The 14th William Blum Lecture
Presented at the 60th AES Annual Convention in Minneapolis, Minnesota
June 18, 1973

Current Distribution on Microprofiles

by

Otto Kardos
M&T Chemicals
Ferndale, Michigan

Recipient of the 1972 AES Scientific Achievement Award

Contents

The 14th William Blum Lecture

Presented at the 60th AES Annual Convention in Minneapolis, Minnesota
June 18, 1973

Current Distribution on Microprofiles

by
Otto Kardos
M&T Chemicals
Ferndale, Michigan
Recipient of the 1972 AES Scientific Achievement Award

Editor's Note: Originally published as *Plating*, **61** (2), 129-138 (1974), this article is a re-publication of the 14th William Blum Lecture, presented at the 60th AES Annual Convention in Cleveland, on June 18, 1973.

ABSTRACT

A survey of experimental facts and theory is given. The three types of cathodic metal distribution on microprofiles (recess/peak thickness ratio = 1, < 1, > 1) are explained. Diffusion controlled inhibition is shown to be the preponderant mechanism of the last type. Cathodic and anodic microthrowing power are compared. Roughness formation on initially smooth surfaces, and its prevention by addition agents or by modulated current, are discussed and possible brightening and leveling mechanisms other than diffusion controlled inhibition are suggested.

1. Introduction

Current distribution on microprofiles was also the subject of two papers written by Dr. Foulke and myself for the 1956 Convention of the American Electroplaters' Society. These papers supplied proofs for a diffusion theory of leveling and "bad microthrow."[1,2] At about the same time, Watson and Edwards[3] developed independently a very similar diffusion theory of leveling and Leidheiser[4] had published the outline of a somewhat different theory.

These papers aroused considerable interest, and many studies on cathodic current and metal distribution on microprofiles, especially on leveling, were made in this and other countries. They generally supplied new or more exact proofs of the diffusion theory of leveling, but some studies reported at the same AES Convention by Thomas,[5] supported another theory which ascribed the increased adsorption of the leveling agent on micropeaks not to a greater local diffusion rate but to "shape-sensitive" adsorption related to the small radius of curvature of the micropeaks.

In view of the great practical importance of leveling, of the possible relevance of a correct theory of leveling to the understanding of brightening, and of the considerable international research effort in this field, it seems useful to summarize the theory, report on the significant contributions of others, and to look at where we are now.

For reviews of the field of microthrowing power see references 6-12.

Cathodic metal distribution on microprofiles, which may be defined as profiles which have a roughness depth or height of less than about 0.5 mm (500 μm, 0.02 in.), shows a surprising variety: on descent from a micropeak into a microdepression, the metal deposit thickness may decrease, remain constant, or increase. One speaks correspondingly of "bad microthrow," "good microthrow" and "true leveling" (excellent microthrow).

Good microthrow or the rather uniform metal deposition into small pores, crevices and scratches was first described by W. Meyer[13] in 1935. All three types of microthrow were described by Gardam in 1947[14] and by Reinhard in 1950.[15] Well-leveling nickel baths[16,17] were available in the late forties.

But in the fall of 1955 when Dr. Foulke and I started to think more intensely about microthrowing power, no general theory was available. As is often the case in electroplating, and in many other technological areas, "art" preceded "science," or empirical technology preceded scientific understanding. However, one type of microthrowing power, namely practically uniform metal distribution ("good microthrow"), was already explained as a benefit from the well-developed theory of macro-throwing power.

2. The theory of macrothrowing power and its contribution to the understanding of microthrowing power

To understand microthrowing power it is necessary to first understand macrothrowing power, that is cathodic current and metal distribution on large-scale profiles, the so-called macroprofiles. The theory of macrothrowing power had been developed much earlier and the classical paper about this theory was published by Haring and Blum 50 years ago.[18] Their paper defined "primary" and "secondary" current distribution, pointed out the influence of the variation of current efficiency with current density on metal distribution, and defined throwing power (which meant at that time, of course, macrothrowing power) as "the deviation (in per cent) of the metal distribution ratio from the primary current distribution ratio." Good reviews on macrothrowing power are found in references 9, 18-25.

Primary current distribution is the current distribution which would be obtained in absence of polarization, which increases with increasing local current density. It would be determined only by the resistance which the electrolyte opposes to the flow of electric current to the different electrode areas. Because of the much higher (often a million times) electrical conductivity of metals as compared to the conductivity of electrolytes, the surface of a metallic electrode can generally be considered to be at practically constant potential, unless the electrode is very long or thin. Finding the primary current distribution on a flat or profiled electrode in the presence of a counter-electrode and of the nonconducting boundaries formed by the walls of the plating cell consists thus in finding the potential distribution between two equipotential surfaces. Mathematical[20,26,27,27A,29A] as well as experimental methods[23,28,28A,29,29A] are available for the determination of primary current distribution. The latter depends on the shape, the relative sizes and positions of the electrodes and of the nonconducting walls of the electrolytic cell, but it is independent of the absolute size of the system, of the electrolyte properties and the conditions of electrolysis.

In primary current distribution the current concentrates on protruding areas not only because of their smaller distance from the counter electrode but, still more, because of their lateral accessibility to the current. Indeed primary current distribution would give infinite current density on ideally sharp peaks and zero current density on the sharp hollow corners of a triangular wave profile.

Figure 1 shows an experimental plot[29] of equipotential lines and, perpendicular to them, current flow lines at and near a triangular wave electrode. The potential difference between two adjacent equipotential lines is constant and the same current flows to the electrodes between two adjacent current flow lines. The local current density is $\sigma|d\phi/dx|$ where σ is the specific electric conductivity of the electrolyte and $|d\phi/dx|$ is the absolute value of the potential gradient. The latter is much greater over the protrusions than over the valleys, and the difference increases with smaller notch (or apex) angles.

Any equipotential line may be replaced by an equally shaped counterelectrode, and any current flow line by a nonconducting boundary, without change of the primary current distribution. The equipotential lines become practically flat at the rather short distance of about half the groove width from the micropeaks.[27]

On a working or "polarized" electrode the "electrode potential" E, which depends on the potential drop in the electric double layer, is different from the equilibrium potential, or - if several reactions occur simultaneously on the electrode - from the rest or zero-current potential. These deviations of E are called overpotential or overvoltage ($\eta = E - E_{eq}$) and polarization ($E - E_{rest}$), respectively. Their presence changes "primary current distribution" into "secondary current distribution."

For the purpose of this paper it will be sufficient to distinguish *activation overpotential* (required to reduce the activation energy of the rate determining step, which is often the "charge transfer" in which ions or electrons are transferred through the electric double layer) and *concentration overpotential* (due to concentration changes in the vicinity of the electrode). Good discussions of overpotential are found in the comprehensive references 30, 31 or the shorter 9, 30A, 32-35 and the very recent 35A.

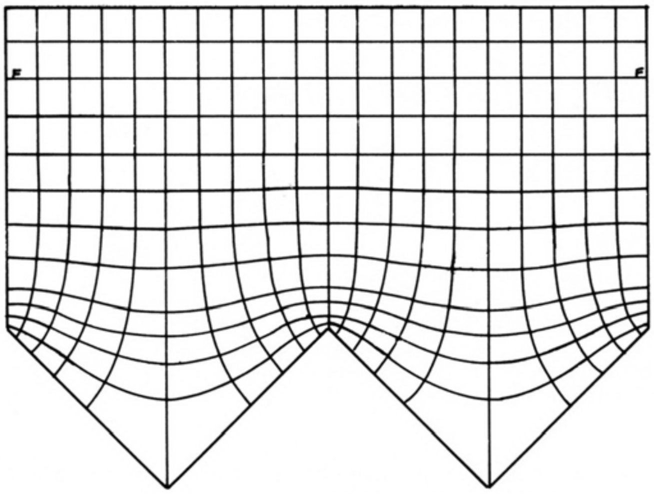


Figure 1 - Primary current distribution, from Rousselot.[29]

Polarization increases with increasing current density current distribution on the peaks, or protruding areas, of a profile produce there a much greater polarization than in the recess or valley areas. This greater overpotential on the peaks tends to oppose current flow and to divert current towards the recess areas. The ohmic resistance to be overcome decreases with decreasing profile depth and, thus, the equalizing effect of polarization should be the greater - and secondary current distribution the more uniform - the smaller the profile depth. On very small-scale profiles, current distribution should consequently become practically uniform. This was pointed out by Kasper,[19] DuRose, Karash and Willson[17] and Wagner.[20]

Before we discuss this very important extension of the theory of macrothrowing power to microprofiles we have to remember that cathodic *metal* distribution on macroprofiles is strongly, and often decisively, influenced by the variation of current efficiency with current density. If the current efficiency decreases with increasing current density, as it generally does in cyanide baths, metal distribution is more uniform than secondary current distribution. If current efficiency increases with increasing current density, as is the case over the entire current density range in chromium plating baths and in the low current density range in nickel baths, metal distribution is less uniform than secondary current distribution.

Wagner[20] developed an approximate method for calculating to what extent uniform current distribution is approached over a small-scale *triangular wave electrode*. The following calculation is a slight modification of his procedure (See also ref. 7, pp. 158-159).

The relative electrode potential E may be represented by the equation:

$$E = \phi_{Me} - \phi_s + \text{constant} \tag{1}$$

where ϕ_{Me} is the potential of the metallic electrode, ϕ_s the potential of the solution side of electric double layer, and where the "constant" depends on the reference electrode.

If one assumes tentatively uniform current distribution over the microprofile with equidistant equipotential lines parallel to the "mean" or "geometric" surface (but not to the "true" surface) and equidistant and parallel current flow lines perpendicular to the equipotential lines, then

$$\phi_p - \phi_r \simeq \frac{di_\infty}{\sigma} \tag{2}$$

where ϕ_p and ϕ_r are the potentials on the solution side of the electric double layer at the peaks (crests) of the triangular wave profile and in the recess depths, respectively, where d is the groove depth, σ the specific conductivity of the electrolyte, and i_∞

the uniform current density at "infinite" distance from the profile (practically a distance of about half the groove width is sufficient) which for this calculation is assumed to be approximately constant also in close vicinity of the profile. On microprofiles i_∞ is also equal to the "apparent" current density.

Combination of Equations (1) and (2) gives

$$E_r - E_p \simeq \frac{di_\infty}{\sigma} \tag{3}$$

Increase of E_r - E_p means that E_r becomes less negative and that consequently the corresponding cathodic current density becomes smaller.

If the angle enclosed by the equal triangle sides is β, then the average current density

$$i_{av} = i_\infty \, sin\left(\frac{\beta}{2}\right) \tag{4}$$

Substitution of Equation (4) into Equation (3) gives

$$E_r - E_p \simeq \frac{d}{\sigma}\frac{i_{av}}{sin\left(\frac{\beta}{2}\right)} \tag{5}$$

Equations (3) or (5) show that the electrode potential *E* is practically uniform over the profile if the profile depth *d* is sufficiently small. The profile depth has to be the smaller the larger the current density, i_∞ or i_{av}, and the smaller the specific electric conductivity, σ.

One may come to the same conclusion by another line of reasoning: Substantial differences of E_r and E_p, and correspondingly of ϕ_r and ϕ_p, would lead to strong currents along the side walls of the microgrooves if the peak to recess distance is small. The current flowing to a micropeak would thus split into two parts: one passing through the electric double layer at the peak, the other flowing along the side wall not only to the deepest recess point but also to intermediate points on the slope.

If one considers only the highest peak and deepest recess point the current along the side wall would be equal to $\sigma(\phi_p - \phi_r)/s$, where *s* is the length of the side wall. This lateral current flow increases with decreasing *s* and tends to equalize current distribution. A more rigorous mathematical treatment of this concept would be useful.

If one wishes to proceed from the potential differences of Equations (3) and (5) to current density differences it is simplest to assume that the same polarization equation applies to all points of the electrode and that it may be linearized at least over a certain current density range;[20,21] compare also,[19] so that

$$E \simeq E' - i\left|\frac{dE}{di}\right| \tag{6}$$

and consequently

$$E_r - E_p \simeq \left(i_p - i_r\right)\left|\frac{dE}{di}\right| \tag{7}$$

From the combination of Equations (5) and (7) one obtains

$$\frac{i_p - i_r}{i_{av}} = \frac{d}{k_c\, sin(\beta/2)} \tag{8}$$

where k_c, the so-called polarization parameter, equals σ|d*E*/d*i*|.

If one wishes to obtain a similar equation for the groove width *a* instead of the groove depth *d* one obtains, because $d = a/[2\tan(\beta/2)]$,

$$\frac{i_p - i_r}{i_{av}} = \frac{a}{2k_c}\frac{cos(\beta/2)}{sin^2(\beta/2)} \tag{9}$$

Equations (8) and (9) show that current distribution becomes practically uniform if the profile depth or width is much smaller than the polarization parameter k_c.

It should be mentioned that De Levie[36,37] proposed a modification of Wagner's method for estimating the uniformity of current distribution on small-scale profiles. As it leads to a more complicated equation the simpler procedure is sufficient for our purpose.

When polarization is predominantly concentration polarization, its slope $|dE/di|$ and consequently k_c increases with increasing current density and becomes infinite at the limiting current density. But concentration polarization does not throw the current into a micro-recess,[2] as we shall see in Sections 3 and 6.

Only activation polarization throws the current into a microrecess. If the electrode potential is sufficiently negative as compared to the equilibrium potential, so that the anodic partial reaction is much smaller than the cathodic partial reaction, $i_a << i_c$, then the cathodic activation overpotential η_{act} is given by the equation:

$$\eta_{act} = -\frac{RT}{\alpha_c F} ln\left(\frac{i}{i_0}\right) = -2.303\frac{RT}{\alpha_c F} log\left(\frac{i}{i_0}\right) \tag{10}$$

which may also be rearranged to the Tafel form

$$\eta_{act} = \frac{2.303RT}{\alpha_c F} log(i_0) - \frac{2.303RT}{\alpha_c F} log(i) \tag{11}$$

or simply

$$\eta_{act} = A - B\log(i) \tag{12}$$

As $\eta = E - E_{eq}$ where E_{eq} is the equilibrium or reversible potential,

$$\left|\frac{dE}{di}\right|_{act} = \left|\frac{d\eta_{act}}{di}\right| = \frac{RT}{\alpha_c F i} = B/2.303i \tag{13}$$

In the preceding equations *R* is the gas constant (8.314 joules), *T* the absolute temperature, *F* the Faraday constant (96500 coulombs), α_c the cathodic transfer coefficient, i_0 the exchange current density at the equilibrium potential where the cathodic and anodic partial reactions, i_c and i_a, are equal, and *A* and *B* are the so-called Tafel constants.

Electrodeposition of multivalent metals is generally a sequence of several reaction steps of which one is rate determining. If no electrons are transferred before the rate determining step, then $\alpha_c = \beta r$, where β is the "symmetry factor" generally equal or close to 0.5, and *r* is the number of electrons transferred in the rate determining step.[30,32] See also Section 6.

Thus, if the first reaction step is rate determining in the reaction sequence

(1) $Cu^{++} + e^- = Cu^+$

(2) $Cu^+ + e^- = Cu$

the expected value of α_c would be 0.5.

This theoretical value of 0.5 for α_c gives a Tafel constant *B* of 0.118 V at 25°C and 0.132 V at 60°C. The experimental values of *B* were about 0.104 V for acid copper at 25°C[38,39,40,162] and 0.1 to 0.11 V for the Watts nickel bath at 60°C.[41,42]

With a Tafel constant *B* equal to 0.1, $|dE/di| = 0.1/2.303\ i = 0.043/i$, or, at, *e.g.*, 0.03A/cm^2, $|dE/di| = 1.43$. With conductivities, σ, for the Watts nickel bath (60°C) of 0.09 ohm^{-1}cm^{-1},[43] for the regular acid copper bath (200 g/L $CuSO_4\cdot5H_2O$, 50 g/L H_2SO_4; 25°C) of 0.18 ohm^{-1}cm^{-1}, and for the high-throw acid copper bath (100 g/L $CuSO_4\cdot5H_2O$, 150 g/L H_2SO_4; 25°C) of 0.5 ohm^{-1}cm^{-1},[44A] one obtains k_c values (see Eq. 8) for activation polarization at 3 A/dm^2 of 0.13 cm, 0.26 cm and 0.72 cm respectively. Note that k_c has the dimension of length.[20]

To obtain a deviation from uniform current distribution of 2% or less and thus $(i_p - i_r)/i_{av} \leq 0.02$, Equation (8) would require $d \leq 0.02\ k_c \sin(\beta/2)$. With $\beta = 90°$ and thus $\sin(\beta/2) = 0.7071$ and $a/2 = d$, a deviation from uniformity of only 2% would require $a/2 = d \leq 0.01414k_c$.

For the Watts nickel bath this would mean that, at a current density of 3 A/dm^2, *a*/2 and $d \leq$ 0.0018 cm. For the two acid copper baths *a*/2 and *d* would have to be equal or smaller than 0.0036 cm or 0.01 cm, respectively. At the ten times smaller current density of only 0.3 A/dm^2 the profile dimensions could, of course, be ten times larger and still the same practically uniform current distribution would be obtained.

The decrease of the thickness ratio h_r/h_p on micro-profiles with increasing current density in electrolytes containing no additives has been frequently confirmed.[1,15,45,138,160] It may be due not only to the decrease of $|dE/di|$ for activation polarization but also to the increasing influence of concentration polarization (See Section 3).

The decrease of h_r/h_p with increasing current density occurs also in electrolytes containing leveling agents[1,45,46,91] except if the leveling agent concentration is higher than the optimum. For more details see Section 7.

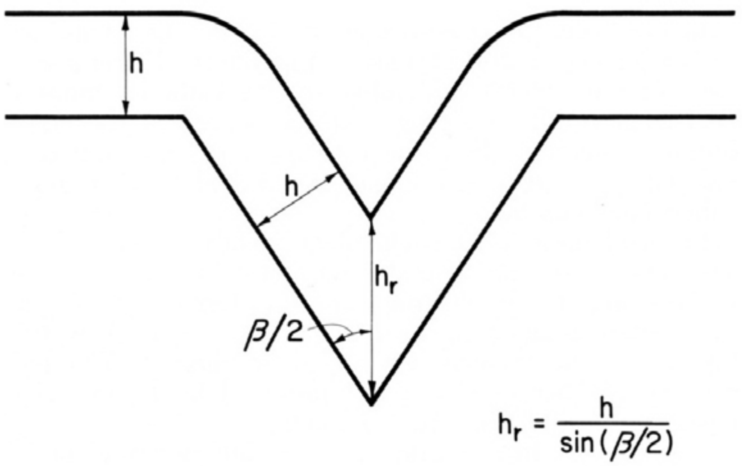


Figure 2 - Geometric leveling at uniform current distribution, from Kardos and Foulke.[7]

It should be mentioned that even uniform current and metal distribution over a microprofile produces leveling, the so-called "geometric leveling", first described by DuRose, Karash and Willson.[17] (See also Ref. 7, pp. 202-203). As can be seen from Fig. 2, a metal deposit of uniform thickness *h* reduces the groove depth by $h_r - h = \left(\frac{1}{\sin(\beta/2)} - 1\right)$. This effect is especially great for small enclosed angles β; for instance for $\beta = 30°$ $\sin\beta/2 = 0.259$ and thus the reduction of groove depth would be $h\ (3.85 - 1) = 2.85h$. The preceding equation becomes invalid for relatively thick deposits and because of the rounding of groove edges; "geometric leveling" proceeds then at a somewhat lower rate. Its rate diminishes also with increasing current density because at higher current densities, especially with small enclosed angle, the supply rate of the metal ions to the groove depth is limited and thus "bad microthrow" starts in the groove depth.[7,9,45]

3. The influence of mass transport on microthrowing power

When in the fall of 1955, Dr. Foulke and I were thinking about an explanation of the various types of microthrowing power, one type, namely "good microthrow" or practically uniform current distribution, was thus already understood, but the two other types, "true leveling" and "bad microthrow" were still unexplained. The change of "good microthrow" into "bad microthrow," or more exactly the decrease of the thickness ratios h_{recess}/h_{peak}, with increasing current density[1,15,45,138,160] could be partly explained by the increase of $E_r - E_p$ and thus E_r becoming less negative according to Equations (3) and (5), or by the decrease of the slope $|dE/di|$ of activation polarization according to Eq. (13). But why should not the increasing concentration polarization push the current into the microrecess?

Why should cyanide baths, which in comparison with noncomplexed acid baths give better macrothrowing power, show worse microthrowing power? And how is true leveling with thickness ratios h_r/h_p often substantially greater than unity explained?

It had been suggested that the complicated phenomena of cathodic metal distribution on microprofiles could only be explainable by a variation of the polarization equation[17,19C] or of current efficiency[19C] over the profile, *e.g.*, depending on surface curvature, but no definite mechanisms were proposed and proved.

I still remember the train of thought leading to our approach to this problem. The question: "What is the difference between microthrowing power and macrothrowing power?" did not yield a quick answer. It changed into the questions: "What is the difference between microprofiles and macroprofiles? Are the characteristic dimensions, such as groove depth or width, of microprofiles smaller, and of macroprofiles larger, than a certain critical dimension? Could this critical dimension be the thickness of the diffusion layer?"

Brenner[47] had obtained by his freezing method a diffusion layer thickness of about 0.4 mm = 400 µm for a non-agitated nickel or acid copper bath and about half this value for an agitated copper bath. These thicknesses were of the right order to separate macroprofiles from microprofiles. On macroprofiles the diffusion layer boundary could follow the contour of the profile, and the diffusion layer thickness would be the same for all profile points, as shown in Fig. 3(a).[48] On a microprofile, which is shown in Fig. 3(b) at about five times greater magnification, the diffusion layer boundary cannot follow the shape of the profile but is flattened out at some distance from it. The diffusion layer thickness is consequently greater over recess areas than over peak areas.

Let us recall the meaning of the diffusion layer. If a species, such as metal ions or addition agents, is consumed at the cathode, there will be a layer near the cathode where its concentration is smaller than in the bulk of the solution. The species can be transported to the cathode by *ionic migration* under the influence of a potential gradient if it carries a positive charge (or away from it if it carries a negative charge), by *convection* due to a movement of the electrolyte, and by *diffusion* under the influence of a concentration gradient.

The electric current is transported by *all* ionic species in the electrolyte. If t_{Me} is the transport number of the depositing metal ion then the ionic migration current is equal to it_{Me} and the remainder, $i\,(l - t_{Me})$, has to be supplied by convection and diffusion. In presence of inert electrolyte (*e.g.*, the sulfuric acid in acid copper) t_{Me} is small; if the metal is deposited from an anion, such as a metal cyanide complex or chromic acid, t_{Me} is negative, that is ionic transport carries the metal-bearing anion away from the cathode. Uncharged addition agents have of course no transport number and thus are brought to the cathode only by convection and diffusion.

In laminar (nonturbulent) flow the relative movement of electrolyte and electrode vanishes on approach to the electrode and thus in the inner part of the diffusion layer only diffusion and ionic migration are effective, and in the case of an uncharged addition agent, only diffusion.

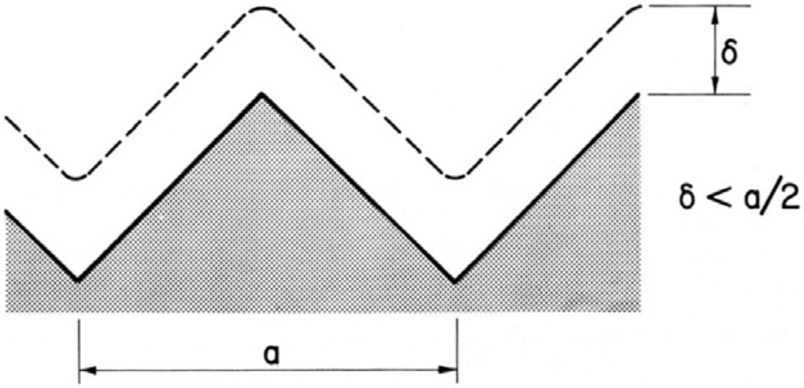


Figure 3(a) - Diffusion layer over a macroprofile, from Ibl.[48]

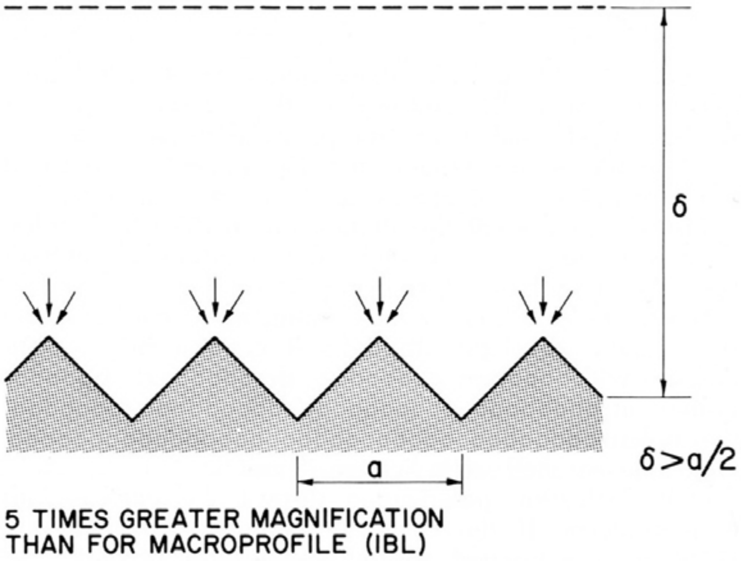


Figure 3(b) - Diffusion layer over a microprofile, from Ibl.[48]

In this paper we shall frequently use the simpler terms diffusion, diffusion control, diffusion theory, etc., where convective diffusion (the combination of convection and diffusion), mass transport, or the synonymous mass transfer, and the corresponding word combinations, would be the more exact terms.

The concentration profiles in the diffusion layer may be obtained by a variety of methods, *e.g.*, by Brenner's freezing method[47] and by interferometric methods[49,50] including laser interferometry.[51]

The diffusion rate j (in moles/cm^2-sec) is given by the equation:

$$j = D\left|\frac{dC}{dx}\right|_{x=0} = \frac{D(C_B - C_E)}{\delta_N} \qquad (14)$$

where D is the diffusion coefficient, frequently of the order of 1 × 10^{-5} cm^2/sec, but about five times as high for hydroxyl ions and 10 times as high for hydrogen ions (compare *e.g.*, Refs. 52 and 95), $|dC/dx|_{x=0}$ is the concentration gradient in immediate vicinity of the cathode, C_B and C_E the bulk concentration and the concentration in immediate vicinity of the electrode, and δ_N the effective or equivalent or Nernst thickness of the diffusion layer. δ_N is really a fictitious term; but it, and not δ, the distance between a profile point and the diffusion layer boundary, has to be used for the calculation of diffusion flow.

If $C_E \ll C_B$ one obtains the equations for limiting diffusion flow

$$j_L = DC_B/\delta_N \tag{15}$$

and for limiting current flow

$$j_L = \frac{nFDC_B}{(1-t_{Me})\delta_N} \tag{16}$$

where *n* is the valency of the depositing metal and *F* is Faraday's constant.

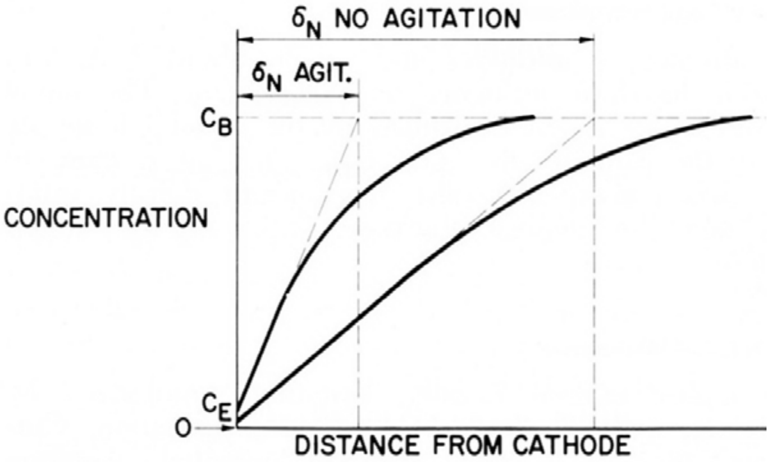


Figure 4 - Concentration profiles in the diffusion layer with and without agitation.

Figure 4 shows two schematic concentration profiles, one without agitation, the other one with a fair rate of agitation. In both cases $C_E \ll C_B$ and diffusion approaches its limiting rate.

It is important to remember that each species consumed at the cathode has its own concentration profile.

The variation of the limiting diffusion flow, or of δ_N, over a microprofile such as the one shown in Fig. 3b is really much greater than the variation of δ, the distance between a profile point and the diffusion layer boundary, because the peaks receive diffusion flow also laterally, they divert diffusion flow from the recess areas. Indeed, if convection does not interfere, the limiting diffusion flow, and correspondingly $1/\delta_N$, varies over a microprofile as much as the current density in primary current distribution. This is due to the formal similarities of the laws of current flow and diffusion flow, such as $i = \delta\,|dE/dx|$ and $j = D\,|dC/dx|$, and was discussed and applied to anodic smoothening by Elmore,[53] Edwards[54] and Wagner.[55] Thus, Fig. 1 may also represent equiconcentration and diffusion flow lines if the boundary of the diffusion layer is sufficiently far away, and the profile small enough, so that convection does not interfere with diffusion between the profile and the flattened equiconcentration line *F* - *F*. This analogy was shown by Edwards[54] to apply to horizontal, laterally shielded, profiled anodes, facing upwards, which under electropolishing conditions dissolved according to primary current distribution, and to a considerable extent also to unshielded anodes, that is in the presence of convection.

For reviews on mass transport, including diffusion, see Refs. 12, 48, 50, 56-59A.

Now back to 1955! We asked ourselves: Could the variation of the diffusion layer thickness, and especially of the effective diffusion layer thickness δ_N, over a microprofile, explain "true leveling" as well as its opposite "bad microthrow" and also be compatible with uniform metal distribution or "good microthrow"? How to obtain a quick answer? It was well-known that increased agitation increases the limiting diffusion rate, or correspondingly decreases the effective thickness of the diffusion layer. It should, consequently, be possible to duplicate current distribution on microprofiles by obtaining polarization curves on flat electrodes at two different agitation rates, *e.g.*, at a certain rate of mechanical agitation and in absence of agitation, that is, at "natural" convection, which is due to the electrolyte density differences developing at the electrodes.

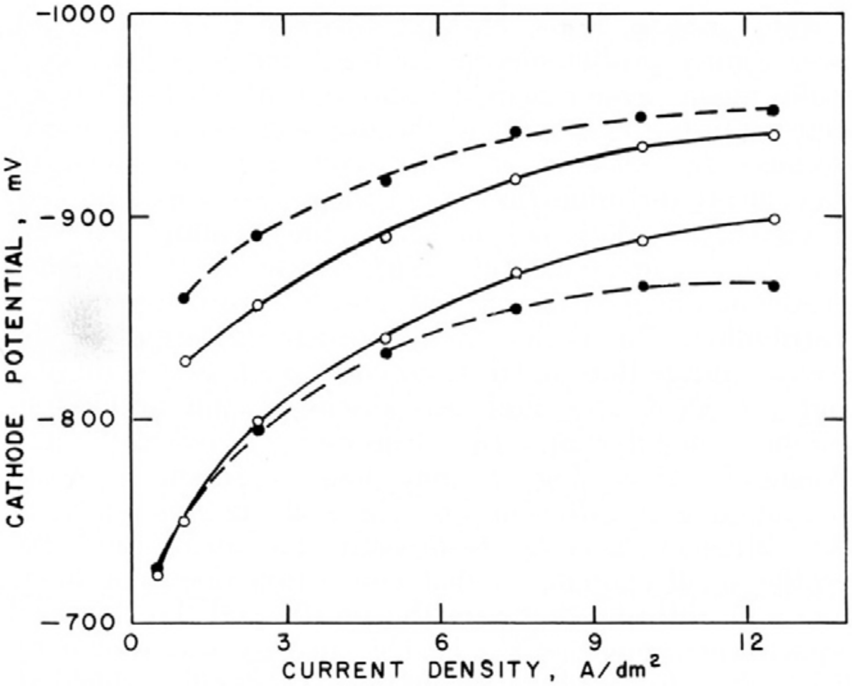


Figure 5 - Polarization curves (versus saturated calomel electrode) in Watts nickel bath (50°C, pH = 3.0) without agitation (○—○) and with agitation (●—●); lower pair with addition agents, upper pair with 0.4 g/L butynediol; from Foulke and Kardos.[1,7,10]

Figure 5 shows such polarization curves obtained without agitation (solid curve) and with mechanical agitation (broken curve). The cathode potentials were measured against a saturated calomel electrode with the help of a Luggin capillary. The lower pair of curves was obtained in a Watts nickel bath (50°C, pH =3.0) containing no additives, the upper pair in presence of 0.4 g/L butynediol.[1] The influence of agitation on the change of current density at a given electrode potential is of three types corresponding to the three types of microthrowing power.

Type I ("Good Microthrow")

In absence of additives and up to about 3 A/dm², agitation has little influence on polarization. The metal deposition rate is not controlled by the metal ion supply rate to the cathode; the ratio $i_{non\text{-}agit}/i_{agit}$ is close to unity and consequently also the current density ratios i_r/i_p and the deposit thickness ratios h_r/h_p should be close to unity.

Type II ("Bad Microthrow")

At higher current density, agitation depolarizes by eliminating part of the concentration polarization. Correspondingly, at a given cathode potential, agitation increases the current density, $i_{non\text{-}agit}/i_{agit} < 1$, and, consequently, also i_r/i_p and h_r/h_p should be smaller than unity. This type of microthrow would be due to the fact that here the metal deposition rate is controlled, to at least some extent, by the supply rate of the depositing metal ions to the cathode.

Type III ("True Leveling")

In presence of 0.4 g/L of the leveling agent butynediol (upper pair of curves in Fig. 5), polarization is, at a given current density, increased by about 100 mV and, correspondingly, current density is strongly decreased at a given electrode potential. Butynediol is a strong "polarizer," in consideration of the first effect, and a strong "inhibitor," in consideration of the second one.

Now agitation increases polarization and inhibition; at a given cathode potential, $i_{non-agit}/i_{agit}$ is greater than unity and, consequently, also i_r/i_p and h_r/h_p should be greater than one. This would be a case of "true leveling", which would be due to the fact that here the metal deposition rate is controlled by the transport rate of the inhibitor butynediol to the cathode.

Comparison of the $i_{non-agit}/i_{agit}$ ratios obtained from each pair of polarization curves showed good agreement with the thickness ratios obtained at the same apparent or, in some cases, peak current density on phonograph record masters, on which the groove depth was about 37.5 µm, the enclosed angle β slightly less than 90° and, consequently, the groove width about twice the groove depth, and the mutual distance of the micro grooves about equal to their width. h_r was measured halfway down the groove slope or at the bottom of the groove, h_p in the middle of the flat area between two microgrooves or at the rim of the groove. If h_r is measured at the bottom of the groove, it does not represent a local deposition rate and even a uniform deposition rate would produce some "geometric leveling." (See Fig. 2 and Section 2)

Similar pairs of polarization curves[1] correctly predicted the strong leveling obtained with 0.2 g/L cadmium, the leveling obtained with 0.2 g/L thiourea, and the bad microthrow obtained with only 0.02 g/L thiourea, all in the Watts nickel bath (50°C, pH = 3.0, 4.3 A/dm^2, mechanical agitation). At 0.02 g/L, thiourea acts as a depolarizer (activator, stimulator) of nickel deposition and its greater supply rate to micropeaks stimulates deposition there more than in the recess areas; consequently bad microthrow results. The complex behavior of thiourea was confirmed by several other studies.[3,6,64,70] See also Section 8 and 9.

Agitation increases polarization in a Watts nickel bath (pH = 3.5, 50°C) containing 1 g/L coumarin up to about 8 A/dm^2. At higher current densities, where, apparently, diffusion control by the metal ion takes over, agitation depolarizes. In the presence of 15 g/L of 1,3,6-naphthalene trisodium sulfonate, agitation depolarizes over the whole current density range (0.5 to 12.5 A/dm^2). If this applies also to the *effective* current densities of nickel deposition, it would mean h_r/h_p ratios smaller than one.

Figure 6 shows similar pairs of polarization curves for cyanide copper, silver and cadmium baths. Agitation strongly decreases the concentration polarization of the cyanide copper and silver bath, which in this case is due not only to a decrease of the concentration of the metal cyanide complex in the vicinity of the cathode but also to a local increase of the concentration of cyanide ions which are freed at the cathode. In the cyanide cadmium bath, agitation depolarizes only slightly, but, nevertheless, $i_{non-agit}$ is considerably smaller than i_{agit} and, for all three baths, i_r/i_p and h_r/h_p ratios considerably smaller than unity are predicted and actually measured on the microprofiles. The case of the cyanide cadmium shows that the change of polarization produced by agitation at constant current density is much less relevant for the prediction of microthrow than the change of current density at constant electrode potential. This agrees with the basic concept that the electrode potential is practically constant over a microprofile.

While on macroprofiles concentration polarization as well as activation polarization tends to throw the current into the recess areas, on microprofiles only activation polarization throws the current into the recess, but concentration polarization throws the current out of the microrecess. This helps to explain why cyanide baths give better macrothrow but worse microthrow than noncomplexed acid electrolytes. Furthermore, on macroprofiles, over which the diffusion layer thickness is practically uniform, metal distribution from cyanide baths is improved by the strong decrease of cathodic current efficiency with increasing current density. On microprofiles the variation of current efficiency over the profile should be much smaller because its decrease with increasing current density should be counterbalanced by its increase with decreasing δ_N (increasing agitation rate).

The successful prediction of cathodic metal distribution on microprofiles from polarization curves obtained with and without agitation strengthens the hypothesis that it is the variation of diffusion layer thickness over a microprofile that causes the two opposite cases of bad microthrow and true leveling.

We knew of course, and expressed this knowledge in our papers,[1,2] that no exact correspondence of the $i_{non-agit}/i_{agit}$ ratios and the thickness ratios could be expected for a variety of reasons.

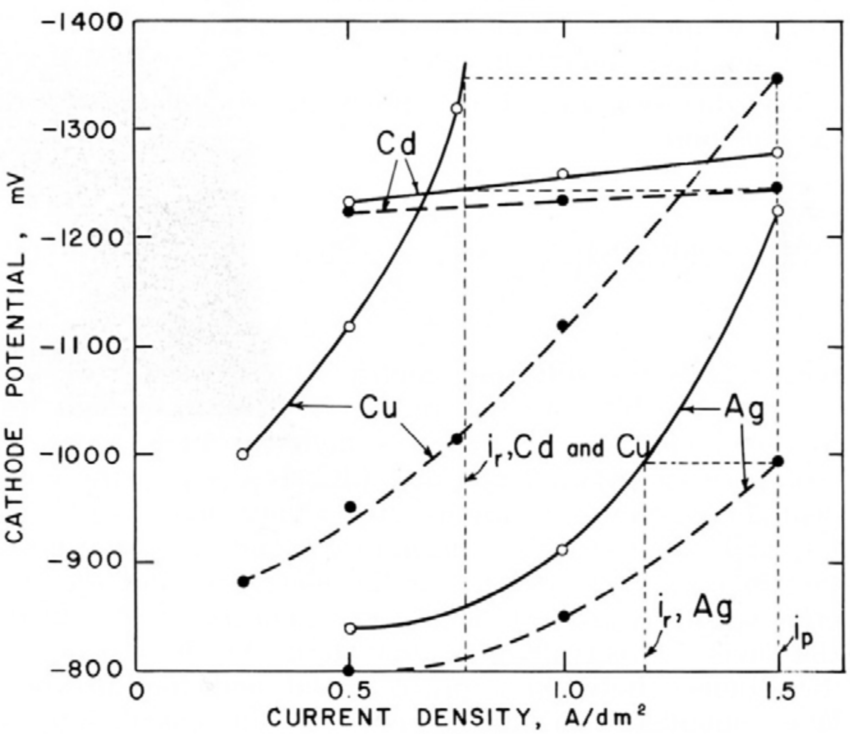


Figure 6 - Polarization curves (versus saturated calomel electrode) in cyanide cadmium, copper and silver baths (25°C) without agitation (○—○) and with agitation (●—●); from Foulke and Kardos.[1,7,10]

The polarization curve obtained with agitation could be made to correspond to the polarization curve on the flat area midway between two microgrooves; but to what point inside the groove would the polarization curve apply which was obtained without agitation?

Another source of error is the ohmic potential drop between Luggin capillary and cathode; this ohmic error increases with increasing current density and, if one corrects for it, the higher current density curve would be displaced towards still higher current density. Thus, the actual nonuniformity of deposit thickness should be greater than the one predicted from the polarization curves.

Another significant source of error is the use of total current densities instead of the partial or effective current densities of metal deposition in our polarization curves. Even in the absence of additives agitation decreases the current efficiency of nickel deposition, especially in the low current density range, because of the increased supply rate of hydrogen ions.[71] Thus over a certain current density range the two polarization curves of the lower pair in Fig. 5 should be less far apart for the effective current densities of nickel deposition than are the curves obtained for total current densities. The lowering of current efficiency of nickel deposition by agitation is still more pronounced in the presence of easily reducible additives such as butynediol,[71,72] because the increased supply rate of the additives, together with hydrogen ions, means increased use of current for their cathodic reduction and because the increased surface coverage by the additives may inhibit nickel deposition more than it inhibits hydrogen evolution, which it may even accelerate as is the case with coumarin.[73,74] This reduction of current efficiency by agitation would shift the i_{Ni} (effective current density of nickel deposition) curve more to the left of the i_{total} curve in presence of agitation than in its absence. Thus, actual leveling should be greater than predicted from the upper pair of polarization curves in Fig. 5.

Although for abnormally high concentrations of additives neglect of current efficiency may lead to a considerable quantitative error in the prediction of the degree of leveling - but not in respect to the presence or absence of leveling - it should be remembered that the average current efficiency of an *industrial* nickel bath is in the middle and high current density range generally higher than about 94% (see, *e.g.*, Ref. 3), and still higher for a leveling acid copper bath, so that the influence of current efficiency on leveling will be rather minor in such industrial baths.

It is difficult to predict the influence of current efficiency on microthrow from the cyanide baths of Fig. 6. It is known that increasing current density at a constant agitation rate *decreases* the cathodic current efficiency of such cyanide baths and that increasing agitation rate at constant current density *increases* their current efficiency. Thus, the opposite effects of increased agitation and increased current density may cancel each other out to a large extent.

4. Diffusion theories of leveling by Leidheiser and Watson and Edwards

It seems that the time was ripe for the development of a diffusion theory of leveling.

While we were conducting experiments to prove (or disprove) our diffusion theory of "bad microthrow" and "true leveling" and were preparing our two papers,[1,2] we received Leidheiser's paper on "The Mechanism of Leveling during the Electrodeposition of Nickel in the Presence of Organic Compounds."[4]

Leidheiser sketched the outline of a theory according to which a greater number of sites for the deposition of nickel will be available in microrecesses than on micropeaks because of the hindered diffusion of organic molecules into the recess. Nickel ions arriving at the micropeaks and finding no free sites for deposition would travel on the surface - or near it - towards the recess area where more deposition sites are available.

Leidheiser related the degree of leveling to the excess polarization produced by the leveling agent. In an earlier paper Roth and Leidheiser[75] had found that with many addition agents, agitation had the same effect on the cathode potential as an increase of the addition agent concentration. Surprisingly they did not make use of this finding for a more quantitative explanation of leveling, but it helped us in the conception of the idea to duplicate current distribution on microprofiles by varying the agitation rate on flat cathodes and observing the current density change produced at constant cathode potential. Already Raub and Wittum[76] had observed increase of polarization by agitation in the presence of some nickel additives, and decrease in presence of others. The depolarizing effect of agitation in the absence of addition agents and at sufficiently high current densities was, of course, generally known.

In December, 1955, Watson and Edwards submitted their paper on the "Mechanism of Leveling in Electrodeposition"[3] to the Council of the British Nonferrous Metals Research Association, but it was presented at the conference of the Institute of Metal Finishing only in April 1957. They proposed a mechanism of leveling practically identical with our own, namely diffusion-controlled inhibition by the leveling agent. Because of the greater diffusion rate to micropeaks as compared to microrecesses the incorporation rate and the inhibiting action of the leveling agent should be greater at the micropeaks. They proved the greater incorporation rate at the "micropeaks" - in this case the flat outside between two microgrooves, the rims of the groove and in some cases the upper part of the groove - by various etching techniques.

For their derivation of an equation for leveling power they made use of the analogy between limiting diffusion flow and primary current distribution, as Edwards had done before in his explanation of anodic smoothing.[54]

Instead of predicting leveling from the change of current density on a flat surface with agitation rate or δ_N as we had done, they predicted it from the change of current density with "equivalent bulk concentration." This method is justified if diffusion and consumption of the leveler occur at the limiting rate (see Eq. 15). Then increase of δ_N to $n\delta_N$ is equivalent to a decrease of C_B to C_B/n. Their method is less suitable if the metal deposition rate depends on the diffusion rate of several species, such as several addition agents, a leveling agent and the depositing metal ion at high i/i_L, a leveling agent and the cobalt ion in nickel-cobalt baths,[77] etc. In such cases, the change of current density with agitation rate, especially on the rotating disk or cylinder electrode, should give more correct predictions of leveling.

Watson and Edwards[3] derived the following equation for leveling power:

$$\frac{i_r - i_p}{i_{av}} = \frac{kC\left(\frac{dE}{dC}\right)}{i_{av}\left(\frac{dE}{di}\right)} \quad (17)$$

where *k* is a constant characteristic of the profile shape, *C* is C_B of the additive, and (d*E*/d*C*) and (d*E*/d*i*) are the slopes of the corresponding polarization curves.

Thus, from two sets of polarization curves (*E* vs. C_B at constant *i*, and *E* vs. *i* at constant C_B) they predicted leveling and their plots of leveling power vs. concentration showed shapes similar to those of the curves obtained by plotting actual thickness ratios, obtained on electroformed phonograph record masters in Watts nickel baths containing coumarin, thiourea, etc., against C_B.

Especially important is their discovery of the occurrence of maxima of leveling power, predicted from Equation 17 and actually measured, at certain concentrations of leveling agents such as coumarin and thiourea. The concentrations of leveling agents required to give maximum leveling increased with increasing current density. The concentration of coumarin required to give maximum leveling in a Watts nickel bath (pH = 4, 55°C, 2 A/dm^2, vertically oscillating cathode), namely, between 0.00022 and 0.0004 M, was about the same whether phonograph record masters with microgrooves 20 μm deep and 32 μm wide, with a mutual distance of 100 μm, were used or diamond ruled surfaces with grooves only 0.1 μm deep and 1 μm wide. Leveling maxima will be discussed in more detail in Section 7.

Watson and Edwards also found that, in a coumarin-containing nickel bath, agitation increases cathode polarization (makes the cathode potential more negative) and that low concentrations of thiourea depolarize and produce "negative leveling" in contrast to the effect of higher concentrations, similarly to what we had found.

It is gratifying that two research groups have independently developed such similar ideas and have, by partly different experimental methods, come to the same conclusions.

5. Various methods for expressing the rate of leveling

In our paper[1] we used thickness ratios, such as h_4/h_1, h_3/h_1 (see Fig. 7) because they should be most directly related to the ratios of (effective) current densities obtained with two rates of convective diffusion, one of which may be the one of natural convection, at constant cathode potential. The terms h_1 and h_2 are, of course, examples of "peak" thicknesses h_p, and h_3 and h_4 of "recess" thicknesses h_r. Because of the surface curvature at the groove rim, h_2 is often somewhat smaller than h_1 if the diffusion of a leveling agent is rate-controlling, and larger than h_1 if the diffusion of the metal ion is rate-controlling. Both features can be seen in Fig. 8, where for the cyanide copper strike $h_2 > h_1$ and for the leveling nickel $h_2 < h_1$.

Figure 8 (0.2 g/L butynediol in an air agitated Watts bath, 50°C, pH = 3.0, 4 A/dm^2) shows a fibrous structure in the lower half of the microgroove and a laminated structure in the relative peak areas. The latter is characteristic for higher bulk concentrations of butynediol than the former. Of course, the bulk concentration was the same, but the surface concentration and the surface coverage were apparently higher on the peak areas than in the recess areas. Figure 8 shows that the deposit at the bottom of the groove of thickness h_3 has not grown from the groove bottom but rather from the side walls. To exclude this "geometric leveling" effect h_4 rather than h_3 should be used (See also Fig. 2 in Section 2).

For practical purposes, however, h_3 is important, as the rate of leveling is often expressed by:

$$\text{leveling percentage} = \frac{d_{initial} - d_{final}}{d_{initial}} \times 100 \quad (18)$$

and $d_{\text{initial}} - d_{\text{final}} = h_3 - h_1$ (See Fig. 7).

Equation (18) is also very suitable if surface roughness is measured with a stylus (or tracer) instrument. Then, the initial and final roughness values (arithmetic average, AA, or root mean square, RMS) are substituted for *d*.

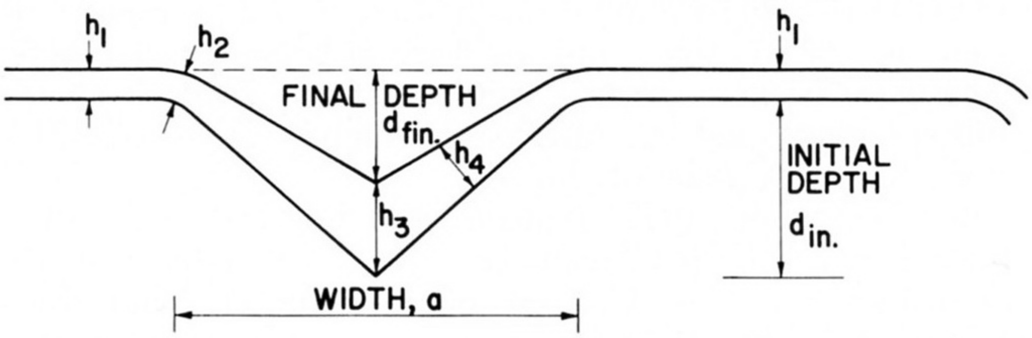


Figure 7 - Thickness measurements on microgrooves, from Foulke and Kardos.[1,7]

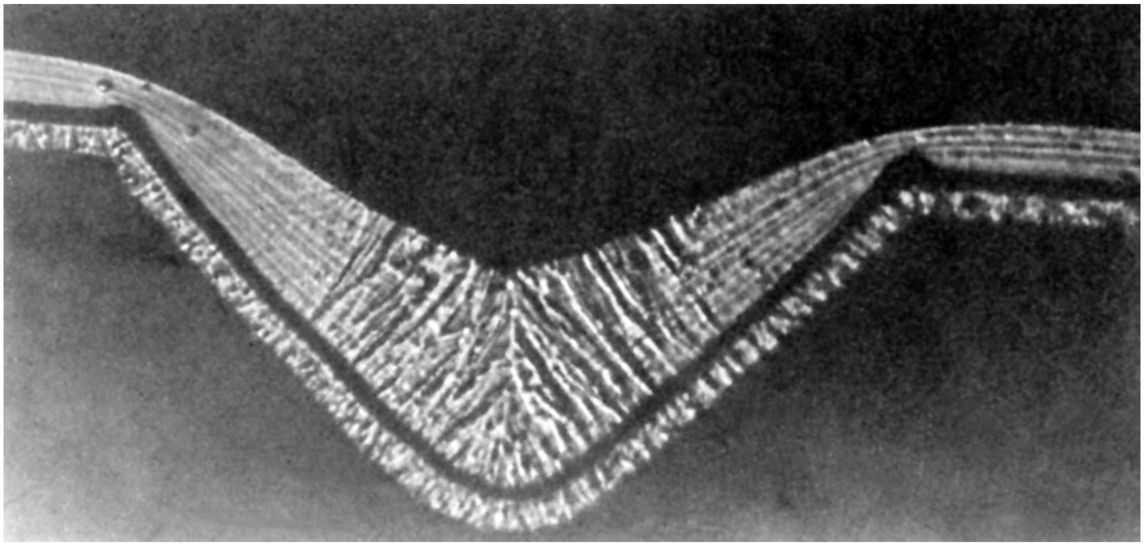


Figure 8 - Photomicrograph of a nickel deposit obtained in the presence of 0.2 g/L butynediol; initial groove depth 37.5 µm; from Foulke and Kardos.[1,7]

Watson and Edwards[3] defined leveling power as $(i_r - i_p)/i_{av}$ or as the corresponding thickness ratios $(h_r - h_p)/h_{av}$; see Eq. (17). These and other expressions for leveling rates were discussed by DuRose.[78] About measurement of surface roughness see also Refs. 17, 79-81.

Kruglikov and coworkers suggested measuring leveling on a sinusoidal profile and proposed the following equation for the leveling power P:

$$P = \frac{2.3a}{2\pi h_{av}} \log\left(\frac{H_0}{H_f}\right) \tag{19}$$

where a is the wavelength of the sinusoidal profile, h_{av} the average deposit thickness and H_0 and H_f the initial and final amplitudes of the profile. P is independent of deposit thickness.[82]

Bertorelle and coworkers[82A] measured leveling on pseudosinusoidal profiles, obtained by winding a fine metal wire around a suitable metal tube, by the decrease of the pseudosinusoidal amplitude. The fact that more than geometric leveling is obtained on such profiles shows that it is not due to shape sensitive adsorption because the initial surface curvature is the same over the wire except at the contact lines.

6. The definition of microprofiles and the meaning of mass transport control

A "typical" microprofile is sufficiently small-scale so that (1) the electrode potential E is practically uniform over the profile, and (2) the effective thickness of the diffusion layer δ_N varies over the profile.

The variation of δ_N leads to a variation of local current density *if* the metal deposition is, at least partly, controlled by the mass transport (mass transfer, or shorter and more familiar, diffusion) of the depositing metal ions or of an addition agent.

In absence of diffusion control, different orientation of crystal facets, or the presence of lattice dislocations, grain boundaries, impurities, etc., may cause a variation of the polarization parameter k_c, and more particularly of i_0 and perhaps α_c, over the profile, but these influences will be rather random, not systematic, between micropeaks and microrecesses, except to some extent on microprofiles produced by electrodeposition. Wagner[83] gave a basic analysis of the effects of a variation of the polarization parameter k_c over an electrode.

If diffusion control is absent and if crystallographic differences can be neglected, the practical uniformity of the electrode potential over a microprofile leads from Equations (10) to (12) to practical uniformity of the current density.

If the metal deposition rate is controlled by the diffusion rate of an inhibitor, but not by the diffusion rate of the metal ions, one may still apply Equations (10) to (12) for activation overvoltage, if one replaces i by $i/(1 - \theta)$, where θ is the fractional surface coverage by the inhibitor. This modification of the equations is based on the simplifying assumption that the inhibiting action consists in a mere reduction of the surface area available for deposition and that the cathodic transfer coefficient α_c is not affected by the inhibitor. Then the practical constancy of E, and consequently of η_{act}, over the microprofile leads to a practical constancy of $i/(l - \theta)$ and to $i_r/i_p \simeq (l - \theta_r)/(l - \theta_p)$. Compare Ref. 78.

If, on the other hand, the metal deposition rate is controlled by the mass transfer rate of the depositing metal ions then the Nernst equation for concentration polarization applies:

$$\eta_{conc} = \frac{RT}{nF} ln(C_E/C_B) = \frac{2.303RT}{nF} log(C_E/C_B) \qquad (19)$$

where n is the valency of the depositing metal.

If one neglects a possible variation of the transport number t_{Me} with current density, Eq. (19) may be transformed into:

$$\eta_{conc} = \frac{2.303RT}{nF} \log(1 - i/i_L) \qquad (20)$$

If the overpotential can be expressed by this equation, practical constancy of E implies practical constancy of i/i_L. Thus, the local current densities would be proportional to the local limiting current densities (which would vary approximately as the current densities in primary current distribution) or, from Eq. (16) inversely proportional to δ_N.

Although in cyanide baths Equations (19) and (20) would have a more complicated form (see, *e.g.*, p. 174 of Ref. 7) we may use Eq. (20) to demonstrate why concentration polarization tends to throw a deposit into a macroprofile but out of a microprofile.[2] Over a macroprofile i_L and δ_N are practically constant. The higher i at a protruding point would thus produce a more negative η_{conc}, that is, a "greater" cathode polarization, which would oppose current flow to the peak points and tend to throw it into the recess. On micropeaks i_L is much greater, or δ_N much smaller, than on the microrecess points and this would allow a proportional increase of the local current density without creating a local increase of overpotential.

At certain values of i/i_L, which will be higher for metals with low exchange current density i_0, such as nickel or iron, than for copper, zinc and especially silver (Ref. 35, pp. 17, 125), Eq. (10) has to be abandoned for Eq. (20). Good microthrow and "true" leveling will then be replaced by bad microthrow. If the formation of a diffusion layer of nonuniform thickness is suppressed by the use of interrupted current, good microthrow, but not true leveling, is restored (see Section 11).

Also, on descent into a microgroove, especially if the enclosed angle β is small and the current density medium to high, Eq. (20) may replace Eq. (10) or bad microthrow ($h_r/h_p < 1$) replace true leveling ($h_r/h_p > 1$) at some point. This may lead to an apparently leveled deposit which contains a void, as shown by Raub in Fig. 9.[45] This figure shows also preferential etching in the peak areas due to greater codeposition rates, and an increase of lamination thickness on descent into the microgroove.

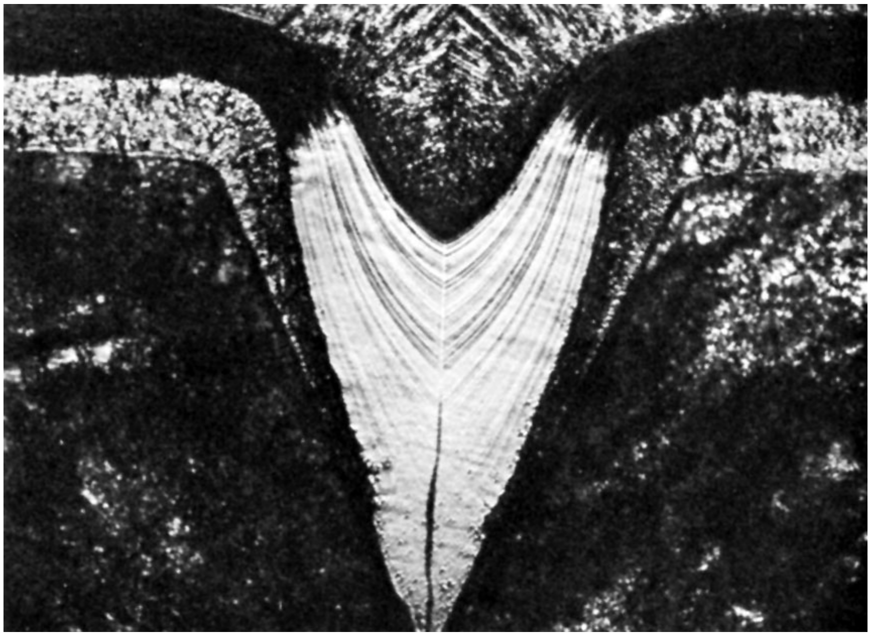


Figure 9 - Photomicrograph of bright nickel deposit; initial groove depth 120 µm; from Raub.[45]

It is surprising that a "typical" microprofile is defined by two independent criteria, namely $E_r \simeq E_p$ (from Eq. 3 and 5) and d or $a/2 << k_c$ (from Eq. 8 and 9) on the one hand, and a groove width a "not much greater" than 2δ, so that δ_N varies over the profile, on the other hand. It is still more surprising that the existence of two independent criteria does not complicate the situation particularly.

It was shown in Section 2 that activation overvoltage would, at 3 A/dm^2 and on a triangular wave profile of included angle β = 90°, produce practically uniform current distribution if the groove depth or half-width is not larger than about 18 µm in the Watts nickel bath, 36 µm in the regular acid copper bath, and 100 µm in the high-throw acid copper bath.

Mass transport into a microgroove should be hindered if the groove width is about twice the diffusion layer thickness. This critical groove width depends on the profile shape. On cylindrical cavities of a U-shaped cross section and 25 mm deep, cyanide copper, which has a relatively high concentration polarization, gave better throwing power than Watts nickel at diameters equal or greater than 6 mm, but a slightly worse throwing power at a diameter of 3 mm. Also, on the wider cavities agitation reduced the throwing power, whereas it improved it on the 3 mm wide cavity.[45] On only 0.084 mm deep trapezoidal grooves the critical groove width was only 0.5 mm.[138] With widths greater than 0.5 mm increased concentration polarization (due, *e.g.*, to higher current density or to lower temperature) threw the cyanide copper deposit into the recess, with smaller widths out of it. On current distribution in narrow and deep slots see also Refs. 44, 84-86.

At very high agitation rates and especially with short cathodic current pulses, the diffusion layer becomes very thin and follows the contours of the profile. Then, *e.g.*, in an acid copper bath, bad microthrow and true leveling disappear and concentration polarization helps to throw the deposit into the recess. See Section 11 and Refs. 133, 134, 178.

Why does the variation of the diffusion layer thickness over a microprofile influence current distribution only in presence of, at least partial, mass transport (mass transfer, diffusion) control? What is the meaning of rate control and rate-determining step?

A reaction occurring at the boundary of two phases ("heterogeneous reaction") such as an electrode reaction comprises at least two steps: the transport of the reacting species to the phase boundary and the (physical, chemical, electrochemical) reaction at the phase boundary.

In the case of metal electrodeposition the latter consists of several steps: transfer of the metal ion through the electric double layer (only about 10^{-7} cm thick as compared to about 10^{-2} cm for the diffusion layer), surface diffusion of the still partly hydrated and probably still partly charged adatoms or adions to suitable sites for incorporation into the metal lattice, and final incorporation. If surface diffusion is hindered by adsorbed addition agents or impurities, or if the growth sites are blocked, the adatom or adion concentration builds up which leads to formation of new nuclei and thereby of new growth sites. The reduction of multivalent metals occurs generally in several steps, *e.g.*, $Cu^{+2} + e^- \rightarrow Cu^+$; $Cu^+ + e^- \rightarrow Cu$.[30,33,38-40,87-90]

For addition agents the steps of the reaction sequence are: diffusion to the cathode, adsorption, which for "reversible" adsorption may be partly counterbalanced by desorption of the unchanged additive, consumption of the additive by incorporation (codeposition) in unchanged or changed form and often by reduction (hydrogenation) to a less adsorbable form, which is desorbed into the electrolyte.

In the pre-steady (transition) state, one of the several steps of a multistep reaction generally proceeds at a lower rate than the other, but, when the steady state is reached, all the steps in a consecutive sequence must proceed at the same rate.[30,33] Nevertheless, one of these steps is *rate-determining* in the sense that the overall reaction rate will be most influenced by a change of the rate of this particular step.

Rate-determining steps in a consecutive sequence are very common in daily life. In an organization an idea or process or product may pass through several departments. One of these departments may be the "bottleneck" and, consequently, the passage through it would be the rate determining step. The same may happen at a particular station of a conveyor line.

One may simplify the reaction sequence by dividing it into only two steps: the mass transport to the electrode and the overall reaction at the electrode. This leads to the equation:

$$k_T(C_B - C_E) = k_S C_E \tag{21}$$

where C_E and C_B are again the concentrations of the reacting species in the bulk and in vicinity of the electrode; k_T, the mass transfer coefficient, is for a neutral species equal to D/δ_N, for a charged species equal to D/δ_N (I - t_{Me}); k_S is the rate constant of the surface reaction.
Rearrangement of Equation (21) gives

$$\frac{C_E}{C_B} = k_T/(k_T + k_S) \tag{22}$$

If the mass transport step is the rate determining step and, consequently, $k_T \ll k_S$, then Eq. (22) gives $C_E \ll C_B$. Equations (14) and (15) show that then an increase of δ_N reduces the mass transport rate most because the increase of δ_N cannot be compensated by a corresponding increase of the concentration difference ($C_B - C_E$), which is already at its maximum. Thus, sensitivity to agitation is the most important criterion of transport control.

If the surface reaction - or one of its steps - is rate determining and thus $k_S \ll k_T$ then, from Eq. (22), $C_E \simeq C_B$. Instead of "surface reaction control" one also uses the terms "electrochemical," "kinetic," "activation" control.

If k_S and k_T are of the same order one speaks of "mixed control." For the preceding compare, *e.g.*, Ref. 58.

To express the metal deposition rate in a manner which fits Eqs. (21) and (22) one may formulate the equation:

$$k_S = \vec{k}\, exp(-\alpha_c F \eta_{act}/RT) \tag{23}$$

where $\vec{k}$ would be the cathodic reaction rate at $C_E = 1$ and $\eta_{act} = 0$. For the meaning of the other symbols see Equations (10) to (13). Equation (23) is valid only if η_{act} is sufficiently negative so that the anodic partial reaction i_a is negligible.

At low η_{act}, k_S is smaller than k_T, $C_E \simeq C_B$, and electrodeposition is under "activation" control. With increasing current density η_{act} becomes more negative, k_S increases exponentially, and becomes first comparable to k_T ("mixed control"), and then larger than k_T ("transport control") which leads to $C_E << C_B$ and thus from Eqs. (19) and (20) to preponderant concentration polarization.

The situation is slightly more complicated for the adsorption and consumption of addition agents. One may formulate two equations, (24) and (25).

$$k_T(C_B - C_E) = k_{ads}C_E(1-\theta) - k_{des}\theta \tag{24}$$

where k_{ads} and k_{des} are rate constants for adsorption and reversible desorption of the unchanged addition agent, respectively, and θ is the fractional surface coverage by the addition agent.
The second equation is

$$k_T(C_B - C_E) = k_{cons}\theta = (k_{inc} + k_{red})\theta \tag{25}$$

where the subscripts refer to total cathodic consumption, incorporation and reduction (generally hydrogenation on nickel and other metals acting as hydrogenation catalysts), respectively.

The terms k_{cons}, k_{inc} and k_{red} should be proportional to the current density i; k_{red} because the reduction rate of organic levelers should depend on the electrode potential in a similar manner as does the current density. k_{red} should increase with increasing hydrogen ion concentration in vicinity of the cathode. Compare Refs. 10, 48, 64, 66.

Because of the proportionality of k_{cons}, k_{inc}, k_{red} to i, we may write Eq. (25) for the case of transport control ($C_E << C_B$) in the form:

$$\theta = \frac{k_T C_B}{k'_{cons} i} = \frac{k_T C_B}{(k'_{inc} + k'_{red})i} \tag{26}$$

θ would thus increase with increasing k_T (increasing agitation, decreasing δ_N), increasing C_B, decreasing i, decreasing k'_{red}, *e.g.*, because of pH increase.

Equation (24) would take the form of Eq. (21) if $k_{des}\theta$ is negligibly small as compared to $k_{ads}C_E(1 - \theta)$ even at high θ, that is for completely irreversible adsorption. Then one can substitute $k_{ads}(1 - \theta)$ for k_S and obtain again Eq. (21). At low θ and for not too low k_{ads} one would have transport control ($k_T << k_S$ and $C_E << C_B$). With increasing θ, k_S would become progressively smaller which would first lead to $k_S \simeq k_T$ (mixed control) and finally to $k_S << k_T$ (surface reaction control). The decrease of k_S with increasing θ may be further accelerated because k_{ads} may decrease with increasing θ because of mutual repulsion of the adsorbed molecules or because at higher θ only less favorable adsorption sites are available.

The critical values of fractional surface coverage θ_{crit} for the fading away and the final disappearance of transport control by a selected leveler occur at a lower C_B for smaller δ_N (therefore, at lower C_B on micropeaks as compared to microrecesses) and, from Eq. (20), for lower current density and often also for higher pH.

If reversible desorption cannot be neglected, a decrease of k_S due to increasing surface coverage θ leads to a faster increase of C_E towards C_B and to a faster disappearance of rate control by the transport of the addition agent.

The action of many, and perhaps all, addition agents is at sufficiently low concentration diffusion controlled. But the critical concentration for the disappearance of diffusion control (at the same k_T and i) varies widely depending on k_{ads}, k_{des}, k_{inc} and k_{red} for the various additives. Compare Section 9.

The various combinations of surface reaction control and transport control, which may be symbolized by SC and TC, respectively, for the metal electrodeposition rate and for the action of additives may be summarized in Table 1.

TABLE 1

Metal deposition	1 SC	2 SC	3 SC	4 TC	5 TC	6 TC
Inhibitor action	0 or SC	TC	---	0 or SC	TC	---
Stimulator action	0 pr SC	---	TC	0 or SC	---	TC
Resulting i_r/i_p	$\simeq$1	>1	<1	<1	?	<1

If metal deposition rate and inhibitor action are both transport controlled, the outcome is uncertain. Transport control of the metal deposition rate tends to produce "bad microthrow" or $i_r/i_p < 1$, transport control of the inhibitor action tends to produce "true leveling" or $i_r/i_p > 1$. At high i/i_L ratios for the metal deposition the former influence should prevail, at lower i/i_L ratios the latter.

Of course, SC for metal deposition in column 2 or 3 means only that the metal deposition rate is directly surface reaction controlled ($k_{S,Me} << k_{T,Me}$ and $C_{E,Me} \simeq C_{B,Me}$) but indirectly by the transport rate of the inhibitor or stimulator.

And, of course, the presence of at least one TC in columns 2 to 6 means that current density (at constant electrode potential) or electrode potential (at constant current density) depends on the agitation rate or, on microprofiles, on the variation of k_T (or δ_N) over the profile.

7. Leveling maxima

The discovery of leveling maxima by Watson and Edwards[3] attracted considerable attention and many plots of leveling vs. addition agent concentration can be found in the literature.[3,72,91-93,99,111]

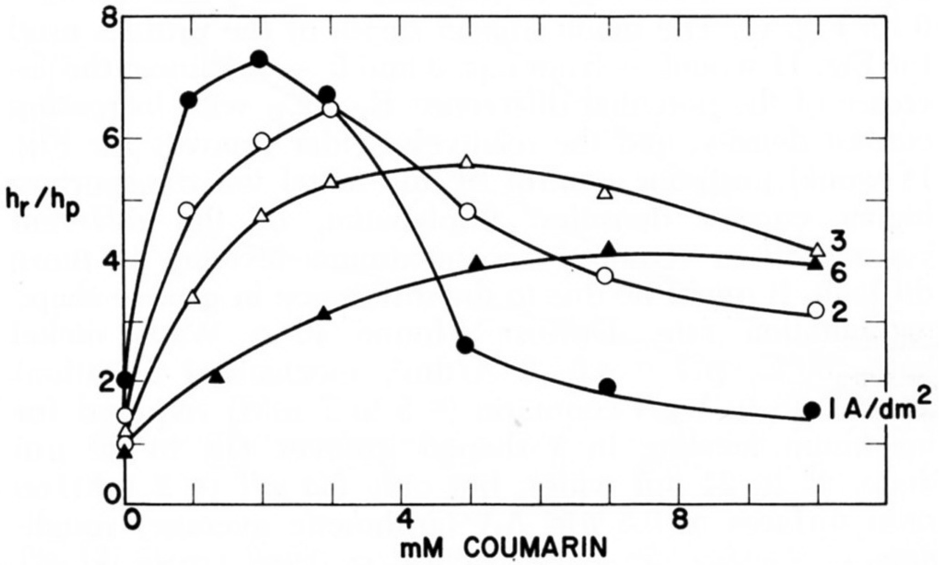


Figure 10 - Thickness ratios of nickel deposits vs. coumarin concentrations at various current densities; initial groove depth 60 μm, notch angle 90°, deposit thickness on flat surface 6 μm; from Voronko.[91]

We show here only two graphs from the less accessible Russian literature. Figure 10[91] shows plots of thickness ratios h_r/h_p against coumarin concentration at various current densities (1 to 6 A/dm^2) obtained with 6 μm deposit thickness (on the flat surface) in 60 μm deep V-grooves, with an enclosed angle of 90°, in a Watts nickel bath (50°C, pH = 4, mechanical agitation). The coumarin concentration required for maximum leveling increases with increasing current density; see also Ref. 3. If a certain leveler concentration is smaller than the concentration required for maximum leveling at a selected current density, then decrease of current density will improve leveling; if it is larger than the optimum for a selected current density, increase of current density will often improve leveling (not true in Fig. 10 for increase from 3 to 6 A/dm^2). Figure 10 shows a decrease of the maximum leveling obtained with increasing current density. This is partly due to the relatively great depth (60 µm) of the microgroove, so that at higher current density the electrode potential is no longer practically uniform (see Eqs. 3 and 5), partly apparently also to incipient transport control, especially at 6 A/dm^2, of the metal deposition rate itself.

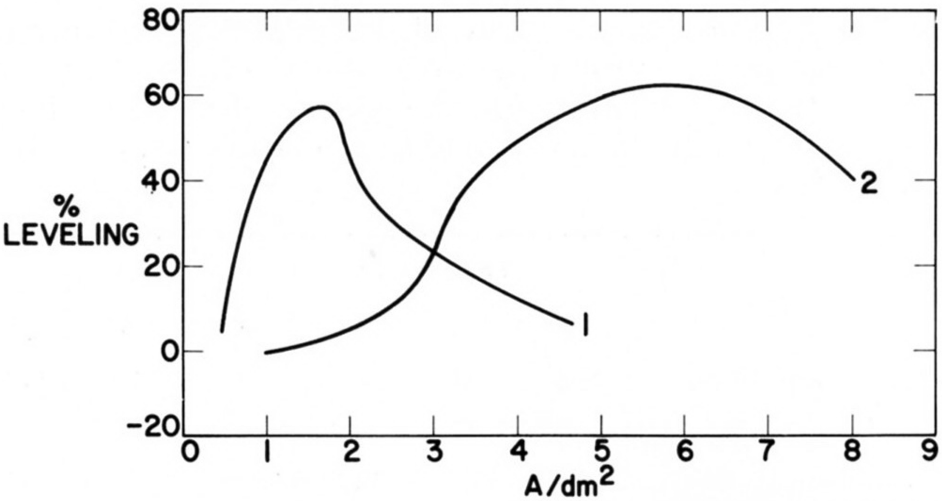


Figure 11 - Leveling percentage vs. current density in Watts nickel bath at two coumarin concentrations, (1) 0.09 g/L and (2) 0.5 g/L; initial groove depth 8.3 µm and width 50 µm, deposit thickness on flat surface 3 µm; from Kruglikov, *et al*.[92]

Figure 11[92] shows plots of leveling percentage against current density for two coumarin concentrations (Curve 1: 90 mg/L = 0.615 mM; Curve 2: 500 mg/L = 3.4 mM) in a Watts nickel bath (50°, pH = 4.1, mechanical agitation) with 3 µm deposit (on the flat) and an initial groove depth of 8.3 µm and groove width of 50 µm. Again, as in Fig. 10, higher current densities require higher leveler concentrations to give maximum leveling. The existence of leveling maxima vs. current density must be considered for the plating of profiled parts, especially because the low current density areas receive, of course, a thinner deposit.

A closer look at Figs. 10 and 11 shows some apparent contradictions between them: decrease of the maximum leveling obtainable with increasing current density in Fig. 10 but not in Fig. 11; higher concentrations required for maximum leveling at 1 to 2 A/dm^2 in Fig. 10 (about 2.5 mM = 0.365 g/L coumarin) than in Fig. 11 (0.09 g/L). The first difference is probably explainable by the great difference in profile depth and shape: groove depth 60 µm for Fig. 10, but only 8.3 µm for Fig. 11; width/ depth ratio = 2 for Fig. 10 (because 0 = 90°) and 50/8.3 = 6 for Fig. 11. The much smaller depth of the profiles used for Fig. 11 would - from Eqs. 3 and 5 - minimize the increase of the potential difference $E_r - E_p$ with increasing current density, and the relatively wider grooves for Fig. 11 would postpone control by the metal ion transport to higher current densities. Explanation of the different concentrations required for maximum leveling is more difficult. It might be due to the difference in groove shape or agitation rate. DuRose[78] found in a Watts nickel bath (60°C, pH = 4.0, 3 A/dm^2, mechanical agitation) about 0.75 to 1 g/L coumarin (= 5 to 7 mM) required for maximum leveling in V-shaped grooves (15 to 20 µm deep, 22 to 24 µm wide), but only 0.3 g/L (= 2 mM) on satin surfaces of 0.5 µm AA (arithmetic average) roughness.

Maxima of leveling were also obtained against temperature,[92] lower temperature requiring higher coumarin concentration, apparently because of the decrease of the diffusion coefficient D.

Watson and Edwards correctly predicted the concentrations required for maximum leveling from their two sets of polarization curves (E vs. i, and E vs. C_B) with the help of Eq. (17).

Raub and Stalzer[93] used an interesting, partly galvanostatic, partly potentiostatic method for the prediction of leveling with the help of a cylindrical cathode which was either static or rotating at a selected rpm value. They maintained a constant current density of, *e.g.*, 3 A/dm^2 on the non-rotating cylinder throughout the experiment. To give 3 A/dm^2 at a certain concentration of the leveling agent C_1 a potential E_1 was required. Then they measured the lower current density obtained with C_1 and at E_1 on the rotating electrode, and continued in the same manner with C_2 and E_2, etc. By plotting the difference in current density ($i_{\text{non-agit}} - i_{\text{agit}}$) against concentration they obtained a maximum, which for butynediol in a Watts nickel bath at 3 A/dm^2 and 40°C was at about 0.6 g/L butynediol.

This technique should roughly predict the position of the leveling maximum for micropeaks protruding from a flat surface in absence of agitation and at 3 A/dm^2. For the prediction of leveling in microgrooves and in the presence of agitation, it should be preferable to keep the current density on the rotating cylinder constant and to proceed otherwise as above.

What is the explanation of the occurrence of leveling maxima? The effective diffusion layer thickness, δ_N, is *n*-times smaller on the micropeak than at a selected recess point, and then under transport control from Eq. (15), $j_{L,p} = nj_{L,r}$. But as discussed in Section 6, transport control will diminish at a certain critical surface coverage. This critical surface coverage is reached on the micropeak at a lower bulk concentration, C_B, than in the recess because of the greater k_T (smaller δ_N) and the smaller local current density (See Eq. 26). Any further increase of C_B will make the ratio of the leveler supply rates to peak and recess, j_p/j_r, decrease until j_p becomes equal to j_r and leveling completely disappears (See section 9 and Fig. 15). Obviously, it is not the relative supply rate as such but the related relative surface coverage which leads to the decrease and final disappearance of leveling (See sections 9 and 10).

8. Polarization measurements on the rotating disc electrode

The rotating disk electrode consists of a metal disk, several mm to cm in diameter, rotating around its axis in a horizontal position and facing downward in a cell containing the electrolyte. All surfaces are insulated except the down-facing surface of the disk. See Fig. 11(a).

As the disk rotates, the adjacent liquid acquires the rotational motion of the disk. This flow pattern, which moves liquid horizontally out and away from the center of the disk, requires an upward axial flow to replenish the liquid at the disk surface. The rotating disk electrode is a "uniformly accessible" surface with a constant thickness of the diffusion layer over the entire surface and thus allows exact calculation of the mass transport by convection and diffusion. The theory of the rotating disk electrode was largely created by Levich in 1942.[94] Compare also Refs. 52, 57-59A, 95.

Levich developed the equation:

$$j = 0.62 D^{2/3} \upsilon^{-1/6} \omega^{1/2} (C_B - C_E) \tag{27}$$

where j is the mass transport rate in moles/cm^2-sec, D the diffusion coefficient, υ the kinematic viscosity, ω the angular velocity (2π rps), C_B and C_E as before the concentrations in the bulk of the solution and in vicinity of the electrode, just outside the electric double layer. Gregory and Riddiford[90,97] provided a minor improvement of Levich's factor 0.62.

Under mass transport control, when $C_E \ll C_B$, Eq. (27) becomes

$$j = 0.62 D^{2/3} \upsilon^{-1/6} \omega^{1/2} C_B \tag{28}$$

By combination of Eqs. (15) and (28), or (14) and (27), one obtains:

$$\delta_N = \frac{1}{0.62} D^{1/3} \upsilon^{1/6} \omega^{-1/2} \tag{29}$$

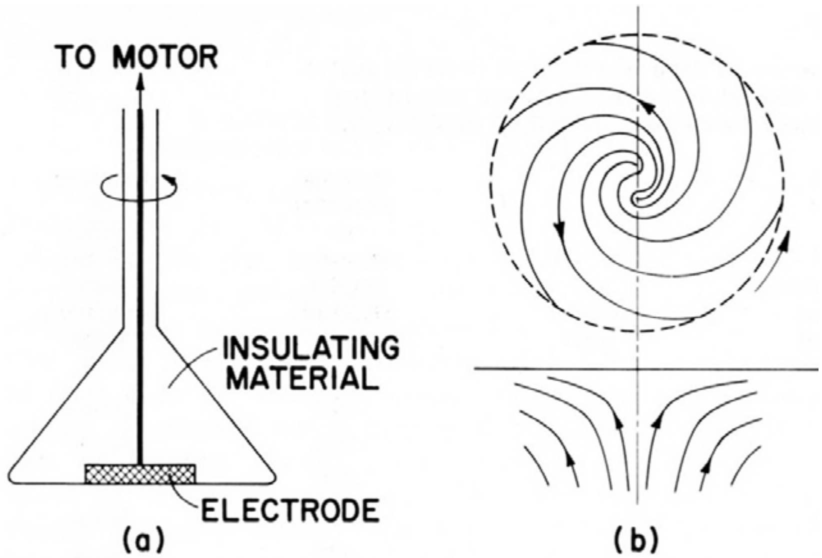


Figure 11 - Rotating disc electrode; (a) cross section, (b) side and bottom view of liquid flow pattern, from Bockris and Drazic.[33]

These equations for laminar (non-turbulent) flow apply up to Reynolds numbers N_{RE} of 10^4 to 10^5, where $N_{RE} = r^2\omega/u$ and r is the disk radius in cm (See *e.g.*, 52, p. 91).

Because of the exact and simple reproducibility of j_L or δ_N the rotating disk electrode is a very valuable tool for the study of transport control of polarization, inhibition, cathodic (or anodic) consumption rates of additives, differential capacities of the electric double layer, etc.

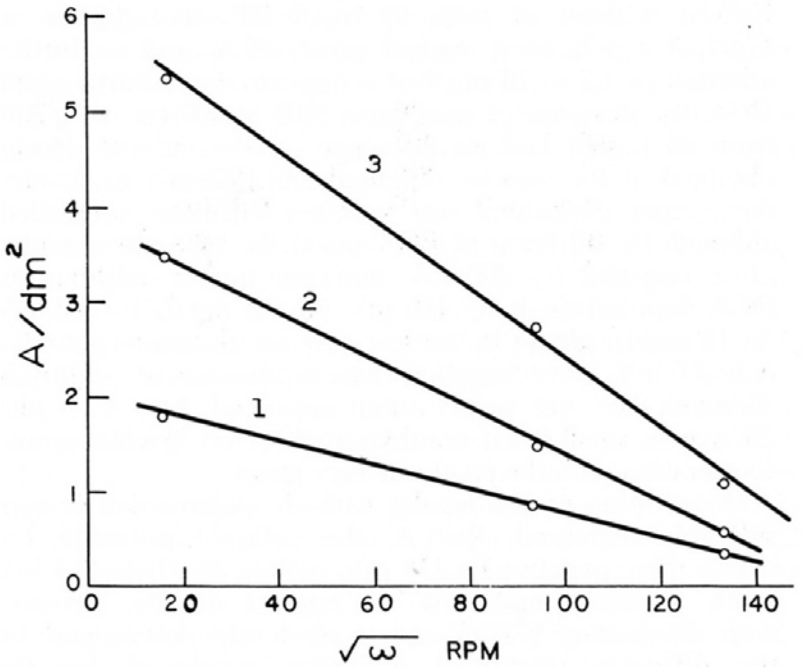


Figure 12 - Current density vs. rotation rate of disk electrode in Watts nickel bath containing 0.15 g/L coumarin at three constant cathode potentials (-700, -725, -750 mV vs. standard hydrogen electrode); from Kruglikov, *et al.*[98]

Kruglikov and his co-workers at the Mendeleyev Institute for Chemical Technology in Moscow measured cathodic polarization on the rotating disk electrode in a Watts nickel bath (50°C, pH = 4.5) containing 0.15 g/L coumarin.[98] Figure 12 shows the decrease of cathodic current density with increasing rpm at three electrode potentials, which confirms the theory that leveling is due to diffusion-controlled inhibition.

They showed again[99] that the inhibiting action of nickel levelers such as coumarin, quinaldine, quinoline, chloral hydrate and thiourea, increases with increasing rotation rate of the disk electrode, and also with decreasing current density. The latter is due to the increase of surface coverage with decreasing i under transport control, as seen from Eq. (26).

Under the same conditions but in absence of coumarin, or in presence of the non-leveler p-toluenesulfonamide,[100] the polarization curves do not depend on the rotation rate and the rather slight inhibiting action of the sulfonamide scarcely varies with current density as evidenced by a parallel shift of the E vs. log i lines.[100]

Under strict transport control, that is, when $C_E << C_B$, Eq. (28) shows that equal products $C_B\sqrt{\omega}$ and evidently also equal $C_B\sqrt{\text{rpm}}$, give equal transport rates of the leveler to the cathode and should thus produce identical polarization curves. Kruglikov and co-workers[101] showed this to be true in a Watts nickel bath (30°C, pH = 4.5) containing coumarin, namely 0.1 g/L at 360 rpm, 0.063 g/L at 900 rpm, 0.048 g/L at 1600 rpm. They also found identical polarization curves for equal $C_B\sqrt{\text{rpm}}$ with thiourea in a nickel bath, but not in an acid copper bath. In the latter, apparently only partial diffusion control of the inhibiting action of thiourea is present.

Because of the equal effects of equal $C_B\sqrt{\omega}$ under transport control Kruglikov, *et al.*[99,101] were able to plot leveling percentage against j_L, or, as D and u did not change, actually against $C_B\sqrt{\omega}$, and to obtain a smooth curve exhibiting a maximum.

The change of current density (preferably of the effective current density) between two rotation rates of the disk electrode at a selected electrode potential characterizes the leveling properties of an electrolyte. In this potentiostatic method, the cathode potential measurement includes the ohmic potential drop between Luggin capillary and rotating disk electrode which increases with increasing current density. To avoid this error, or its somewhat elaborate correction, Kruglikov and co-workers preferred to apply a galvanostatic method and use the potential difference $\Delta E = E_{360} - E_{4000}$, that is, between 360 and 4000 rpm, for the prediction of leveling[102,103] of many organic compounds. The more negative E_{4000} is as compared to E_{360} and consequently the greater ΔE, the greater is the expected leveling. The degree of leveling predicted by ΔE (at three values each of C_B and i) agreed essentially with the available knowledge of levelers, the known role of substituents, of hydrogenation, etc. ΔE may also be used for the determination of the concentration of a leveling agent such as coumarin.[101]

Rogers and Taylor's important studies performed with the help of the rotating disk electrode[73,74,105,106] will be discussed in Section 9, as they concern cathodic consumption rates of levelers as well as the inhibition produced by them. Here we mention only that they proved that increasing concentrations of coumarin or butynediol strongly reduce at constant electrode potential the *effective* or *partial* current density of nickel deposition, i_{Ni}, and not only the total cathodic current density. They also obtained a smooth plot of i_{Ni} against the rate of coumarin consumption, which over a wide range of $C_B\sqrt{\omega}$ was strictly transport controlled and followed the Levich Eq. (28) for j_L.

Encouraged by these interesting results, I had made polarization measurements on the rotating disk electrode several years ago and, more recently, my associate Ron J. Lash performed some in the acid copper bath.

We selected as the reference state a cathodic current density of 5 A/dm^2 and a rotation rate of 3600 rpm. This reference state may represent a micropeak, or the flat surface separating two microgrooves, at strong agitation. At the cathode potentials required to give 5 A/dm^2 at 3600 rpm under various conditions we then reduced the rotation rate and measured the steady state current density obtained. This method is similar to the partly galvanostatic - partly potentiostatic method used by Raub and Stalzer[93] with a once static, once rotating cylindrical cathode. One difference is that we used the highest agitation rate for the reference points. Table 2 and Fig. 13 show the results obtained.

Table 2 - Cathode potentials required to give 5 A/dm^2 at 3600 rpm in acid copper bath (220 g/L $CuSO_4•5H_2O$, 60 g/L H_2SO_4 without and with additives and influence of decreasing $\sqrt{rpm}$ on current density obtained at these potentials.

Experiment No.	Cl^- mg/l	PCA g/l (Polarizing Control Agent)	DCA mg/l (Depolarizing Control Agent)	Leveler mg/l	Cathode Potential *vs* Saturated Hg_2SO_4 Electrode mV	Increase of Current Density with Decreasing $\sqrt{rpm}$
1	-	-	-	-	-510	None
2	60	-	-	-	-500	None
3	60	1	-	-	-700	None
4	60	1	1.5	-	-570	None
5	60	1	15	-	-537	None
6	60	1	15	1	-655	Weak
7	60	1	15	5	-724	Strong
8	60	1	15	10	-744	Moderate
9	-	1	15	5	-662	None

In the copper bath (220 g/L $CuSO_4•5H_2O$, 60 g/L H_2SO_4) without or with 60 mg/L Cl^-, on addition of 1 g/L of a polarizing control agent, PCA, and on further addition of 1.5 to 15 mg/L of a depolarizing control agent, DCA, the decrease of rpm from 3600 to 900 (or of $\sqrt{\text{rpm}}$ from 60 to 30) had no influence on the current density obtained at the various potentials. In absence of leveler, the copper deposition rate was not diffusion controlled, although the addition of PCA made the cathode potential more negative by 200 mV and the further addition of DCA depolarized it by 130 mV (at 1.5 mg/L) to 163 mV (at 15 mg/L), giving in the last case an electrode potential only 27 mV more negative than in absence of additives. Although the net polarization produced by PCA plus DCA is so small, their combined effect on brightness and cooperation with the leveler is very great.

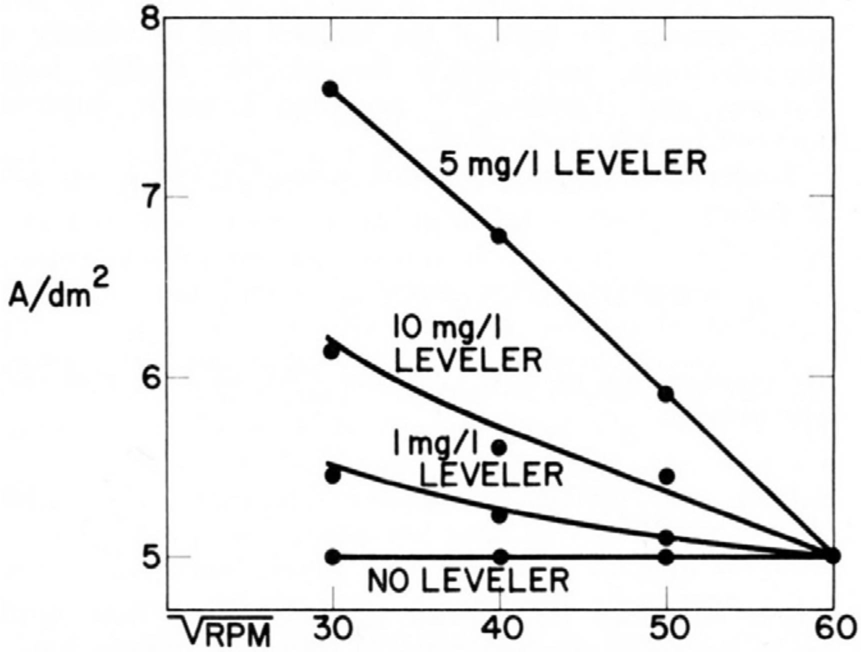


Figure 13 - Current density vs. rotation rate of disk electrode in acid copper bath containing 60 mg/L Cl^-, 1 g/L polarizing control agent (PCA), 0.015 g/L depolarizing control agent (DCA), and various concentrations of leveling agent. For each bath composition cathode potential gives 5 A/dm^2 at 3600 rpm (Lash and Kardos).

On addition of the leveler, cathode polarization is considerably increased, that is, the cathode potential becomes more negative by 118 mV (with 1 mg/L) to 207 mV (with 10 mg/L), and now the current density increases with decreasing $\sqrt{\mathrm{rpm}}$ and is obviously determined by the diffusion controlled inhibition produced by the leveler. The leveler concentration giving maximum leveling predicted from Fig. 13 would be around 5 mg/L, which seems somewhat high judging from our experience with leveling on surfaces of initial AA roughness of 0.25- 0.5 µm.

Very surprisingly, omission of the 60 mg/L chloride ion causes a loss of all diffusion control and of about 62 mV polarization (compare experiments 9 and 7). We do not yet have a full explanation of this strange phenomenon, but know that in absence of chloride no substantial leveling is produced on scratched panels and brightness is strongly reduced. Compare, *e.g.*, Ref. 179.

As diffusion controlled inhibition is absent in experiments 1 to 5 and 9 one would expect no true leveling under these conditions. Indeed, none occurs under the condition of experiments 1, 2, 3 and 9, but, as we shall discuss in more detail in Section 13, a fair amount of leveling is obtained under the conditions of experiment No. 4 (and after a predip or preplate in solution No. 5 even in solution No. 3) by a completely new leveling mechanism discovered by Dr. J. Schulz-Harder.[107]

It should be mentioned that in our experiments no correction was made for the ohmic potential drop between disk and Luggin capillary. As this ohmic error increases with increasing current density, the corrected curves corresponding to experiments 6, 8, and especially 7 should show a stronger increase of current density with decreasing $\sqrt{\mathrm{rpm}}$ than they show in Fig. 13.

9. Cathodic consumption and codeposition rates of leveling agents

While we were preparing our two papers on "Current Distribution on Microprofiles,"[1,2] we were not quite satisfied with the only semi-quantitative prediction of leveling from polarization measurements made with and without agitation. We looked for a more quantitative proof of the diffusion theory of leveling and hoped to find it in the cathodic consumption rates of leveling agents. As pointed out in Section 6 the cathodic consumption of levelers should, under strict transport control, occur at its limiting rate, $j_L = DC_B\delta_N$ (Eq. 15), as C_E should be much smaller than C_B. Then the variation of δ_N over the microprofile would have its maximum effect on the local supply rate of leveling agent, the resulting surface coverage by the leveler and the local inhibition of metal deposition, because an increase of δ_N could not be compensated by a corresponding increase of (C_B - C_E).

We used butynediol because its concentration is easily determined by bromine addition to the triple bond in presence of a catalyst and back-titration of the excess bromine. To our satisfaction its cathodic consumption rate showed all the signs of diffusion control: it was proportional to C_B, increased only moderately with increasing current density, decreased to one-half when mechanical agitation was omitted, and gave reasonable values of D/δ_N.

Later experiments, reported in Ref. 7, p. 182, gave in a Watts nickel bath (60°C, pH = 4.0, 6.6 A/dm^2, air agitation) at a concentration of 2 mM the following j/C_B values: 3.0×10^{-3} cm/sec for butynediol, 2.9×10^{-3} for butenediol, 2.3×10^{-3} for coumarin, but only 0.05×10^{-3} for the non-leveling control agents benzenesulfonic acid and m-benzenedisulfonic acid and 0.09×10^{-3} for saccharin. In consideration of the larger molecular weight of coumarin (146, vs 86 and 88 for butyne-and butenediol), and its consequently smaller diffusion coefficient D, the first three values indicate consumption at the limiting transport rate and consequently strict diffusion control, and the much smaller j/C_B values for the non-leveling control agents indicate absence of diffusion control.

Edward's radioactive tracer studies show that the codeposition rates of sulfur from saccharin or p-toluene-sulfonamide,[62-65] and apparently also their total cathodic consumption rates, are diffusion controlled only up to about 0.1 mM, which is much below the concentrations used in industrial plating processes. Even in the concentration range where the codeposition of sulfur is diffusion controlled they do not act as levelers because they are too weak inhibitors or even slight stimulators.[3,91,100,103,104]

A practical consequence of the great difference of the relative cathodic consumption rates j/C_B for leveling and non-leveling additives at the concentrations used in industrial processes is the necessity of formulating different makeup and maintenance mixtures of additives.

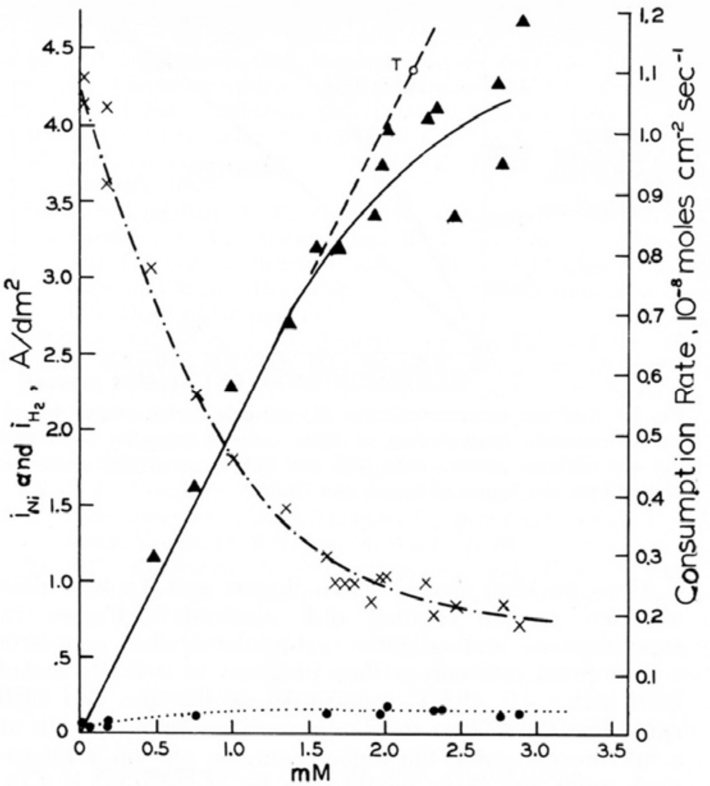


Figure 14 - Rates of cathodic coumarin consumption, nickel deposition and hydrogen evolution vs. coumarin concentration on rotating disk electrode (-960 mV$_{SCE}$, 980 rpm); from Rogers and Taylor.[74]

The rotating disk electrode is, of course, a very valuable tool for the study of transport control of addition agent consumption. We shall first report the results obtained by Rogers and Taylor.[73,74,105,106] The ascending curve in Fig. 14,[74] shows that the consumption rate of coumarin from a Watts nickel bath (48.5°C, pH = 4.0) at a rotating disk cathode (980 rpm) and at an electrode potential of - 960 mV$_{SCE}$ is exactly proportional to the coumarin concentration and follows exactly the Levich equation for i_L (Eq. 28), but with the slightly improved coefficient proposed by Gregory and Riddiford,[96,97] up to a certain critical concentration of about 1.5 mM or to a critical consumption rate of about 0.7 × 10^{-8} mol/cm^2-sec. Point T (and the line going through it and the origin) were calculated from the slightly modified Levich equation using the experimental values of $D = 7.85 \times 10^{-6}$ cm^2-sec^{-1} and $u = 1.12 \times 10^{-2}$ cm^2-sec^{-1}, both obtained at 48.5°C.

The critical coumarin concentration for the disappearance of strict diffusion control decreases with increasing rpm, decreasing (less negative) cathode polarization and consequently decreasing current density, and with increasing pH. This agrees with Eq. 26, as on the rotating disk electrode k_T is proportional to $\sqrt{\text{rpm}}$ and k_{red} decreases with increasing pH.

The two other curves in Fig. 14 show how the effective current density of nickel deposition, i_{Ni}, strongly decreases, and how the much lower current density for hydrogen evolution, i_{H2}, increases, with increasing coumarin concentration.

Butynediol gives cathodic consumption rates and i_{Ni} curves[105] which are very similar to those shown in Fig. 14 for coumarin. At pH = 4.0, a cathode potential of -960 mV$_{SCE}$, and 48.5°C, the cathodic consumption rates are proportional to C_B up to a consumption rate of 3 × 10^{-8} mol/cm^2-sec, or more than four times higher than for coumarin. The slope of the j vs. C_B line was only slightly greater than for coumarin, which, in consideration of the smaller molecular weight and consequently greater diffusion coefficient of the butynediol, gives again very good agreement with the Levich equation for j_L (Eq. 28). At -1100 mV$_{SCE}$ no deviation from strict diffusion control occurred even at a consumption rate of 8 × 10^{-8} mol/cm^2-sec.

The possible relation of the disappearance of strict diffusion control of leveler consumption rates to the occurrence of leveling maxima was discussed in Section 7. Here we shall show it from Rogers and Taylor's data obtained on the rotating disk electrode.[73] Figure 15 superimposes and slightly extrapolates the coumarin consumption rate curves they obtained in a Watts nickel bath (pH = 4,0, 48.5°C, - 960 mV) at 485 rpm and 2250 rpm. The lower rpm may represent the agitation rate at a microrecess point, the higher rpm the one on a micropeak point. δ_{Nr}/δ_{Np} would then be $\sqrt{2250/485}$ = 2.15. From a critical coumarin concentration upwards j_p/j_r and presumably θ_p/θ_r decreases until at still higher concentration $j_p = j_r$ and $\theta_p = \theta_r$. We would expect that at or near the first critical concentration (about 0.75 mM) the maximum of leveling is reached; and that at the second critical concentration (about 4 mM) true leveling should completely disappear. This method would predict the leveling maximum and the disappearance of leveling for a selected cathode potential. Indeed in Fig. 14 above the critical concentration of 1.5 mM (at 980 rpm and -960 mV) both the coumarin consumption curve and especially the i_{Ni} curve become increasingly flatter, and from the critical consumption rate of 0.7 × 10^{-8} mol/cm²-sec (at -960 mV) upwards the i_{Ni} curve vs. total consumption quickly flattens.[73]

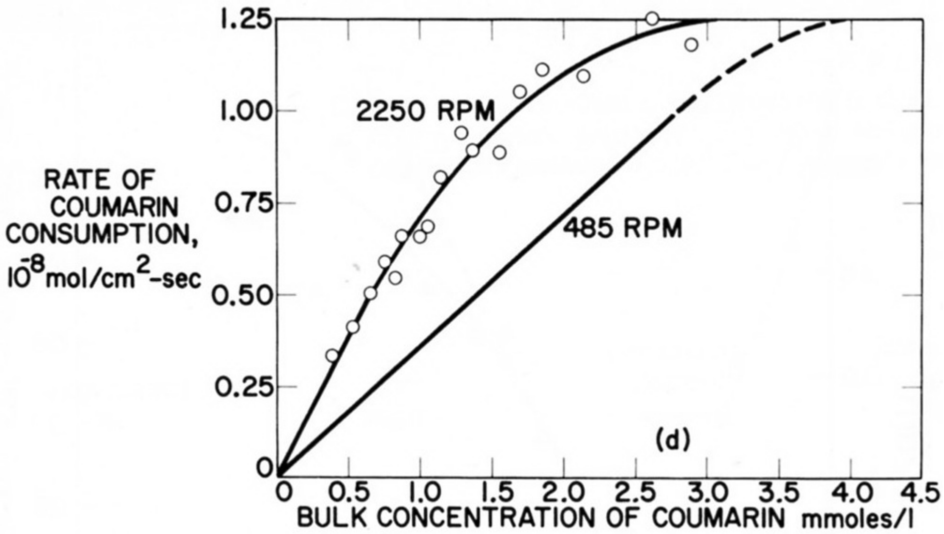


Figure 15 - Cathodic consumption rate of coumarin during nickel deposition vs. coumarin concentration at same cathode potential (-960 mV) but with different rotation rates (485 and 2250 rpm) of disk electrode; plotted from two figures of Rogers and Taylor.[73]

But would not polarization, inhibition, leveling and leveling maxima better relate to codeposition rates than to total cathodic consumption rates? This is quite possible. Chemical analysis of codeposited carbon and radiotracer studies with C-14 containing nickel levelers show that only a small percentage, of the order of about 1%, or more generally about 0.3 to about 6%, of the cathodically consumed coumarin,[8,73,74] butynediol,[8,108,109] N-methylquinolinium iodide[110] is co-deposited (or "incorporated"). The remainder is reduced, or more specifically hydrogenated, to less adsorbable compounds[66,68,105,106,109] and released back into the electrolyte. Compare the important papers on addition agents, especially for nickel plating, by DuRose,[41] Saubestre[112] and Brown.[113-115]

It is true that the, let us say, 3% of leveler to be codeposited contribute to surface coverage and inhibition until they are covered by several atomic layers, or one multiatomic layer, of nickel and that the 97% of leveler to be hydrogenated and released into the electrolyte will stay adsorbed only a shorter time, will have a shorter "lifetime" or "stay time" as adsorbed molecules, but we do not know how much shorter. It would be extremely surprising if 94 to 99% or more of a leveler used in nickel plating would be "wasted," that is, would not perform a useful function in surface coverage, brightening and leveling. It is much more probable that they perform this useful function, but by not being incorporated do not impair the physical properties of the nickel deposits.

The radiotracer or chemical studies of addition agent incorporation by Edwards,[60-64] Edwards and Levett,[65-69] Beacom and Riley,[116-119] Doty and Riley,[120] Vyagis and co-workers,[108] and Matulis[109] are very important for the understanding of the action and cooperation (synergism) of addition agents. Some of these studies report a similar trend of the codeposition curves and the polarization curves, *e.g.*, against concentration of coumarin, Ref. 64, Fig. 17, or butynediol,[108,109] but not, for instance, for codeposition of N-allylquinaldinium bromide and polarization in dependence on the sodium allylsulfonate concentration above 0.5 g/L, Ref. 120, Fig. 4.

Detailed discussion of these interesting studies is beyond the scope of this paper. To my knowledge they do not supply data on codeposition rates or percentages, which would be directly useful for the prediction of leveling and leveling maxima such as Fig. 14 does for consumption rates at constant potential and constant agitation against concentration, or Fig. 15 does for two agitation rates, or as a plot of consumption rates at constant potential against $C_B\sqrt{\omega}$ would do.

Such data, and similar data on surface coverage, would show whether total cathodic consumption rates or incorporation rates or surface coverage give the best correlation to leveling. The one study of surface coverage[100] which is directly relevant to this subject will be discussed in Section 10.

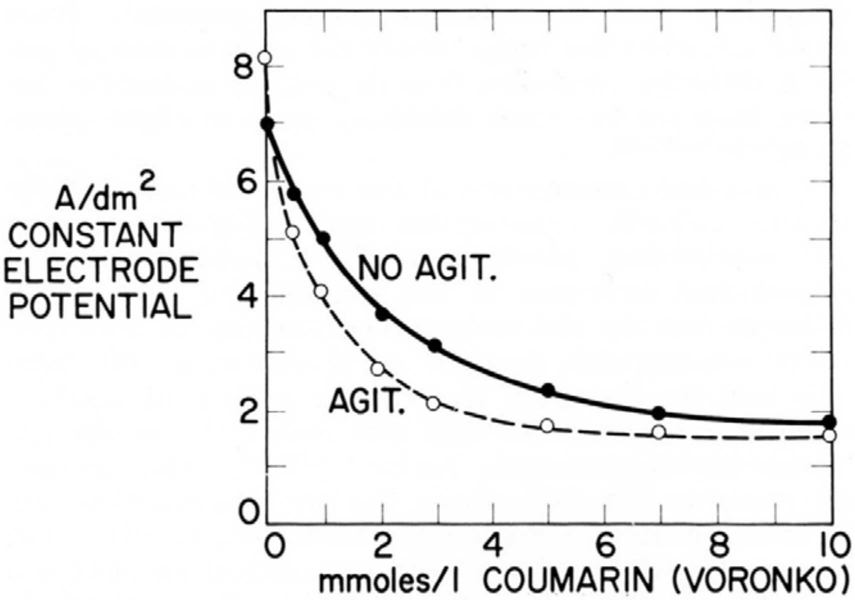


Figure 16 - Current density of nickel deposition vs. coumarin concentration in Watts nickel bath (50°C, pH = 4.0) at same cathode potential (-890 mV_{SCE}) without and with agitation; from Voronko.[91]

Just as Fig. 15 plots two consumption vs. concentration curves at two different agitation rates, one could plot two i_{Ni} vs. concentration curves at two different agitation rates. Voronko[91] has done something similar by plotting i_{total} at constant potential without and with agitation against coumarin concentration. Figure 16 shows that at first addition of coumarin inhibits nickel deposition more with agitation than without. This is expected from Eqs. 15 and 26 because of the smaller δ_N, or larger k_T, in presence of agitation. But the critical surface coverage for the disappearance of strict transport control is first reached in presence of agitation and from then on an increase of coumarin concentration produces a smaller decrease of current density with agitation than without until finally, at about 10 mM = 1.46 g/L coumarin, both curves practically coincide and leveling should disappear. At the concentration where the difference ($i_{non\text{-}agit}$ - i_{agit}) or the ratio $i_{non\text{-}agit}/i_{agit}$ reaches a maximum (at about 3mM = 0.45 g/L) also the rate of leveling should have its maximum. The maximum ratio could be directly observed if i were plotted on a logarithmic scale because $\log(i_r/i_p) = \log i_r - \log i_p$.

Of course, the leveling maxima predicted from Figs. 14-16 would apply to a selected electrode potential. For practical purposes, one is more interested in leveling maxima at a selected current density. Unfortunately, purely galvanostatic methods are not directly applicable because it is the electrode potential and not the current density which is constant over a microprofile. Consequently one would have to use a partly galvanostatic-partly potentiostatic method, comparable to the one used by Raub and Stalzer[93] and by Lash and myself for obtaining Fig. 13.

Before concluding this section we have to summarize the many interesting studies on cathodic consumption and incorporation rates of thiourea, H_2NCSNH_2. See the survey by Ibl.[48]

In a Watts nickel bath the incorporation rates of sulfur (but not of carbon) are equal to the cathodic consumption rates[70] and both show all the characteristics of diffusion control over a very wide range of conditions.[48,60,70,121,122] They are proportional to the thiourea concentration, rather independent of current density (and correspondingly the sulfur content of the deposits strongly decreases with increasing current density), and on the rotating disk electrode proportional to $\sqrt{\text{rpm}}$.[48,121,122]

The incorporation rate of carbon is much lower: the atomic ratio C/S in the nickel deposit varies between 0.015 and 0.05 at 55°C and pH = 4[60] and 0.1 and 0.4 at 20°C and pH = 2.5.[70] Brightness, cathode polarization and leveling show similar trends with increasing thiourea concentration as does the C/S incorporation ratio.[70,123] The depolarizing (or stimulating) action of thiourea in the lower concentration or current density range[3,60] is apparently related to the depolarizing effect of H_2S or NiS.[60] Compare also Ref. 124.

In the acid copper bath cathodic consumption rates of thiourea[125] and incorporation rates of sulfur[126] show also strong features of diffusion control above 2 to 3 A/dm^2, but strongly decrease with decreasing current density below this critical current density. In contrast to the nickel bath the cathodic consumption rates in the acid copper bath are about 3 to 4 times larger than the incorporation rates of sulfur.[125] The atomic C/S ratios are higher than in the nickel bath and often close to 1.[127,127A]

10. Diffusion control of surface coverage as revealed by the differential capacitance of the electric double layer

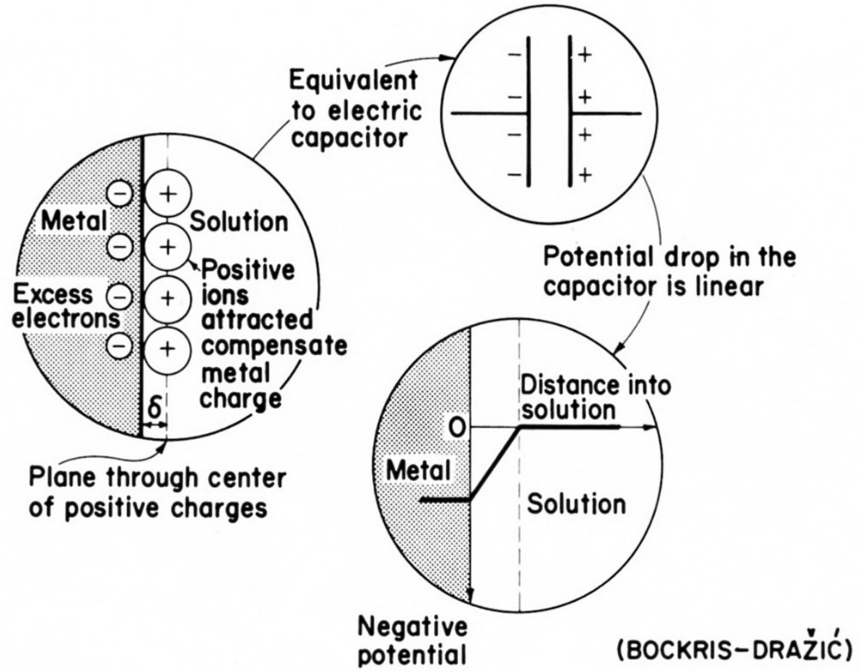


Figure 16A - The simplest imaginable electric double layer; from Bockris and Drazic.[33]

Like any capacitor (condenser) the electric double layer (see Fig. 16A) has a capacitance (or capacity), or for small changes of charge Q and potential *E* a differential capacitance *C*, which is given by the equation:

$$C = \frac{\Delta Q}{\Delta E} = \frac{i\Delta t}{\Delta E} = \frac{i}{\Delta E/\Delta t} \qquad (30)$$

$\Delta E/\Delta t$, and herewith *C*, may be obtained by superposition of AC or, less exactly, from the decay of the overpotential after current interruption.

Organic inhibitors often, but not always, decrease the capacitance of the electric double layer by displacing adsorbed water molecules, which in most cases have a greater dielectric constant than the organics.

The fractional surface coverage by the organic addition agent is given by the equation:

$$\Theta = \frac{C_0 - C}{C_0 - C_{sat}} \qquad (31)$$

where C_0, C and C_{sat} are the capacitances at zero coverage, coverage Θ, and saturation coverage.

On the relation of adsorption and capacitance decrease see for instance Refs. 30, 33, 128-130. Volk and Fischer[131] studied the decrease of differential capacitance produced by various nickel additives and found for uncharged compounds such as butynediol or propargyl alcohol a decrease of C_0 - C with more negative cathode potential. They ascribed this change of C with E (or i) to dependence of the surface coverage by the inhibitor on the electrode potential. Balakrishnan and Fischer[124] reported the decrease of capacitance produced by thiourea. Raub, Baba, Knödler and Stalzer[72] used the capacitance decrease, together with the increase of overpotential and in some cases of cathodic film resistance, produced by acetylenic and other additives for their classification.

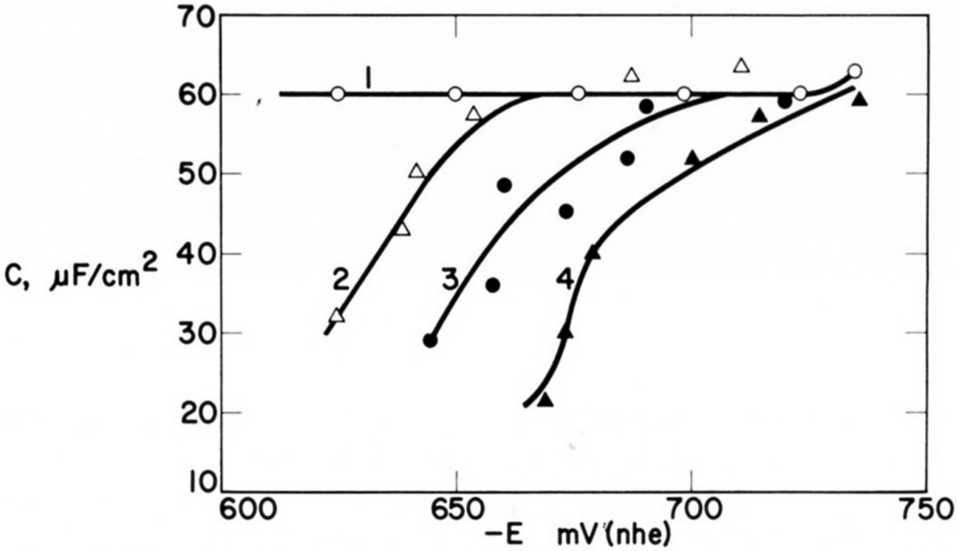


Figure 17 - Electric double layer capacitance vs. cathode potential in Watts nickel bath (30°C, pH = 4.5) (1) without addition agent at 400 to 4000 rpm and (2) with 0.2 mmol/L coumarin at 400 rpm, (3) 1540 rpm, (4) 4000 rpm; from Kruglikov, *et al.*[100]

Most relevant for the subject of this paper is the study by Kruglikov, Kudryavtsev and Sobolev.[100] Figure 17 shows the decrease of differential capacitance (measured by the potential decay method) produced by 0.2 mmole/L of coumarin in a Watts nickel bath (30°C, pH = 4.5). C_0 - C, and consequently from Eq. (31) surface coverage, strongly increases with the rpm of the rotating disk electrode, which indicates strong diffusion control of the surface coverage. C_0 - C and surface coverage decrease with increasing cathode polarization, but - because of diffusion control revealed by the dependence of C on rpm - this decrease should, at least partly, be due to diffusion control according to Eq. (26). Figure 17 suggests that C_{sat} is between 10 and 20 microfarad/cm², which is confirmed by similar capacitance curves obtained with 2 mmole/L coumarin.

Curve 2 in Fig. 18 shows that 1 mmole/L of the non-leveling control agent p-toluenesulfonamide lowers the double layer capacitance to about 35 pf/cm², but in this case C_0 - C, and consequently surface coverage, are constant over a wide potential and current density range, and are not influenced by a variation of the rotation rate of the disk electrode. Evidently, surface coverage by PTSA is not diffusion-controlled. Curve 4 shows the synergism of the two addition agents.

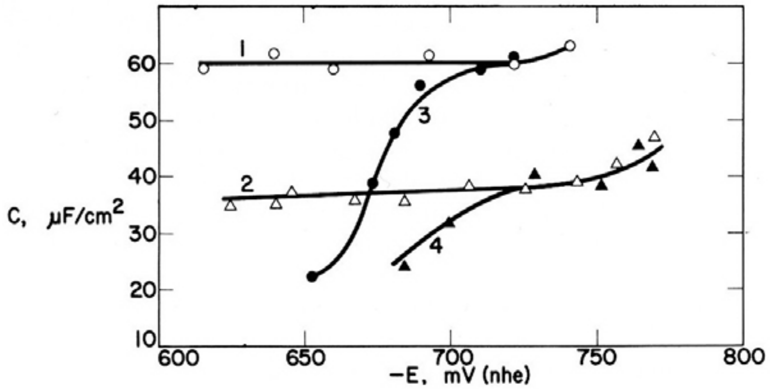


Figure 18 - Electric double layer capacitance vs. cathode potential in Watts nickel bath (30°C pH = 4.5; 1540 rpm) (1) without addition agent, (2) with 1 mmol/L p-toluenesulfonamide, (3) with 0.2 mmol/L coumarin and (4) with both addition agents; from Kruglikov, *et al.*[100]

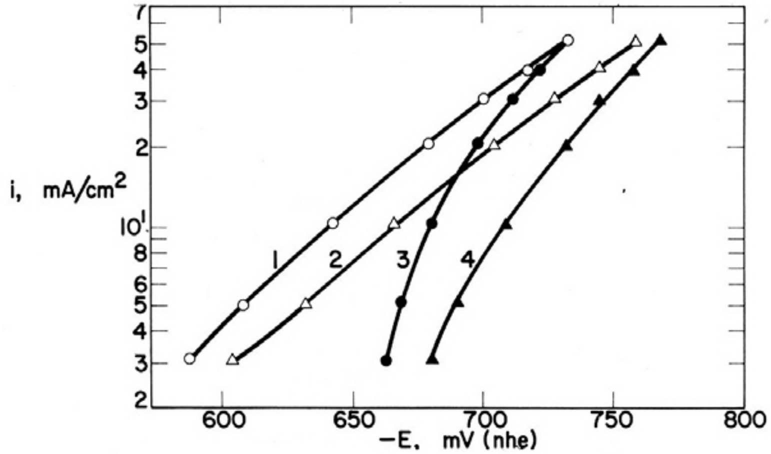


Figure 19 - Polarization curves in Watts nickel bath (30ºC, pH = 4.5, 1540 rpm); (1) without addition agent, (2) with 1 mmol/L p-toluenesulfonamide, (3) with 0.2 mmol/L coumarin, and (4) with both addition agents; from Kruglikov, *et al.*[100]

Figure 19 shows the corresponding polarization curves. The extra polarization ($-\Delta E$) produced by the additives is closely related to the decrease of capacitance, C_0 - C, produced by them, and to the corresponding surface coverage. For the diffusion-controlled coumarin, $-\Delta E$, just like C_0 - C and Θ, strongly increases with decreasing current density (as predicted by Eq. 26). For the not diffusion-controlled PTSA, $-\Delta E$, C_0 - C, and Θ are constant over a very wide potential and current density range. The correspondence between $-\Delta E$ and C_0 - C produced by various additives was also shown by Volk and Fischer.[131]

11. The disappearance of diffusion control with some types of interrupted current

In linear diffusion, that is diffusion to a flat electrode, the thickness of the diffusion layer would continuously increase with time if convection were absent. In the presence of convection, however, the diffusion layer reaches its steady state thickness in a few seconds after switch-on of the current. See *e.g.*, Ref. 33, p. 134. After interruption of the current, the concentration of the consumed species in the diffusion layer is replenished by diffusion. The decay time of the diffusion layer is several times longer than its formation time and decreases with increasing agitation.[98,101,132] If, after the decay of the diffusion layer, the current is switched on again (*e.g.*, at 4 A/dm^2) the initial overpotential in a coumarin-containing nickel bath may be more negative than its steady state value by as much as 150 mV.[98,101,132] At high coumarin concentration and low current density (0.5 g/L, 0.1 A/dm^2), where diffusion control is absent ($C_E \simeq C_B$), no such initial excess overpotential occurs.[98]

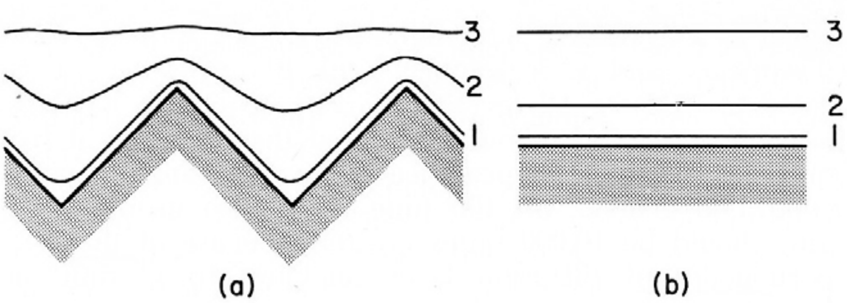


Figure 19A - Schematic comparison between nonstationary diffusion on (a) a rough homogeneous surface and (b) a flat homogeneous surface. Lines 1, 2 and 3 indicate equiconcentration planes for times $t_1 < t_2 < t_3$. From DeLevie.[36]

It should be kept in mind that over a microprofile the diffusion layer boundary is, for the fraction of a second after the current switch-on, very close and parallel to the profile contour.[12,36,133,134,178] Then the diffusion layer boundary gradually recedes and flattens and its local thickness varies more and more until after a few seconds the steady state is reached; (Fig. 19A). The length of the time after current switch-on during which the diffusion layer thickness is practically uniform over a microprofile strongly decreases with decreasing profile size.

One would thus expect a decrease of leveling if, with periodically interrupted current, the cathodic electrolysis time during each cycle, t_e, is not long enough to produce the maximum nonuniformity of δ over the profile, and if the interruption time, t_i, is sufficiently long to destroy the incipient diffusion layer formed during the preceding pulse. If t_e is so short that the diffusion layer thickness is still uniform over the profile, and t_i long enough to destroy this very thin diffusion layer, all leveling, except, of course, geometric leveling, should disappear. Exactly this is shown in Fig. 20, obtained by Kruglikov, Kudryavtsev and co-workers[101] (compare also Refs. 98 and 132) which plots the percentage of leveling in a coumarin-containing nickel bath against the pulsation frequency. Leveling was determined on V-shaped microgrooves on the rotating disk electrode, initially 50 µm deep, with an included angle of 60°. Deposit thickness on the flat area was 4 µm. The Watts nickel bath (30°C, pH = 4.5) was saturated with coumarin. With $t_e/t_i = 1/4$ (curve 2), when the frequency becomes greater than about 0.1 cycle/sec or t_e becomes smaller than 2 sec, leveling begins to decrease. At a frequency equal to 1 cycle/sec or t_e equal to 0.2 sec most leveling disappears, and at a frequency of 10 cycles/sec or t_e equal to 0.02 sec all leveling, except geometric leveling, has disappeared. It should be noted that the critical frequencies for the disappearance of leveling, and diffusion control in general, on 100 times less deep grooves (0.5 µm) should be 10,000 times greater, because of the proportionality of diffusion layer thickness to $\sqrt{\text{time}}$ or $1/\sqrt{\text{frequency}}$.[133]

The 50% leveling shown in Fig. 20, obtained on an initial groove depth of 50 µm thickness (on flat), is quite substantial and corresponds to a h_3/h_1 ratio (see Fig. 7) of more than 7.[98,132]

If t_e/t_i is too great (*e.g.*, 3/2 in curve 4), then the diffusion layer developed during a pulse is only partly destroyed during the following interruption time and thus its thickness increases during each cycle until it reaches its normal value. Consequently, leveling is scarcely diminished.

Figure 20 is a very strong proof of the diffusion mechanism of leveling in coumarin-containing nickel baths, at least on grooves of the examined depth (30 and 50 µm). It is difficult to imagine that other leveling mechanisms such as the shape-sensitive adsorption suggested by Thomas[5] or the cyclic mechanism of Zak[179] would show a similar dependency on pulse frequency.

If the pulse time is short enough, and the interruption time sufficient to destroy the rudimentary diffusion layer formed in the preceding pulse, also the unfavorable influence of rate control by the mass transport of the depositing metal ions should disappear. Thus "bad microthrow," increase of original surface roughness, formation of dendrites and metal powder can be avoided.[133,134,178] See also Ref. 133A on the induction time required for the appearance of diffusion controlled amplification of surface roughness.

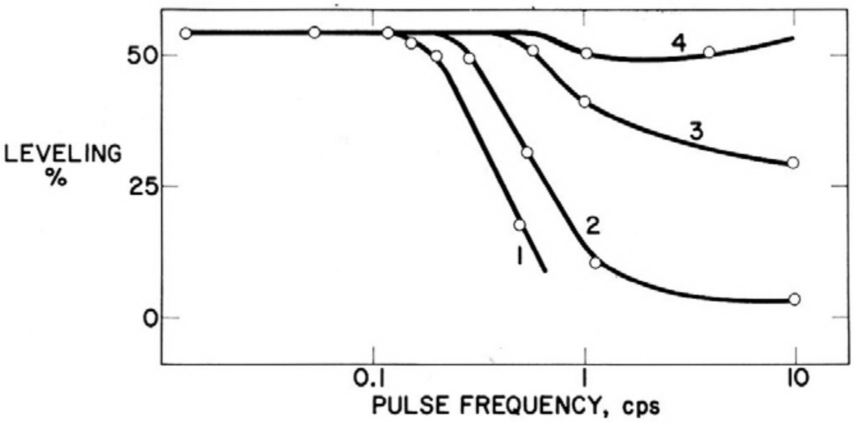


Figure 20 - Leveling vs. pulse frequency in nickel bath (30°C, pH = 4.5, 4 A/dm^2, 430 rpm) saturated with coumarin; initial groove depth 50 µm, notch angle 60°, deposit thickness on flat surface 4 µm. Electrolysis time/interruption time = (1) 1/12, (2) 1/4, (3) 1/1, (4) 3/2. From Kruglikov, *et al.*[101]

While the diffusion layer thicknesses obtained in electroplating are generally between 20 and 200 µm, and most intense mechanical agitation may reduce it to 0.8 µm, Braun and Ibl[134,178] obtained with pulse times of 0.7 to 30 microseconds (µsec) diffusion layer thicknesses of only 0.025 to 0.2 µm. The boundaries of such thin diffusion layers can follow the contours of even very fine surface roughness and are smaller than the radius of the finest dendrite tips. Consequently, diffusion-controlled roughening of the metal surface is avoided, even at a current density as high as 25,000 A/dm^2 during the cathodic pulse and an average current density during the cycle of 37.5 A/dm^2, in an acid copper bath flowing at a velocity of 2 m/sec. A similar effect is obtained with high-frequency (*e.g.*, 10,000 cycles/sec) pulsation of the cathode potential.[133]

With a uniform diffusion layer thickness over the microprofile, electrodeposition at the limiting current density even improves the uniformity of metal deposition and concentration polarization throws the deposit into the microrecess just as it does on macrorecesses.[l34,178]

Interrupted current of a more usual type (*e.g.*, t_e = 3 sec, t_i = 12 sec, i_{av} = 3 A/dm^2) reduces roughness formation in acid copper baths.[177] Various cycles of interrupted current are useful in industrial cyanide plating where they reduce roughness formation and improve microthrow, especially in the high current density range.

12. Quantitative prediction of leveling

Idle arguments for a diffusion theory of leveling assembled in the preceding sections are many and seem to be very strong. They seem to explain the general features and trends of metal deposition on microprofiles. It is thus surprising that very few attempts were made to predict or explain quantitatively the thickness ratios obtained in a microgroove of a specific shape and under specific conditions. Such attempts were made by Gladshtein and Kadaner[135] and were apparently quite successful, as far as I can judge from my unreliable translation of the Russian original and from the short abstracts in English.[136] These authors predicted thickness ratios on a V-shaped groove (β = 60°, *depth* = 0.25 mm) and a rectangular groove (0.1 mm deep and wide) from a coumarin-containing nickel bath, for instance, by the following method: They made models of the two grooves on semiconductive paper, on which they determined the primary current distribution ratios (i_n/i_{10})pr for the 10 equal sections of the grooves, sections 8 to 10 being situated on the flat surface. Because of the analogy of limiting diffusion flow and primary current distribution $j_{Ln}/j_{L10} = (in/i_{10})$pr. From Eq. (15) they obtained the "equivalent" coumarin concentrations $C_n/C_{10} = j_{Ln}/ j_{L10}$ and, combining these two equations, $C_n/C_{10} = (i_n/i_{10})$pr. From polarization measurements they predicted the local current density on each groove section corresponding to the local "equivalent" coumarin concentration at the electrode potential required to give the selected current density at section 10. The predicted and the actually measured current density and thickness ratios agreed remarkably well. This success should encourage similar attempts at quantitative prediction of deposit thickness ratios on microprofiles.

The influence of the microprofile shape on microthrow and leveling is easily predictable: As well on isolated V-grooves as on triangular wave profiles increase of the enclosed angle (notch angle) β makes primary current distribution and thus diffusion flow at constant C_E more uniform.[29] Consequently bad microthrow, *e.g.*, from cyanide baths or from acid copper baths at high current densities, improves with increasing β, or as tan (β/2) = (width/2 × depth) with increasing width/depth ratio. On the other hand, true leveling, and from Fig. 2 also geometric leveling, decrease with increasing notch angle. These expectations were confirmed by Raub,[45] Müller and Raub[45A] and Cheh,[160] and on trapezoidal grooves by Sundarayan, Rayagopalan and Reddy.[138]

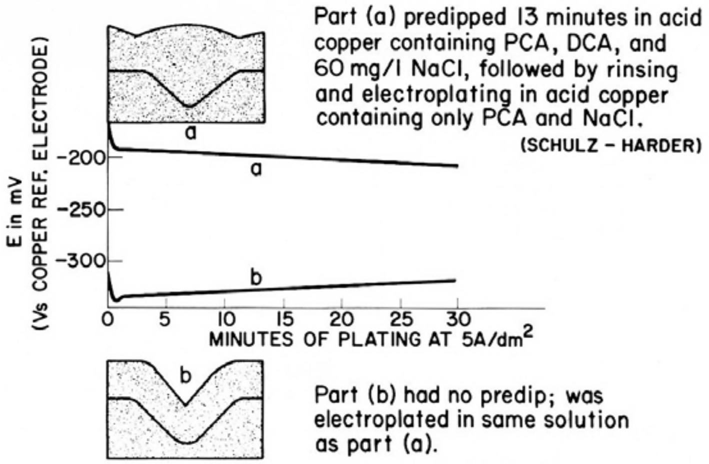
A triangular wave profile should give a greater variation of j_L, and δ_N, than V-grooves of the same notch angle β. This seems to agree with DuRose's[78] finding that less coumarin is required for maximum leveling on satin surfaces than on isolated notches.

Overplating should be avoided to minimize the influence of geometric leveling.[45A] If one wishes to study the influence of groove size on leveling, it is therefore recommended to decrease deposit thickness in proportion to groove depth.

13. A new and completely different leveling mechanism

Until recently, only two main cathodic leveling mechanisms were known: diffusion-controlled inhibition producing "true leveling" and uniform current distribution producing "geometric leveling." A less frequent mechanism was described by Sundarayan and co-workers.[138] They obtained moderate leveling in trapezoidal grooves from a cyanide copper bath containing no additives at high rotation rates of the cylindrical cathode. They ascribed this to turbulent flow within the grooves leading to increased supply of the complexed metal ions.

But in fall 1972 Professor Ibl sent me a copy of the doctoral thesis of Dr. Ing. J. Schulz-Harder[107] in which the latter described a completely new and different leveling mechanism. Schulz-Harder obtained substantial leveling by predipping or preplating an electroformed copper panel containing V-shaped grooves (30 µm deep) in an acid copper bath containing 60 mg/L sodium chloride, a polarizing control agent, PCA, and a depolarizing control agent, DCA, similar to, but not identical with, those we had used in the experiments leading to our Fig. 13 and Table 2, rinsing it in an acid copper bath containing no additives, and finally plating it in a copper bath containing only chloride and PCA.



Part (a) predipped 13 minutes in acid copper containing PCA, DCA, and 60 mg/l NaCl, followed by rinsing and electroplating in acid copper containing only PCA and NaCl.
(SCHULZ – HARDER)

Part (b) had no predip; was electroplated in same solution as part (a).

Figure 21 - Copper deposits on microgrooves (30 µm initial depth) and cathode potentials (at 5 A/dm^2) from non-leveling acid copper bath (a) with activating predip and (b) without predip; replotted from Schulz-Harder.[107]

The upper photomicrograph in Fig. 21 shows the copper deposit obtained after 13 min predip in the PCA + DCA + Cl^- bath (similar to solution No. 5 in Table 2), followed by rinsing and final plating (32 min at 5 A/dm^2) in the PCA + CP bath free of DCA (similar to solution No. 3). It shows strong leveling and even "superleveling" because of the hump formation over the groove. The lower photomicrograph b in Fig. 21 shows the non-leveling copper deposit obtained in the PCA + Cl^- bath without predip. The graph shows the cathode potentials (against a copper wire) during the plating of deposit (a) after predip and deposit (b) without predip. The preceding predip, although followed by a rinse, depolarizes copper deposition by about 150 mV, just as the addition of 15 mg/L DCA to a copper bath containing 60 mg/L Cl^- and 1 g/L of a PCA depolarized by 163 mV (Experiment No. 5

vs. 3 in Table 2). (It should be noted that the cathode potentials of Fig. 21 are measured against a copper wire and are consequently much less negative than those given in Table 2 for similar additives against the saturated mercurous sulfate electrode.) The copper surface thus shows a "memory" for the pretreatment which only slightly decreases during the 32 min plating time.

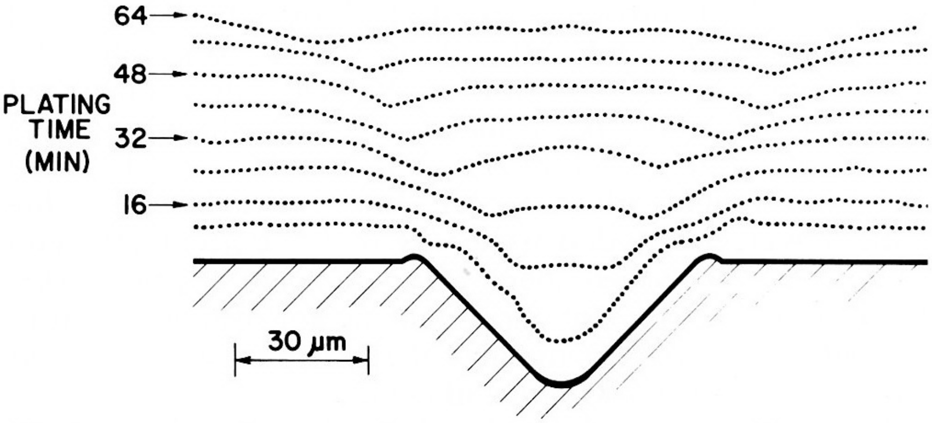


Figure 22 - Copper deposits in dependence on plating time after activating predip as in Fig. 21A; from Schulz-Harder.[107]

Figure 22 shows successive deposit thicknesses obtained after predip under the same conditions as Fig. 21A.

Schulz-Harder's interesting explanation of these phenomena is based on a fact and a hypothesis. The fact is that uniform metal deposition reduces the surface area over a microgroove, increases it over a micropeak, and leaves it unchanged over a flat area. The hypothesis is that the "catalyst" (stimulator, depolarizer) DCA is relatively slowly adsorbed and still more slowly incorporated or desorbed. During the predip the copper surface becomes evenly but not completely covered by DCA, but during the following plating the surface area over the groove bottom shrinks and consequently ends up with a higher surface coverage by DCA and thus will grow faster than the other areas. The opposite happens over micropeaks or convex surface areas. This hypothesis assumes that the copper grows below the adsorbed catalyst and "pushes it up" or "carries it along" while growing.

Preplating (8 min) in the PCA + DCA + Cl^- bath No. 5 followed by rinsing and plating (24 min) in the PCA + Cl^- bath No. 3 gives results similar to those described in Figs. 21 and 22. For some other DCA compounds only the preplating and not the predip method produces leveling.

Also a predip (5 min) in the acid copper bath No. 4 containing chloride + PCA + only 10% of the regular DCA concentration followed by plating (32 min at 5 A/dm^2) in the same bath gives moderate leveling. We confirmed this on a scratched Hull Cell panel and also found that the predip is not required. However, in both cases the leveling is considerably lower than can be obtained in the presence of a typical leveling agent, that is, a diffusion-controlled inhibitor.

Concentrations of the catalyst DCA in predip, preplating solution and, with the just described procedure, in the plating bath itself, and predip or preplate time are somewhat critical. If surface coverage is at or near saturation on all profile points, then shrinkage of the surface area in the groove cannot produce any, or at least not much, increase of the surface coverage by the catalyst and of the metal deposition rate.

This new "surface controlled catalysis" mechanism of leveling, discovered by Schulz-Harder, is bound to attract considerable attention as soon as it becomes more widely known. It should strongly contribute to the understanding of addition agent action, but it seems that in strongly leveling industrial plating processes the presence of diffusion-controlled inhibitors, that is of the regular type of levelers, will continue to be indispensable.

The "memory effect" discovered by Schulz-Harder is remarkably long-lasting. It brings to mind other memory effects such as the influence of the substrate structure on the deposit structure, the persistence of fingerprints on the substrate even through fairly thick electrodeposits if cleaning is insufficient, and the preplate influence described by Edwards[64] and Edwards and Levett.[67]

These authors showed that a preplate in a nickel bath containing inactive saccharin and either succinonitrile or quinoline methiodide, followed by a rinse, increases subsequent codeposition of sulfur from a nickel bath containing radioactively labeled saccharin. They ascribed this effect to the creation of adsorption sites (or could they be reduction sites?) for saccharin in the preplate bath containing the mentioned additives (but not in a preplate bath containing, *e.g.*, only inactive saccharin). This memory effect fades rather quickly; after 2.5 sec plating in the second bath, it decreased to less than one third of the magnitude it had at only 0.5 sec plating time.

A predip effect observed by Vagramyan and Baraboshkina[141] will be discussed in Section 14.

The "pushing up" or the "carrying along" of the adsorbate by the growing metal deposit required by Schulz-Harder's leveling mechanism (unless the latter is explainable by the creation of especially active growth sites) could have some relation to the formation of laminations. The replica electron micrographs and especially the transmission electron micrographs of thin foils of a proprietary bright nickel deposit, obtained with a special technique by Weil and Jacobus,[143] reveal a finer grain structure of the lamination boundaries ("dark bands" developed by electropolishing or etching) which the authors relate to periodic fluctuation of the concentration of adsorbed or codeposited additives. Could it be that "some or all" of the adsorbed additives are "pushed up" until at a critical surface concentration of "some or all" they are incorporated? The situation becomes especially interesting and complex because all proprietary bright nickel baths contain control agents (see DuRose's definition[41]) such as aromatic or otherwise unsaturated sulfonates and sulfonamides which require splitting of the C-S bond by hydrogenolysis[41,113-115] before sulfur (and sometimes also carbon[120]) is codeposited and, on the other hand, leveling brighteners which become less adsorbable by hydrogenation.[66,68,105,106,109,113-115] What is then "pushed up": only the control agents or also the leveling brighteners? Do the dark bands contain only more codeposited sulfur or also more codeposited carbons? Compare also the related papers by Weil and co-workers.[142,144,145]

14. Brightening

The brightness of a surface is related to the practical absence of surface roughness of the order of the wavelengths of light, namely 0.4 to 0.8 µm for violet and red light, respectively.

Weil and Paquin[139] showed that the eye evaluation of the brightness of various nickel deposits corresponds to the percentage of specular reflection (angle of reflection = angle of incidence) of light from them and to the fraction of surface area free of roughness of 0.15 µm or more depth. The following equation shows the dependence of the ratio of diffuse reflection (R_d) to total reflection (R_t) on the RMS roughness of the surface (σ) and the wavelength of light (λ):[140]

$$\frac{R_d}{R_t} = \left(\frac{4\pi\sigma}{\lambda}\right)^2 \tag{31A}$$

To get a high degree of brightness, that is, a low R_d/R_t, the RMS roughness of the surface should thus be substantially smaller than the wavelengths of light.

It is important to distinguish between brightening of a matte surface and brightness maintenance, that is, suppression of roughness formation on an originally bright substrate. Both effects were studied by Vagramyan and Baraboshkina.[141] With the help of a specially designed instrument, including a photocell, they measured specular reflection from nickel deposits during plating in a variety of nickel baths. They used two substrates: matte nickel and bright nickel. Most crystallites on the former were four-sided pyramids of 0.7-1.0 µm width and with valleys between them of an average depth of 0.3-0.4 µm. The surface of the bright nickel, deposited from a Watts nickel bath containing 0.3 g/L thiourea, appeared smooth even at 16,000× magnification.

Figures 23 to 25 show the dependence of reflectivity (expressed as microamperes flowing through the photo-cell) on deposit thickness. Standard conditions were 40°C, pH = 4.0, 4 A/dm², no agitation, in a well-purified Watts nickel bath.

The ascending curve in Fig. 23 shows the rapid increase of the reflectivity of the matte nickel substrate in nickel baths containing the leveling brighteners butynediol (1 g/L) or thiourea (0.3 g/L). With about 3 µm deposit thickness, full brightness is reached. The upper curve shows the excellent brightness maintenance during plating on a bright substrate. In absence of additives, the reflectivity would fall until the initial value of the ascending curve is reached with about 12 µm deposit thickness.

Figure 24, obtained in presence of 1 g/L coumarin, shows the rapid increase and decrease, respectively, of brightness to the semibright level which is characteristic for deposits from a coumarin-containing bath. Compare also the interesting electron micrographs of Weil and Cook.[142]

Figure 25, obtained in presence of 2 g/L saccharin, shows a much slower rate of brightness increase to a semibright level but a rather good brightness maintenance.

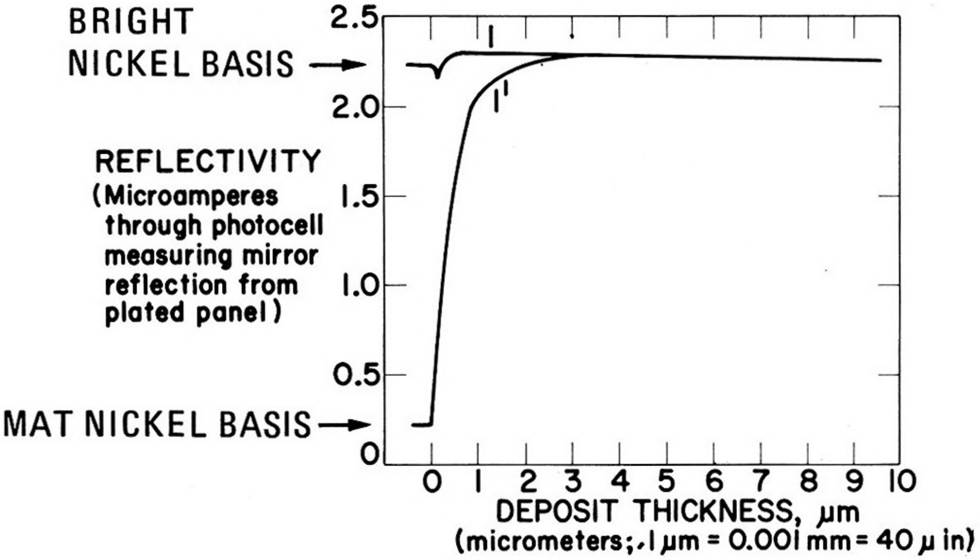


Figure 23 - Change of specular reflection with nickel deposit thickness on bright nickel substrate (1) and mat nickel substrate (V). Watts nickel bath (40 C, pH = 4.0, 4 A/dm^2, no agitation) containing 0.3 gL thiourea or 1 g/L butynediol; from Vagramyan and Baraboshkina.[141]

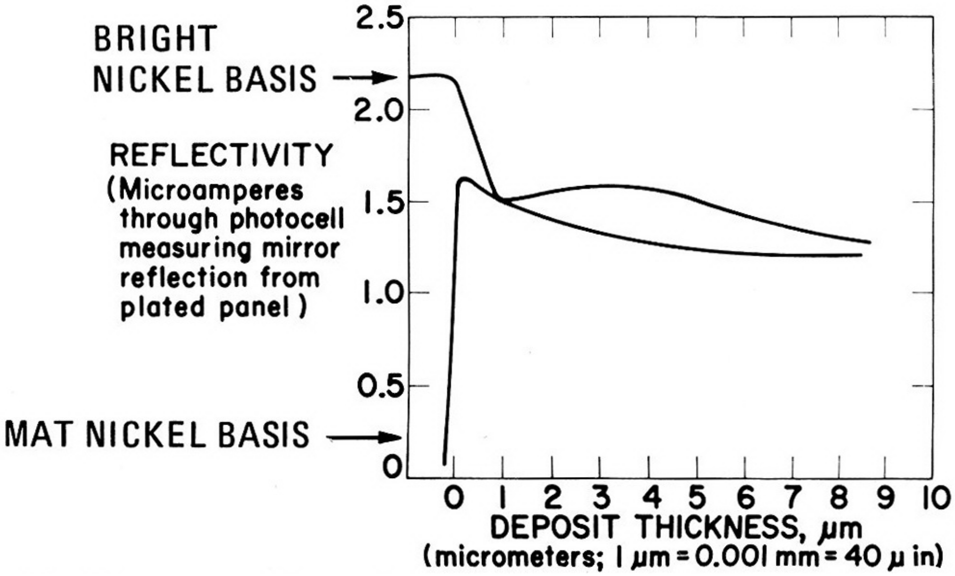


Figure 24 - As Fig. 23 but with 1 g/L coumarin as the addition agent.[141]

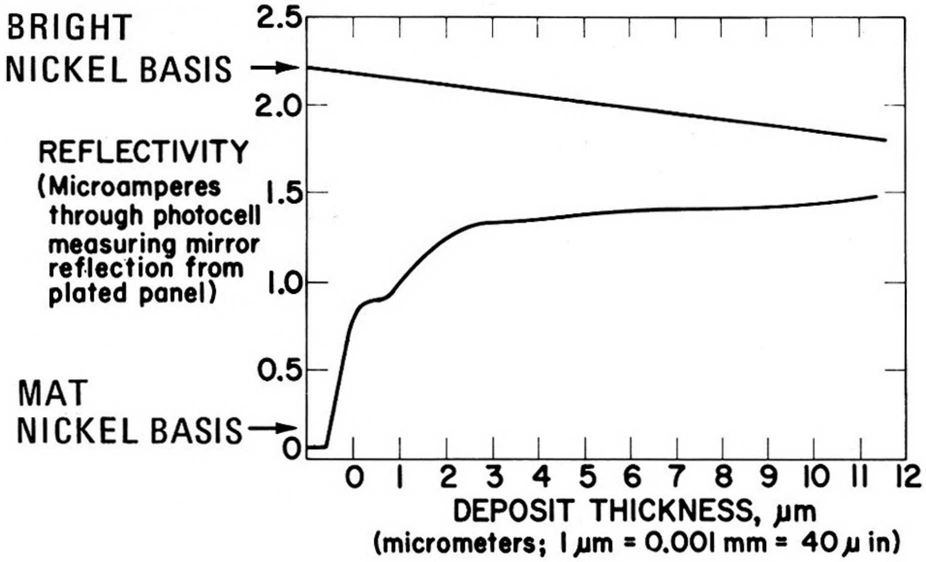


Figure 25 - As Fig. 23 but with 2 g/L saccharin as the addition agent.[141]

How does one interpret these results, especially those referring to the *brightening of matte substrates*, which is obviously a smoothening or leveling process? To compare the rate of leveling over a microgroove 0.35 µm deep and over another one 25 µm deep one should keep deposit thicknesses proportional to the groove depths. The 100% leveling obtained in Fig. 23 on a 0.35 µm roughness with 3 µm deposit would require a 70 times thicker deposit, that is 210 µm, for the 25 µm deep groove. Apparently, the rate of leveling over the matte nickel is of the right order, but somewhat smaller than expected. This applies also to the apparently geometric leveling in Fig. 25 and may perhaps be due to the absence of agitation. Evidently, a much more detailed and quantitative comparison would be desirable.

Vagramyan and Baraboshkina bring two arguments against the existence of a diffusion-controlled leveling mechanism on such fine profiles. First they argue that with a roughness of, *e.g.*, 0.3 µm, and a diffusion layer thickness of, *e.g.*, 140 µm, the diffusion layer thicknesses over micropeak and microrecess would be 140 µm and 140.3 µm, respectively, and thus $\delta_r/\delta_p \simeq 1$. This is correct as far as it goes but the ratio of limiting diffusion rates j_{Lp}/j_{Lr} is equal to the ratio of the *effective or equivalent* diffusion layer thicknesses δ_{Nr}/δ_{Np}, which remains unchanged if the profile size is reduced, just as primary current distribution is independent of profile size or of the distance of the anode if the latter is sufficiently far away. This is because a micropeak receives more diffusion flow not only because it is nearer - and in the case of very fine-scale roughness, just a trifle nearer - to the diffusion layer boundary, but mainly because it diverts diffusion flow toward itself by being accessible from several directions.[146]

Vagramyan and Baraboshkina's second argument against diffusion control on very fine-scale roughness and for "specific" or "shape-sensitive" adsorption in the sense of Thomas[5] or Beacom and Riley[116,117] is based on the following experiment: they dipped a still active matte nickel deposit in an aqueous thiourea solution, rinsed it in distilled water, and obtained leveling during subsequent plating in a nickel bath containing no additives. This "memory effect" (see Section 13) seemed to indicate "selective" or "specific" adsorption, instead of diffusion-controlled adsorption, on the micropeaks. Their experiment requires further analysis. Immediately after the immersion of the matte nickel into the thiourea solution, there would be no diffusion layer present. Then a diffusion layer would form, first of equal thickness, then of unequal thickness over the profile. Finally, after the surface becomes saturated with thiourea or one of its reaction products with nickel hydride, namely nickel sulfide,[61] the diffusion layer would decay. It would, consequently, be important to know which stage was reached in the predip. Furthermore, considering the depolarizing or stimulating effect of thiourea at certain concentrations, or at very low current density even at all concentrations,[3] one could wonder whether the leveling obtained after the predip would not be of the Schulz-Harder type described in Section 13.

The experiments reported in Section 9[48,60,70,121,122] show conclusively that the overall adsorption and consumption rate of thiourea in nickel baths is, during the "steady state" of nickel plating reached after a few seconds, diffusion controlled. That means that peaks, valleys, flats will adsorb and "consume" all the thiourea molecules arriving at the limiting diffusion rate, and consequently more on micropeaks than on microrecesses, unless it can be proved that the difference of limiting diffusion rates to micropeaks and microrecesses disappears on very fine-scale profiles. Vagramyan and Baraboshkina's first argument did not seem to prove this and the presently available experimental data seem to disprove it. One may cite here Watson and Edwards's finding[3] that maximum leveling is obtained at about the same coumarin concentration whether the microgrooves are 20 µm or 0.1 µm deep (see Section 3) and the prevention of roughness formation at high current density with interrupted current[133,134,178] which was shortly discussed in Section 11.

Thus, my peace of mind was not disturbed until I received a letter from Dr. Schulz-Harder, dated January 31, 1973. I would like to translate some of the significant passages in this letter from the original German:

"*First I would like to express my opinion concerning your thesis that the diffusion-controlled inhibitor mechanism applies also to roughnesses the dimensions of which are very small, e.g., in comparison with Nernst's diffusion layer thickness. This assumption is correct if the inhibitor consumption occurs on all points of the surface at the limiting rate and consequently the concentration of the inhibitor in vicinity of the surface becomes zero. This concept applies only in rough approximation. In reality surface concentrations*" (this applies obviously to C_E and Θ of this paper) "*must be different to make leveling possible . . .*

"*In this case there exists a characteristic length* L_D, *which indicates the order of the profile dimensions, from which on substantial decrease of these dimensions produces no more difference in the surface concentrations of the inhibitor and consequently no more leveling*."

This parameter L_D is similar to Wagner's polarization parameter k_c and Schulz-Harder calculates it as (if we use some of the symbols of this paper):

$$L_D = \left(\frac{dC_E}{dj_{ads}}\right)^D = \frac{D}{k^\circ} \tag{32}$$

where k^o is a complex reaction constant calculated from the adsorption, desorption, and consumption rate constants of the inhibitor. (These ideas were developed by Dr. Schulz-Harder in cooperation with Professor Dr. J. Osterwald).

If reversible (unchanged) desorption can be neglected and surface coverage is far from saturation, k^o is equal to k_{ads} (see Eq. 24). Then an equation similar to (8), but for adsorption rates instead of current densities, results:*

$$\frac{j_{ads\,p} - j_{ads\,r}}{j_{ads\,av}} = \frac{d}{L_D \sin(\beta/2)} = \frac{d}{(D/k_{ads})\sin(\beta/2)} \tag{33}$$

If $d/\sin(\beta/2)$ - and consequently the smaller groove depth d itself - is substantially smaller than D/k_{ads}, adsorption rates should become practically uniform unless, of course, k_{ads} varies over the profile and is *e.g.*, greater on micropeaks. However, the critical adsorption or diffusion parameter $L_D = D/k_{ads}$ decreases with increasing k_{ads}. As shown in Section 6, $k_{ads} >> k_T$ is characteristic of strict diffusion control. Diffusion-controlled inhibition (or stimulation) should thus exist down to very fine profile sizes if k_{ads} is sufficiently large.

Consideration of the inhibitor diffusion from micropeak to microrecess, which reduces adsorption on the peak and increases it on the recess, leads to a similar conclusion (Compare Section 2). This diffusion rate is equal to $D(C_p - C_r)/s$, where s is the length of the groove side. To obtain $j_{ads\,p}/j_{ads\,r} \simeq 4$, one would need $C_p/C_r \simeq 4$ (if the influence of a variation of θ can be neglected; see Eq. 24.). But the resulting diffusion flow from peak to recess is, of course, 10 times smaller with $C_p = 0.004C_B$ and $C_r = 0.001C_B$ than with $C_p = 0.04C_B$ and $C_r = 0.01C_B$.

---

* From $j_{ads\,p} = k_{ads}\,C_p$, $j_{ads\,r} - k_{ads}\,C_r$, and the simplification $j_{ads\,av} = j_{diff\,av} \simeq \frac{D(C_p - C_E)\sin(\beta/2)}{d}$

Similar considerations apply to metal deposition in absence of inhibitors, where C_p and C_r would refer to the metal ion concentrations. In this case, transport-controlled roughness increase of the very fine initial roughness is so well-proven[12,133,134,155,156,178] that strict transport control must exist down to a very fine scale of roughness.

Now to roughness formation and its suppression by inhibitors, or "*brightness maintenance*."

In absence of mass transport control, roughness develops on polycrystalline substrates because of the different growth rates of crystallites of different orientation[147,148] and on single crystals, or on the individual crystallites of a polycrystalline surface, by the bunching of monoatomic layers to polyatomic layers ("macro-steps"), the development of ridges, growth spirals, pyramids, blocks, etc., by mechanisms discussed in Refs. 33, 88, 89, 90, 140, 147-154.

Transport control strongly increases the rate of roughening because, except with pulsed current or potential of sufficiently high frequency or of sufficiently short cathodic pulses and sufficiently long rest periods,[133,134,178] the diffusion layer thickness is smaller over the micropeaks than over the microvalleys. This diffusion-controlled roughness formation was studied especially by Ibl and associates[48,56,134,155,156,178] and was recently surveyed by Despic and Popov.[12,133,133A]

A special case of diffusion-controlled roughness formation is dendritic (tree-like) growth. According to the theory initiated by Barton and Bockris[157] and further developed in Refs. 158 and 159, a growth spiral or pyramid becomes, after the required induction time,[133A] tall and steep under diffusion control until it penetrates the diffusion layer characteristic of the substrate. Then linear diffusion is replaced by spherical diffusion and Eq. (16) is replaced by the corresponding equation for spherical diffusion

$$i_L = \frac{nFDC_B}{r(1-t_{Me})} \tag{34}$$

where r is the radius of curvature of the dendrite tip. If r is much smaller than the diffusion layer thickness of the substrate, the dendrite will grow at a much faster rate than the rest of the surface. See also Rets. 12, 33, 89.

How do inhibitors suppress roughness formation? Hoar[161] suggested that the production of a bright surface (other than by mechanical means) involves the deposition, or in the anodic case removal, of surface atoms in a random manner. He proposed two mechanisms by which equalization of the growth rates on different crystal planes and consequently brightening would occur (compare Ref. 88). One mechanism is due to nearly complete surface coverage by an additive which is reversibly adsorbed and desorbed; metal deposition would then occur through the randomly forming holes in this adsorbed film and would consequently be uniform. The other mechanism consists in preferred adsorption of the inhibitor on the more active faces or growth sites, which would also lead to an equalization of the local deposition rates. DuRose[78] has placed nickel brighteners in one of these two groups, or in an intermediate group, according to their adsorption and inhibition mechanism.

Some growth sites, which are generally more active than others but need not be so, are especially sensitive to adsorbed inhibitors in respect to the change of crystal structure and surface roughness. This applies especially to screw dislocations,[153] including the emerging screw dislocation (or group of dislocations) which operates at the apex of a pyramid.[90,162]

Could a diffusion-controlled inhibition mechanism contribute to brightness maintenance? Perhaps in the case of the leveling brighteners butynediol, thiourea, coumarin (Figs. 23 and 24) but not with saccharin (Fig. 25) which gives no leveling, except geometric leveling, and shows at 2 g/L no signs of diffusion-controlled inhibition or consumption on flat surfaces.

Epelboin, Froment and Wiart[164] measured by differential interferometry the maximum amplitude, e_M, of the microprofile formed by plating 10 µm of nickel on an initially smooth rotating disk electrode from nickel baths containing butynediol. They found $1/e_M$ and consequently brightness strongly increasing with $\sqrt{\text{rpm}}$ until a plateau was reached at e_M equal to about 0.02 µm for 0.6 to 2 mmoles/L butynediol, but higher plateaus for smaller concentrations. Thus, brightness maintenance by butynediol shows certainly signs of diffusion control but it is questionable whether this diffusion control applies only to the overall surface coverage or also to the greater coverage on incipient very fine micropeaks.

A related type of roughness suppression was described by Ibl, Javet and Stahel.[156] They found that roughness formation in an acid copper bath ($0.1N\ CuSO_4 + 0.3N\ H_2SO_4$) beginning at $i/i_L = 0.8$ was suppressed by addition of 0.2 g/L thiourea up to at least $i/i_L = 1.3$. With a 4 µm deposit the surface roughness was less than 0.2 µm from $i/i_L = 0.3$ to 1.3, while in absence of thiourea it increased to about 1.6 µm at $i/i_L = 1.2$. Is this suppression of roughness formation due to a suppression of all incipient "electrocrystallographic" (that is not diffusion controlled) roughening, *e.g.*, by blockage of all screw dislocations, or does diffusion control by the inhibitor overwhelm diffusion control by the metal ion? (Compare column 5 in Table 1).

A detailed discussion of brightening, inhibitor action, decomposition products of addition agents, cooperation and antagonism between addition agents in respect to brightening, leveling, polarization, codeposition is beyond the scope of this paper. See, *e.g.*, Refs. 41, 42, 60-69, 72, 78, 105, 106, 111-115, 118-120, 131, 140, 154, 163, 164.

15. Through-hole plating of printed circuit boards

The cylindrical holes in printed circuit boards produce - after suitable preparation and electroless copper deposition - an interesting type of microprofile with some features of a macroprofile. Their diameters, ranging from about 0.375 to 2.5 mm, and depths, varying from about 0.2 to 5 mm, are in their upper ranges somewhat large for typical microprofiles. But the fact that a thickness ratio between the midpoint of the hole and the flat surface H/S (or h_r/h_p) of one or almost one can be obtained,[165-169A] and occasionally of even more than one;[168,168A,169A] makes these circuit board holes microprofiles.

Similarly to the rectangular slots studied by Garmon and Leidheiser[84,85] the side walls of the hole (area = πBD) should at primary current distribution receive only as much current - and even less because of the edge effect - as areas equal to the two circular entrance areas ($=\pi D^2/2$) receive on the board surface, where B is the board thickness and D the hole diameter. The ratio average current density in hole/average current density on board surface should thus be $D/2B$ at primary current distribution. The presence of polarization makes secondary current distribution, of course, much better. But still the hole/surface thickness ratio H/S strongly increases with increasing D/B even at secondary current distribution.[166-168]

Both Dini[166] and Rothschild[167] showed that the hole/surface thickness ratio H/S increases with increasing *macrothrowing* power, as measured *e.g.*, in the Haring-Blum throwing power cell. It is perhaps surprising that it is *macrothrowing* power and not *microthrowing* power which, together with the D/B ratio, determines the H/S thickness ratio on printed circuit boards. Solutions with high concentration polarization, and, less surprisingly, high conductivity, such as low metal-high acid high-throw copper, pyrophosphate copper, cyanide copper, cyanide gold, high-throw tin or tin-lead give the highest H/S ratios on printed circuit boards.

Apparently, diffusion into the holes is not, or is scarcely, hindered because the holes are open on both sides and because very often the circuit boards are oscillated perpendicularly to the board surface so that electrolyte is forced into the holes.[165,169] If mass transport into the holes is not hindered, then not only activation polarization but also concentration polarization throws the deposit into this type of "microgroove." This agrees with Dini's[166] finding that the H/S ratio from copper pyrophosphate or (regular) sulfate copper may increase with increasing current density. The slope $|dE/di|$ of activation polarization decreases, and the slope of concentration polarization increases, with increasing current density (see section 2). Thus, on *typical* microprofiles throwing power always decreases with increasing current density.[1,15,45,160]

The H/S thickness ratios greater than one[168,168A] obtained from cyanide, pyrophosphate and high-throw acid copper baths were explained by Saubestre and Khera[168A] by "higher ionic mass transport which occurs in the holes." Such a higher mass transport rate in the holes could easily be produced by the oscillating movement perpendicularly to the board, but may occur also in absence of this movement. One is reminded of the leveling which Sundarayan and co-workers[138] obtained on trapezoidal grooves at high agitation rates from a cyanide copper bath containing no additives, which they ascribed to turbulent flow, and consequently greater mass transport, in the grooves.

In these cases, Fig. 6 would apply with the important difference that here the agitation rate in the hole would be larger than on the board surface. The effect of this is partly counteracted by the cathode potential being less negative in the central regions of deep holes.

It should be worthwhile to measure *H*/*S* thickness ratios at various *D*/*B* values in dependence on the mass transport rate in the hole (j_H), on the board surface (j_S), and on the ratio j_H/j_S.
Pinkerton and Smith[169A] obtained *H*/*S* thickness ratios greater than one from hot cyanide copper baths by using periodic reverse current, which also reduces edge buildup.

It would be very interesting to learn much more about mass transport in printed circuit board holes, especially if their diameter becomes smaller and the multiple board thickness increases. Printed circuit boards are, of course, a kind of "porous electrode,"[36,170,171] but with relatively large pore diameters.

16. Anodic current distribution

Relatively slow anodic smoothing or leveling is produced by equal dissolution rates of metal from all points of the microprofile.[54] This is similar to "geometric" leveling in metal deposition. But Edwards[54] showed that anodic smoothing of copper (40 µm initial roughness) during electropolishing in phosphoric acid (50 vol%) proceeds at a much faster rate. If the upward facing anode was shielded, the local dissolution rates were diffusion-controlled and could be exactly predicted from primary current distribution as had been suggested by Elmore.[58] Electropolishing of unshielded anodes, and thus in presence of convection, gave a slightly slower rate of anodic smoothing, and so did anodic smoothing under etching conditions. Smoothing in chemical polishing and bright-dip solutions occurred at a still lower rate, which however was still much faster than would be obtained by uniform dissolution.

It is important to note that anodic smoothing is produced by "bad microthrow," or $i_r < i_p$, in contrast to cathodic smoothing.

Opinions are divided whether it is the diffusion of the dissolved metal salt from the anode[58] or of "acceptors" such as anions or water to the anode[54,55] which is rate determining. A recent paper by Kojima and Tobias[180] supplies strong evidence in favor of the first hypothesis in the case of the anodic dissolution of copper in phosphoric acid.

Hoar and Mowat[172] suggested that during electropolishing a thin solid film is present on the anode which prevents etching. Removal of metal ions from the lattice depends then no more on the crystal structure but occurs randomly into the random cation vacancies in the film. This mechanism of anodic brightness maintenance corresponds to one of the mechanisms proposed by Hoar[161] for cathodic brightness maintenance.

Diffusion-controlled inhibitors of anodic dissolution, if they exist, would, of course, reduce the rate of smoothing and even produce roughening, just the opposite to what they are doing in cathodic metal deposition. Correspondingly, diffusion-controlled stimulators, including anionic reactants, increase the rate of anodic smoothing.

The anodic pulse in periodically reversed (PR) plating exerts its smoothing and brightening action probably by diffusion-controlled dissolution of incipient roughness, by "geometric" anodic leveling even at uniform current distribution and by increasing the formation time of the cathodic diffusion layer during the cathodic pulse and destroying this layer during the anodic pulse.[7,8,173] Heiling[174] discussed the possible role of a cuprous oxide film formed in the anodic phase for the leveling of cyanide copper with periodic current reversal.

For surveys on anodic processes including anodic polishing see Hoar[175] and Hoar and Rothwell[176] and on transport control of metal dissolution (and deposition) the recent chapter by Despic and Popov.[12] The latter describes a variety of other possible electropolishing mechanisms. One of them would be due to the higher free surface energy of the micropeaks as compared to microrecesses due to the small radius of convex curvature of the former. This would be "shape sensitive" dissolution, comparable to "shape sensitive" adsorption.[5]

17. Summary

Much work has been done in many countries on the diffusion-controlled inhibition mechanism of cathodic leveling. Much work has also been done on "bad micro-throw," if one includes roughness formation on apparently smooth surfaces, where roughening is initiated by preferential growth of certain crystal faces or on dislocations and then accelerated by transport control.

Anodic current distribution is somewhat outside the scope of this paper. Consequently, I discussed it only briefly in Section 16, but its similarities to, and differences from, cathodic current distribution are certainly worthwhile thinking about.

Obviously, there are many reaction steps in metal deposition and dissolution, and in addition agent adsorption, transformation, incorporation and desorption. Most of them are less simple and less well-understood than current flow and mass transport, and they are certainly worth intense study. But the study of the role of mass transport in the total reaction makes important and relatively easily obtainable contributions to the whole picture. And from a practical standpoint: if a reaction sequence or an effect is under transport control, it is relatively simple to find means to enhance it (*e.g.*, metal deposition rate, leveling) or to suppress it (*e.g.*, roughening).

Now a more personal remark: I believe that cooperation is a very important feature of science. Besides the frequent cooperation of several persons on a research project or on a paper and the exchange of information and opinion between scientists interested in the same field, there is the wider cooperation of those who write and who read scientific papers. The author of a paper cooperates with those who are interested in the subject and invites their cooperation. I have described how I was influenced by the publications of others and I hope that my papers were and are useful to others.

18. Acknowledgements

Finally, I wish to thank those who have helped me directly in my work in this field: During many years as a committee member of AES Research Project 16, I learned much from Professor Bockris and his associates and I wish to thank them for it. Thanks also to Professor Ibl for the interesting exchange of ideas throughout the years and to Dr. Schulz-Harder for the same during recent months.

Thanks to my associates at M&T Chemicals Inc. and to its management who helped me in many ways to prepare this paper. Last, but not least, I would like to thank the American Electroplaters' Society for honoring me with the William Blum Scientific Achievement Award, for encouraging Dr. Foulke and me with the Carl E. Heussner Award for 1956-1957, and for the pleasure and instruction I received from its publications, its meetings and from my participation in project research committees.

19. References

1. D.G. Foulke and O. Kardos, *Proc. Am. Electroplaters' Soc.*, **43**, 172 (1956).
2. O. Kardos, *ibid.*, 181.
3. S.A. Watson and J. Edwards, *Trans. Inst. Metal Finishing*, **34**, 167 (1957).
4. H. Leidheiser, *Z. Elektrochemie*, **59**, 756 (1955).
5. J.D. Thomas, *Proc. Am. Electroplaters' Soc.*, **43**, 60 (1956).
6. E.B. Leffler and H. Leidheiser, *Plating*, **44**, 388 (1957); AES Research Report, Serial No. 37.
7. O. Kardos and D.G. Foulke, "Electrodeposition on Small-Scale Profiles," in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, Ed. C. W. Tobias, Interscience, New York, 1962.
8. O. Kardos and D.G. Foulke, "Symposium on Electrodeposition and Metal Finishing," India Section of the Electrochem. Soc.,Bangalore, 1957; p. 7.
9. E. Raub and K. Müller, *Fundamentals of Metal Deposition*, Elsevier Publishing Company, Amsterdam and New York, 1967.
10. O. Kardos, *Proc. Internat. Conf. (Basel)*, "*Surface 66,*" Forster Verlag, Zurich; p. 62.
11. S.S. Kruglikov, "Surface Leveling in the Electrodeposition of Metals," in *Achievements of Science, Electrochemistry 1965*, Ed. S. S. Kruglikov (English translation for U.S. Dept. of Commerce).

11A. N.P. Gnusin and N.J. Kovarskii, "Roughness of Electrodeposited Surfaces," Academy of Science USSR, 1970, (In Russian).

12. A.R. Despic and K.I. Popov, "Transport-Controlled Deposition and Dissolution of Metals," in *Modern Aspects of Electrochemistry*, No. 7, Ed. B. E. Conway and J. O'M. Bockris, Plenum Press, New York, 1972.
13. W. Meyer, *Proc. Am. Electroplaters' Soc.*, **23**, 116, 135 (1935); **24**, 135 (1936).
14. G.E. Gardam, *J. Electrodepositors' Tech. Soc.*, **22**, 155 (1947).
15. C.E. Reinhard, *Proc. Am. Electroplaters' Soc.*, **37**, 171 (1950).
16. K.S. Willson and A.H. DuRose, *Plating*, **36**, 246 (1949).

17. A.H. DuRose, W.P. Karash and K.S. Willson, *Proc. Am. Electroplaters Soc.*, **37**, 193 (1950).
18. H.E. Haring and W. Blum, *Trans. Electrochem. Soc.*, **44**, 313 (1923).
19. C. Kasper, *ibid*., (a) **77**, 353, 365 (1940); (b) **78**, 131, 147 (1940); (c) **82**, 153 (1942).
20. C. Wagner, *J. Electrochem. Soc.*, **98**, 116 (1951).
21. C. Wagner, "The Scope of Electrochemical Engineering," in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, Ed. C. W. Tobias, Interscience, New York, 1962.
22. J. Kronsbein, *Plating*, **37**, 851 (1950); **39**, 165 (1952); **40**, 898 (1953).
23. R.H. Rousselot, *Metal Finishing*, **57**, 56 (Oct. 1959).
24. H.L. Pinkerton, "Current and Metal Distribution," in *Electroplating Engineering Handbook*, Ed. A. K. Graham, 3rd Ed., Van Nostrand Reinhold Co., New York, 1971.
25. A.T. Yagramyan and Z.A. Soloveva, *Technology of Electrodeposition*, Robert Draper Ltd., Teddington, 1961.
26. E. Weber, *Electromagnetic Fields*, Vol. I, Wiley, New York, 1950.
27. E. Weber, *Swiss Bull. Electrical Eng.*, **51** (20), 1011 (Oct. 1960).
27A. J.A. Klingert, S. Lynn and C.W. Tobias, *Electrochim. Acta*, **9**, 297 (1964).
28. G.F. Kinney and J.V. Festa, *Plating*, **41**, 380 (1954) or *Proc. Am. Electroplaters' Soc.*, **41**, 66 (1954).
28A. J.J. Christie and J. Thomas, *Plating*, **52**, 855 (1965).
29. R.H. Rousselot, *J. Rech. Centre Nat. Rech. Sci., Lab. Bellevue, Paris*, (*S. et O.*), No. 52 (Sept. 1960).
29A. K.C. Clements-Jewery, *Electroplating Metal Finishing*, **26**, (4) 24 (1973).
30. J. O'M Bockris and A.K.N. Reddy, *Modern Electrochemistry*, 2 volumes, Plenum Press, New York, 1970.
30A. J. O'M Bockris, *J. Chem. Educ.*, **48**, 353 (1971).
31. K.J. Vetter, *Electrochemical Kinetics*, Academic Press, New York, 1967.
32. D.B. Matthews and J. O'M Bockris, "The Mechanism of Charge Transfer from Metal Electrodes to Ions in Solutions," in *Modern Aspects of Electrochemistry*, No. 6, Ed. Bockris and Conway, Plenum Press, New York, 1971.
33. J. O'M. Bockris and D. Drazic, *Electrochemical Science*, Taylor & Francis Ltd., London, 1972.
34. E.H. Lyons, *Introduction to Electrochemistry*, D.C. Heath & Co., Boston, 1967.
35. J.M. West, *Electrodeposition and Corrosion Processes*, 2nd Ed., Van Nostrand Reinhold Company, New York, 1970.
35A. T.P. Hoar, *Plating*, **61**, 35 (1974).
36. R. de Levie, "Electrochemical Responses of Porous and Rough Electrodes," in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 6, Ed. P. Delahay, Interscience, New York, 1967.
37. R. de Levie, *Electrochim. Acta*, **10**, 113 (1965).
38. E. Mattson and J. O'M. Bockris, *Trans. Faraday Soc.*, **55**, 1586 (1959).
39. J. O'M. Bockris and M. Enyo, *ibid*., **58**, 1187 (1962).
40. J. O'M. Bockris and H. Kita, *J. Electrochem. Soc.*, **109**, 928 (1962).
41. A.H. DuRose, *Trans. Inst. Metal Finishing*, **38**, 27 (1961).
42. R. Wiart, *Oberfläche-Surface*, **9**, 213, 241, 275 (1968).
43. W.A. Wesley and E.J. Roehl, *Trans. Electrochem. Soc.*, **86**, 419 (1944).
44. L.B. Garmon and H. Leidheiser, *Proc. Am. Electroplaters' Soc.*, **46**, 50 (1959).
44A. W. Blum and G.B. Hogaboom, *Principles of Electroplating and Electroforming*, 3rd Ed., McGraw-Hill, New York, 1949; p. 434.
45. E. Raub, *Plating*, **45**, 486 (1958).
45A. K. Müller and E. Raub, *Metalloberfläche*, **15**, 357 (1961); E. Raub and K. Müller, *ibid*., **17**, 97 (1963).
46. D.G. Foulke, *Metal Finishing*, **54**, 52 (Oct. 1956).
47. A. Brenner, *Proc. Am. Electroplaters' Soc.*, **28**, 95 (1940); *ibid*., **29**, 28 (1941).
48. N. Ibl, *Proc. Internat. Conf.* (*Basel*) "*Surface 66*", Forster Verlag, Zurich, p. 48.
49. N. Ibl and R. Miiller, *Z. Elektrochem*., **59**, 671 (1955).
50. N. Ibl, *Galvanotechnik ir Oberflächenschutz*, **4**, 265 (1963).
51. A. Tvarusko and L.S. Watkins, *Electrochim. Acta*, **14**, 1109 (1969).
52. R.N. Adams, *Electrochemistry of Solid Electrodes*, Marcel Dekker, New York, 1969.
53. W.C. Elmore, *J. Appl. Phys*., **10**, 724 (1939); *ibid*., **11**, 797 (1940).
54. J. Edwards, *J. Electrodepositors' Tech. Soc*., **28**, 133 (1951-1952); *J. Electrochem. Soc*., **100**, 189C (195.3); *ibid*., 223C.
55. C. Wagner, *J. Electrochem. Soc*., **101**, 225 (1954).
56. N. Ibl, "The Formation of Powdered Metal Deposits," in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, Ed. C. W. Tobias, Interscience, New York, 1962.

57. V.G. Levich, *Chemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, New Jersey, 1962.
58. L.L. Bircumshaw and A.C. Riddiford, *Quart. Rev.* (*London*), **6**, No. 2, 157 (1952).
59. J. Newman, "Transport Processes in Electrolytic Solutions," in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 5, Ed. C.W. Tobias, Interscience, New York, 1967.
59A. A.R. Arvia and S.L. Marchiano, "Transport Phenomena in Electrochemical Kinetics," in *Modern Aspects of Electrochemistry*, No. 6, Ed. J. O'M. Bockris and B. E. Conway, Plenum Press, New York, 1971.
60. J. Edwards, *Trans. Inst. Metal Finishing*, **39**, 33 (1962).
61. *Ibid*., **39**, 45 (1962).
62. *Ibid*., **39**, 52 (1962).
63. *Ibid*., **41**, 140 (1964).
64. *Ibid*., **41**, 169 (1964), or 42, 22 (1964).
65. J. Edwards and M.J. Levett, *ibid*., **41**, 147 (1964).
66. *Ibid*., **41**, 157 (1964).
67. *Ibid*., **44**, 27 (1966).
68. *Ibid*., **45**, 12 (1967).
69. *Ibid*., **47**, 7 (1969).
70. Yu.K. Vyagis, A.I. Bodnevas and Yu.Yu. Matulis, *Protection of Metals* (*Zashchita Metallov*), **1** (4), 318 (July-Aug. 1965); **1** (5), 468 (Sept.-Oct. 1965); **2** (2), 168 (March-April 1966); **2** (4), 388 (July-Aug. 1966), Consultants Bureau, New York.
71. E. Raub, A. Knodler, A. Disam and H. Kawase, *Proc. Internat. Conf.* (*Hannover*), "*Interfinish 68*", Eugen G. Leuze Verlag, D-7968, Saulgau, Wurtt., p. 52; *Metalloberfläche*, **23**, 293 (1969).
72. E. Raub, N. Baba, A. Knodler and M. Stalzer, *Trans. Inst. Metal Finishing*, **42**, 108 (1964).
73. G.T. Rogers and K.J. Taylor, *Electrochim. Acta*, **8**, 887 (1963).
74. G.T. Rogers and K.J. Taylor, *Trans. Inst. Metal Finishing*, **43**, 75 (1965).
75. C.C. Roth and H. Leidheiser, *J. Electrochem. Soc*., **100**, 553 (1953).
76. E. Raub and M. Wittum, *Z. Elektrochem*., **46**, 71 (1940); *Metal Ind*. (*London*), **38**, 206, 315, 429 (1940).
77. J. Edwards in discussion of reference 99, p. 136.
78. A. DuRose, *Proc. Internat. Conf.* (*Hannover*), "*Interfinish 68*", Eugen G. Leuze Verlag, D-7968 Saulgau, Wurtt., p. 54.
79. American Standard ASA B46.1-1962, Surface Texture, Am. Soc. of Mechanical Engineers, New York.
80. H.L. Kellner, *Proc. Am. Electroplaters' Soc*., **37**, 105 (1950).
81. A.G. Strang and F. Ogburn, *ibid*., **37**, 125 (1950).
82. S.S. Kruglikov and T.A. Smirnova, *Proc. 8th Internat. Metal Finishing Congress*, (*Basel*) "*Interfinish 1972*," Forster Verlag, Zurich, 1973; p. 105; S.S. Kruglikov, N.T. Kudryavtsev, G.I. Medvedev and T.M. Izmailova, *Protection of Metals* (*Zashchita Metallov*), **8** (6), 668 (Nov.-Dec. 1972), Consultants Bureau, New York, and *Galvanotechnik*, **63**, 955 (1972).
82A. E. Bertorelle, I.R. Bellobono and C. Bordonali, *Trans. Inst. Metal Finishing*, **35**, 231 (1957-58).
83. C. Wagner, *Electrochim. Acta*, **12**, 131 (1967).
84. L.B. Garmon and H. Leidheiser, *Plating*, **48**, 1003 (1961).
85. C. Wagner, L.B. Garmon and H. Leidheiser, AES Research Report No. 50 (1962).
86. C. Wagner, *Plating*, **48**, 997 (1961).
87. B.E. Conway and J. O'M. Bockris, AES Research Report, Serial No. 41; *Plating*, **46**, 371 (1959).
88. J. O'M. Bockris and G. A. Razumney, *Fundamental Aspects of Electrolystallization*, New York, Plenum Press, 1967.
89. J. O'M. Bockris and A. Damjanovic, "The Mechanism of the Electrodeposition of Metals" in *Modern Aspects of Electrochemistry*, No. 3, Ed. J. O'M. Bockris and B.E. Conway, Washington, Butterworths, 1964.
90. A. Damjanovic, AES Research Report Serial No. 55 (1966); *Plating*, **52**, 1017 (1965).
91. A. A. Voronko, *Zh. Prikiad. Khim*., **35**, 2802 (1962).
92. S.S. Kruglikov, N.T. Kudryavtsev and R.P. Sobolev, *Tr. Mosk. Khim.-Technol. Inst. Mendeleyev*, **32**, 259 (1961).
93. E. Raub and M. Stalzer, *Metalloberfläche*, **17**, 134 (1963).
94. V.G. Levich, *Acta Physicochim. USSR*, **17**, 257 (1942).
95. A.C. Riddiford, "The Rotating Disk System" in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 4, Ed. P. Delahay, New York, Interscience, 1966.
96. D.P. Gregory and A.C. Riddiford , *J. Chem. Soc.,* 3756 (1956).
97. J.D. Newson and A.C. Riddiford, *J. Electrochem. Soc.,* **108**, 695 (1961).

98. S.S. Kruglikov, G.F. Vorobeva, N.T. Kudryavtsev, M.M. Yarlikov, A.Ya. Antonov and R.G. Erenburg, in *Theory and Practice of Bright Plating*, *Proc. All-Union Conference in Vilnyus* (*Dec. 1962*), p. 20 (English translation for U.S. Dept. of Commerce).
99. S.S. Kruglikov, N.T. Kudryavtsev, A.Ya. Antonov and A.V. Dribinski, *Trans. Inst. Metal Finishing*, **42**, 129 (1964).
100. S.S. Kruglikov, N.T. Kudryavtsev and R.P. Sobolev, *Electrochim. Acta*, **12**, 1263 (1967).
101. S.S. Kruglikov, N.T. Kudryavtsev, G.F. Vorobiova and A.Ya. Antonov, *ibid*., **10**, 253 (1965).
102. S.S. Kruglikov, N.T. Kudryavtsev and E.V. Semina, *Proc. Internat. Conf*. (*Hannover*) "*Interfinish 68*," E.G. Leuze Verlag, D-7968 Saulgau, Wurtt, p. 66.
103. S.S. Kruglikov, N.T. Kudryavtsev and E.V. Semina, "*3rd Internat. Congress on Corrosion, Moscow 1966*," Vol. 3, pp. 323-332.
104. S.S. Kruglikov, E.V. Semina and N.T. Kudryavtsev, *Protection of Metals* (*Zashchita Metallov*), **3** (1), 69 (1967), Consultants Bureau, New York.
105. G.T. Rogers and K.J. Taylor, *Electrochim. Acta*, **11**, 1685 (1966).
106. G.T. Rogers and K.J. Taylor, *ibid*., **13**, 109 (1968).
107. J. Schulz-Harder, Doctoral Thesis, Technische Universitat, Berlin (1971), D 83.
108. Yu. K. Vyagis, A. V. Skuchene and A. I. Bodnevas in *Electrodeposition of Metals*, *Proc. 10th Lithuanian Conference of Electrochemists* (1968) (English translation for U.S. Dept. of Commerce), p. 8.
109. Yu.Yu. Matulis, *Proc. 8th Internat. Metal Finishing Congress* (*Basel*), "*Interfinish 1972*," Forster Verlag, Zurich, 1973; p. 110.
110. S.S. Kruglikov and V.A. Volkov, *Soviet Electrochemistry* (*Elektrokhimiya*), **6**, 1690 (Nov. 1970), Consultants Bureau, New York.
111. S.A. Watson, *Trans. Inst. Metal Finishing*, **37**, 144 (1960).
112. E.B. Saubestre, *Plating*, **45**, 1219 (1958).
113. H. Brown, *ibid*., **55**, 1047 (1968).
114. H. Brown, *Trans. Inst. Metal Finishing*, **47**, 63 (1969).
115. II. Brown, *Proc. 8th Internat. Metal Finishing Congress* (*Basel*) "*Interfinish 1972*," Forster Verlag, Zurich, 1973; p. 114.
116. S. E. Beacom and B.J. Riley, *J. Electrochem. Soc.,* **106**, 309 (1959).
117. S. E. Beacom and B. J. Riley, *ibid*., **107**, 785 (1960).
118. S. E. Beacom and B. J. Riley, *ibid*., **108**, 758 (1961).
119. S. E. Beacom and B.J. Riley, *Record Chem. Progr*., **24**, No. 2, 75 (1963).
120. W. R. Doty and B. J. Riley, *J. Electrochem. Soc.,* **114**, 50 (1967).
121. Ph. Javet, N. Ibl and H. E. Hintermann, *Galvanotechnik Oberflächenschutz*, **8**, 231 (1967).
122. Ph. Javet, "Contribution à la connaissance de la cinétique du transport et de l'action de la thiourée lors de la deposition électrolytique," Thesis, Microtecnic Scriptar S. A., 1001 Lausanne (1966).
123. N. Ibl, *Traitements de Surface*, 20 (March 1967).
124. K. Balakrishnan and H. Fischer, *Trans. Inst. Metal Finishing*, **43**, 192 (1965).
125. Ph. Javet, N. Ibl and H.E. Hintermann, *Electrochim. Acta*, **12**, 781 (1967).
126. S.S. Kruglikov, N.T. Kudryavtsev and U.I. Sinyakov, *Trans. Inst. Metal Finishing*, **44**, 152 (1966).
127. T. Mine, R. Tominaga and T. Seiyama, *Denki Kagaku*, **35** (7), 472 (1967).
127A. E. Raub and T. Schiffner, *Metalloberfläche*, **25**, 114 (1971).
128. H.A. Laitinen and B. Mosier, *J. Am. Chem. Soc*., **80**, 2363 (1958).
129. A.N. Frumkin and B.B. Damaskin, "Adsorption of Organic Compounds at Electrodes" in *Modem Aspects of Electrochemistry*, No. 3, Ed. J. O'M. Bockris and B. E. Conway, Butterworths, Washington, 1964.
130. B.B. Damaskin, O.A. Petrii and V.V. Batrakov, *Adsorption of Organic Compounds on Electrodes*, Plenum Press, New York, 1971.
131. O. Volk and H. Fischer, *Electrochim. Acta*, **4**, 251 (1961).
132. S.S. Kruglikov, N.T. Kudryavtsev, R.P. Sobolev and A.Ya. Antonov, *Plating*, **53**, 78 (1966).
133. A.R. Despic and K.I. Popov, *J. Appl. Electrochem*., **1**, 275 (1971); K.I. Popov, B.J. Lazarevic and M. Kostic, *ibid*., **3**, 161 (1973).
133A. A.R. Despic, *Proc. 8th Internat. Metal Finishing Congress* (*Basel*) "*Interfinish 1972*," Forster Verlag, Zurich, 1973; p. 89.
134. M. Braun and N. Ibl, *Oberfläche-Surface*, **14**, 49 (1973); *Proc. Internat. Metal Finishing Congress* (*Basel*) "*Interfinish 72*," Forster Verlag, Zurich, 1973; p. 142.

135. M.Sh. Gladshtein and L.I. Kadaner, *Issled. Elektro-osazhden. Rastvoren. Metal* (*1971*), Ed. A.N. Frumkin, Nauka, Moscow, pp. 11-17.
136. *Chem. Abstr.*, **76**, 30048h (1972) and Kadaner in Discussion of ref. 137.
137. Yu.Yu. Matulis and B.M. Zileniene, *Proc. 3rd Internat. Congress on Corrosion*, *Moscow 1966*, **3**, 316 (In English) Swets-Zeitlinger, Amsterdam.
138. K. Sundarayan, S.R. Rajagopalan and A.K.N. Reddy, *Electrochim. Acta*, **8**, 831 (1963).
139. R. Weil and R.A. Paquin, *J. Electrochem. Soc.*, **107**, 87 (1960).
140. I. Epelboin, M. Froment and G. Maurin, *Plating*, **56**, 1356 (1969).
141. A.T. Vagramyan and N.K. Baraboshkina, *ibid.*, **54**, 930 (1967).
142. R. Weil and H.C. Cook, *J. Electrochem. Soc.*, **109**, 295 (1962).
143. R. Weil and W.N. Jacobus, *Plating*, **53**, 102 (1966).
144. R. Weil and H.K. Tsourmas, *ibid.*, **49**, 624 (1962).
145. R. Weil, W.N. Jacobus and S.J. DeMay, *J. Electrochem. Soc.*, **111**, 1046 (1964).
146. O. Kardos, discussion of ref. 141 in *Plating*, **55**, 90 (1968).
147. G.G. Storey and S.C. Barnes, *Trans. Inst. Metal Finishing*, **37**, 11 (1960).
148. A. Damjanovic, T.H.V. Setty and J. O'M. Bockris, *J. Electrochem. Soc.*, **113**, 429 (1966).
149. A. Damjanovic, M. Paunovic and J. O'M. Bockris, *J. Electroanalyt. Chem.*, **9**, 93 (1965); *Electrochim. Acta*, **10**, 111 (1965).
150. M. Fleischmann and H.R. Thirsk, "Metal Deposition and Electrocrystallization" in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 3, Ed. P. Delahay, Interscience, New York, 1963.
151. H.J. Pick, G.G. Storey and T.B. Vaughan, *Electrochim. Acta*, **2**, 165, 179 (1960).
152. H. Fischer, *Angew. Chemie, Internat. Edit.*, **8** (2), 108 (1969).
153. H. Seiter, H. Fischer and L. Albert, *Electrochim. Acta*, **2**, 97 (1966).
154. H. Fischer, *Electrochim. Acta*, **2**, 50 (1966); *Plating*, **56**, 1229 (1969); *Elektrolytische Abscheidung und Elektrokristallisation von Metallen*, Springer Verlag, Berlin, 1954.
155. N. Ibl and K. Schadegg, *J. Electrochem. Soc.*, **114**, 54 (1967); N. Ibl in discussion of this paper, *ibid.*, 1267.
156. N. Ibl, Ph. Javet and F. Stahel, *Electrochim. Acta*, **17**, 733 (1972).
157. J.L. Barton and J. O'M. Bockris, *Proc. Royal Soc., London*, **A 268**, 485 (1962).
158. D.R. Hamilton, *Electrochim. Acta*, **8**, 731 (1963).
159. A.R. Despic, J. Diggle and J. O'M. Bockris, *J. Electrochem. Soc.*, **115**, 507 (1968); *ibid.*, **116**, 1503 (1969).
160. H.Y. Cheh, *ibid.*, **117**, 609 (1970).
161. T.P. Hoar, *Trans. Inst. Metal Finishing*, **29**, 302 (1953).
162. D.R. Turner and G.R. Johnson, *J. Electrochem. Soc.*, **109**, 798, 918 (1962).
163. H. Fischer, "Modes of Inhibiting Electrode Processes," *Werkstoffe Korrosion*, **23**, 445 (June 1972) (In English); *Electrodeposition Surface Treatment*, **1** (3), 239; **1**, (4), 319 (1972-73) Elsevier Sequoia S.A., Lausanne.
164. I. Epelboin, M. Froment and R. Wiart, *C. fl. Acad. Sciences, Paris*, **260**, 3379 (1965).
165. R.W. Couch and R.G. Bikales, *Proc. Am. Electroplaters' Soc.*, **48**, 176 (1961).
166. J. W. Dini, *Plating*, **51**, 119 (1964).
167. B. F. Rothschild, *ibid.*, **53**, 437 (1966).
168. M. W. Jawitz in *Proc. Second Plating in the Electronics Industry Symposium*, Am. Electroplaters' Soc., (Feb. 1969), p. 5; *Metal Finishing*, **71**, 31 (July 1973).
168A. E.B. Saubestre and R.P. Khera in *Proc. Third Plating in the Electronics Industry Symposium*," Am. Electroplaters' Soc., (Feb. 1971), p. 230.
169. L.J. Quintana, *Proc. Am. Electroplaters' Soc.*, **51**, 170 (1964).
169A. H.L. Pinkerton and J.W. Smith, *Plating*, **59**, 672 (1972).
170. I.G. Gurevich and V.S. Bagotskii, *Electrochim. Acta*, **9**, 1151 (1964).
171. J.G. Sohm, *ibid.*, **7**, 629 (1962).
172. T.P. Hoar and J.A.S. Mowat, *Nature*, **165**, 64 (1950).
173. A. Hickling and H.P. Rothbaum, *Trans. Inst. Metal Finishing*, **34**, 53 (1957).
174. H.H. Heiling, *Metall*, **9** (17/18), 764 (1958).
175. T.P. Hoar, "The Anodic Behaviour of Metals" in *Modern Aspects of Electrochemistry*, No. 2, Ed., J. O'M. Bockris, Butterworths, Washington, 1959.
176. T.P. Hoar and G.P. Rothwell, *Electrochim. Acta*, **9**, 135 (1964).

177. N.Ya. Kovarskii and N.P. Gnusin, *Protection of Metals* (*Zashchita Metallov*), **2**, 190 (March-April 1966), Consultants Bureau, New York.
178. N. Ibl and M. Braun, *Chemie-Ing. Technik*, **45** (4), 182 (1973).
179. T. Zak, *Trans. Inst. Metal Finishing*, **49**, 220 (1971).
180. K. Kojima and C.W. Tobias, *J. Electrochem. Soc.*, **120**, 1026 (1973).

20. About the author

This piece was written at the time Dr. Kardos was announced as the recipient of the 1972 Scientific Achievement Award:

The AES Scientific Achievement Award Selection Committee has chosen **Dr. Otto Kardos** to be the 1972 recipient of the award. The selection of Dr. Kardos was announced by chairman of the committee, Arthur H. DuRose, at the Opening Session of the 59th AES Annual Technical Conference in Cleveland on June 19, 1972.

Dr. Kardos retired from M&T Chemicals Inc., a wholly owned subsidiary of American Can Company, after 28 years in research on electroplating processes. He was a pioneer in developing modern bright plating processes and is the inventor of basic patents in this field. His contribution to modern theories of leveling in bright smooth electrodeposits is recognized internationally.

Dr. Kardos was born in 1907 in Vienna, Austria, where he received his primary and secondary education. In 1932, he obtained his Ph.D. degree in chemistry from the University of Vienna. He wrote his thesis on the kinetics of catalytic reactions involving peroxides and inorganic iodine compounds under Professor Emil Abel. His first job was as a chemist in the electroplating supply firm of "Galvapol" in Vienna. This introduction into electrodeposition led to his life work and interest in this field.

After the political upheaval in Austria in 1938, he left his native country and lived in France until 1942. While there he worked as an electroplating consultant, specializing in anodizing, coloring and electroplating on aluminum.

In 1942 he came with his wife and small daughter to New York. He worked briefly as an analytical chemist in an electroplating job shop, and then as a research electrochemist at a slide-fastener manufacturer, Conmar Products in Newark, New Jersey. In 1944 he joined the Hanson-Van Winkle-Munning Company at Matawan, New Jersey, which later became a part of M&T Chemicals, as a research electrochemist, and through the years was promoted to senior research associate. After the merger with M&T Chemicals Inc., he transferred in 1965 to the company's Detroit research laboratory.

Dr. Kardos specialized in the development of bright plating processes for nickel, copper, silver, zinc, cadmium and cobalt and is the inventor or co-inventor of 30 U. S. patents along with corresponding foreign patents. Among these is a basic pioneering patent on which most modern bright leveling nickel plating processes are based. He developed - in cooperation with Dr. D.G. Foulke - a now generally accepted theory on the mechanism of leveling and microthrowing power during electrodeposition on small-scale profiles. For papers published in 1957 he received the American Electroplaters' Society's highest award for the best technical paper published in the Society's publications. Dr. Kardos reviewed the theories for leveling and microthrowing power in the field of electroplating in a chapter in *Advances in Electrochemistry and Electrochemical Engineering*, *Vol. II*, edited by Professor Charles Tobias of the University of California and published in 1962. He was invited to update his theories on the mechanism of leveling in a paper which he presented at the International Metal Finishing Conference in Basel, Switzerland, in November 1966.

He was a member of various Research Project Committees of the American Electroplaters' Society for many years. He is a member of the American Electroplaters' Society, Electrochemical Society, the American Chemical Society and the American Association for the Advancement of Science.

He resides in Ferndale, Michigan. His married daughter, her husband and their young son live nearby in Detroit.

In his retirement he plans to continue as a consultant for M&T Chemicals. Besides consulting in electrochemistry, Dr. Kardos plans to enjoy reading in scientific fields, listening to classical music, playing the piano, gardening, walking, and - last but not least - babysitting for his grandson.