JOURNAL OF APPLIED ELECTROCHEMISTRY **21** (1991) 565–574

REVIEWS OF APPLIED ELECTROCHEMISTRY 29

Some fundamental aspects of levelling and brightening in metal electrodeposition

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Received 29 March 1990; revised 22 October 1990

This review concerns fundamental aspects of levelling and brightening in the electrodeposition of metals. The most important effects of additives, such as the grain refinement of the deposit, polarization of the cathode, incorporation of additives in the deposit, the change of the orientation of crystals and the synergism of additives are presented. The mechanisms proposed to explain the action of additives in metal electrodeposition are classified taking into account the rate determining step of the process. The main mechanisms are discussed.

1. Introduction

In modern electroplating practice it is well-known that the introduction of small amounts of certain substances in the plating bath leads to marked changes in the nature of the metallic deposit obtained at the cathode. The quantity of additive agents required is surprisingly small and their action is often specific for a particular bath.

Although advances have been made in the study of the kinetics of metal plating processes, there are still many unknown aspects concerning the action mechanisms of the additives used as levelling or brightening agents. Also, the number of these additives used in electrodeposition is very large and it is difficult to classify them. However, a tentative classification can be made as given in Table 1. Some of the criteria used herein were proposed earlier [1]. Examples of additives used in some particular cases of metal electrodeposition processes are presented in Tables 2 to 4 [2–21].

Levelling has been defined by Thomas [22] as the ability of an electroplating solution to produce deposits relatively thicker in small recesses and relatively thinner on small protrusions with an ultimate decrease in the depth or height of the small surface irregularities. One must distinguish between 'geometric levelling' which is produced by uniform current distribution, and 'true levelling' which may appear in the presence of organic additives because of larger current densities on recess areas than on protrusions of a microprofile [23].

Brightening can be defined as the ability of an electroplating solution to produce fine deposits which consist of crystallites smaller than the wavelengths of visible light, i.e. smaller than 0.4 μm [24, 25] and having oriented grain structure [26]. A small grain size is a necessary, but not a sufficient, condition for brightness; likewise not all fine-grained deposits are bright. It has been found that the brightness depends on the degree to which morphological components of the surface of electrodeposits are in the same plane [27].

Some additives may act simultaneously as levellers and brighteners, like thiourea in Watts-type nickel electroplating baths [28]. Watson and Edwards [29] have shown that, as a function of its concentration, coumarin used as additive in a nickel plating bath may produce maximum levelling and milky brightness at 0.00034 M, less levelled but fully bright deposits at 0.001 M and deposits completely without brightness and only geometrically levelled at 0.005 M. A satisfactory explanation for this behaviour has not yet been found.

In many cases, to satisfy both conditions, combinations of levelling and brightening agents are used.

The specific action of particular agents in certain baths is one of the characteristics that is hardest to explain. It is well known that some small variations in

Table 1. Classification of additives used in the electrodeposition of metals

Properties	*Classification*
Chemical nature	Organic compounds Inorganic compounds
Interfacial activity	Surfactants: – anionic – cationic – nonionic Tensioinactive substances
Dimensions of particles	Molecular solutions Colloids
Mechanism of adsorption on the cathode [1]	Rapid adsorption-desorption Class I Brighteners ('Carriers', 'Control agents') Specific adsorption Class II Brighteners ('Levellers', 'Polarizers')
Effect on the deposit	Levelling agents Brightening agents

Table 2. Organic compounds used as levelling agents in lead electrorefining and electrodeposition

	Additives	*Electrolyte*	*References*
1.	Ligninsulphonate + animal glue	$H_2SiF_6 + PbSiF_6$	[2]
2.	Ligninsulphonate + aloes extract	$H_2SiF_6 + PbSiF_6$	[3]
3.	Ligninsulphonate + flavones or flavanones	$H_2SiF_6 + PbSiF_6$	[4]
4.	Ligninsulphonate + quinones	$H_2SiF_6 + PbSiF_6$	[4]
5.	Ligninsulphonate + chestnut extract	$H_2SiF_6 + PbSiF_6$	[5]
6.	Ligninsulphonate + block-copolymer of ethylene oxide with propylene oxide	$H_2SiF_6 + PbSiF_6$	[6]
7.	Ligninsulphonate + red cedar extract	$H_2SiF_6 + PbSiF_6$	[7]
8.	Goulac + mimosa extract	$H_2SiF_6 + PbSiF_6$	[8]
9.	Dibenzenesulphonamide + aloin	$HBF_4 + Pb(BF_4)_2$	[9]
10.	Ligninsulphonate + antraquinonesulphonate	acid solution	[10]
11.	Phenol + ethanol + gelatin	$PbCl_2 + CH_3COONH_4 + CH_3COOH$	[11]

the structure of a brightener can ruin its brightening ability and there are few chances to use one and the same agent in different baths [30].

Of course, there also exist exceptions such as saccharin, which may be used in Watts and in sulphamate nickel plating baths [31] but also in weak acidic zinc plating baths [32] and in copper electroplating baths [13]. Furfural and furfurilic alcohol are brightening agents in nickel electroplating [33, 34] and also in zinc electroplating [35, 36], tin electroplating [37] and copper electroplating from cyanide baths [38].

It is very difficult to establish a relationship between the nature and the structure of addition agents and the nature of the metal being plated.

The correlations found up to the present are applicable only in particular cases and are based on empirical observations. Thus, it was observed that all the organic compounds which have in their molecules sulphur bound directly to an atom of carbon, may be successfully used in bright silver plating, and substances with a triple bond $-C\equiv C-$ are efficient in nickel electroplating [13].

Some correlations have been made between polarizing properties and the structure of organic compounds. Thus, in the case of lead electrorefining with flavone or flavanone compounds as levelling agents, the results appeared to indicate that the necessary structural requirement for strong polarization properties was the presence of a hydroxyl group (–OH) in proximity to the aromatic ketonic group (–C–O) [4].

Such correlations may also be established in other cases, but the existence of efficient levelling and brightening agents which belong to very different classes of substances, led to the conclusion that in the levelling and brightening process more general factors than the chemical structure are implied. An argument is provided by the different behaviour of compounds from the same class. Thus, p-benzoquinone and anthraquinone, both quinones, have no levelling effect in lead electrorefining, while another quinone, naphthoquinone is an efficient levelling agent [39]. In this case, the lack of levelling capacity of p-benzoquinone and anthraquinone was attributed to the lack of the molecular dipole moment, this leading to their inability to interact with the inhomogeneous electric field at the metal/solution interface.

An attempt was made to correlate the electronic structure of organic compounds to their electrosorbtive properties which have an inhibiting effect on the cathodic reduction of metallic ions. In zinc electrodeposition, it was found that compounds which present maximum wetting and electrosorption properties have an ionization energy of $\sim 9.4\,eV$, which corresponds to the ionization potential of Zn/Zn^{2+} [18]. The ionization potentials of organic compounds were determined by studying their adsorption on several oxides (ThO_2, Al_2O_3, SnO_2, etc.) with known ionization potentials. The adsorption of organic compounds was maximum on the oxides with ionization potentials close to those of the organic compound being studied (resonance potential). Based on these results, the authors conclude that the wetting and adsorption capacities of the tensioactive organic compounds are independent of the nature and the

Table 3. Inorganic compounds used as brightening agents in silver electrodeposition

	Additives	*Electrolyte*	*Reference*
1.	Compounds of telurium	cyanide	[12]
2.	NaSCN or NH_4SCN	cyanide	[13]
3.	SbF_3 + (organic oxiacids)	cyanide (KCN + KOH)	[14]
4.	Sb_2O_3 + KOH + (triethanolamine)	cyanide ($KCN + K_2CO_3$)	[15]
5.	Sodium selenate + $Na_2S_2O_3$	cyanide	[16]
6.	$(NH_4)_2S_2O_3 + Na_2SO_3$ anh. (+CH_3COOH)	cyanide	[17]

Table 4. Types of surfactant used as additives in electrodeposition

	Type of surfactant	*Additive*	*Metal*	*Reference*
1.	Anionic	Sodium laurylsulphonate	Zn	[18]
		Dioctylsodiumsulphosuccinate (+ o-chlorobenzaldehyde)	Zn/acid	[19]
		Sodiumligninsulphonate	Pb/H_2SiF_6	[2–7, 20]
2.	Cationic	Tetra-alkylammonium salts	Sn, Pb, Zn, Cd alkalyne solutions	[21]
3.	Nonionic	Blockcopolymer of ethylene oxide with propylene oxide	Pb/H_2SiF_6	[6]

dimensions of their molecules, but dependent on their electronic structure i.e. their first ionization potential.

It is evident that developing a complete theory about the role and the mechanism of action of additives used as levelling and brightening agents in electrodeposition processes is a difficult task.

Unfortunately, the existing theories explain levelling and brightening only partially and offer satisfactory explanations only for some effects of additives. The purpose of this paper is to present the most important effects of levelling and brightening agents and their main action mechanisms in the electrodeposition process.

2. Effects of additives on cathodic deposits

2.1. *Grain refinement of the deposit*

A refinement of the deposit in regard to crystal size is found in all the cases of levelling and brightening. The dimensions of grains are determined by the number of grain-producing dislocations as well as by the number of nuclei which appear during the electrodeposition of metal. Except for coupled screw dislocations, the probability of two different grains merging into a single one is practically negligible for purely geometric reasons. Hence, the lines of coalescence form grain boundaries in the deposit. Consequently, the deposit will have a finer grain structure the larger the density of grain precursors, and therefore all the factors promoting formation of dislocations or nucleation contribute to reduction of the grain size [40]. These factors are: (i) high overpotential and/or current density, leading to a high degree of supersaturation of the surface by adatoms; and (ii) foreign molecules (impurities or additives) adsorbed at the surface which create disorder in the incorporation of adatoms into the lattice or inhibit surface diffusion of adatoms towards growing centres. These factors may appear simultaneously or separately.

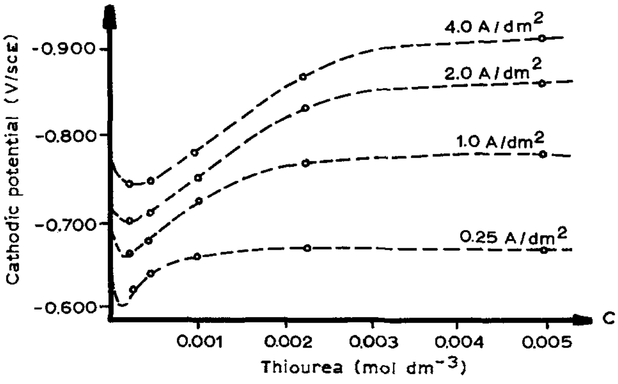


Fig. 1. Cathode potential against concentration of additive for nickel solutions containing thiourea.

As mentioned earlier, grain refinement is a necessary, but not a sufficient, condition for the production of bright and evenly levelled deposits. Thus, for example, in lead electrorefining the Na-ligninsulphonate used as additive, acts as a grain refiner, supposedly by blocking the growth of individual crystals, and thus resulting in an increased nucleation rate for lead crystallites. However, the presence of ligninsulphonate alone in lead refining electrolyte does not give good levelling of the cathodic deposit; both ligninsulphonate and another agent (animal glue, aloin, flavonoid compounds a.s.o.) must be present [3–5].

2.2. *The polarization of the cathode*

A large number of additives used in electrodeposition of metals increase the polarization of the cathode, i.e. they decrease the current density obtained at a given electrode potential. Roth and Leidheiser [41] measured the cathodic polarization in nickel plating baths in the presence of many additives. The slopes of the (ε against c) curves (where ε is the potential of the cathode and c is the bulk concentration of the additive) decreased in most cases with increasing concentration of the additive and frequently a more or less flat polarization plateau was reached. The initial slope of the polarization curve and the polarization obtained at the plateau varied strongly with the type of addition agent used.

Watson and Edwards [29] also detected polarization plateaux for coumarin, thiourea and saccharin in nickel plating baths (Fig. 1).

The maximum polarization for the first two compounds was about 0.1 V higher than that obtained without an addition agent, whereas saccharin had little effect.

The increase of cathode polarization was also observed in the case of lead electrorefining [3, 4]. The slopes of the cathode polarization against current den-

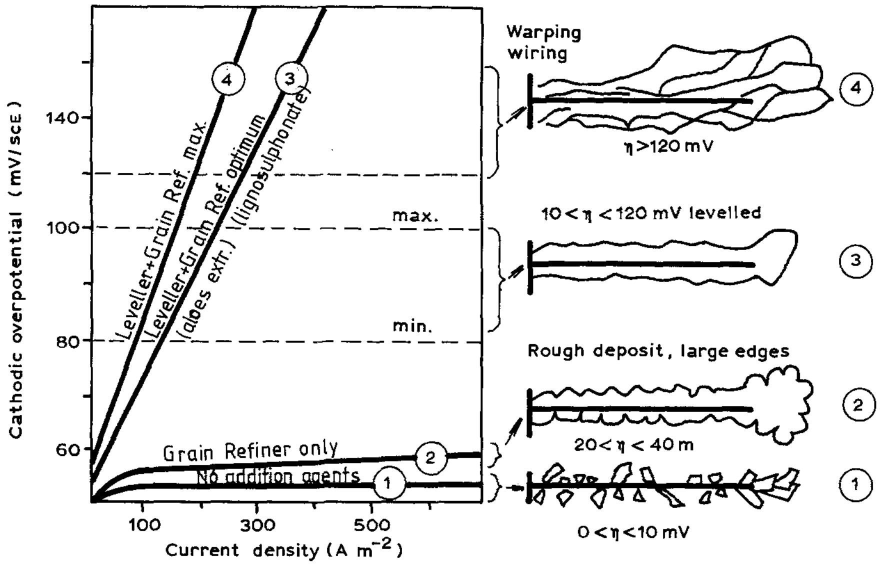


Fig. 2. Cathode polarization and cathode deposit quality in lead electrorefining. Conditions: $T = 20°\mathrm{C}$, $[\mathrm{Pb}^{2+}] = 70\,\mathrm{g\,dm}^{-3}$, $\mathrm{H_2SiF_6} = 90\,\mathrm{g\,dm}^{-3}$, $i = 200\,\mathrm{A\,m}^{-2}$.

sity curves are very low without addition agents, remain low with ligninsulphonate only and rise from 0.3 to $0.6\,\mathrm{mV\,(A\,m^{-2})^{-1}}$ in the presence of an optimum combination of aloes and ligninsulphonate; when the slope of the curve exceeds $0.6\,\mathrm{mV\,(A\,m^{-2})^{-1}}$ the deposit changes from a good, smooth, to a very unacceptable and warped deposit (Fig. 2).

Cathode polarization decreases with increasing stirring rate, temperature or lead concentration in the electrolyte. If the reaction is controlled by the diffusion of the additive, the limiting currents are sensitive to stirring rate [21, 23].

A strong influence of the additives on the polarization curves was used as selection criteria for efficient levelling agents [4], but as already mentioned, a large slope of the polarization curves is not always associated with good levelling properties of the additive [23].

This apparently unexpected behaviour may be explained by the very strong adsorbtion of these additives onto the surface of the metal without any possibility of the subsequent migration of their molecules to the sites with local irregularities which have to be levelled.

The change of electrode polarization in the presence of additives was used, in some cases, for quantitative determination of these additives in electroplating baths. Thus, the rotating disc electrode technique was used to determine the concentration of polyethyleneglycol (PEG) and polypropyleneglycol (PPG) in acid copper plating baths [42].

A constant electric current is passed through a plating cell and the voltage difference between the copper plated cathode and a reference electrode is measured. Varying amounts of PEG are added to the solution and the cathode potential is recorded at equilibrium. The potential against the known amount of additive is plotted to provide a standard curve for determining unknown amounts of the same additive.

The main cause of the changes in the potential of the cathode is the electrosorption of additives at the electrode interface. Coverage of the electrode by additive molecules increases the effective current density, and consequently, the overvoltage [43]. Furthermore, the electrode reaction kinetic parameters can also be modified, resulting in a change of overvoltage. Unfortunately, these effects are difficult to determine on solid metals.

There are situations when additives decrease the cathodic polarization. Thus, Weiner and Klein [44–46] mentioned the depolarization effect of some additives used in cyanide plating baths. An interesting case is that of thiourea, used as brightening agent in a Watts-type nickel plating bath [29]. As shown in Fig. 1. thiourea decreases cathode polarization at concentrations less than 0.001 M and increases it considerably at higher concentrations.

In the simultaneous use of more than one additive it is possible that the cathodic potential remains unaffected; one of the additives acts as a polarizing agent and the other as a depolarizing one, thus being mutually counteractive [47, 48].

2.3. *Incorporation of additives in the deposit*

Electroplating practice shows a consumption of additives during metal electrodeposition; therefore, concentration must be corrected during the process.

The consumption of additives takes place by removal with the plated objects, by their incorporation in the deposit (codeposition) and by reaction on the plated object.

Several methods are used to determine the consumption rates and the form in which the additives are included in the deposits. There are direct methods (radiotracer, mass spectrometry, etc.) and indirect methods (determination of the bulk concentration, determination of deposit resistivity, etc.).

The radiotracer method is successfully used when the levelling or brightening agent is a compound with known structure and in which one of the constituent atoms may be replaced with its radioactive isotope, easily detectable after incorporation into the deposit. Using this method Bedcom and Riley [49–51] demonstrated that sodium allylsulphonate, used as levelling agent in a nickel plating bath, is deposited preferentially at high points of a rough surface. The organic addition agent was added to the solution in the form of radioactive sodium allylsulphonate containing the S–35 radioactive isotope.

The preferential adsorption of the radiotracer is consistent with the fact that, in levelling, less metal is deposited on the peaks and more metal is deposited in the recesses of an irregular surface. Rogers, Ware and Fellows [28] arrived at the same conclusion during an investigation of the behaviour of labelled thiourea in a nickel plating bath. These authors have demonstrated, not only the higher rate of incorporation of thiourea at the peaks, but also the dependence of incorporation on the stirring rate and on the current density. It was showed that brightening and incorporation are strongly controlled by the diffusion of thiourea through the boundary layer at the metal-solution interface. Since in all experiments only the presence of S–35 isotope was detected, no conclusion could be made concerning the form in which the additive was incorporated.

Several theories exists regarding the form in which the incorporation of an additive takes place. While some investigators have shown that certain addition agents are apparently codeposited with the metal in an unchanged or unreduced form [29], others assert that additives are reduced on the cathode [52]. If the reduction products are less adsorbable, they may return to the bulk of the solution and this could partially explain the difference between the consumption and the incorporation rate of additives observed in some cases [23].

In some cases, the reduction or dimerization products of additives are responsible for the levelling of the cathodic deposit. Thus in their study on zinc electrodeposition, Loshkarev *et al.* [53] observed the levelling effect of the partial reduction products of cotarnine, used as brightening agent.

Another direct method used for the study of codeposition of additives was mass spectrometry.

The concentration of organic matter in the deposit is compared to a reference concentration obtained for a clean electrodeposit. This method was used to investigate the behaviour of coumarin and p-toluenesulphonamide in the electrodeposition of Pt on Ir and W from sulphate-dinitroplatinous acid, i.e., $H_2Pt(NO_2)_2SO_4$ [54, 55].

2.4. *The change of the orientation of crystals in the deposit*

The preferential orientation of crystals in deposits is the result of a great number of variables, including the base crystal, bath compositions and plating conditions. There is a well known tendency of the electrodeposit at the very beginning to continue the structure of the base metal (epitaxy). After the influence of the substrate becomes less important, the observed orientation in electrodeposits is more likely to be determined by bath composition and plating conditions. In the presence of additives, the crystals may adopt a preferred orientation, which may be observed by X-ray diffraction analysis. This preferred orientation is a result of different rates of growth of different crystal faces. The difference is enhanced by preferential adsorption of foreign molecules such as impurities or additives [56].

A direct relationship between the degree of preferred orientation and brightness has not yet been found. However some investigators have mentioned that the fibre axis of some nickel deposits is related to the type of structure observed (i.e. platelet, equiaxed crystallite, or spyral-type) and the addition agents in the plating bath [27]. It was concluded that the brightness depends on the degree to which the structural components of the deposits are in the same plane. This, in turn, is determined by several factors such as grain size and orientation, the degree of preferred orientation and codeposition of foreign substances. As mentioned above, small grain size is not a sufficient condition for brightness. Deposits showing spyral-type structures were dull even though some were very fine grained because this type of growth results in crystals which have no light-reflecting plane parallel to the surface. The orientation of the crystals which determines whether or not a light-reflecting plane is parallel to the surface therefore affects the brightness.

The ability of some organic additives to interfere with the normal tendency of certain plating baths to continue the propagation of a metal single crystal must be mentioned (i.e. thiourea in an acid copper plating bath) [30]. The interference operates on the growing crystals on the (1 1 1) and (1 0 0) faces of the single crystals, limiting their growth.

In the case of electrodeposition of zinc from acidic baths containing animal glue [57], strong preference for (1 0 1) orientation was observed. This orientation is attributed to the fact that the additive preferentially increases the overpotential on certain crystalline faces, thus increasing the nucleation rate and diminishing the size of the zinc grains.

2.5. *The synergism of additives*

The literature contains much information about the conjoint use of additives producing high quality cathodic deposits. When used alone, certain additives do not produce sufficiently good deposits, but their levelling or brightening effect is remarkable in synergetic combinations with other additives.

Dextrin is generally used with thiourea and enhances brightening in the electrodeposition of copper from a sulphate solution [58]. Calcium or sodium ligninsulphonates, used as additives in lead electrorefining baths, produce a relative smooth plate, but with heavy edges. However, conjoint use of the ligninsulphonates and aloes [3, 21], ligninsulphonates and flavanonic combinations [4] or ligninsulphonates and a water soluble block copolymer of propylene oxide and ethylene oxide [6] has the effect of smoothening the edges and, in general, of producing a much more uniform plate, essentially free of nodules and trees.

In nickel electrodeposition from Watts type baths it is recognized that two addition agents are usually required to produce full brightness and that a synergistic effect takes place [50]. In the case of using a combination of sodium allyl sulphonate and N-allylquinaldinium bromide, it was suggested that the charged groups of both of these additives would be arranged alternately on the surface. This arrangement of alternate negative and positive ions might be thought of as 'ion-pairs', which suggests a neutralization of repulsive forces and an enhancement of attractive forces, which may contribute to a greater blockage of the surface, thus promoting levelling.

2.6. *The extension of the current density range*

The use of additives influences the working current density range. The more efficient the levelling agent, the higher the current densities at which acceptable electrodeposits are obtained. Thus, in silver electroplating from an electrolyte containing sodium selenate, by adding 100–150 g dm^{-3} KNO_3, the current density may be increased from 4 A dm^{-2} to 10 A dm^{-2} [59].

In the case of organic surface active additives, the levelling capacity of an agent can be correlated with its ability to block the irregularities of the cathode by surface diffusion; so, it may be expected that an increase in current density, which promotes an increase in surface growth rate may be countered by a compound with higher mobility (diffusivity).

3. Mechanisms of levelling and brightening

It is well known that the electrodeposition of a metal from a solvated ionic species present in the solution occurs in several steps [40], namely,

- mass transfer of the electroactive species to the outer limit of the electrode double layer followed eventually by their electrosorption;
- charge transfer from the cathode to the partially desolvated and uncomplexed ions, with the formation of adatoms on the cathode surface;
- lateral diffusion of adatoms on the metal surface until their incorporation into the crystal lattice.

Each of these steps is characterized by a definite overvoltage (transport, activation and electrocrystallization-overvoltages, respectively). In most cases, in the absence of additives, the final result is an unsatisfactory cathodic deposit (dendritic, powdery, etc.).

A dendrite-free, levelled, compact and adherent deposit requires such values of overpotentials as to provide a sufficiently high nucleation rate, a moderate charge transfer rate and a sufficiently high crystallization overpotential. In such a way nucleation is provided simultaneously with growth of grains and with surface diffusion of adatoms to the thermodynamically favoured growth centres. These conditions may be fulfilled by adequate choice of parameters and, especially, by using proper levelling and brightening agents in appropriate concentrations.

The mechanisms proposed to explain the action of additives in metal electrodeposition differ, not only from one metal to another, but also from certain working conditions to others during the deposition of the same metal. A classification of these mechanisms is difficult and there are so far few reviews published on this subject [23, 60]. However, taking into account the rate determining step of the process, the mechanisms can be classified as either *diffusion controlled mechanisms* (the rate determining step is the diffusion of electroactive species or of the additives to the electrode) or *non-diffusional mechanisms* (the rate determining steps are the charge transfer or adatom incorporation in the crystal lattice).

3.1. *Diffusion controlled mechanisms*

The electrodeposition process rate may be controlled by mass transfer of the metallic ions, and the additives (which may sometimes act as complexing agents) or of the hydrogen ions.

In most cases, the rate determining step is the transport of additives towards the cathode. The possibility that the electrodeposition reaction over a certain current density range may be controlled by the mass transfer of additives and not of the metal ions is obviously due to the fact that the latter are usually present in 100 to 10^5 times larger molar concentrations and that generally the current density, i, is much lower than the limiting current density, i_l, for the metal ions [23].

It can be assumed that in the case of diffusion controlled levelling, more levelling agent diffuses to, and is adsorbed at, elevations rather than the recesses and this drives the metallic adatoms to migrate over the surface into the recess areas until they find free sites available for incorporation into the lattice [61].

The reaction control by convective diffusion of an additive may be revealed by the influence of stirring on polarization and by the dependence of the consumption rate of the additive on its bulk concentration, current density and boundary layer thickness. In these cases, studies of codeposition of additive revealed the following features of diffusion control: preferred codeposition on micropeaks, increase of codeposition with increased stirring, reasonable constancy of the codeposition rate, proportionality of the codeposition rate to the concentration of the additive [23].

The surface diffusion of adions or adatoms was identified as the rate determining step in silver electrodeposition at potentials not far from the equilibrium potential [62]; at higher current densities this diffusion plays only a secondary role.

The decrease of levelling as a consequence of pH lowering in a bath for nickel electroplating in the presence of coumarin [61] as well as of an acetilenic compound [63] suggests that the diffusion rate of H^+ ions may also affect the electrodeposition rate, probably by influencing the rate of hydrogen evolution on the electrode [60].

The diffusion rate of metal ions may become important at high current densities and/or large diffusion layer thickness.

In the case of a complex formation between the organic additive and the metal ions, it is possible that the transport properties of the electroactive species are modified and, thus, the levelling mechanisms may be diffusion controlled.

Several diffusional mechanisms are proposed to explain the role of colloidal additives in the electrodeposition of metals. The colloids may adsorb onto their surface the metal ions and some organic species resulting in sizable aggregates which possess altered transport properties. As an example, in the electrorefining of lead, the sodium or calcium ligninsulphonate, whose colloidal properties are well known, provide a suspension of colloidal particles on which a second additive (i.e. a flavonoid agent) and its lead complex are adsorbed and dispersed throughout the diffusion layer of the cathode [4]. This function facilitates levelling of the deposit by the flavonoid compound (the leveller).

It is clear that, even in the case of diffusional mechanisms, there are several different alternatives concerning the rate determining step. Furthermore, consideration needs to be given to the substrate surface on which the electrodeposition process is to take place, because its preparation and microgeometry affect the diffusion layer significantly. A wide variety of surface treatments are now available (grinding, abrading, polishing, etching etc.) and each of the different surfaces obtained will result in a different physical form of the substrate.

3.2. *Non-diffusional mechanisms*

It is not possible to explain all the types of levelling and brightening through a diffusional mechanism. Among the non-diffusional factors which may be involved in levelling are the inner crystalographic differences of the metallic deposit, the curvature of the surface, the electrodeposition, the complexing properties of the metallic ions, etc.

The rate determining step in these cases becomes the charge transfer or the incorporation of metal adatoms into the crystal lattice.

Taking into account the large number of particular cases, we can conclude that the following main types of non-diffusional mechanism exist: (i) mechanisms based on electrosorption, (ii) mechanisms with complex formation, (iii) ion-pairing mechanisms, (iv) mechanisms with changing interfacial tension, and (v) mechanisms based on chemical filming of the electrode.

The boundaries between these mechanisms are not strict. Certain factors (e.g., electrosorption) may be involved in several types of mechanisms. The present classification has been made taking into account the predominant non-diffusional factor.

3.2.1. Mechanisms based on electrosorption. A number of theories concerning the mechanisms of levelling start from the premise of electrosorption of additives at the metal/electrolyte interface taking into account the surface active character of the majority of these additives. However, not every surfactant gives level deposits, thus leading to the idea that the surface active character of the additive must be related to other parameters which promote levelling [39, 64].

Considering the fact that the concentration of the brightener or leveller is always much less than that of the metal ion, it seems reasonable that its action is localized mainly at the electrode interface.

Several electrosorption mechanisms may be postulated of which the following are described.

'Structure sensitive' electrosorption [30] supposes that the adsorption of the brightener is selective, so that only molecules of a certain size, shape, and chemical structure can be electrosorbed on the metal surface. This corresponds in some respects to chemisorption and may require a suitable spacing between metal atoms on the surface of the electrodeposit to hold the organic molecules.

In the electrosorption of aromatic molecules at metal electrodes the electrosorptive effects were attributed to the interaction of π-electrons with the electrode. The energetic analysis shows that charge transfer takes place between the adsorbed molecule and the metal; the transfer should depend on the Fermi level of the metal, i.e. the work function and the ionization potential and electron affinity of the adsorbate [65].

It seems likely that this mechanism of electrosorption of molecules that act as levelling and brightening agents is similar to the mechanisms of action of additives in other fields such as in corrosion inhibition [66].

Another type of electrosorption may be termed 'current density sensitive' or 'shape sensitive' [30]. In this case, the electrosorption of the brightener on the cathode surface occurs regardless of the nature of the crystalline structure of the cathode, but dependent on the profile of the electrode. This situation seems to be present in certain bright baths, in which the expected low current density areas (the recess areas) grow faster than high current density areas (the peak areas), suggesting the possibility that the high current density areas are blocked preferentially by these compounds.

Structure sensitive and shape sensitive electrosorption may be viewed as physically independent, but not necessarily always separated. In some cases, one type of mechanism operates exclusively, but in most situations, contributions from each mechanism will be found.

There are further models proposed for the explanation of the specific double layer effects occurring when a surfactant (a neutral species or an anion) is electrosorbed at the interface [67, 68]. They are: (a) 'bridging' models where the surfactant facilitates or blocks the electron transfer and the rate constant is a linear function of the surface coverage; (b) 'electrostatic interaction' models where the activation energy is lowered or enhanced by the surfactant and the logarithm of the rate constant is a linear function of the surface coverage; (c) 'coadsorption' models where the electroactive species coadsorbs with the surfactant and the reaction proceeds via and adsorbed state and the rate constant is proportional to the surface excess of the reactant.

The adsorption of the surfactant takes place preferentially on the protrusions of the growing surface leading to the displacement of metal adatoms toward the recesses of the microprofile, followed by their deposition, the final effect being levelling and/or brightening. Investigations by autoradiography and counting techniques showed that Na-allyl sulphonate [49, 50] or thiourea [28] from a Watts-plating solution used in nickel electrodeposition are deposited preferentially at the high points of an irregular surface, thereby substantiating a part of the levelling theory.

The primary mechanisms by which additives exert their influence are blocking adsorption and/or non-blocking adsorption which occur both on the active sites of the crystal planes of the substrates and on the emerging surfaces of the crystallizing phases themselves [69].

Non-blocking adsorption can cause changes in the nucleation and in the growth rate of crystals growing via the screw dislocation mechanism. Non-blocking additives are in equilibrium with the bulk solution and hence are pushed along ahead of the steps from the crystal faces (they are mobile).

Blocking adsorption is particularly important in the later stages of crystal growth, coming after a steady growth during which the nearest neighbours have coalesced into a layer of product. Blocking adsorption occurs when additives are irreversibly adsorbed at interfaces, a fact that is most easily achieved by large organic molecules and colloids. Animal glue, used as additive in many electrodeposition processes, acts as an efficient blocking additive, being both a colloid and a tetra-alkyl-ammonium salt. Sodium ligninsulphonate, a colloidal additive, used in lead electrorefining, acts as a grain refiner, supposedly by blocking the growth of individual crystals, resulting in a greatly increased nucleation rate for lead crystallites (blocking adsorption) [4]. Another typical colloid is gelatin, used as additive in lead [11, 70], zinc [71] and copper [72] electrodeposition, acting probably as mentioned previously.

During the growth of the crystal surface, when the distance between two neighbouring adsorbed additive molecules is less than the diameter of a critical nucleus, C, the 'squeeze' of a step between these molecules creates a curved edge that has a higher energy than the straight edge from which it originated (Fig. 3). Consequently, the average growing velocity in the presence of additives is smaller than in their absence. Furthermore, if the additive molecules are sufficiently close together, the curvature of the edge exceeds that of the critical nucleus and growth stops entirely.

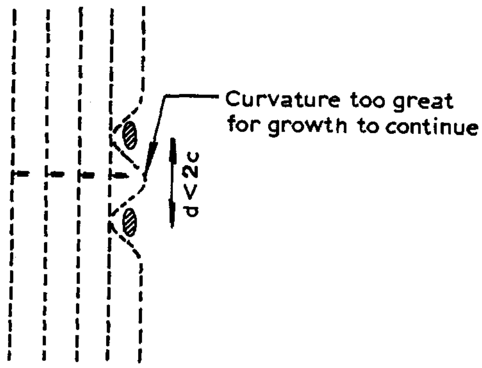


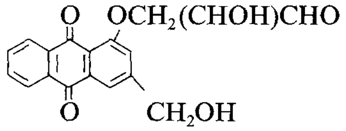
Fig. 3. Blockage of growth steps by additive molecules less than $2c$ apart.

Mechanisms based on electrosorption are the most common and, whatever the opinion about whether additive adsorption takes place, there is general agreement that the additive is essentially acting only as a foreign body which interferes with some process or furnishes localized spots on which reactions can occur [60].

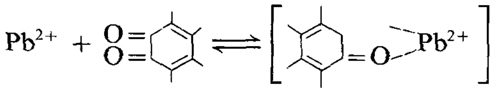
The primary requirement of an additive that acts by this mechanism is not its chemistry. It merely has to be able to attach itself to the surface and be approximately the right size. This adsorbed material presumably leads to localized polarization, which partially inhibits the deposition of metal at the peaks of an irregular surface and diverts current flow to recessed areas.

3.2.2. *Mechanisms with complex formation.* It is postulated that, in the case of metal electrodeposition, the adsorbed additive may complex metal ions, increasing the amount of the latter adsorbed on the electrode and thus increasing the rate of reduction (induced adsorption) or accelerating the rate of flow of electrons through the additive from the electrode to the metal ion (ion bridging) [60].

One of the mechanisms proposed to explain the levelling of lead deposits in the Betts baths containing sodium ligninsulphonate and aloes extract suggests the formation of a complex of lead ions with the main component of the aloes extract, the aloin [4], with the proposed formula



This mechanism explains the increase in electrode polarization with increase in Pb^{2+} ion concentration, but some doubt is cast on the proposed structure of aloin, because it appears impossible for the p-phenol structure to complex the Pb^{2+} ions as does the o-quinone structure:



There are some cases in which the reduction of metal ion takes place in several steps and the intermediate valence ions interact with the organic compound present in the electrolyte. Thus, in the electrodeposition of copper in the presence of acrylic acid, the surface reaction of Cu^+ with acrylic acid leads to a profound change in the nature of the adsorbed particles and of the kinetics and mechanism of Cu^{2+} electroreduction [73].

3.2.3. Ion-pairing mechanisms. In different cases of electrodeposition the reacting complex ion varies in charge. In some cases it is negative, while in others it is positive. The negative ion faces a repulsion barrier to the electrosorption on the cathode. A quaternary ammonium salt, which can form an ion pair with the negative ion, lowers this energy barrier and therefore accelerates the rate of reduction of the negative ion in an adsorption controlled reaction.

The beneficial influence of ammonium quaternary salts was demonstrated in the case of electrodeposition of amphoteric metals such as zinc and tin from their negative anions in alkaline baths and in the electrodeposition of cadmium from cyanide complex ions [21].

In the case of electrodeposition of alloys it was found that the mass ratio of metal plated from a negatively charged ion to that from a positively charged ion increases with addition of a quaternary ammonium salt, as expected from the rule of ion-pairing [74].

There are also exceptions from the ion pairing rule, in which the expected behaviour would not be obtained upon addition of the quaternary salt to a solution of a negatively charged metal complex, exceptions which are well summarized by Franklin *et al.* [21]:

(a) the rate of the reduction process is not adsorption controlled (e.g. the reduction of lead from a negative plumbite in basic solution is transport controlled and hence the surfactant does not affect the limiting current);

(b) the reacting ion is not the predominant one in the solution; in some cases the ion which is in small concentration reacts more rapidly than the species of higher concentration. In these cases, the most important factor for predicting the ion pairing effect is the electric charge of the species which is controlling the rate of reduction, not the charge of the predominant ion;

(c) the additive has a high surface activity and a film is formed on the electrode. The levelling action is not due to the ion pairing but to the ability of the surfactant to adsorb on the electrode surface. Thus, for example, the addition of $[(Bu)_4N^+Br^-]$ causes a marked increase in the lead to thallium ratio in electrodeposited alloys because the additive probably protects from dissolution by the NaOH solution the lead compound precipitate formed on the electrode by the codeposition of hydrogen.

The ion pairing mechanism explains the synergistic effect of some additives like sodium allyl sulphonate and N-allyl quinaldinium bromide in a Watts-type nickel plating bath [49, 51] (see § 2.5).

3.2.4. Mechanisms based on change of interfacial tension. One common factor present in most existing theories of levelling and brightening is the electrosorption of additives, leading to a substantial change in the interfacial free energy.

In studies of the electrodeposition of zinc in the presence of strong fluorosurfactants, it was concluded that levelling and brightening is due to the tendency of adsorbed surfactants to kept the interfacial free energy uniform all over the exposed deposit surface, thus facilitating latteral diffusion of adatoms until they reach growth sites.

The adsorption of a strong surfactant may also affect the deposition by a strong hydrophobization of the substrate surface [48, 60, 75, 76]. The hydrophobic film formed below the critical micellar concentration has a much lower interfacial tension and wets hydrogen and other hydrophobic substances at the interface and thus aids their removal from the surface. In some cases these films, if charged, attract the reducible ions to the surface. In other cases, the low interfacial tension allows some non-polar compounds to wet the surface [60].

As the concentration of surfactant in solution increases, organized multilayers appear. Hence, the surface properties change alternately from hydrophobic to a hydrophilic and back. This probably accounts for some of the reported effects observed when the concentration of surfactant changes [48]. The hydrophobization or hydrophilization of the growing surface may influence the deposition mechanism of a modified electrode.

3.2.5. Mechanisms based on chemical film formation of the electrode. Some levelling agents may influence the deposit morphology without being adsorbed on the surface. The interaction in these cases may be of chemical nature, as in the case of thiourea in the electrodeposition of copper from cyanide baths, when a thin CuS film is formed on the electrode [13, 58]. It can be assumed that thiourea decomposes on the cathode, resulting in H_2S and NH_4CN. The H_2S reacts with the cathode, giving CuS. The incorporation of sulphur into the deposit modifies the crystalline structure. The CuS appears to act by blocking the growing centres and inhibiting the surface diffusion of copper adatoms, thus causing the nucleation of new growth centres.

A similar mechanism is proposed for the action of l(-)cystine in the electrodeposition of copper from a sulphate solution [58].

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