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Preparation of metal powders from sulfamate baths - II) Discussion

R. PIONTELLI, B. MAZZA, P. PEDEFERRI, F. SINISCALCO *

Laboratory of Electrochemistry, Chemical Physics and Metallurgy of the Polytechnic School of Milan (Laboratory of the Group: Electrolytes and Electrochemical Processes of C.N.R.)

RIASSUNTO - *PREPARAZIONE DI POLVERI METALLICHE PER ELETTRODEPOSIZIONE DA BAGNI SOLFAMMICI. II) DISCUSSIONE* - Viene discusso il problema delle condizioni di ottenimento dei depositi incoerenti, distinti in varie sottoclassi morfologiche.

Viene discussa l'influenza del « grado di sovrassaturazione elettrochimica » e del « potere di penetrazione » catodico alle diverse scale di dimensioni, e vengono analizzati i diversi fattori.

Viene fatto cenno alle possibili ragioni delle interessanti possibilità dei bagni solfammici in questo campo di applicazione.

ABSTRACT - The problem of the conditions leading to incoherent deposits is discussed, distinguishing various morphological classes.

The influence is discussed of the « electrochemical oversaturation degree », and of the cathodic « throwing power » at the different scales of dimensions, and the various factors are analysed.

The possible reasons of the potentialities of the sulfamate baths in this field are pointed out.

In the first part of the present research (1) the potentialities of the sulfamate baths, in the production of incoherent deposits by electrolysis, have been systematically investigated for the metals: Cu, Ag, Zn, Cd, Ni, Co, Pb, Sn, In.

To discuss our experimental results and in the aim of better defining the potentialities of the sulfamate baths in the field of the production of metal powders, it appears necessary to investigate, from a general point of view, the influence of the various factors involved. We shall be concerned here only with the direct production of powdery or spongy deposits.

The opinions advanced about the mechanism, by which the cathodic deposition leads to such a kind of products, are rather divergent.

The factors taken into account, as directly responsible of this anomalous structure are:

1. *inhibition phenomena* of the crystal intergrowth, deriving from:

α) hydrogen: adsorbed, or in form of bubbles;

β) oxide or hydroxide formation;

γ) colloidal substances, from sources also different from: β).

2. *complex-ions formation;*

3. *depletion of the cathodic film* in respect of the metal.

The influence of the factors themselves depends upon: the nature of the metal, of the bath, and the operative conditions (current density (c.d.); mass transfer and so on).

The depletion of the cathode film appears to be considered, at present, as the main factor involved, at least in the case of the metals presenting a step polarization curve (those belonging to the classes whose electrochemical kinetic behaviour is: « intermedium », or « inert »).

According to Ibl (2):

1. « The powder formation starts when the limit current is reached, i.e. when the concentration of metallic ions at the cathode-solution interface is zero ».

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* University of Naples.

2. In general, the nucleation rate increases with decreasing concentration. In the limit c.d. range, the rate of formation of new nuclea is high.

3. Moreover, instability of growth derives from the fact that the local current has to adjust itself to such a value that the mass transfer may be granted.

4. The intervening of the limit current condition is favored by: low concentration, high c.d., low temperature, stationary electrolyte and presence of neutral salts [*].

In view of our present purposes the main structural types of cathodic deposits may be classified as indicated in the following scheme and fig. 1:

I. *compact,* or basis-selective *deposits* (3), among which one may conventionally distinguish the deposits:

Iα. *fine-grained* corresponding to a high nucleation rate;

Iβ. *large-grained,* obtained when the nucleation rate is low enough (the limit condition corresponding to the epitaxial growth of oriented single-crystal cathodes);

II. *incoherent deposits,* among which one should distinguish:

IIα. deposits formed by *large trees or leaves* (*dendrites*). These may present the tendency to grow with their main axis either perpendicular to the cathode surface (orthogonal tropism), or, on the contrary, without any preferred direction (random tropism);

IIβ. *sponge deposits,* which are a first degenerative step of the structure IIα) of the random type;

IIγ. *coarse powdery deposits,* which may be considered either a degenerative step of IIα) or of Iα);

IIδ. *cathodic blacks,* which constitute a second degenerative step of Iα), or a first one of IIγ) [**].

Also before analysing the possible influence of the various intervening factors, we may advance some general points (4).

The incoherent deposits are grown, in any case, starting from tridimensional nuclea: mutually independent and in respect to the basis metal.

The *possibility* of formation of tridimensional nuclea is thus a *necessary* condition in view of the separation of incoherent deposits.

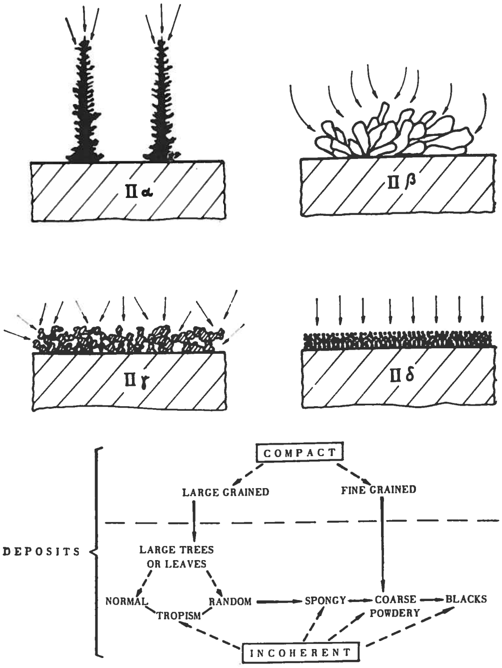

Fig. 1 Structural classes of cathodic deposits.

This possibility subsists in a wide range of conditions. The kind of incoherent deposit obtainable then depends: upon the relative rate of the formation of these nuclea in respect of the concurrent growth processes, and upon the « degree of isotropy » of the resulting growth rate.

We may foresee that when the conditions are just favorable to the development of few accidentally formed new nuclea, the kind of incoherent deposits, which can be obtained, belongs to the classes IIα) or IIβ).

This accidental formation may occur thank to the unavoidable existence, on the electrode surface, of any kind of structural defects and microgeometrical irregularities.

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[*] The fact that for metals, such as Zn and Cd, the formation of spongy deposits from neutral solutions occurs also in a very low c.d. range and is favored by temperature increments, is considered due to the decreasing of the hydrogen overvoltage and thus to the increased pH of the cathode film, followed by hydroxide formation.

[**] The blacks of the « normal metals » (as Pb) may consist of very small dendrites (Wranglen (5)).

The preferential growth of the nuclea themselves may be foreseen, in the cases of low or very low throwing-power, also at a microscopic scale of dimensions.

The formation of deposits of the classes IIγ) and IIδ) presupposes a high or very high relative rate of formation of these tridimensional nuclea, in conditions favouring a tendential growth-isotropy of the nuclea themselves. On the basis of these rather obvious principles, the main aspects to be considered, in view of the electrolytic direct formation of incoherent deposits, are:

1. the relative formation rate of tridimensional nuclea;
2. the distribution in space of the vectorial growth rate of the nuclea themselves.

I. Formation-rate of tridimensional nuclea

Mention has been already given of the accidental circumstances, which may promote the formation of tridimensional nuclea. We shall now consider the circumstances of more general significance.

The first one to be considered is the local « oversaturation degree ». In the case of the crystallization from melts or solutions, the oversaturation degree may be defined, on a simple thermodynamic basis, as the difference between the chemical potential of the chemical species to be exchanged, respectively: in the origin phase, and in the newly formed one.

In the case of the electrocrystallization processes, the oversaturation degree must be defined on the basis of the available electrochemical affinity.

Let us consider, for sake of simplicity, as the concurrent processes, the only ones, by which the metal ions $M^{Z+}_{(\varepsilon)}$, contained in the bath ε, become:

1. constituents of the growing lattice ($M_{(c)}$);
2. « potential constituents » ($M_{A_{III}}$) of new tridimensional nuclea (perhaps in the form of losely « adsorbed atoms ») *.

We may express these processes by the equations:

1. $M^{Z+}_{(\varepsilon)} + Z\,e^{-}_{(M)} \rightarrow M_{(c)}$;
2. $M^{Z+}_{(\varepsilon)} + Z\,e^{-}_{(M)} \rightarrow M_{A_{III}}$, respectively.

The electrochemical affinity, or « driving work », is thus given by: $(\tilde{\mu}^{\varepsilon}_{M^{Z+}} + Z\tilde{\mu}^{e}_{M}) - \mu^{c}_{M}$, in in the former case, and by: $(\tilde{\mu}^{\varepsilon}_{M^{Z+}} + Z\tilde{\mu}^{M}_{e}) - \mu^{A_{III}}_{M}$ in the second one, μ^{c}_{M} and $\mu^{A_{III}}_{M}$ being the chemical potentials of $M_{(c)}$, or $M_{A_{III}}$ respectively; $\tilde{\mu}^{M^{Z+}}_{\varepsilon}$ and $\tilde{\mu}^{M}_{e}$ the electrochemical potentials of M^{Z+} in ε and of e^{-} in $M_{(c)}$ respectively.

Of course: $\mu^{A_{III}}_{M} > \mu^{c}_{M}$ and thus the process 1) may be considered as preferred from a thermodynamic point of view. The process 2) may become possible only when an adequate oversaturation degree in respect to 1) is available.

When the oversaturation degree is high, the differences in the driving-works, available for the two concurrent processes, becomes scarcely significant in respect to the total, thus placing the processes on rather similar levels from the thermodynamic point of view.

We are thus lead to consider that the circumstances, which increase the local oversaturation degree, promote also the tridimensional nucleation at the electrode surface.

To better define the meaning of the quantity above and its relations with the measurable overvoltage, let us admit this last to be determined by utilizing a reversible iso-electrodic ** reference electrode (RE), in equilibrium with ε at the electrode surface.

The measured voltage is then expressive of the « true overvoltage », and it is given, in absolute value ***, by:

$$\left| \frac{\tilde{\mu}^{M}_{e} - \tilde{\mu}^{M'}_{e}}{\mathscr{F}} \right| = \left| \frac{\tilde{\mu}^{\varepsilon}_{M^{Z+}} + Z\tilde{\mu}_{e} - \mu^{c}_{M}}{Z\mathscr{F}} \right|$$

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* The condition of « potential constituents » of bidimensional nuclea, oriented following the basis, may be considered: intermedium amongst the two limit conditions, above defined for the discharged ions. The expression: « potential constituents » means: atoms whose thermodynamic level (as measured by μ and eventually spatial situation, enable them to cooperate in the formation of new nuclea.

** That is one for which the electrode reaction is again:

$$M^{Z+}_{(\varepsilon)} + Z\,e^{-}_{(M')} \rightleftarrows M_{(c)}$$

*** Following the hypotheses above:

$$Z\tilde{\mu}^{M'}_{e} = \mu^{M'}_{M} - \tilde{\mu}^{M'}_{M^{Z+}} = \mu^{c}_{M} - \tilde{\mu}^{\varepsilon}_{M^{Z+}}$$

By accepting the usually admitted partition of the electrochemical potentials in two terms: chemical and electrical, we obtain *:

$$\mu^{\overset{\varepsilon}{\circ}}_{M^{Z+}} + RT \ln {}^{\circ}a^{\varepsilon}_{M^{Z+}} + Z \mathscr{F} V^{\varepsilon} + Z \mu^{M}_{e} -$$
$$- Z \mathscr{F} V^{M} - \mu^{c}_{M} = \mu^{\overset{\varepsilon}{\circ}}_{M^{Z+}} + RT \ln {}^{\circ}a^{\varepsilon}_{M^{Z+}} +$$
$$+ Z \mathscr{F} [(V^{\varepsilon} - V^{M})_{eq} + \Delta\varphi^{\varepsilon M}] + Z \mu^{M}_{e} -$$
$$- \mu^{c}_{M} = Z \mathscr{F} \Delta\varphi^{\varepsilon M}$$

We thus conclude that the absolute value of the true overvoltage, as above defined, expressive of the excess in the electric potential difference between the two phases at the electrode surface, in respect of the equilibrium conditions, measures also the available electrochemical affinity.

Of course, only the true overvoltage is expressive of the local oversaturation degree at the electrode surface.

The contributions to the true overvoltage, deriving for instance from « electrochemical inertia » or « inhibition » are thus contributions also to the local oversaturation degree at the electrode surface.

On the contrary, such contributions to the « apparent overvoltage » (the one usually measured), as the ohmic drop or the concentration-polarization, cannot be considered to be contributions also to the local oversaturation degree.

II. Throwing power influence

The formation of tridimensional nuclea may derive, as previously indicated, either from accidental peculiarities at the electrode surface or from an adequate local oversaturation degree.

Also the influence of throwing power may be active at different scales of dimensions and result in different classes of incoherent deposits **.

In order to get large trees or leaves presenting orthogonal tropism, the metal deposition must be essentially guided by the electric and concentration gradients in the solution, in the absence of appreciable influence of the basis metal and of excessive overvoltages, due either to intrinsic electrochemical inertia of the metal, or to strong inhibition.

This class of deposits is thus essentially peculiar for the « normal » metals, in conditions of low throwing power also at the macroscopic scale. In order to get incoherent deposits, suitable for application, neither excessive sizes of these growth forms *** nor marked orthogonal tropism are wanted, however; modest sizes (and thus frequent interruption in growth) and random tropism being on the contrary required. For normal or intermedium metals, when deposited from simple salt-solutions, this conditions, which leads to spongy deposits, may result satisfied, in practice:

1. under moderate inhibition (due to: anion, OH^-, hydrogen, colloidal matter ****);

2. when the ratio: c.d. to metal content of the cathodic layer, although strong, is kept not excessively high, as to lead to the successive degenerative steps (which we shall consider in what follows).

This conditions range includes not a few of the optimum conditions we found for preparing spongy deposits of the normal or intermedium metals.

Let us now consider the formation conditions of the subclasses: IIγ) (coarse powdery deposits) and IIδ) (blacks). In order to get deposits of these classes, not only the

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* Being:

$$Z \mathscr{F} (V^{\varepsilon} - V^{M})_{eq} = \mu^{c}_{M} - (Z \mu^{M}_{e} + \mu^{\overset{\varepsilon}{\circ}}_{M^{Z+}} +$$
$$+ RT \ln {}^{\circ}a^{\varepsilon}_{M^{Z+}}) .$$

$\mu^{\overset{\varepsilon}{\circ}}_{M^{Z+}}$ is the chemical potential of the ion M^{Z+} in ε in standard conditions, while ${}^{\circ}a^{\varepsilon}_{M^{Z+}}$ is the activity of the ions themselves in ε in the actual conditions, referred to the standard state; $\mathscr{F} = 96500$ coulomb/equiv.; V^{M} and V^{ε} are the macroscopic electric potentials in ε and $M_{(c)}$ at the electrode interface.

** In the study of the electrode processes the « throwing power effects » must be considered at different scales:
α) the macroscopic scale (in the range of cm); β) the microscopic one (in the range of the large multiples of μ); γ) the « submicroscopic » one (in the range of the fractions of μ), and δ) the « molecular » one.

*** We do not consider here the formation of whiskers.

**** In a way not to make the electric and concentration gradients to be decisive for the growth of the deposits. Also the mechanical action of the eventually developed hydrogen hinders the growth of large size dendrites, thus supporting the transition from the structure II α) to the II β) one.

tridimensional nuclea are required to be numerous, independent (mutually and in respect of the basis metal); but, moreover, they must be characterized by a tendentially isotropic growth.

As a matter of fact, when high values of the local oversaturation degree are coupled with high relative values also of the tangential (that is parallel to the electrode surface) growth rate, fine-grained but compact deposits are obtained. This occurs for instance, in the cases of plating of inert metals under usual conditions, or in the presence of strong inhibition.

To get incoherent deposits, not only the oversaturation degree must be adequately high but, moreover, neither of the vectorial growth-rate components:

1. parallel to the cathode surface (and thus tending to lead to a « tangential tropism »);

2. normal to the surface itself (thus tending to give a « field-oriented axial growth », or orthogonal tropism), must become overwhelming in respect to any other.

We are thus facing a problem of « throwing power » at the micro-or submicroscopic scale of dimensions, or of « micro-distributive power » of the deposition.

Concerning this aspect of the problem, one must recall:

1. that while the local oversaturation degree mainly depends upon the absolute value of the various contributions to the true overvoltage; the micro-distributive power of the deposition depends upon the rate of change with c.d. of the contributions themselves (that is to say, upon the slope of the diagram in which these contributions are plotted as functions of the local value of c.d.);

2. that we may control, in practice, only the current intensity and thus the apparent or average c.d., while the actual local values of the c.d., at the different scales of dimensions, may result enormously different from this average value.

The predominating role, played by the « limit c.d. conditions », in the production of this kind of deposits, may thus be explained, when one considers also the fact that, in the range itself, the secundary inhibition effects, due to hydrogen or colloidal matter are promoted too.

In the range of adequately high values of the ratio: c.d. to metal ions activity, in the areas where the cathodic c.d. tends to become high, the local depletion of the sources of the metal to be separated, when the mass transfer rate is adequate, involves strong concentration polarization, which tends to deviate the electrode process towards areas, formerly less favoured, in respect of the electrode process.

Thus the conditions, promoting this local depletion, may constitute a very effective incentive to the growth isotropy, or growth interruption of the tridimensional nuclea, and lead to powdery or black deposits.

The ensemble of factors, which may promote the intervening of the limit c.d. conditions, is too well known to make necessary any further comment on it.

III. Influence of the various involved factors

On the basis of the above general conclusions, we may now discuss the influence of the main factors involved in the production of incoherent deposits.

1) *Nature of the metal*

The influence of the nature of the metal is multiform, of course. The main property, however, is the « degree of electrochemical inertia ». For « normal metals », deposited by simple-salts solutions, the true overvoltage is very low, in the absence of strong inhibitive influences. Thus also the local oversaturation degree is low.

The accidental formation of tridimensional nuclea initiates a deposition sequence, essentially in the form of dendrites, whose main axis is directed following the electric and concentration gradients, while the structural peculiarities may be decided by crystallographic factors *.

The intervention of moderate (direct, or secundary) inhibition, and of adequately high ratios: c.d. to metal content at the cathode surface ** may involve the transition from the structure IIα) to the

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* For instance, the dendrite axis is often directed following the closest packed directions in the lattice (Wranglen (5)).

** As a consequence on the one hand, of the bulk composition and on the other, of the mass-transfer conditions.

IIβ) one. For very high values of this ratio, in a way to attain both adequately strong local oversaturation degree and micro-distributive power, we may get also blacks of these metals (again tendentially formed by very small dendrites). The conclusions above may be applied in particular to: Pb, Sn, Tl, Ag.

The behaviour of Cd and Zn on the one hand, and of Bi and Sb, on the other, is rather peculiar.

Cd and Zn give blacks by deposition also in a relatively low c.d. range, when the OH^- ions concentration is adequately high at the cathode surface.

This behaviour may be considered a consequence of the specific affinity of these ions for the metal, on which they may act as efficient crystal-growth inhibitors. Cd may also give, however, spongy deposits in conditions corresponding to those in which also the other normal metals are separated in this form.

Cathodic blacks are also obtainable for these metals in the limit c.d. range.

The marked tendency to give very disperse (even amorphous) deposits, presented by Bi and Sb is perhaps a consequence of inhibition phenomena due to hydrogen in some conditions and to anions in others *.

In the case of the metals affected by « electrochemical inertia », the very existence of important contributions to the true overvoltage, involves also high values of the local oversaturation degree.

The relative rate of formation of new tridimensional nuclea is thus tendentially high. This circumstance is entirely compatible with the formation of compact fine-grained deposits, in the conditions in which the tangential component of the vectorial growth rate is especially high, thus leading to an uninterrupted side soldering of the different nuclea.

The high relative value of this tangential component corresponds to a strong influence of the basis metal as the preferred seat of the separation of discharged atoms **.

The strong directive influence of the basis metal and of the preferred positions on the surface, which may be accounted for by considering strong differences in the chemical potential of the adatoms, according to their situation on the surface itself, may explain some peculiarities of the plating of the inert metals. In the deposition with adequately low ratios: c.d. to metal concentration at the cathode surface, in the absence of any contamination source for the surface of the metallic phase, the local values of the oversaturation degree, arising from the inertia contribution to the true overvoltage, may result inadequate to cancel the directive influence of the basis metal, thus allowing also an epitaxial growth ***.

When the formation of tridimensional nuclea is promoted either by surface irregularities or by the true overvoltage attaining adequately high values (as a consequence of c.d. increments or of inhibitive effects), the deposit, instead of being epitaxial in respect to the basis metal, tends to become fine-grained but compact ****.

By further accentuating of the circumstances above, the tendency intervenes towards random structures of the class IIγ), or also IIδ) (once more especially favoured by the limit c.d. conditions).

2) *Bath composition*

We shall consider here the following aspects:

1. metal content;
2. anion;
3. pH;
4. foreign salts;
5. direct inhibitors.

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* The strong tendency towards the hydride formation is well known, for these metals, while the possibility of formation of « amorphous » deposits, presenting high chloride contents, is well known for Sb. This tendency increases in the order Bi, Sb, As, this last being always deposited in amorphous form from aqueous solutions. The inhibition due to hydrogen is probably responsible also of the wanting tendency towards the dendritic deposition, presented by In in a wide range of conditions and of the relatively good throwing power in the In plating (rather exceptional for sulfamate baths).

** In the case of the inert metals, the high mobility, possessed by the adsorbed atoms of the normal metals, may be excluded.

*** This condition has been realized in this Laboratory, for istance with Ni and Co single crystals (6).

**** The orientative effect of the basis metal, although inadequate to impose epitaxial growth, leading to relatively high tangential component of the vectorial growth rate.

For the reasons already discussed, in order to promote the separation of incoherent deposits of the classes IIβ), IIγ), or IIδ), the metal content of the bath must be kept adequately low, especially in the absence of strong inhibitive effects. In the same sense the presence of foreign salts (competitive in the transference processes, or also in the discharge process) may result effective.

When one discards the point of view, according to which the complex-ions formation is especially important for the formation of powdery or spongy deposits *, the possible anion influence appears to be limited to:

1. the direct structural influence of the anion;

2. that exerted through the mass-transfer factors (transference numbers, diffusion, viscosity and so on);

3. the one exerted on the formation of oxides, hydroxides in the cathode layer, that is through the buffering power of the bath, the influence on the structure and properties of the colloidal substances and on the oversaturation and precipitation phenomena of the eventually formed basic compounds.

In the frame above, what is the situation of the sulfamate baths? These solution, by the lack of interference with the electrode processes, are not characterized by any peculiar tendency to direct inhibition, and on the contrary they are moderately preventive (by tendentially opposing the abrupt pH changes in the cathodic layer, and the precipitation of colloidal basic compounds) of the possible sources of secondary inhibition.

Thus the production of incoherent deposits from sulfamate baths may occur: 1) for Cd and Zn, in the conditions of strong inhibition due to OH^- ions; 2) for all the normal and intermedium metals, in the form of spongy or coarse powdery deposits, in conditions sufficiently near to those of limit c.d.; 3) for some intermedium and for inert metals, in the form of finely powdery up to black deposits.

In the conditions 2) and 3), the peculiar characteristics of the sulfamate baths allow a condition of separation of incoherent deposits without contamination of the deposits from oxides, hydroxides and so on.

In this respect it appears especially noteworthy the peculiar absence of this kind of contamination for copper powder deposited from sulfamate baths **, compared with the greater one of those obtained from sulfate baths, and the strong contamination of the powders from acetic or perchloric baths.

In this case, one must take into account also the intervention of the peculiar relationships of the sulfamic ion with the Cu^+, on which we shall return in detail in a study on the chemical and electrochemical behaviour of the copper sulfamate baths.

The influence of pH may result multiform. The H^+ ions are first of all a concurrent, in respect of M^{z+}, both in transference and discharge. Moreover the hydrogen discharge may involve direct or indirect inhibition while the mechanical action of the developed hydrogen may result both in promoting the mass-transfer and in influencing the deposit texture.

The pH influence is especially strong in the cases (as the one of Zn and Cd), in which the inhibitive influence of the OH^- ions result decisive in the separation of very disperse deposits, or when a similar (although much weaker) influence is due to the colloidal matter precipitated at high enough pH on the electrode surface.

3) *Other operative factors*

Among the other operative factors, we shall consider only:

1. temperature;
2. c.d.;

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* From the solutions of stable complexes (as those of cyanides), the production of powdery deposits occurs again in the « limit current » range, while in the lower c.d. range, the structure of the deposits, although tendentially fine-grained, is compact till to brightness. In this respect the situation may appear to be comparable with the one encountered with inert metals, in the conditions involving strong contributions to the true overvoltage. As a matter of fact the two deposition conditions of the inert metals and from complex-salts baths (in which case the true overvoltage may be also definitely modest), in spite of the common aspects mentioned above, present radical differences, which we shall discuss elsewhere.

** Correlated also with the morphology of the powders themselves (see (1)), which indicates the lack of any marked inhibition.

3. mass-transfer controlling circumstances.

Temperature increments, by decreasing overvoltages and direct inhibition and by increasing the mass-transfer rate exert a tendentially contrary influence, in respect of the separation of incoherent deposits. Only in the cases of indirect inhibition, deriving from hydrolitic products *, temperature increments may promote the formation of incoherent deposits.

The apparent c.d. increments are, as a rule, and for the previously indicated reasons, definitely favorable to the formation of incoherent deposits. In this respect the limit c.d. condition is often critical.

The circumstances promoting the mass-transfer supply of the metal at the cathode surface exert a tendentially opposite influence to the one of the c.d. increments.

Also in the case of the metal deposition by displacement, the transition from incoherent to compact deposits by adequate stirring, has been discovered long time ago (7) by one of the present Authors. Of course the influence of c.d., acting also through the true overvoltage, is not confined to the depletion of the cathodic film, and thus cannot be entirely contrasted by mass-transfer promotion.

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* As the possible sources of cathodic inhition, one may consider especially: I) eventual additives; II) anions (the one of the salt of the metal to be separated, or also OH^- and others); III) hydrogen; IV) colloidal matter, formed by precipitation of basic compounds (oxides, hydroxides, basic salts), at the cathode surface as a consequence of the local pH increments.

The sources I) apart, the others tend to be promoted by the conditions in which the current efficiency deviates from the theoretical value. The specificity and the efficiency of these different sources are strongly dependent upon the nature of the metal. The influence of hydrogen may be at work in different manners (adsorption, gaseous films, mechanical action).

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