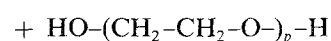
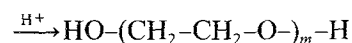
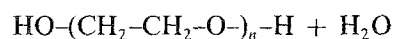


It is quite possible that when SSP is used as an additive that it is reduced at the cathode to MPS. This is a possible explanation for why the results obtained with the two different additives are so similar. However, the acid stability of the MPS is not likely to be as good as SSP because the active mercapto- group can undergo acid hydrolysis more rapidly than the disulphide group:



However, this reaction is slow at room temperature and the MPS present in the solutions was only decomposed over a period of weeks; thus the validity of the results presented should not be too much affected by decomposition of the MPS. From a commercial point of view, stability of the sulphur containing compounds is very important, which explains why in most of the patents [1-5] the disulphide (SSP) rather than the sulphide is patented. Thus for any commercial application, only the disulphide would be suitable.

3.5.2. Polyethers. Polyethers generally have quite good acid stability. High molecular weight polymers have some susceptibility to acid hydrolysis which can cause chain scission and lead to a lowering of the average molecular weight. For example, with polyethylene glycol:



where n is an integer representing the number of ethylene oxide units in the original polymer and m and p represent the number of ethylene oxide units in the fragments after acid hydrolysis. Note that $n = m + p$ to balance the equation. It is reasonable to consider that this hydrolysis effect is too slow to affect the experimental results obtained in this paper.

When the effect of molecular weight was studied, this was done using the same weight percentage for all tests. This would mean that the molecular concentration would vary. However, the concentration of polymer used was sufficient to be close to the top of the curve illustrated in Fig. 15. Thus differences in molecular concentration would not be expected to have a significant influence on the results obtained.

4. Conclusions

1. By the use of pulsed reverse current on acid copper electrolytes containing certain organic additives, it is possible to obtain a more even metal distribution at low current densities than when direct current is used.

2. When polyethers are added to acid copper electrolytes, the deposition potentials for a given current density are higher than the corresponding deposition potentials in the absence of this additive. This phenomenon is believed to be caused by a surface blocking effect caused by the adsorption of the polyether on the cathode surface. This surface blocking effect increases with increasing molecular weight of the polymer until above a certain molecular weight, steric factors prevent uniform adsorption. The maximum effective molecular weight of polyether was determined experimentally to be around 50 000. The addition of these polyethers also causes a shift in the rest potential to more negative values and a reduction in the exchange current density. Chloride ions appear to play some part in the adsorption mechanism and increases in the chloride ion concentration tends to cause the rest potential to become more negative.

3. When sulphopropyl sulphides are added to acid copper electrolytes, the deposition potentials for a given current density are less negative than the corresponding deposition potentials without this additive present. This is due to a catalytic effect of the active sulphur containing groups. Thus the addition of these additives causes a shift in the rest potential to less negative values and an increase in the exchange current density.

4. In additive free solutions and when either polyethers or sulphopropyl sulphides are present singly, a plot of log current density against potential gives a straight line relationship over the current density range studied in the experiments. This behaviour was

noted using both pulsed reverse and direct current, which implies that (i) the system was essentially under activation control, i.e. concentration polarization was negligible, and (ii) the system obeyed Tafel kinetics.

5. When both additives were present, the rest potential and calculated exchange current densities were close to those obtained from solutions containing only the sulphopropyl sulphide.

6. When both additives were present, a plot of log current density against potential gave a straight line using direct current, but a significant change in slope at higher current densities with pulsed reverse current. It was concluded from this that pulsed current produced desorption of the sulphopropyl sulphide at higher current densities. This could then cause a shift in the polarization potential to more negative values owing to adsorption of the polyether.

7. From the experimental results, it was determined on the basis of the magnitude of the change in slope of the polarization curve when pulsed reverse current was used, that the most effective concentration ranges of the additives were as follows: (i) mercaptopropane sulphonic acid (or its disulphide), 10 to 40 p.p.m.; (ii) polyalkylene glycol (25% propylene oxide), molecular weight 50 000, 70 p.p.m. to 1 g l^{-1} ; (iii) chloride ion, 100 to 200 p.p.m.

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