# A tartrate-based alloy bath for brass-plated steel wire production

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The plating of brass on steel from a tartrate based alloy bath has been studied using electrochemical methods and surface analysis techniques. The coating composition obtained using both direct current (d.c.) and pulsed current (p.c.) electrolysis was examined for a variety of temperatures, current densities and bath compositions. The dissolution process of a suitable composition of brass anodes was studied using small amounts of nitrate as depolarizing agent. Tests in a pilot plant showed that when electrolysis is carried out *in continuo* the coating composition remains constant with time  $(\pm 1\%)$ . Tests were performed at cathode current densities of industrial interest (20–30 A dm<sup>-2</sup>). The Auger and XPS analyses combined with Ar<sup>+</sup> etching indicated a homogeneous composition throughout the coating.

# 1. Introduction

The use of a tartrate-based alloy bath offers certain advantages in the production of brass-plated steel cords, widely used in industry (world production  $\sim 2 \,\mathrm{M}$  tonne year<sup>-1</sup>) in the manufacture of radial tires for passenger vehicles, trucks and of high pressure hoses. The present production process employs a carbon steel rod with diameter of 5.5 mm and pearlitic structure. After scarfing the rust by thermal and mechanical means and electrolytic pickling in an acidic environment, the rod is drawn to obtain a steel wire with diameter of between 0.7 and 1.45 mm. This wire is then thermally treated at around 1000° C and subsequently patented at 550°C to restore the pearlitic structure. After electrolytic pickling ( $H_2SO_4$  25%) at high current density, it is then brass-plated. Copper is first electrodeposited by means of acid (sulphate) or alkaline (pyrophosphate) galvanic baths and, after washing, zinc is then electrodeposited using a ZnSO<sub>4</sub>/  $H_2SO_4$  bath. The alloy is obtained by diffusion in the solid state through the Joule effect or using induction furnaces.

The resulting brass-coated wire is still covered with a ZnO film which is removed by subsequent acid pickling, generally in phosphoric acid. Depending on the wire diameter, the plating thickness ranges from 1 to  $2 \mu m$  (from 4 to  $6.5 \text{ g kg}^{-1}$ ). The brass-coated wire is then drawn with a suitable lubricant and the coating thickness diminishes to  $0.1-0.3 \mu m$  depending on the ultimate steel wire diameter (from 0.15 to 0.37 mm). In this drawing process brass coverage losses do not usually exceed  $0.2 \text{ g kg}^{-1}$ . However, particularly in the case of small diameter wires, brass coverage of the surface is not complete; in a fraction of it, 5–15%, the underlying iron is exposed.

For these types of coatings, i.e galvanic shortcir-

cuited iron/brass couple, and Zn less than 40%, the iron acts as anode [1]. In addition, the ferrous oxides do not adhere to the rubber during the curing process [2]. Discontinuity in the brass coating may also be due to the diffusion which occurs through the Joule effect. In fact the electric contacts are not always perfect because of vibrations in the wire which move through the plant at a speed of  $25-60 \text{ m min}^{-1}$ . This may lead to microsparking which damages the galvanic coating\*. Another problem concerns the brass composition. The best adhesion to rubber is obtained, depending on compound characteristics, with a specific brass surface composition [3]. Unfortunately, this composition almost always corresponds to the  $\beta$  phase which is not mechanically workable [4]; consequently, a coating with a bulk composition ranging between 63 and 68 Cu% ( $\alpha$  phase) is produced.

Many of the above mentioned inconveniences can be overcome using an alloy bath; however of the many processes suggested the only one applied in industry utilizes the complex ions of copper and zinc with alkaline cyanide [5–7]. This bath is falling into disuse for obvious environmental reasons. The advantages of using a tartrate galvanic bath for brass-plating lie in its cost, stability and non toxicity of the reagents. This bath has been studied, but only in laboratory conditions [8–12].

The aim of this work was to extend earlier research: (i) to geater cathodic current densities (from 0.5 to  $30 \text{ A dm}^{-2}$ ); (ii) to study the anodic processes in order to assess continuous operation; (iii) to improve the coating's morphology and, finally, (iv) to identify all the operating conditions required for obtaining a predetermined and constant coating composition.

\* Diffusion using induction furnaces is little used now both for high plant costs and low current yield.



Fig. 1. Diagram of the pilot plant: (1) clutched uncoiler, (2) wire guides, (3) current carrying rollers in stainless steel and Cu/graphite, (4) sulphuric pickling units with Pb anodes,  $35^{\circ}$  C,  $100 \text{ A dm}^{-2}$ , (5) rubber wire pinchers, (6) free-flow washing units, (7) brass-plating baths, (8) phosphoric acid 10% pickling, (9) compressed air dryers, (10) distribution systems for wire on reels, (11) coilers with adjustable linear speed at  $\pm 2 \text{ cm min}^{-1}$ .

#### 2. Experimental details

#### 2.1. Electrochemical methods

Cathodic polarization and anodic dissolution of brass were carried out using an AMEL apparatus (models 550, 564, 560, 667) and an EG & G potentiostat (mod. 283).

Simulations of the industrial process were performed in a purpose built pilot plant (Fig. 1) having an overall length of around 12 m. This plant allows treatment of several kilos of steelwire which can move at a rate of between 1 and  $20 \,\mathrm{m\,min^{-1}}$ . The plant consists of a series of easily interchangeable electrolytic tanks each with its own thermostat  $(+1^{\circ}C)$ . The wire was negatively polarized. In the present investigation the following set up was used: an acidic pickling tank, 25% H<sub>2</sub>SO<sub>4</sub>,  $35^{\circ}$ C, ccd around 100 A dm<sup>-2</sup>, lead anodes; a free-flowing water wash; a brass-plating bath, two brass anodes with the same composition as the desired brass plate and of the same length as the electrolytic tank; a second water wash; a phosphating bath (10%  $H_3PO_4$ ); a final water wash; a high pressure air blower and a wire coiling device. The wire tension was maintained by means of special band clutches and did not exceed a 10 kg load between the decoiler and the coiler. The wire distribution on the spool was regulated by a double-pitch screw. The wire speed was linearly adjusted with a precision of  $\pm 0.02 \,\mathrm{m \, min^{-1}}$ .

Stainless steel rollers, with a copper/graphite pin, for current supply fed by AMEL 555B potentiostatgalvanostat were used for DC simulations. When pulsating current was required, a JCT Controls Ltd. PDM 2040 instrument (max. frequency 5 kHz) was used.

#### 2.2. Surface analyses

XPS analyses were performed with an ESCALAB MK II spectrometer (Vacuum Generator Ltd, UK). The vacuum system consists of a turbomolecular pump, fitted with a liquid nitrogen trap and a titanium sublimation pump. The residual pressure in the spectrometer during the data acquisition was always lower than  $5 \times 10^{-7}$  Pa. The specimens were mounted on a modified nickel sample holder. The X-ray source was Al  $K_{\alpha}$  (1486.6 eV) and it was run at 20 mA and 15 kV. All the spectra were obtained in the digital mode (VGS 1000 software on APPLE IIe). A constant energy of 20 eV was set across the hemispheres of the electron

analyzer operated in Fixed Analyzer Transmission (FAT) mode, giving a full width at half maximum (FWHM) value of 1.1 eV for the Ag  $3d_{5/2}$  transition.

For the calibration of the instrument the Au  $4f_{7/2}$  line at 83.9 eV, the Cu  $2p_{3/2}$  line at 932.5 eV, the Cu LMM signal at 567.9 eV and the Ag  $3d_{5/2}$  at 368.2 eV were taken. To compensate for sample charging during the analysis all the binding energies were referred to the carbon 1s signal at 285.0 eV.

The depth profiles were obtained by sputtering with Argon ions and recording the Auger spectra in FRR mode.

#### 2.3. Cells, electrodes and measurements

Two types of cell were used. In both cases the cells were thermostated  $(\pm 0.1^{\circ} \text{C})$  and the solution was magnetically stirred and deaerated with purified nitrogen. The electrode terminals were protected in both cases and did not partake in the electrochemical process.

The cathodic polarization measurements were performed in a three electrode cell: as working electrode a stainless steel wire (1.4 mm diameter), as counter electrodes two graphite bars placed symmetrically on each side of the working electrode in separate compartments, and as reference electrode a saturated calomel electrode (SCE).

The investigations on the anodic dissolution process of brass were carried out using a brass coaxial cylinder with a steel wire, as cathode and a SCE as reference electrode.

Stainless steel electrodes employed here had pearlitic structure and the following bulk composition: C% 0.68-0.73, Mn% 0.58-0.68; S% < 0.03; S + P% < 0.06; Si% < 0.2; Cu% < 0.1; Cr% < 0.5; Al% < 0.01; Ni% < 0.1; N% < 0.01. The electrodes were mechanically polished with 600 mesh emery paper, washed with water and rinsed with ethanol.

Cathodic polarization measurements were performed at  $0.5 \,\text{mV}\,\text{s}^{-1}$  scan rate starting after 300s of initial delay at the open circuit potential.

#### 2.4. Reagents and solution preparation

The solutions were prepared with bidistilled water and reagent-grade chemicals. Concentrations are given in M (mol dm<sup>-3</sup>). Starting from cupric carbonate basic (56.0% Cu) and zinc carbonate basic (57.4% Zn), L-tartaric acid in a stoichiometric amount correspond-

Table 1. Range of compositions and characteristics of the 37 galvanic baths examined

Reagent	Range of concentration (M)		
	min	max	
$Cu^{2+}$ ion, total	0.1	0.4	
$Zn^{2+}$ ion, total	0.04	0.25	
Tartrate ion	0.4	2.0	
Sodium hydroxide	2.0	3.0	
Specific conductivity (S)	0.15	0.24	
Density $(kg dm^{-3})$	1.14	1.30	
Alkalinity (M)			
free	1.4	2.0	
total	3.0	4.2	

ing to the sum of the two cations, potassium sodium tartrate and sodium hydroxide were added.

The solutions were prepared so that the carbonates reacted with the tartaric acid until the  $CO_2$  had completely evolved (~24 h). Potassium sodium tartrate and sodium hydroxide were added, making up the volume at 20° C. After 24 h the solution was filtered, when necessary, and density, specific conductivity at 30° C, copper and zinc concentrations, free and total alkalinity (by conductimetric titration) were measured. Table 1 shows the range of composition and the chemico-physical characteristics of the 37 solutions examined while the composition of the specific solutions used in the test are indicated in each figure.

In order to study the dependence of plating composition on the concentrations of copper and tartrate ions, two series of solutions were tested:

*Ist series:* (solutions 27, 28, 29, 30) Bath composition 0.1 M zinc ion 1.75 M tartrate 2.5 M NaOH 0.05 M triethanolamine 0.1, 0.15, 0.2, 0.25 M copper ion

density =  $1.285 \text{ kg dm}^{-3}$ free alkalinity = 1.8 Mtotal alkalinity = 4.2 M0.195 S < conductivity < 0.154 S

2nd series: (solutions 29, 31, 32, 33) Bath composition 0.1 M zinc ion 1.00, 1.25, 1.50, 1.75 M tartrate 2.5 M NaOH 0.05 M triethanolamine 0.2 M copper ion

 $\begin{array}{ll} 1.204 \, kg \, dm^{-3} < density < 1.292 \, kg \, dm^{-3} \\ 1.58 \, M < free alkalinity < 1.72 \, M \\ 3.06 \, M < total alkalinity < 4.18 \, M \\ 0.197 \, S < conductivity < 0.170 \, S. \end{array}$ 

The following solution was utilized for the tests with pulsed current (p.c.): 0.20 M copper ion; 0.10 M zinc ion; 1.25 M tartrate; 2.50 M sodium hydroxide; 0.05 M triethanolamine. Characteristics: density  $(kg dm^{-3})$ 

1.234; free alkalinity 1.74 M, total alkalinity 3.40 M; conductivity (S) 0.193. Electrolysis was carried out with p.c. at a frequency of 1, 3, 5 kHz.

For the tests in the pilot plant, solution No. 30 was used with the following composition: 0.25 M copper ion, 0.10 M zinc ion, 1.75 M tartrate, 2.50 M sodium hydroxide, 0.05 M triethanolamine, 0.03 M potassium nitrate.

The brightening and deoxidation agents described further on were gradually added to the solutions. The most effective deoxidizer was found to be the ion  $NO_3^-$ . As far as brightening agent is concerned, triethanolamine is effective and under these experimental conditions is not volatile.

# 2.5. Brass plate analyses

The brass coatings were dissolved in concentrated  $HNO_3$  and analysed by means of a Perkin-Elmer Model 603 Atomic Absorbtion Spectrophotometer or by determining the copper iodometrically and the zinc by the difference. As far as the pilot plant tests are concerned coating composition was determined on samples taken at the head, tail and middle of each length of wire, and the results were in good agreement within the experimental errors.

#### 3. Results and discussion

#### 3.1. Solutions

The prepared solutions remained stable for at least six months for a maximum of 0.15 M zinc ion and provided that the sodium hydroxide and tartrate ion concentrations were not less than 2.5 and 1.0 M, respectively. Under these conditions the ions typically present in the solution are:

 $Cu(OH)_2(C_4H_4O_6)^{2-}$   $(K_i = 7.3 \times 10^{-20})$ 

and

$$Zn(OH)_4^{2-}$$
 ( $K_i = 2 \times 10^{-13}$ )

#### 3.2. Cathodic polarization curves

The cathodic polarization curves for different experimental conditions are given in Figs 2–6. The brass discharge potential lies between those of copper (solution 5) and zinc (solution 4) as shown in Fig. 2. The increase in tartrate ion (Fig. 3) or sodium hydroxide (Fig. 4) concentration results in lower current densities at each potential value, whereas the current density tends to increase with temperature (Fig. 5).

These findings have also been reported by other investigators [9] for lower current density ranges. By changing the Cu/Zn ratio from 1.28 to 2.43 (Fig. 6) only a slight decrease of the current density is observed.

The addition of small amounts (up to 0.05 M) of triethanolamine, as brightening agent, does not cause significant variations in the polarization curves.

From these results it may be inferred that: (i) the solutions may be utilized for a long time at typical



Fig. 2. Zinc, copper and brass discharge potentials (curves 4, 5 and 6, respectively); the curve is also shown of solution No. 30 which is then employed in the pilot plant tests;  $40^{\circ}$  C,  $V_{scan} = 0.5$  mV s<sup>-1</sup>.

production levels; (ii) at more negative potentials of -1.5 V/SCE the hydrogen evolution reaction overlaps that of the brass discharge; (iii) the brass discharge potentials are affected to a greater extent by variations in tartrate ion concentration and temperature.

#### 3.3. Plating compositon and morphology

Figure 7 shows the effect of the current density at different temperatures (30, 40 and 50° C) on brass plate composition, in a  $[Cu^{2+}]/[Zn^{2+}] = 1.5$  bath



Fig. 3. Effect of tartrate ion concentration on brass discharge potential;  $40^{\circ}$  C,  $V_{sean} = 0.5$  mV s<sup>-1</sup>.



Fig. 4. Effect of sodium hydroxide concentration on brass discharge potential;  $40^{\circ}$  C,  $V_{scan} = 0.5 \text{ mV s}^{-1}$ .

(solution No. 28). At low current density values  $(1.5 \,\mathrm{A} \,\mathrm{dm}^{-2})$  the plating is predominantly copper.

A high percentage of copper in the brass plate is observed at low current densities whereas above  $5 \text{ A dm}^{-2}$  the composition remains more or less steady. This value corresponds to the discontinuity observed in the polarization curves of Fig. 6. This finding may be explained by the simultaneous deposition of copper and zinc from the alloy bath. By increasing the temperature it is possible to achieve the desired coating composition (Cu% = 63) operating in the most desirable current density range.

With all of the first series of solutions listed in the experimental section, 6-8 electrolyses were carried out



Fig. 5. Effect of temperature on brass discharge potential;  $40^{\circ}$  C,  $V_{scan} = 0.5$  mV s<sup>-1</sup>.



Fig. 6. Effect of  $[Cu^{2+}]/[Zn^{2+}]$  ratio on brass discharge potential; 40° C,  $V_{scan} = 0.5 \text{ mV s}^{-1}$ .

at different current densities and temperatures obtaining diagrams very similar to those shown in Fig. 7. Electrolysis performed on the second series of solutions, showed that for current densities in the range from 4 to  $16 \,\mathrm{A}\,\mathrm{dm}^{-2}$ , varying the tartrate ion concentration between 1.0 and 1.75 M produced no noticeable effect on coating composition. The operating conditions for the pilot plant were deduced from working diagrams similar to those of Fig. 8. The percentage of copper in the deposited alloy is shown as a function of the  $[Cu^{2+}]/[Zn^{2+}]$  ratio in the alloy bath for the different temperatures and current densities. In this way the bath composition, current density and temperature values required for plating were found so as to obtain a 63-68% Cu composition which ensures the best cord to rubber adhesion.



Fig. 7. Example of correlation between copper percentage in the alloy and current density  $([Cu^{2+}]/[Zn^{2+}] = 1.5; 1.75 \text{ M}$  tartrate; 2.5 M NaOH; 0.05 M triethanolamine). ( $\bigstar$ ) 50, ( $\bigstar$ ) 40 and ( $\bullet$ ) 30° C.

Operating the electrolysis in direct current and at low current densities the plating was coherent, bright and reddish in colour due to the high copper content of the alloy. At between 5 and 12 A dm<sup>-2</sup>, the plating was coherent, bright and yellow; for current density values above  $16 \text{ A dm}^{-2}$  it became black and noncoherent.

#### 3.4. Cathodic efficiency

The cathodic current efficiency, in direct current (d.c.) is 100% only at the lower current densities  $(1-2 \,\mathrm{A} \,\mathrm{dm}^{-2})$ . At higher values the brass discharge is always accompanied by parasitic reactions, mostly the discharge of hydrogen ions. A typical example of cathodic efficiencies is shown in Table 2.

Cathodic efficiency tends to increase with temperature increase for each value of current density. For current densities ranging between 5 and  $16 \text{ A dm}^{-2}$ , i.e. in the region where the plating composition is constant, the average cathodic efficiency in d.c. and at  $40^{\circ}$  C is estimated to be 52  $\pm$  2%.

Table 2. Examples of cathodic efficiency. Bath composition: 1.5 M tartrate, 2.5 M NaOH;  $[Cu^{2+}]/[Zn^{2+}] = 2$ 

30°	С	<i>40</i> °	С	50°	С
$\frac{(Adm^{-2})}{}$	(Cu%)	$(A dm^{-2})$	(Cu%)	$(A dm^{-2})$	(Cu%)
0.75	101	0.70	102	0.70	100
1.45	100	1.80	97	2.00	100
2.80	73	2.40	90	2.40	90
7.00	63	6.00	83	6.00	90
11.50	57	9.40	56	8.30	79

<u>solution</u>; Cu<sup>++</sup> 0.10-0.15-0.20-0.25 M; Zn<sup>++</sup> 0.1 M; tartrate 1.75 M; NaOH 2.5 M; triethanolamine 0.05 M; d (Kg dm<sup>-3</sup>) 1.28±0.01;  $\chi$  (S) 1.285 ±0.005; alcalinity free 1.80, total 4.2 M.



Fig. 8. Curve of correlation between copper/zinc ratio in the galvanic bath and percentage of copper in the alloy at various ccd and temperature values.

#### 3.5. Tests with pulsed current

A series of tests was carried out with pulsed current (p.c.) at frequencies of between 1 and 5 kHz to improve cathodic efficiency and plating quality. An example of the results is shown in Fig. 9. The three curves refer to different ratios of  $t_p/t_b$  and  $V_p/V_b$  (where  $t_p$  and  $t_b$  represent the current pulse duration and the interval between the two pulses, respectively, and  $V_p$  and  $V_b$  are the corresponding potential values). The average potential  $V_{av}$  is given by

$$V_{\rm av} = [t_{\rm p}/(t_{\rm p} + t_{\rm b})]V_{\rm p} + [t_{\rm b}/(t_{\rm p} + t_{\rm b})]V_{\rm b}$$

where  $V_{\rm b}$  is taken as -0.8 V/SCE corresponding to zero current density (see Fig. 2).

In general the correlation between plating composition and cathodic current density is similar to that



Fig. 9. Curve of correlation between brass composition and ccd with pulsated current electrolysis operation (40° C; 1 kHz;  $V_b = -0.8 \text{ V/SCE}$ ;  $V_p (\blacktriangle) - 2.0$ ; ( $\bigstar$ ) -3.0; ( $\blacklozenge$ ) -4.0 V/SCE).

obtained in the d.c. mode, though all the curves are shifted to higher current densities. Up to  $10 \,\mathrm{A}\,\mathrm{dm}^{-2}$ the plating consists almost entirely of copper and appears coherent but reddish in colour (Cu%  $\ge 90$ ). To obtain a composition of 60–65% Cu, current densities of between 10 and 30 A dm<sup>-2</sup> were required depending on the different  $t_p/t_b$  duty cycles employed and on the  $V_p$  values.

The curves in Fig. 9 were used to define the operating conditions in the pilot plant with p.c. input. The advantages of using pulsed current are known [13]. In the rest stage between the current pulses,  $t_b$ , the reagent concentration in the diffusion layer is re-established, reducing the concentration overvoltage, increasing the cathodic efficiency and improving the plating morphology because of the reduced hydrogen evolution.

As a result it is possible to obtain bright and coherent platings at higher current densities compared to those permitted by d.c. electrolysis. In addition the plating appears to be better distributed on an electrode with a rough surface like that of the steel wire employed in brass-plated cord production, since the wires used have undergone a drawing process resulting in long lengthwise grooves (with an amplitude of  $1-2 \mu m$ ).

#### 3.6. The anodic process

To keep electrolysis going for months the Cu/Zn ratio in the plating bath needs to be kept constant. The anodes had the following composition 67.5% Cu, 32.5% Zn. The plating bath used in these tests consisted



Fig. 10. Selectivity coefficient of the dissolution of brass anodes (68% Cu, 32% Zn) in a solution containing 1.25 M tartrate ions and 2.50 M sodium hydroxide. The curve is averaged over 67 experimental plots.

of 1.25 M tartrate ion and 2.50 M sodium hydroxide at  $25^{\circ}$  C, 0.03–0.09 M NO<sub>3</sub><sup>-</sup> ion (as KNO<sub>3</sub>) depolarizing agent was added to the solution.

The Cu/Zn ratio is monitored versus time and related to the anode composition defining a selectivity coefficient Z:

$$Z = \frac{(p.p.m. Zn/p.p.m. Cu)_{in the solution}}{(Zn\%/Cu\%)_{in the anode}}$$

The results (Fig. 10) show that initially more zinc is dissolved ( $Z \ge 1$ ) and that after approximately 1 h Zn and Cu dissolution occurs with Z = 1. No appreciable effect was detected by varying the nitrate ion concentration in the range 0.03–0.09 M (Table 3).

Table 3. Selectivity coefficient values Z for different nitrate concentrations at  $25^{\circ}$  C in 1.25 M tartrate and 2.50 M NaOH. Anodic current density = 0.45 A dm<sup>-2</sup>, cathodic current density 15 A dm<sup>-2</sup>.

Time (min)	$NO_1^-(M)$		
	0.03	0.06	0.09
0	3.56	5.40	2.71
4	1.56	1.87	1.51
8	1.40	1.40	1.30
10	1.27	1.29	1.30
20	1.24	1.31	1.32
30	1.16	1,17	1.17
40	1.06	1.14	1.25
50	1.09	1.10	1.06
60	1.06	1.10	1.02
75	1.03	1.03	1.01
90	1.03	1.03	1.01
120	0.99	1.00	1.01
180	0.96	1.00	0.97

#### 3.7. Pilot plant tests

The tests were performed following the procedures described in the experimental section using the galvanic bath No. 30 (see experimental section). Operating conditions were the following: temperature  $40 \pm 1^{\circ}$ C; brass anodes 68/32; p.c. input at 1, 3 or 5 kHz frequency; duty cycles 50%, i.e.:  $t_p/t_b = 1$ . Each test lasted 3 days.

The results obtained (Table 4) indicate an almost constant plating composition and the repeatability of the different tests. The cathodic efficiency was greater



Fig. 11. XPS copper and zinc signals and Auger depth profiles up to  $\sim 2 \,\mu m$  from the surface.

Electrolysis type	Frequency (kHz)	Current density (A dm <sup>-2</sup> )	Cathodic efficiency (%)	Cu in the deposit (%)
		16.0	25	62.4
a.c.	-	16.0	33 50	62.4
p.c.	L	10.0	30	03.4
p.c.	5	10.4	85	63.5
p.c.	1	12.8	67	62.0
p.c.	3	16.0	68	65.8
p.c.	5	14.4	72	66.0
p.c.	3	14.4	71	63.8
p.c.	1	14.4	71	63.8
p.c.	3	14.4	70	63.8

with p.c. than with d.c. In all cases the platings were coherent, yellow and bright.

# 3.8. Characterization of the plating obtained in the pilot plant

The Auger composition profiles and the Cu2p and Zn2p XP-spectra are shown in Fig. 11. These spectra were recorded on a brass coated steel cord (6.12 g kg<sup>-1</sup>, 62.4% Cu) deposited in d.c. mode at 30° C. The Auger composition profile shows the percentages of Cu and Zn are constant up to about 1  $\mu$ m from the surface. This distinguishes the plating deposited from a tartrate alloy bath from that obtained with a traditional method, i.e. solid state diffusion of two layers of copper and zinc where the composition profile indicates discontinuities in the coating.

The XP-spectra reveal the presence of a surface layer mainly constituted of  $Cu_2O$  and ZnO. A thin contamination layer, which disappears after ~ 60 s of sputtering, is present in the outermost part of the coating. C, K, N signals due to adsorbed species are detectable. Since neither Auger nor XPS show the presence of the iron signal the surface is entirely coated.

### 4. Conclusions

The tartrate based alloy bath allows plating of steel with brass of a predetermined composition in a single electrochemical operation. This result has been obtained both in laboratory tests and in the pilot plant utilizing d.c. and p.c. modes. For current densities higher than  $6 \text{ A} \text{ dm}^{-2}$  and up to  $16 \text{ A} \text{ dm}^{-2}$  plating composition is independent of cathodic current density and this facilitates the use of this alloy bath at an industrial level.

Pilot plant tests have demonstrated that the bath can be successfully run for several months and that the brass-plating composition is constant with time. The characterization of the plating by Auger and XPS analyses reveals that the plating composition is homogeneous throughout its depth and that iron is exposed only at the brass/steel interface.

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