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Physical properties of pulsed current copper electrodeposits

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Square-wave unipolar pulse electroplating and bipolar pulse reverse electroplating of copper using an acid copper electrolyte of the type used for printed circuit board production has been studied. The effects of pulse-plated coatings on cathode efficiency and on the coatings properties, such as surface roughness, microhardness, stress–strain characteristics and elongation, are reported. The results show that microhardness, tensile strength and elongation are directly affected by the pulse technique used.

Nomenclature

A	Cross-sectional area (m^2)
CE	Relative cathode efficiency
i	Current density (A dm^{-2})
i_m, i_P	Mean, peak current density (A dm^{-2})
M_a	Actual deposit mass (g)
M_t	Theoretical mass (g)
R_a	Average roughness
R_{tm}	Mean roughness
t	Coating thickness (m)
t_{off}	Off-time (ms)
t_{on}	On-time (ms)
ϕ	duty cycle (%)
ρ	density (g m^{-3})

1. Introduction

The main practical difference between direct current (d.c.) and pulsed current for electrodeposition is that with d.c. plating only voltage (or current) can be controlled, but with pulse plating three parameters – on-time, off-time and the peak current density – can be varied independently. Such variables are believed by many authors to be able to create a mass transport situation, an electrocrystallization condition, and adsorption and desorption phenomena which are not otherwise possible [1, 2].

The anticipated advantages of pulse plating based on previously reported work can be enumerated:

(i) improved physical properties including increased hardness [3–5] as a result of finer grained structure [6], reduced porosity, [7–11] and also increased density, ductility and electrical conductivity [12, 13];

(ii) increased deposition current density, and hence plating rate, by virtue of operating nearer the instantaneous limiting current density [1, 2];

(iii) improved adhesion of the deposit to the substrate, possibly due to oxide film reduction [1];

(iv) improved plating distribution and thickness uniformity especially in relation to recesses [1, 2]. An optimized electrolyte may also lead to increased solution conductivity and reduced polarisation.

The model electrolyte solution selected was a highly conductive acid copper sulphate with the option of some additives typical to those used for printed circuit board manufacture, because of the improved throwing power achieved [2, 6].

Using a number of pulsed current programmes results for weight-gain measurements (used to calculate the cathode efficiency for unipolar pulse plating only), surface roughness and microhardness measurements for unipolar pulse and direct current plating, and stress–strain characteristics with elongation measurements for unipolar pulse, bipolar pulse reverse and direct current plating, are reported.

2. Experimental procedure

The experimental arrangement employs a current pulse unit having a microprocessor-controlled electronic switch which allows programming of up to nine channels and also allows various parameters, such as frequency, duty cycle and the pulse direction, either forward or reverse, to be stored.

The power source used for d.c. and unipolar pulse plating was a Farnell H30/100 (30 V, 100 A) and, for bipolar pulse reverse, the second power supply used was a Farnell AP30-80 (30 V, 80 A). The power sources were set in constant current mode.

The electrolytes were prepared from "analar" grade chemicals. The electrolyte solutions consisted of a standard acid copper solution (I), $CuSO_4{\cdot}5H_2O$ (0.3 M), H_2SO_4 (2.25 M) and Cl^- (50 p.p.m.), solution (II) containing LeaRonal proprietary additives of a mixture of polyethylene glycol, mercaptopropyl sulphonic acid and aromatic sulphonic acid, and solution (III) consisted of a standard acid copper solution without the addition of any chloride ions. Basically, electrolytes I and II were used as stock solutions [6, 14, 15]; electrolyte III was used to examine whether chloride ions had any effect on measured properties.

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TABLE I Experimental frequencies, duty cycles and electrolytes used under unipolar pulse conditions

Frequency (Hz)	Duty cycle (%)	Electrolyte
20, 100, 500, 1×10^3, 2×10^3, 3×10^3, 4×10^3, 5×10^3	25, 50, 75	I
20, 100, 500, 1×10^3, 2×10^3, 3×10^3, 4×10^3, 5×10^3	25, 50, 75	II
100	25, 50, 75	III

TABLE II Experimental conditions for bipolar pulse plating using different electrolytes (t_{on} is in ms, i_p is in A dm^{-2})

$i_{p(c)}/i_{p(a)}$	$t_{on(c)}/t_{on(a)}$			
	10/0.2		10/0.5	
	I	II	I	II
1/1	√	√		
1/2	√	√		
1/3	√		√	√
1/4	√	√		

The agitation used in all trials was cathode reciprocation combined with air agitation. The cathode reciprocation was set at 0.6 m min^{-1} and a constant air flow rate of 4.5 dm^3 min^{-1}, typical of those used on plating lines such as printed circuit board industries [6]. The plating tank was 2.5 dm × 2 dm × 3.5 dm in length × width × depth having a 17.5 dm^3 volume capacity.

The unipolar pulse and bipolar pulse reverse plating conditions are given in Tables I and II, respectively, for different electrolytes, the choice of the conditions being derived from an earlier study [16, 17]. The electroplating was carried out at a mean current density of 3 A dm^{-2} for d.c., unipolar pulse and bipolar pulse reverse conditions. The formulation for mean current density is defined as

$$i_m = i_p \phi \quad (1)$$

The duty cycle, is defined as

$$\phi = [t_{on}/(t_{on} + t_{off})] \quad (2)$$

where t_{on} is time on and t_{off} is time off. The mean current density, i_m, for bipolar pulse reverse plating is given by

$$i_m = \{[i_{p(c)} t_{on(c)}] + [i_{p(a)} t_{on(a)}]\}/[t_{on(c)} + t_{on(a)}] \quad (3)$$

The electroplating was carried out using two copper anodes having an exposed area of 1.8 dm^2 each, positioned at either sides of the cathode. The grade of anodes was phosphorus deoxidized copper with high residual phosphorus.

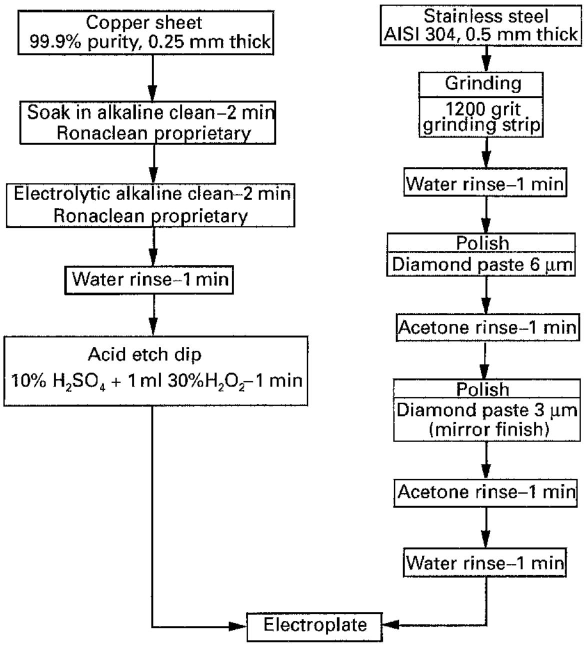

Figure 1 Flow chart showing the pretreatment stages used prior to electroplating.

The cathodes used for pulse cathode efficiency, microhardness and surface roughness measurements under d.c. and unipolar pulse conditions were copper sheets with an exposed surface area of 0.7 dm^2 (i.e. length × width × thickness of 1 dm × 0.34 dm × 0.01 dm); however, for tensile strength and elongation studies the plating was carried out on stainless steel with an exposed surface area of 1.5 dm^2. The use of stainless steel was preferred because the poor deposit adhesion allowed foils to be removed for individual testing. Plating was carried out on both sides of the cathodes. The pretreatment of copper and stainless steel samples was carried out as shown in Fig. 1.

The average plating thickness adopted for the examination of pulse cathode efficiency, surface roughness and microhardness was 25 μm, and for tensile strength and elongation, the average plating thickness was 50 μm. Table III shows the experimental properties examined for electrolytes I, II and III.

TABLE III Experimental properties examined under d.c., unipolar pulse reverse electroplating for electrolytes I, II and III

Property	D.c.			Unipolar pulse		Bipolar pulse reverse	
	I	II	III	I	II	I	II
Cathode efficiency	√	√	√	√	√		
Surface roughness	√	√	√	√	√		
Microhardness	√	√	√	√	√		
Tensile strength	√	√		√	√	√	√
Elongation	√	√		√	√	√	√

TABLE IV Weight gain and calculated pulse cathode efficiency values obtained under d.c. and unipolar pulse conditions for electrolytes I–III

Conditions	Weight gain (g)[a]			Efficiency (%)[b]		
	I	II	III	I	II	III
D.c.	1.6008	1.5193	1.5696	102.42	97.20	100.40
100 Hz, 25%ϕ	1.4189	1.5512	1.5592	90.78	99.25	99.76
100 Hz, 50%ϕ	1.4741	1.5485	1.5523	94.36	99.07	99.32
100 Hz, 75%ϕ	1.5218	1.5777	1.5549	97.36	100.94	99.48

[a] To four decimal places.
[b] To two decimal places.

The cathode efficiency was calculated from total deposit mass, as described in the Appendix [18]. Each copper cathode was weighed before and after plating and then the weight difference or weight gain of the coatings was calculated. The efficiency values were only calculated for unipolar pulse and coated samples under d.c. conditions. The efficiency expression (Equation A1) described in the Appendix is used to provide an indication of the effectiveness of different pulse conditions rather than the charge transfer phenomena ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{\circ}$ or $Cu^{2+} \rightarrow Cu^{\circ}$) which may exist [6].

A Rank Taylor-Hobson, model 10 Talysurf was used to provide information on surface texture (roughness) of the coating. Two types of roughness measurements were used: the first roughness measurement is termed average roughness, R_a, and the second roughness is known as mean roughness, R_{tm}. The R_a is the average area measurement of a coating, and the R_{tm} is the measurement from peak to trough of a coating. The measurements were repeated four times and the average of the four values was taken in micrometers; they were carried out for unipolar pulse conditions, for electrolytes I and II, and for d.c. conditions for electrolytes I, II and III. For comparative purposes, the unipolar pulse results were compared to d.c. as literature data in this area are sparse. The R_a and R_{tm} values of the as-rolled copper sheets were 0.08 and 0.6 μm, respectively.

Microhardness measurements were carried out using the Vickers microhardness tester on a Reichert MeF2 microscope using a 20 g load and averaging five values (in $\text{kg}\,\text{mm}^{-2}$). The plated samples were mounted in cross-section in bakelite, ground using 1200 grit and then polished using 6 μm followed by 3 and 0.5 μm diamond pastes.

Tensile strength and elongation studies were carried out using electrolytes I and II. Standardized tensile specimens were prepared from the stripped copper foils and uniaxial tensile properties were evaluated using a J.J. Lloyd testing machine (T5002) fitted with a 500 N load cell and an X–Y chart recorder, according to ASTM: D 638: (1972). All the samples were carefully examined for any tear or imperfections left from separation, cutting or punching.

3. Results and discussion

3.1. Deposition efficiency

The efficiency of deposition is calculated by weight measurement [18], Equation A1, for unipolar pulse and d.c. plating conditions. The results are based upon the coated deposits for a particular plating time of 37 min to obtain a coating thickness of 25 μm, the mean plating current density being $3\ \text{A}\,\text{dm}^{-2}$. In this study, the theoretical mass was calculated from the volume and density of deposit for pulse cathode efficiency values (Equation A2). Such calculation gives a theoretical mass value of 1.563 g. Any increase or decrease in the actual deposit mass value is indicative of an increase or decrease in efficiency of deposition, respectively.

Table IV shows the weight gain and efficiency values obtained for unipolar pulse and d.c. plating conditions using electrolytes I, II and III. The weight gain value obtained under d.c. for electrolyte II is 1.5193 g and, in comparison to the calculated theoretical mass of 1.563 g, it indicates that in real terms, the plating process is inefficient. The highest efficiency value was obtained for the d.c. condition (Table IV) when no additive was present in the electrolyte I, and the lowest efficiency was obtained when a mixture of additives was used, II. In electrolyte III, where no chloride ions were present, the efficiency under d.c. is reduced compared to electrolyte I. Under pulse plating condition, however, the situation is reversed for electrolyte III and, from surface roughness values obtained, it was found that electrolyte II provided a much improved (and more acceptable) coating than those for I and III. The cathode efficiency values obtained under pulsing conditions were always near 100% and it was also observed that the coating appearance under pulsing was better when the deposition efficiency was high. Similar observations have been reported by Popov *et al.* [19] and it is further indicated that improved pulsing efficiency can lead to a better coating structure. An overview of the effectiveness of different electrolytes for a particular process and vice versa is shown in Table V.

Finally, from the results obtained, it can be deduced that (a) the electrolyte constituents affect the cathode efficiency, (b) the cathode efficiency is dependent upon the pulsing conditions assuming all other conditions (such as pretreatment, etc.) remain equal, and (c) a small concentration of chloride ion in solution improved surface finish under both d.c. and pulsing conditions; this is attributed to the passivation prevention nature of chloride ions at the electrode surface.

3.2. Surface roughness

The surface roughness of the coated deposits was measured for electrolytes I, II and III. A summary of the

TABLE V A general overview of results identified for unipolar pulse (UP), bipolar reverse pulse (PR), and d.c. plating conditions. The comparison is based on different electrolytes and plating techniques adopted. Expected highest (>) or lowest (<) or equivalent (≡) values for each mode are described. Results obtained for pulse plating are frequency and duty-cycle dependent

Physical properties	Effectiveness of different electrolytes for a particular plating process	Comparison between different plating processes for a particular electrolyte
Cathode efficiency	D.c.:I > III > II UP: II > I > III	I: d.c. > UP II: UP > d.c.
Surface roughness	D.c. and UP: I ≡ III > II	I and III: d.c. ≡ UP II: d.c. > UP
Microhardness	D.c.: I > II > III UP: I > III > II	I and II: d.c. > UP III: UP > d.c.
Tensile strength	D.c., UP and PR: I > II	I and II: UP and PR > d.c.
Elongation	D.c, UP and PR: II > I	I and II: UP and PR > d.c.

surface roughness results is given in Table V. It was found that under unipolar pulse conditions, deposits from electrolyte I were rougher, in terms of R_a and R_{tm}, than those from electrolyte II. This is due to the presence of levelling additives, as expected. By comparison, the R_a and R_{tm} values of the deposits under unipolar pulse conditions for electrolyte I are somewhat similar to d.c. and, the R_a and R_{tm} values are less dependent on frequency and duty cycle, Fig. 2. However, for electrolyte II, the roughness values under d.c. are higher than those of unipolar pulse conditions, Fig. 3. The R_a and R_{tm} values are frequency and duty-cycle dependent. For electrolyte III, the R_a and R_{tm} values obtained are similar to those for electrolyte I. It must be pointed out that without the presence of any chloride ion in solution, electrode passivation may occur, as observed during this study, thereby making it commercially non-viable. However, electrolytes I and III produce a rough deposit texture compared to electrolyte II, Fig. 4. The results obtained are comparable with the findings by Chéne *et al.* [20], that using electrolyte I the R_a value of the deposit is around 1 µm for d.c. but for unipolar pulse-plated coatings it is dependent on the pulsing conditions.

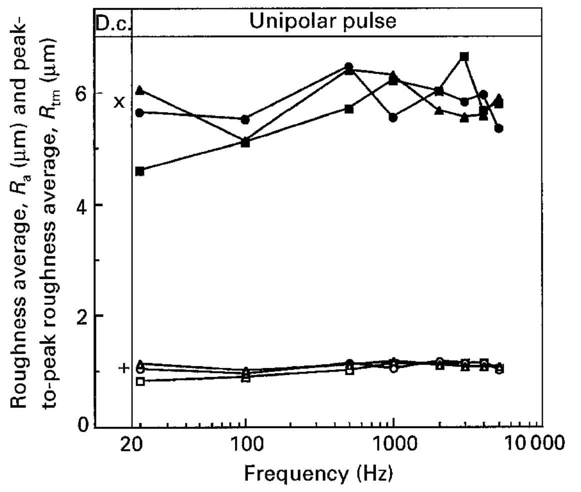

Figure 2 (□, ○, △, +) R_a and (■, ●, ▲, ×) R_{tm} plotted against unipolar pulse frequency for different duty cycles and also for (+ , ×) d.c., using electrolyte I: (□, ■) 25%, (○, ●) 50%, (△, ▲) 75%.

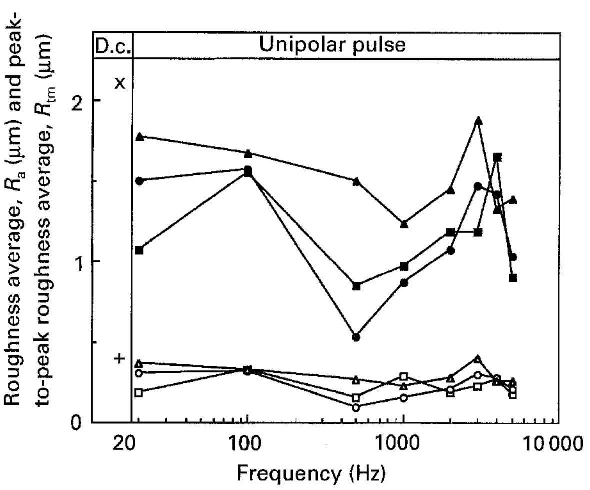

Figure 3 (□, ○, △, +) R_a and (■, ●, ▲, ×) R_{tm} plotted against unipolar pulse frequency for different duty cycles and also for d.c., using electrolyte II. (□, ■) 25%, (○, ●) 50%, (△, ▲) 75%.

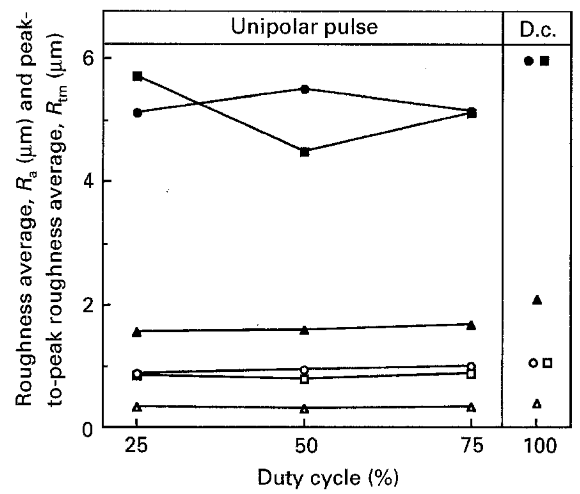

Figure 4 (□, ○, △) R_a and (■, ●, ▲) R_{tm} plotted against duty cycle using electrolytes (○, ●) I, (△, ▲) II and (□, ■) III at a frequency of 100 Hz, and also d.c. values for the three electrolytes.

From Figs 2 and 3 it can be deduced that under pulsing condition, the R_a and R_{tm} values of electrolyte II are improved by a factor of about 2.5 and 4.0 fold, respectively. This, of course, has a pulse-condition dependency; consequently, the surface roughness of the electrolyte II was better than other electrolytes used. Finally, the increase in the R_a and R_{tm} values for pulsed coatings may be associated with the electron transfer phenomenon ([1] pp. 84-7, [20]).

3.3. Microhardness

The microhardness values of the plated samples for electrolytes I, II and III under d.c. condition are 142 HV, 130 HV and 92 HV, respectively. The hardness values obtained for electrolytes I and II under unipolar pulse conditions are always less than for d.c., Figs 5 and 6. For electrolyte III, the hardness values for unipolar pulse conditions were higher than for the equivalent d.c. plated samples, Fig. 7. The results

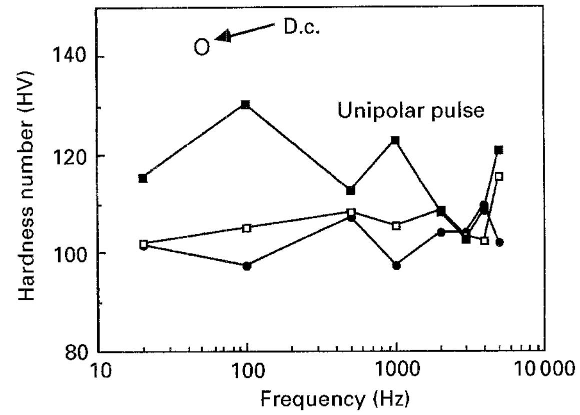

Figure 5 Hardness number plotted against unipolar pulse frequency for different duty cycles and also for d.c., using electrolyte I: (●) 25%, (□) 50%, (■) 75%.

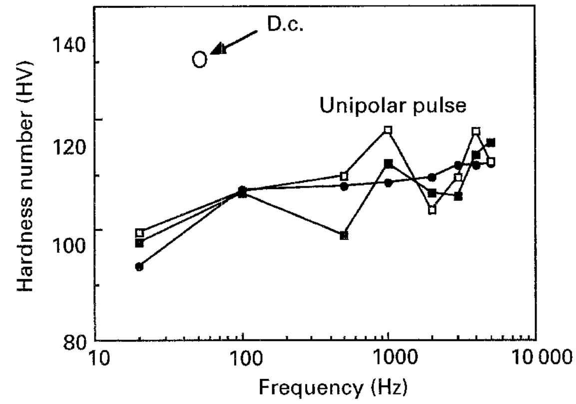

Figure 6 Hardness number plotted against unipolar pulse frequency for different duty cycles and also for d.c., using electrolyte II: (●) 25%, (□) 50%, (■) 75%.

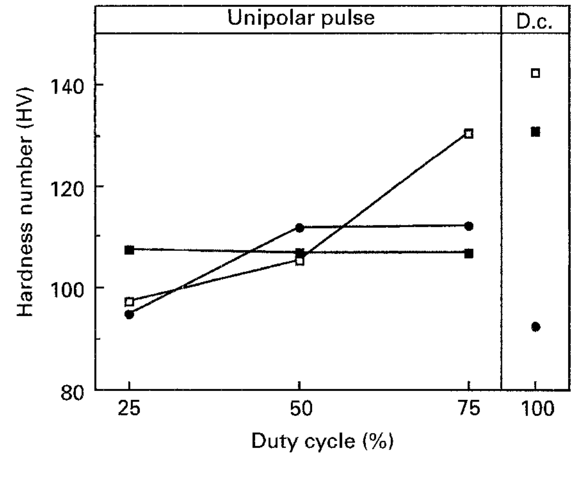

Figure 7 Hardness number plotted against duty cycle using electrolytes (□) I, (■) II and (●) III at a frequency of 100 Hz, and also d.c. values for the three electrolytes.

indicate that the hardness value is dependent on chloride-ion concentration in the electrolyte and also the pulsing conditions.

It was found that for electrolyte I, Fig. 5, the hardness value was highest at a low frequency of 100 Hz and a duty cycle of 75%, but for electrolyte II, this was not the case. For electrolyte II the highest hardness value was obtained at a frequency of 1000 Hz and duty cycle of 50%, Fig. 6. However, for electrolyte III (Fig. 7) it was found that the hardness values increased as the duty cycles increased at a frequency of 100 Hz. The increase at 100 Hz for electrolyte III is similar to that of electrolyte I. This phenomenon can be related to surface roughness, Fig. 4, and also the fact that no additive was present in the electrolytes I and III. Because the addition of additives affects the coating structure/grain size, it is normal to think that some grain refinement has taken place when hardness values are high and also the reverse is true. This behaviour has also been observed with different pulsing conditions.

It should be noted that electrolyte III contained no chloride ions and the hardness values under d.c. conditions are lower than those occurring using electrolyte I. With regard to electrolyte II, it can be seen that even under d.c. conditions the hardness values are affected, indicating the important role of the additives. In comparison, electrolyte II produces more uniform hardness values and its dependence on pulse conditions is less than electrolytes I and III, Figs 5–7. An overview on the effectiveness of different electrolytes for a particular process and comparison between different plating processes under a particular electrolyte is shown in Table V. Finally, from the results it can be deduced that the hardness values are dependent upon (a) pulsing conditions, (b) electrolyte constituent, and (c) coating structure, which is the consequent of surface texture and efficiency of the deposition [21].

3.4. Tensile strength

The tensile strength values obtained for deposits from electrolyte I under d.c. conditions produced almost the highest value of 313 $\mathrm{N\,mm^{-2}}$, but for unipolar pulse plated samples the tensile strength values were lowest at low frequency and duty cycle and increased as the frequency increased, Fig. 8. The highest tensile strength was obtained under unipolar pulse conditions at a frequency of 4 kHz and a duty cycle of 75% (348 $\mathrm{N\,mm^{-2}}$). The reason for this high value is not known but it may be associated with either

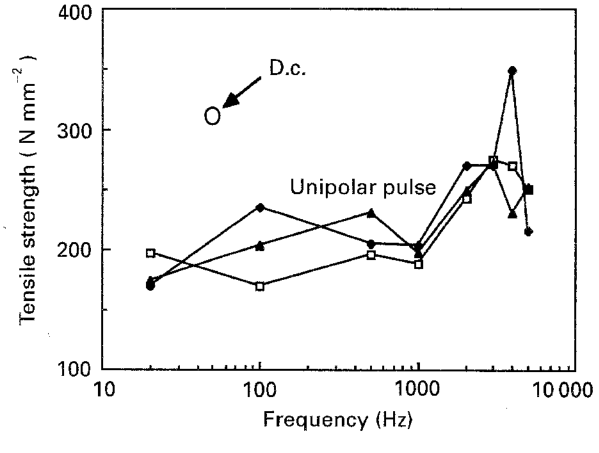

Figure 8 Tensile strength plotted against unipolar pulse frequency for different duty cycles and also for d.c., using electrolyte I: (□) 25%, (▲) 50%, (◆) 75%.

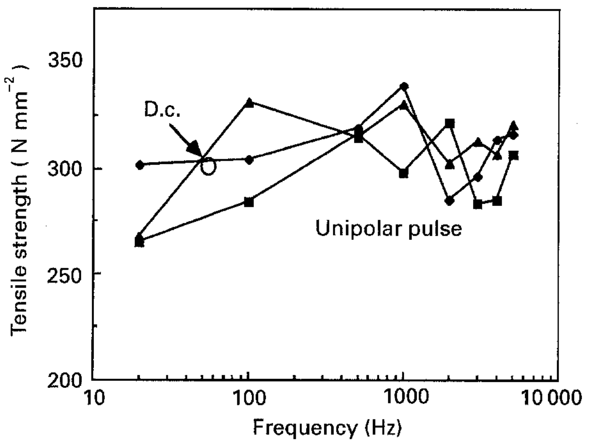

Figure 9 Tensile strength plotted against unipolar pulse frequency for different duty cycles and also for d.c., using electrolyte II: (■) 25%, (▲) 50%, (◆) 75%.

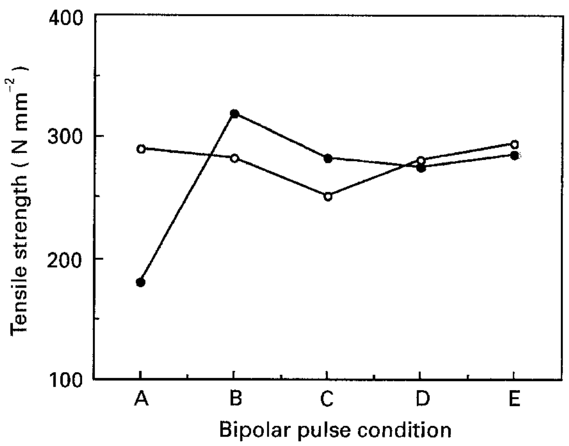

Figure 10 Tensile strength plotted against bipolar pulse conditions ($t_{on(c)}$ /$t_{on(a)}$; $i_{p(c)}$ /$i_{p(a)}$) using electrolytes plotted (●) I and (○) II: A, 10/0.5, 1/3; B, 10/0.2, 1/1; C, 10/0.2, 1/2; D, 10/0.2, 1/3; E, 10/0.2, 1/4.

experimental variance or the specific effect this pulsing condition may have with electrolyte I.

The tensile strength values obtained for deposits from electrolyte II were dependent upon the unipolar pulse conditions used when compared to d.c., Fig. 9. The tensile strength values were at their lowest at a frequency of 20 Hz irrespective of the duty cycle but it can be expected to obtain tensile strength values higher than d.c., for example the highest tensile strength values were 338 N mm^{-2} at unipolar pulse conditions of 1 kHz and 75% compared to 301 N mm^{-2} for d.c. However, comparing the electrolytes I and II, Figs 8 and 9, it can be seen that in the majority of unipolar pulse conditions the tensile strength values obtained using electrolyte II were higher than those of electrolyte I. This is surprising, because under d.c., the tensile strength value for electrolyte II is less than electrolyte I indicating that unipolar pulsing can increase the tensile strength. There remain two main factors affecting the tensile strength values: firstly, the additives present in electrolyte II and secondly, the pulsing conditions. The behaviour of a decrease in tensile strength value for electrolyte II compared to I under d.c. and also increase in tensile strength value of electrolyte II compared to I under unipolar pulse, is in direct contrast to cathode efficiency and surface texture results.

The tensile strength values obtained under bipolar pulse reverse for electrolyte I were higher under certain pulse conditions than electrolyte II, Fig. 10. Furthermore, the tensile strength values obtained for electrolyte II have a smaller range compared to electrolyte I, Table VI, mainly due to the nature of the additives used and possible degradation of the additives during the pulse reverse mode or negative polarity, as has been indicated by Pearson and Dennis [2]. This phenomenon has not been specifically investigated in this programme.

3.5. Elongation

The elongation values obtained using unipolar pulse conditions are similar in terms of overall pattern to those of tensile strength, such that for electrolyte I the elongation value is higher under d.c. compared to the majority of the unipolar pulse conditions studied and is at its lowest at low frequency and low duty cycle, Fig. 11. The results show that elongation is frequency and duty-cycle dependent, whilst for electrolyte II, the elongation is at its lowest for d.c. compared to unipolar pulse, Fig. 12. The results obtained indicate that the elongation data from electrolyte II were lower than electrolyte I under d.c. but it is possible to expect higher tensile strengths under unipolar pulse with

TABLE VI Tensile strength and elongation values obtained in this research work and their comparison with other authors' results

Reference	Tensile strength (N mm^{-2})		Elongation (%)	
	Electrolyte		Electrolyte	
	Without additive	With additive	Without additive	With additive
Ogden *et al.* [24, 25][a]				
d.c.	372	327[b]	15	22[b]
Present work[c]				
d.c.	313	301[d]	7.1	6.7[d]
unipolar pulse	169–348	265–338[d]	2.5–9.8	11.3–11.8[d]
bipolar pulse	180–319	251–294[d]	5.3–9.2	7–10[d]

[a] 0.75 M $CuSO_4$, 1.875M H_2SO_4, 50 p.p.m. Cl^-

[b] Bath containing proprietary additives – not specified.

[c] – 0.30M $CuSO_4$, 2.25M H_2SO_4, 50 p.p.m. Cl^-.

[d] Bath containing mixtures of polyethylene glycol, mercaptopropyl sulphonic acid and aromatic sulphonic acid additives.

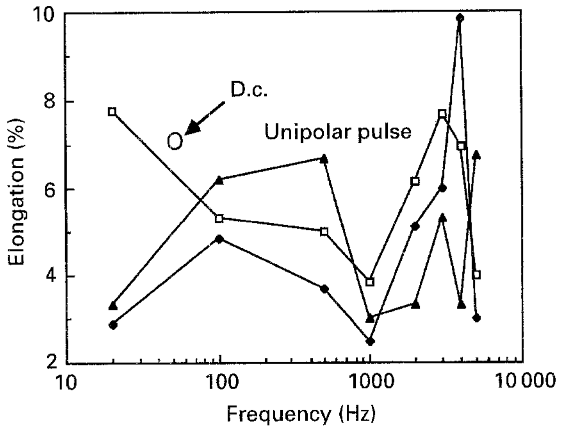

Figure 11 Percentage elongation plotted against unipolar pulse frequency for different duty cycles and also for d.c., using electrolyte I: (□) 25%, (▲) 50%, (◆) 75%.

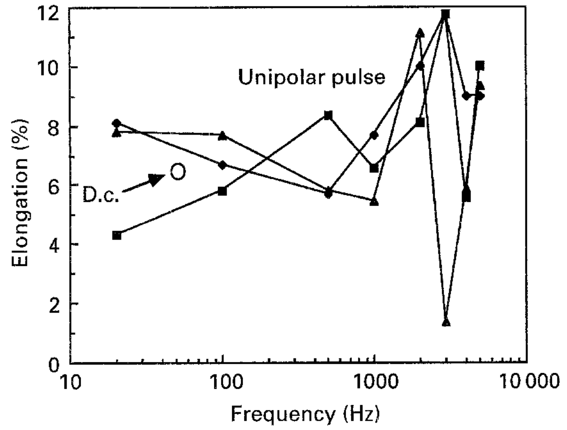

Figure 12 Percentage elongation plotted against unipolar pulse frequency for different duty cycles and also for d.c., using electrolyte II: (■) 25%, (▲) 50%, (◆) 75%.

electrolyte II. There appears to be a general trend that samples produced at higher frequencies have greater elongation; such a trend clearly indicates that the unipolar pulse can assist in improving the physical properties of deposit.

The elongation values obtained under bipolar pulse reverse for electrolytes I and II are varied, Fig. 13, but are found to have a dependency on pulsing conditions. In general, the elongation is directly proportional to tensile strength values for these samples. A general overview on the effectiveness of different electrolytes for a particular process and comparison between different plating processes under a particular electrolyte is shown in Table V.

Examination of tensile strength and elongation values have been previously reported by Ogden *et al.* using copper pyrophosphate [22, 23] and acid copper sulphate [24–26] baths, typical of those electrolytes used in printed circuit board industries. The results obtained in this research work are compared with those of Ogden *et al.* [24, 25], Table VI. In general, the tensile strength and elongation values under d.c., unipolar pulse and bipolar pulse for the electrolytes I and II were lower than those found by Ogden *et al.*; however, the low tensile strength and elongation values may be due to the lower concentration of sulphuric acid, Table VI. The results clearly show that, by modifying the pulse plating parameters, it is possible to achieve a wide range of tensile strength and elongation values leading to specialized use opportunities.

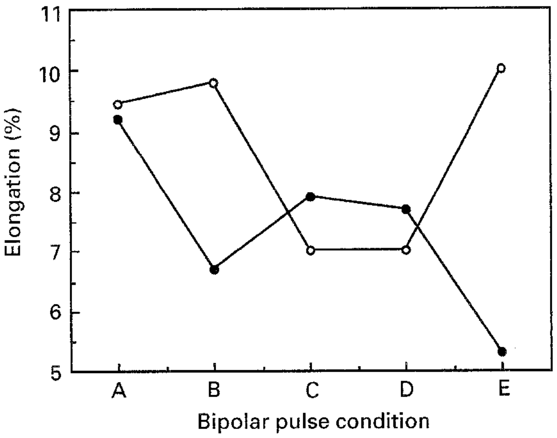

Figure 13 Percentage elongation plotted against bipolar pulse conditions ($t_{on(c)}/t_{on(a)}$, $i_{p(c)}/i_{p(a)}$) using electrolytes (●) I and (○) II: A, 10/0.5, 1/3; B, 10/0.2, 1/1; C, 10/0.2, 1/2; D, 10/0.2, 1/3; E, 10/0.2, 1/4.

Finally, it can be concluded that the results are similar to those reported in the literature. In terms of industrial usage, pulse plating can certainly produce a better and wider range of tensile strengths and elongation properties than the d.c. condition.

4. Conclusion

The cathode efficiency increased under certain unipolar pulse conditions. It is dependent primarily on electrolyte constituents, i.e. the presence of chloride ions and additives, and pulsing conditions.

The average roughness value of the deposit for electrolyte I is approximately 1 μm under d.c. but for unipolar pulse it is dependent on the pulsing conditions. For electrolyte II the roughness values are lower than those of electrolyte I. The average roughness and peak-to-peak roughness average values for electrolytes I and III are higher than for electrolyte II, indicating that electrolyte II produces a smooth surface texture which is mainly due to the presence of additives. Consequently, the surface roughness from electrolyte II is better than other electrolytes used. Under pulsing conditions, the R_a and R_{tm} values of electrolyte II are improved by a factor of 2.5 and 4.0 fold, respectively.

The microhardness values showed that the presence of chloride ions produced a significant increase in the hardness values. Electrolyte II produced more uniform hardness values and shows some dependency on pulsing conditions. In general, it was noted that hardness is dependent on electrolyte constituents and the pulsing conditions.

The tensile strength and elongation values were found to have good correlation with those in the literature. It is noted that the tensile strength and elongation values under bipolar pulse reverse are somewhat less than for unipolar pulse and direct current. This is believed to be due to the additive behaviour, as they may be effected during the pulse reverse or negative polarity mode. Finally, the tensile strength and elongation values are clearly affected by pulsing conditions.

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Appendix. Method of calculating cathode efficiencies for electroplated coatings [18]

The relative cathode efficiency, CE, can be defined as the ratio of the actual deposit mass, M_a, to the theoretical mass of electroplated materials, M_t, as follows

$$CE(\%) = (M_a/M_t) \times 100 \qquad \text{(A1)}$$

M_t, the theoretical mass is calculated thus

$$M_t = \rho A t \qquad \text{(A2)}$$

Therefore, the theoretical mass is

$$M_t = (8.93 \times 10^6)(0.7 \times 10^{-2})(25 \times 10^{-6}) = 1.563 \text{ g} \qquad \text{(A3)}$$

to three decimal places.

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