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# Electrolyte for copper deposition based on aqueous polyaniline dispersion

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The properties of an electrolyte for acid bright copper deposition have been investigated. The influence of polyaniline dispersion, polysafranine dye (levelling component), poly(alkylene oxide) (wetting agent) or dialkyl disulfides (brightener) and combinations of these additives on the quality of electrodeposited coatings were studied. The presence of polyaniline dispersions increased the levelling ability by 16% and at the same time the concentration of the other additives could be considerably reduced. The electrolyte containing polyaniline dispersion could also be efficiently used under production conditions.

Keywords: *copper electrodeposition*, *polyaniline*, *polyaniline dispersion*

## 1. Introduction

The electrodeposition of multilayer copper–nickel–chromium coatings is the most important method for the anticorrosion treatment of metals. As the copper layer is in direct contact with the protected metal surface and supports the next metal layers, it is expected to possess a number of specific properties, including a high degree of levelling. The novel noncyanic electrolytes for acid bright copper deposition with high levelling ability permit the removal of all manual operations and provide the possibility for fully automated processing. These electrolytes contain poly(alkylene oxides) as wetting agents [1–3], organic disulfides as brighteners [4] and polysafranine dye derivatives as levelling additives [5].

The preparation of polysafranine dye derivatives in good purity is difficult due to the multistep method of synthesis, the high toxicity of intermediates and the large amount of waste. The use of dye-free electrolytes is suitable for some copper coatings, but not sufficient for multilayer copper–nickel–chromium ones. That is why the substitution of the polysafranine dye derivative by other levelling additives, including polymers, has been sought.

Polyaniline [6, 7] (PANI) is one of the most studied electrically-conducting polymers. It can exist in a variety of forms [8, 9] that differ in the degree of oxidation and/or protonation and, consequently, in physicochemical properties. It is easily prepared by the chemical or electrochemical oxidation of aniline. When such a preparation proceeds in the presence of a steric stabilizer, a suitable water-soluble polymer (e.g. poly-*N*-vinylpyrrolidone), dispersions of submicrometre polyaniline particles are obtained [10]. Polyaniline dispersions [11] can then be used in electrodeposition experiments [12, 13]. Because of its electrochemical properties, the use of polyaniline in the anticorrosion treatment of metal surfaces has also been proposed [14–16]. This paper reports the results of the application of polyaniline dispersions as a levelling agent in acid bright copper electrodeposition.

## 2. Experimental details

### 2.1. *Electrolyte*

The main electrolyte was composed of 220 g $dm^{-3}$ copper sulfate pentahydrate, 50 g sulfuric acid (98%) and 0.09 g $dm^{-3}$ sodium chloride. All components were of analytical grade (Fluka, Switzerland). The electrolyte also contained a dialkyl disulfide as a brightener, poly(alkylene oxide) as a wetting agent and polysafranine dye or polyaniline dispersion (or both) as levelling additives.

Disodium *bis*-sulfopropyl disulfide was prepared from 1,3-propane sultone and disodium disulfide, and separated from polysulfides [4]. The symmetrical pentablock copolymer [17] of ethylene oxide (EO)

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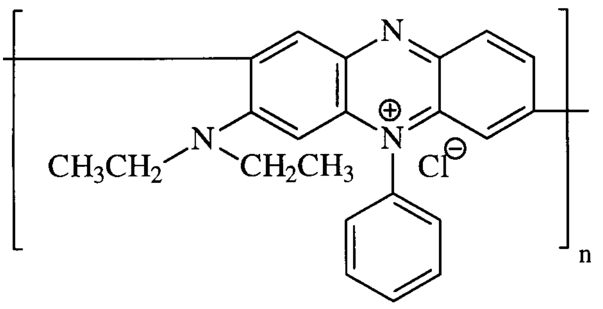
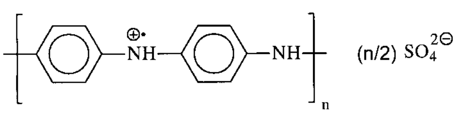
and propylene oxide (PO), $(EO)_8(PO)_{15}(EO)_{10}(PO)_{15}(EO)_8$, was used as a wetting agent. The synthesis was initiated by the action of potassium hydroxide on a decamer of ethylene oxide followed by ring-opening anionic polymerization of PO at 140–160 °C in a nitrogen atmosphere. The last blocks were produced by addition of ethylene oxide. The weight-average molecular weight of the pentablock copolymer was $M_w = 3400$ and the weight-to-number molecular weight ratio $M_w/M_n = 1.3$ (by gel-permeation chromatography); the copolymer composition was 46 mol % EO (by NMR). Polysafranine dye derivative, poly[5-phenyl-7-(*N*,*N*-diethylamino) phenazinium] chloride,



$n \simeq 20$ was prepared by decomposition of the diazonium salt of 3-amino[5-phenyl-7-(*N*,*N*-diethylamino)phenazonium] chloride [5]. The latter compound was obtained by the procedure described elsewhere [5].

Polyaniline dispersion was prepared as folows: aniline sulfate (569 mg, 2 mmol) was dissolved in 5 ml of 4 wt% aqueous solution of poly(*N*-vinylpyrrolidone) (PVP; Fluka, Switzerland; $M_w = 360\,000$), 0.5 ml of water was added and the dispersion polymerization of aniline [10] was started by introduction of 4 ml of 1 M aqueous ammonium peroxodisulfate (= 4 mmol) at room temperature. Polyaniline (green emeraldine sulfate form [8, 9]),



$n > 100$ [9], was completed in about 30 min. The resulting PANI dispersion is stable. All low-molecular weight components were removed by dialysis (Spectra/Por1 Dialysis Membrane, Spectrum, USA). The concentration of polyaniline in the dialysed dispersion, 0.024 g ml$^{-1}$, was determined by spectrophotometry [18], the average particle diameter, 370 nm, by dynamic light scattering (DLS; AutoSizer Lo-C, Malvern Instruments, UK) after dilution with 1 M hydrochloric acid. The concentration of PVP was 0.013 g ml$^{-1}$.

### 2.2. *Levelling*

The deposition of copper was carried out in a 1 dm$^3$ electrolytic cell at 20 °C using a cathode current density 5 A dm$^{-2}$ and air bubbling under the cathode. Elliptical (70 mm × 35 mm) phosphor (0.04–0.07%) alloyed copper bars were used as anodes. The cathodes (20 mm × 10 mm) were made of a gramophone-record nickel master mould with model microprofile with V-shaped groove and 90° angle in the groove. The average groove depth was 30 $\mu$m with a distance of 150 $\mu$m between two adjacent groove bottoms. The levelling effect was determined with a profilograph–profilometer (Perthen, Germany) on 20 $\mu$m copper coatings. Five measurements over 5 mm intervals were done. The levelling was calculated as $L(\%) = 100\ (R_1 - R_2)/R_1$, where $R_1$ is the initial roughness and $R_2$ the final one.

### 2.3. *Brightness*

The brightness was assessed visually from plates deposited in a Hull cell (0.25 dm$^3$) which provided a range of current densities $I = 0.10$–11.0 A dm$^{-2}$ at a cathode current density of 2.0 A dm$^{-2}$. The deposition of copper was carried out at 20 °C for 10 min.

### 2.4. *Mechanical properties*

A 40 $\mu$m thick copper coating was deposited on the stainless steel cathode (180 mm × 85 mm) in the 1 dm$^3$ electrolytic cell at 20 °C. The coating could readily be sheared. The tensile strength and the relative elongation (ductility) were measured on 12 spade-shaped foil samples at stretch rates of 100 mm min$^{-1}$ and a load of 50 kg.

## 3. Results and discussion

The effect of PANI dispersion used in the presence of low-molecular weight organic and polymeric additives on the properties of copper coatings was investigated. Each component was introduced separately or in combination into a fresh portion of the main electrolyte. A remarkably high levelling effect was observed for electrolyte containing the combination of PANI dispersion, pentablock copolymer, polysafranine dye and alkyl disulfide (4 in Table 1). The copper coatings deposited from this electrolyte had mirror brightness over a large range of current densities. The reflectivity of these samples was 87%. The tensile strength was 204 kg cm$^{-2}$ and the ductility about 40%. No burned spots were found on V-shaped samples with current densities up to 8 A dm$^{-2}$.

An 1 dm$^3$ electrolytic cell was operated for 25 days with this electrolyte under production conditions. Concentration corrections of the main electrolyte were made by introducing the additives in half of the quantities listed in Table 1 after 20 A h charge. It was found that the choice of the relative proportions of the additives ensured their steady consumption, without any deterioration in the deposit quality by the prolonged operation or the many concentration corrections.

Entries 6 and 7 in Table 1 show a 7% increase in levelling after substitution of the polysafranine lev-

*Table 1. Influence of polyaniline dispersion on the brightness and levelling of copper coatings electrodeposited from electrolytes of various composition**

| *No.* | *Concentration of additives* / mg dm$^{-3}$ | | | | *Mirror brightness at I* / A dm$^{-2}$ | *Levelling* / % |
|---|---|---|---|---|---|---|
| | *PANI* | *WA* | *LA* | *B* | | |
| 1 | 4.5 | – | – | – | none | – |
| 2 | 4.5 | – | – | 11.0 | none | – |
| 3 | 4.5 | – | 5.6 | 11.0 | none | – |
| 4 | 4.5 | 4.5 | 5.6 | 11.0 | 0.1–11 | 95$^{\dagger}$ |
| 5 | 4.5 | 4.5 | 2.5 | 11.0 | 0.1–11 | 90 |
| 6 | 4.5 | 4.5 | – | 11.0 | 1.5–11 | 86 |
| 7 | – | 4.5 | 5.6 | 11.0 | 0.1–11 | 79 |
| 8 | – | – | 5.6 | 11.0 | none | – |
| 9 | – | – | – | 11.0 | none | – |
| 10 | – | – | 5.6 | – | none | – |

* PANI denotes polyaniline dispersion, WA wetting agent (pentablock copolymer), LA levelling agent (polysafranine dye derivative) and B brightener (dialkyl disulfide).

† The surface of the sample shown in Fig. 1(c).

elling agent with the same concentration of PANI dispersion. This result indicates that PANI, especially in dispersion form, may become a substitute for polysafranine dyes, which are in common use now, without sharing their drawbacks.

With the addition of PANI dispersions, a certain amount of the steric stabilizer, poly(*N*-vinylpyrrolidone), was also introduced into the electrolyte. If the PANI dispersion was replaced by PVP, the levelling effect was considerably reduced (Table 2). This means that PVP alone is not responsible for the high levelling efficiency of PANI dispersion.

The surface of the samples, which were prepared for levelling studies, were also investigated by scanning electron microscopy (Fig. 1). After deposition of copper in the presence of PVP, the difference between peaks and grooves (Fig. 1(a)) was reduced (Fig. 1(b)) and became nearly invisible when PANI dispersion was used as additive (Fig. 1(c)), in agreement with the observed high levelling (Table 1).

Experiments also showed that copper plating in the absence of the pentablock copolymer (1–3, 8–10 in Table 1) was not successful; the coatings thus obtained were matt, with poor wetting properties and defects at high current densities. Thus, the fundamental role of poly(alkylene oxides) in the electrochemical levelling of copper coatings [19] has once more been confirmed.

The role of poly(alkylene oxides) during acid bright copper plating has been studied by several authors [20, 21] but a general understanding of the mechanism of this process is lacking. Mircheva *et al.* [19] proposed a model according to which the high levelling effects of poly(alkylene oxide) block copolymers are due to the formation of block copolymer micelles in the electrolyte and of the solubilization of low-molecular weight components in part of these micelles. Micelles containing low-molecular weight components in its core adsorb predominantly on the peaks of the uneven cathode surface, thus blocking copper deposition there. This results in a high degree of levelling of the copper coatings.

In the present case, the pentablock copolymer forms micelles in the electrolyte. Micelles are considerably smaller (hydrodynamic radius $R_h = 36$ nm) than particles of the polyaniline dispersion ($R_h = 185$ nm). It is reasonable to assume that particles of PANI dispersion efficiently fill the large cavities of the uneven cathode surface. Since PANI particles are electrically conducting this process does not lead to passivation of the electrode. Indeed, after introduction of PANI dispersion, the levelling increased by 16% (cf. 4 and 7 in Table 1).

The electrodeposition of polyaniline dispersions has been observed by Eisazadeh *et al.* [12, 13]. The nature of the transport of polyaniline particles to the cathode, is, however, not completely understood. Protonated polyaniline (2) is a polycation. Although, due to its insolubility in water, the dissociation of the ionic groups is limited, the motion of polyaniline

*Table 2. Influence of poly(N-vinylpyrrolidone) on the brightness and levelling of copper coatings electrodeposited from electrolytes of various composition**

| *No.* | *Concentration of additives*/mg dm$^{-3}$ | | | | *Mirror brightness at I* / A dm$^{-2}$ | *Levelling* / % |
|---|---|---|---|---|---|---|
| | *PVP* | *WA* | *LA* | *B* | | |
| 1 | – | 4.5 | – | 11.0 | none | 60 |
| 2 | 2.0 | 4.5 | – | 11.0 | none | 60 |
| 3 | 2.0 | 4.5 | 2.5 | 11.0 | 0.1–11 | 80$^{\dagger}$ |

* PVP denotes poly(*N*-vinylpyrrolidone), the meaning of other symbols is the same as in Table 1.

† The surface of the sample shown in Fig. 1(b).

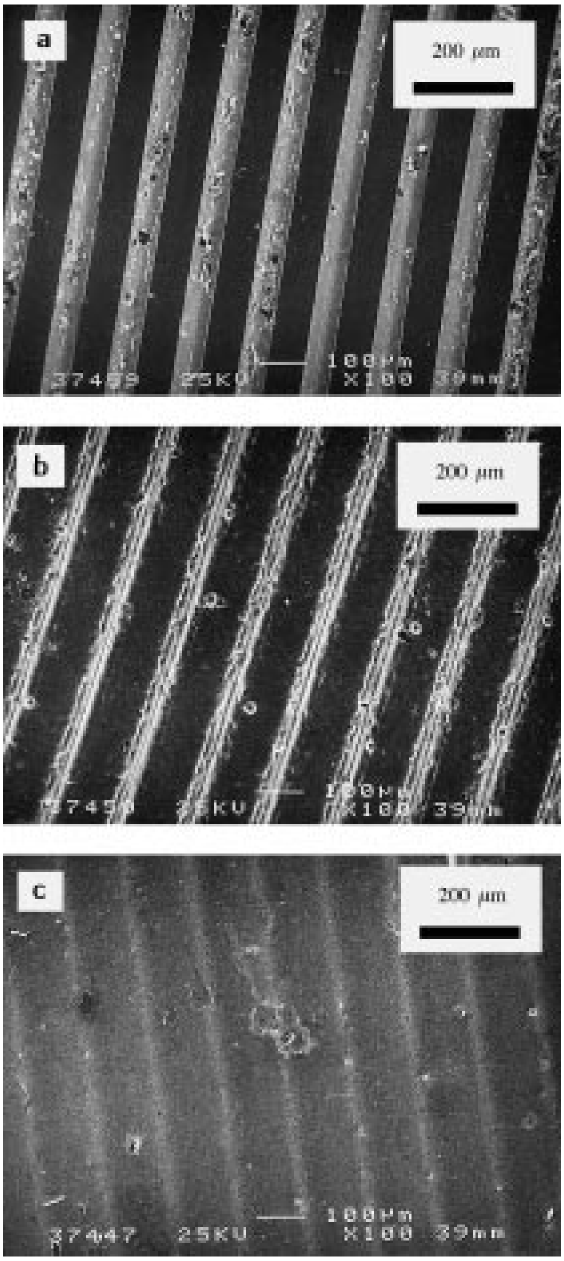


Fig. 1. Surface of the gramophone-record nickel master mould (a) before copper electrodeposition and after deposition in the presence (b) of poly(*N*-vinylpyrrolidone) and (c) of polyaniline dispersion stabilized with poly(*N*-vinylpyrrolidone).

particles is oriented towards the cathode. When polyaniline particles are placed in an electric field, even at low field strengths, they organize into chains due to the induced dipoles [22]; these effects can also affect transport phenomena. The behaviour of the system may, moreover, be influenced by the interaction among the components: preliminary dynamic light-scattering experiments have shown that the hydrodynamic radius of PANI dispersion particles increased by 25% after the introduction of the pentablock copolymer, that is, micelles formed by this copolymer are likely to adsorb onto PANI dispersion particles. The block copolymer further interacts with the copper cations [3] and the resulting objects thus may carry an overall positive charge . All these effects are likely to influence the formation of copper deposits on the cathode surface, their final quality and the degree of levelling.

The influence of the nature of the steric stabilizer used for the preparation of PANI dispersions and of the dispersion particle size on the properties of copper layers will be the subject of future studies.

## 4. Conclusions

The results suggest that electrolytes containing a polyaniline dispersion as additive will find practical applications because of the high levelling effect, the mirror brightness of surfaces over a broad range of current densities, the good mechanical deposit properties deposits, the stability of the electrolyte, and the reproducible properties of the coatings under prolonged work conditions, as well as to the relatively simple composition of the electrolyte.

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