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Guidelines for setting the useful range of Pulse Plating parameters

Jean-Claude Puippe

www.steiger.ch

8th European Pulse Plating Seminar
2nd March 2018, Vienna

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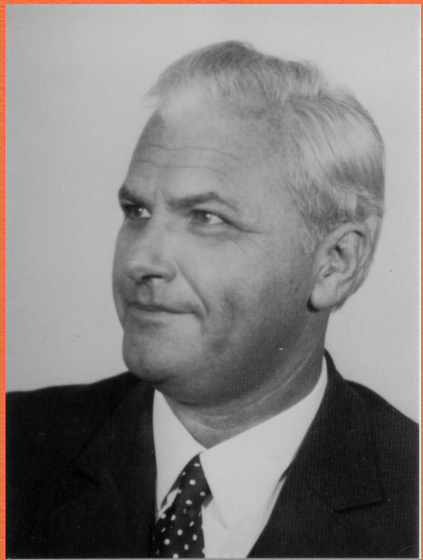
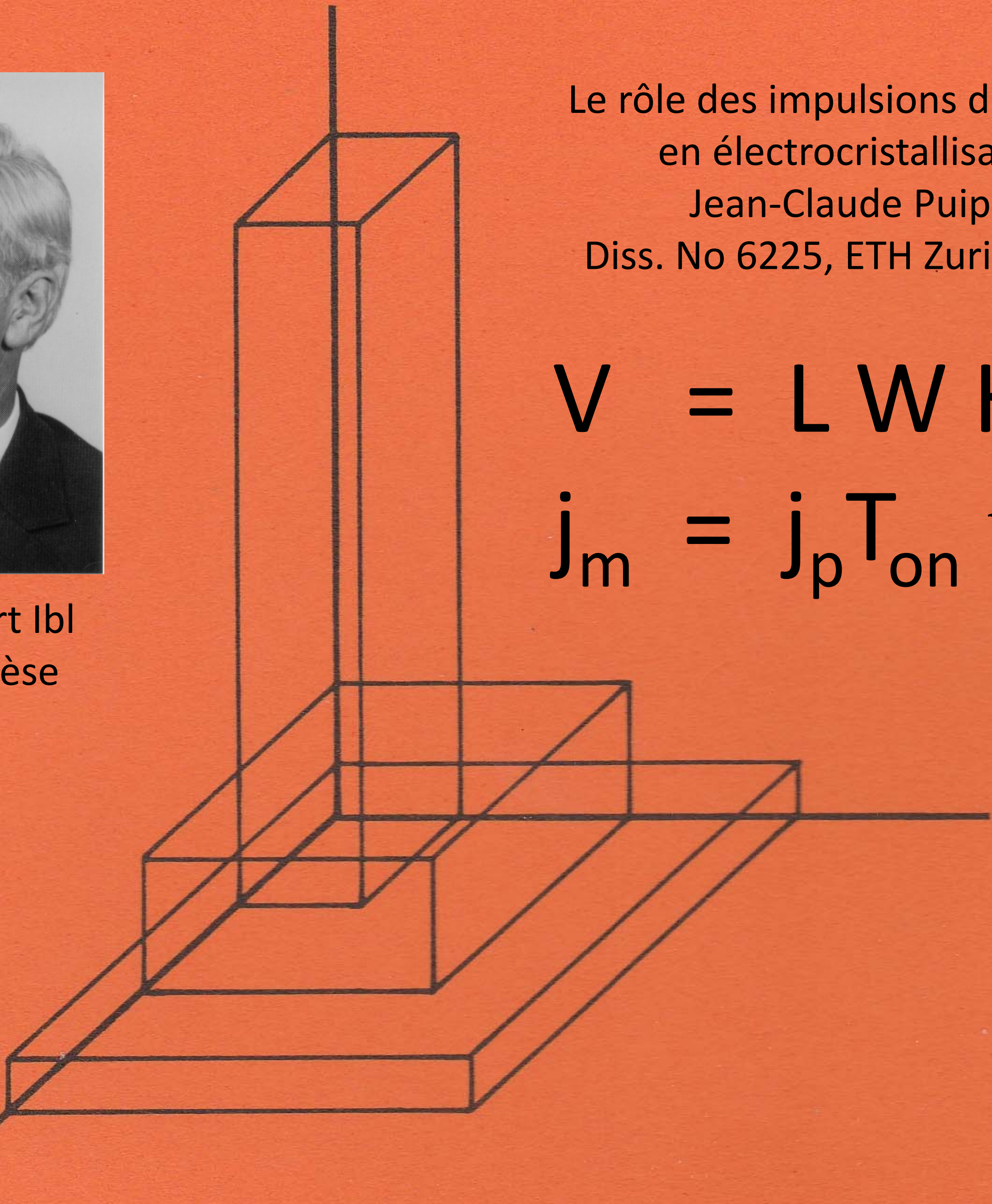


Prof. Dr. Norbert Ibl
Directeur de thèse



Le rôle des impulsions de courant
en électrocristallisation
Jean-Claude Puippe
Diss. No 6225, ETH Zurich, 1978

$$V = L\,W\,H$$

$$j_m = j_p T_{on}\,\nu$$

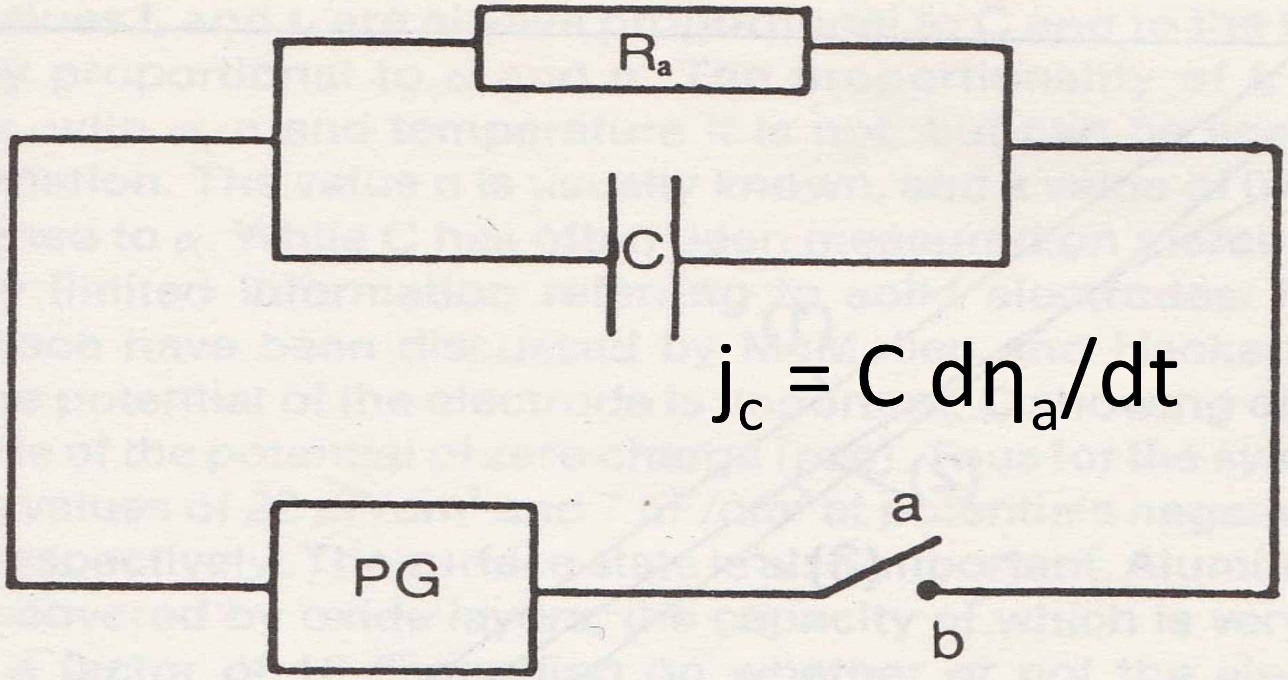
Limiting factors of Pulse Plating parameters

- The lower limit of the pulse duration depends on the **capacity effects** of the electrical double layer at the electrode.

- The upper limit of the pulse duration depends on the mass transport of electroactive ions through **diffusion** at the electrode.

Capacity effects

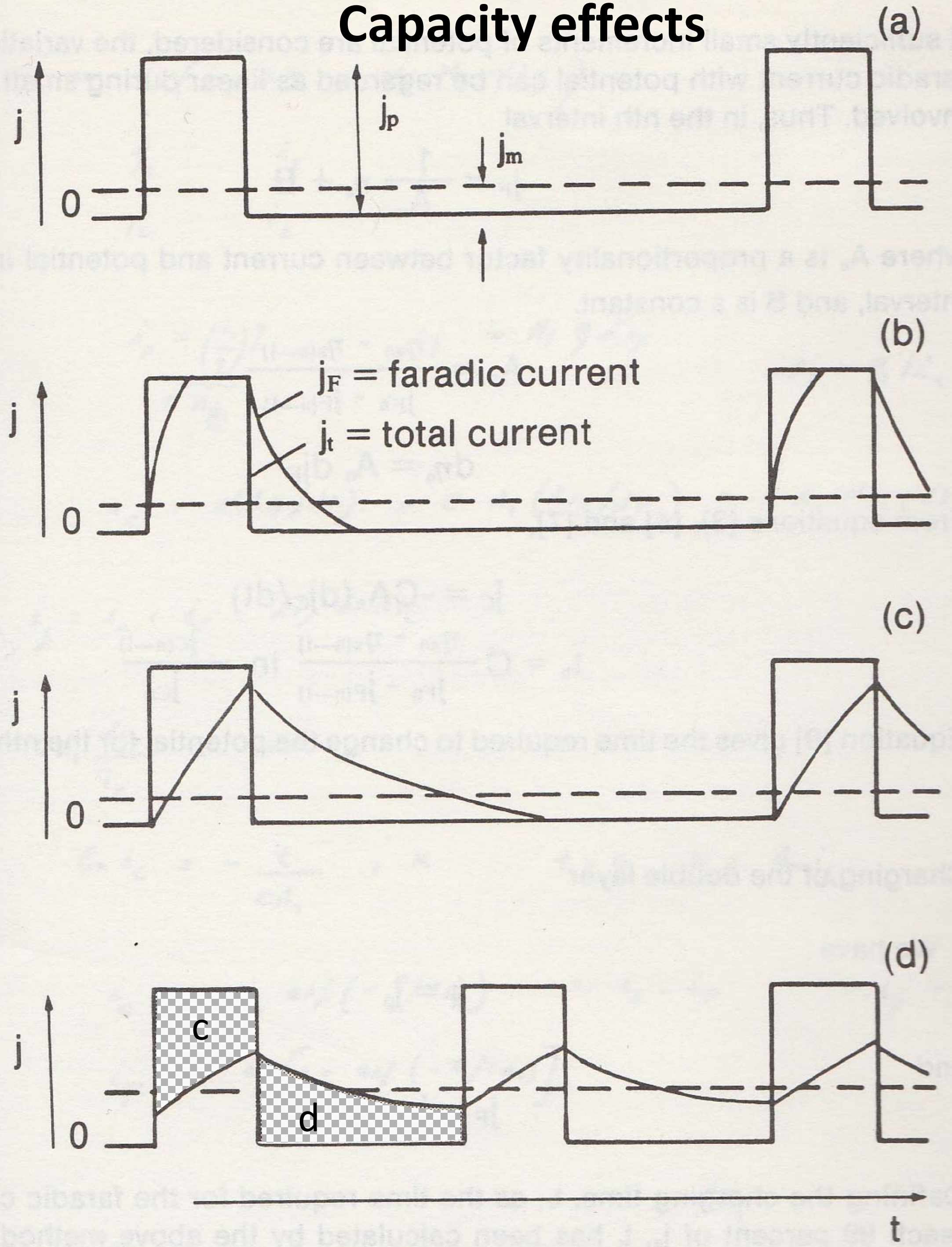
Charge and Discharge of Electrical Double Layer



$$j_c = C\, d\eta_a/dt$$

Fig. 4.4—Equivalent circuit of an electrode.
Position a: off-time, external circuit open;
Position b: on-time, external circuit closed;
PG, pulse generator;
C, capacitor;
R_a, resistance.

Capacity effects



No damping of faradic current

small damping of faradic current

strong damping of faradic current

Flattening of faradic current

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Computation of charging time t_c of double layer

t_c = time required for the faradic current to reach 99% of j_p

The charging time is segmented in increments corresponding to 1 mV steps. Within one step, the faradic current can be considered as constant. It is readjusted according to Butler Volmer equation for each step.

$j_c = dQ / dt = C\, d\eta_a/dt$

$dj_F = - dj_C$ (for galvanostatic pulse)

$j_F = j_o\,(\exp(\alpha zF\eta_a/RT) - \exp((1-\alpha)zF\eta_a/RT))$

$t_n = C\,((\eta_{an} - \eta_{a(n-1)}) / (j_{Fn} - j_{F(n-1)}))\ \ln\,(j_{C(n-1)} / j_{Cn})$

$t_c = \sum t_n$ from $j_F = 0$ till $j_F = 0.99\, j_p$

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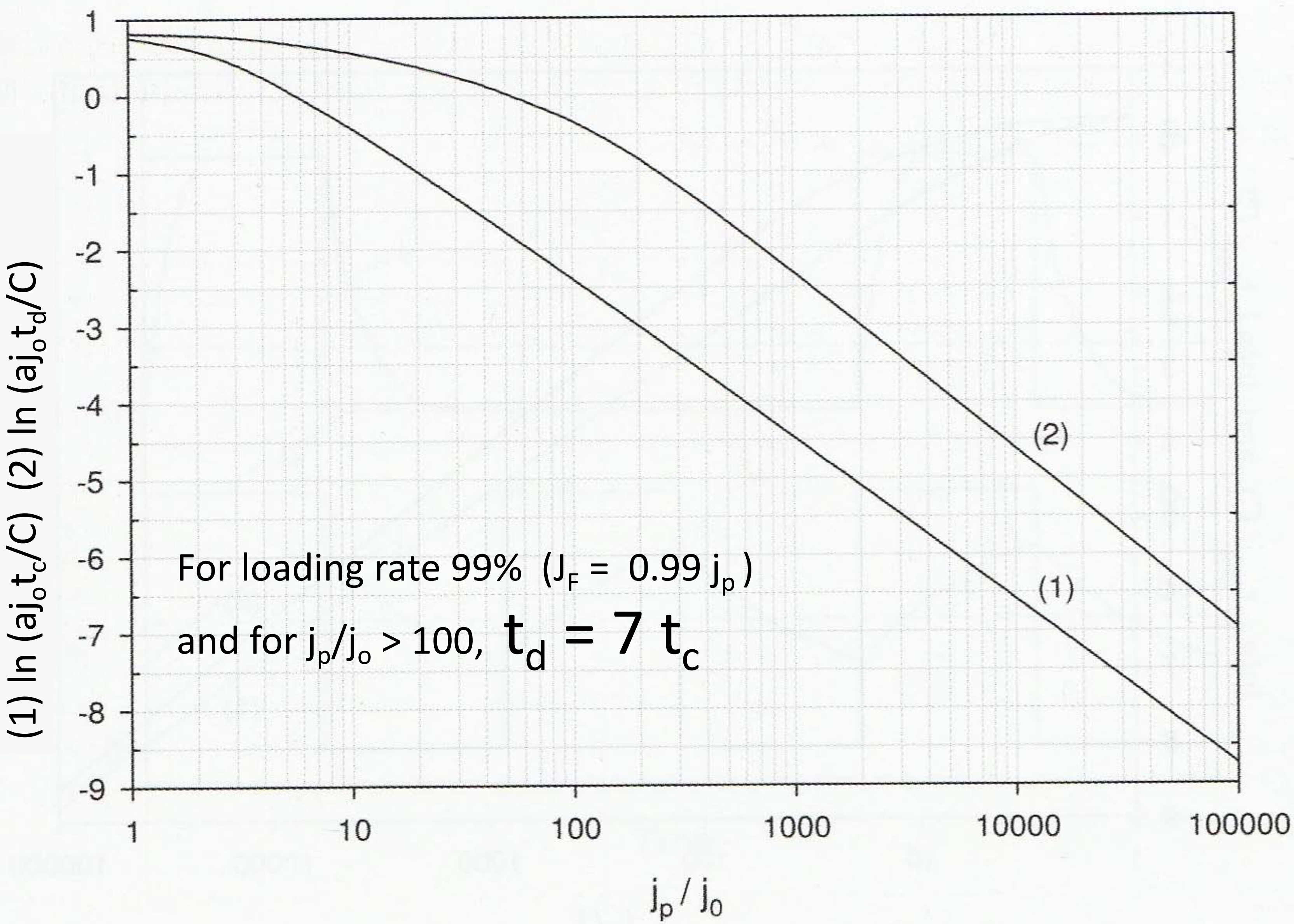


Dimensionless representation of t_c and t_d as a function of the ration j_p / j_o ,
where a = αnF/RT and (□n = 1; T = 289 °K; C = 50 µF/cm^2)

Computation of charging time of double layer

For the following conditions:

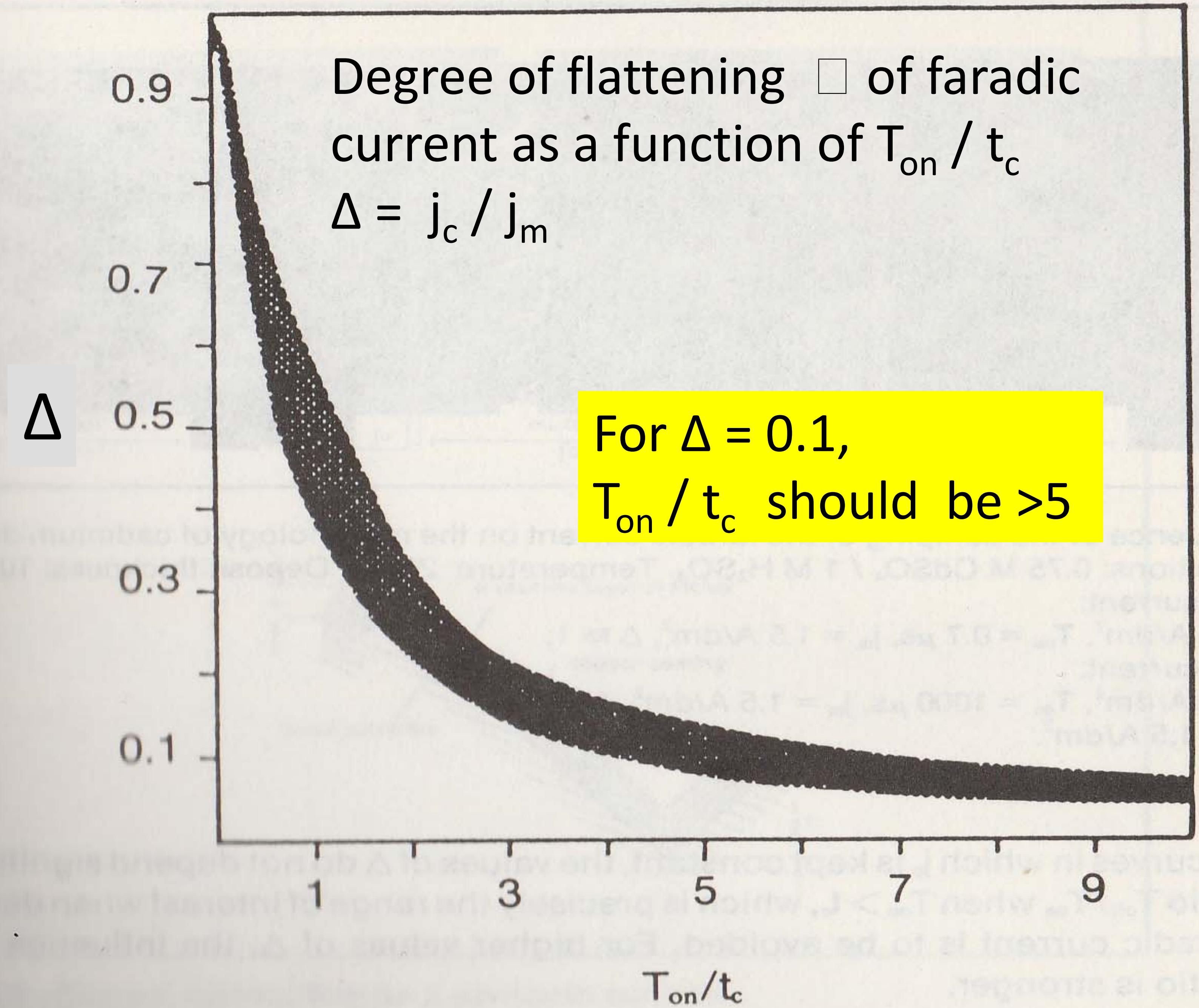
- $J_F = 0.99\ j_p$
- $J_p / j_o > 100$
- $C = 50\ \mu F / cm^2$
- $\alpha n = 1$

$$\mathbf{t_c = 0.017 / j_p \quad \text{and} \quad t_d = 0.120 / j_p}$$

where t_c and t_d are given in [ms] and j_p is given in [A/cm^2]

Degree of flattening □ of faradic current as a function of T_{on} / t_c

$\Delta = j_c / j_m$



For $\Delta = 0.1$,
T_{on} / t_c should be >5

Lower limits of Pulse Plating parameters

The lower limits of T_{on} and T_{off} which are dictated by the charging and discharging time of the electrical double layer.

For a degree of flattening (j_c/j_m) $\Delta < 0.1$,
$T_{on} > 5\, t_c$ and Toff $> t_d$. Therefore,

$$T_{on} > 0.085 / j_p \quad \text{and} \quad T_{off} > 0.12 / j_p$$

Where T_{on} and T_{off} are given in [ms] and j_p in [A/cm^2]

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Mass transport limitations through diffusion

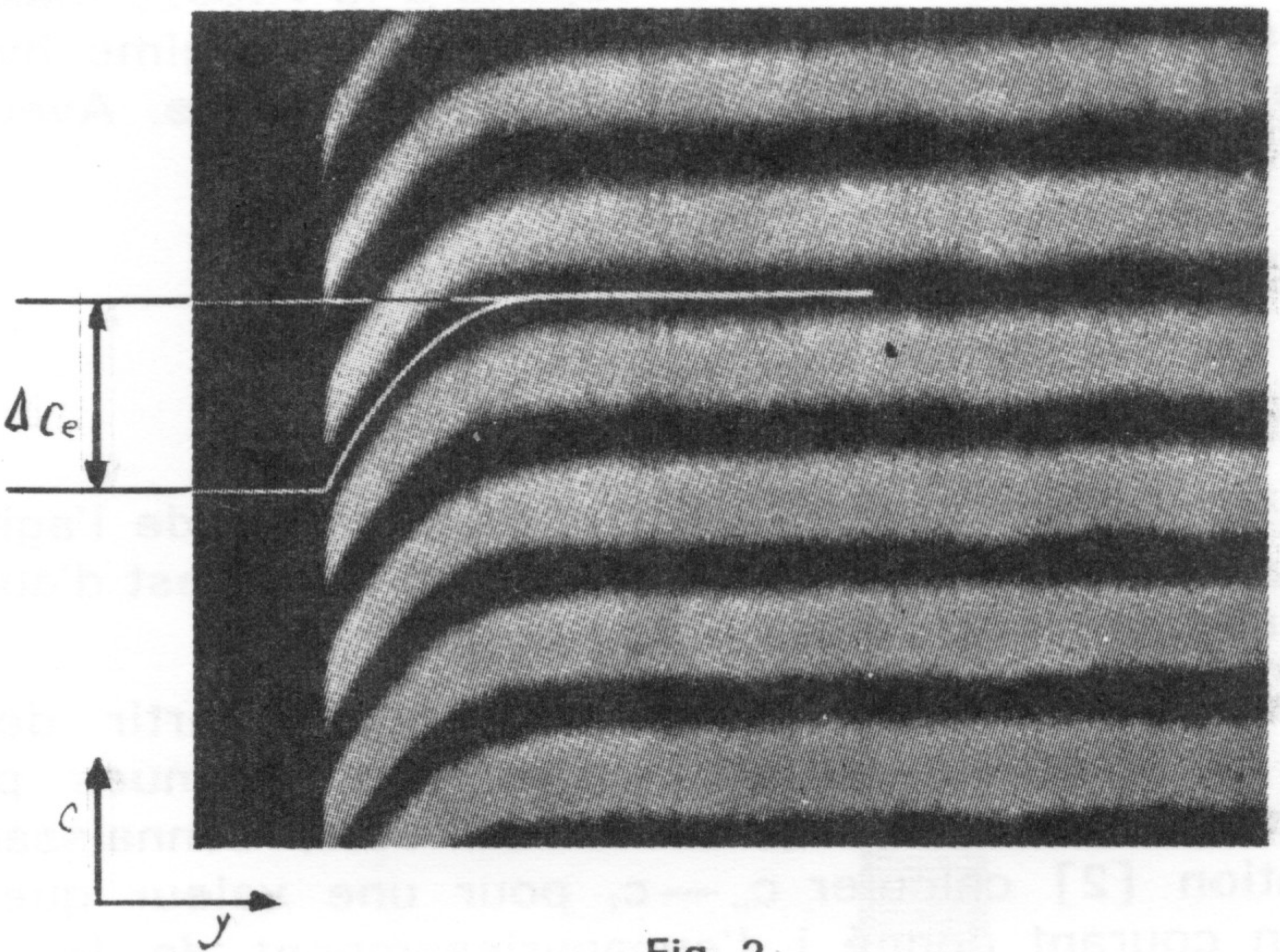

Fig. 2.

Image interférométrique de la couche de diffusion (dépôt de cuivre à partir d'une solution de $CuSO_4$, avec cathode verticale en convection naturelle) (1).

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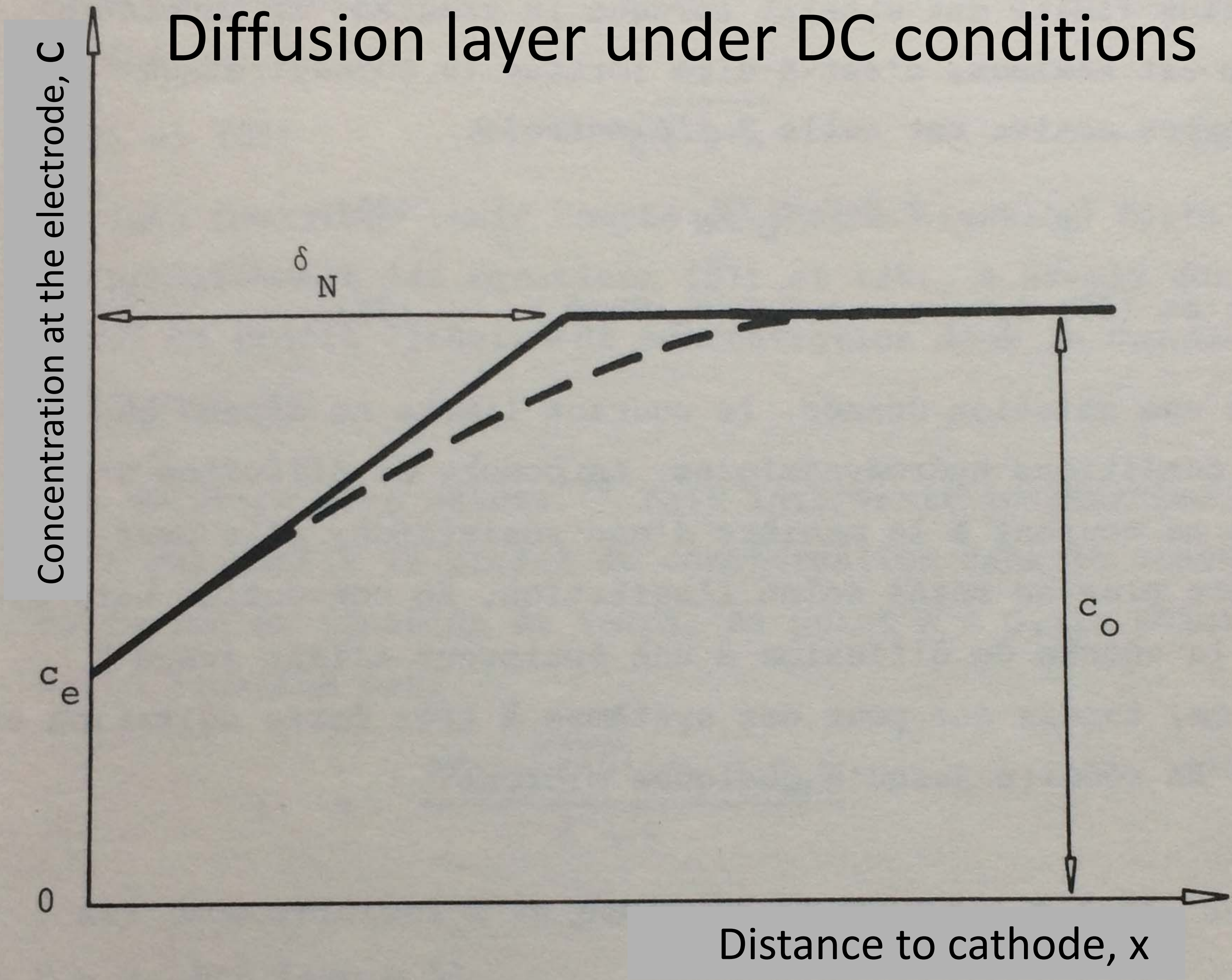
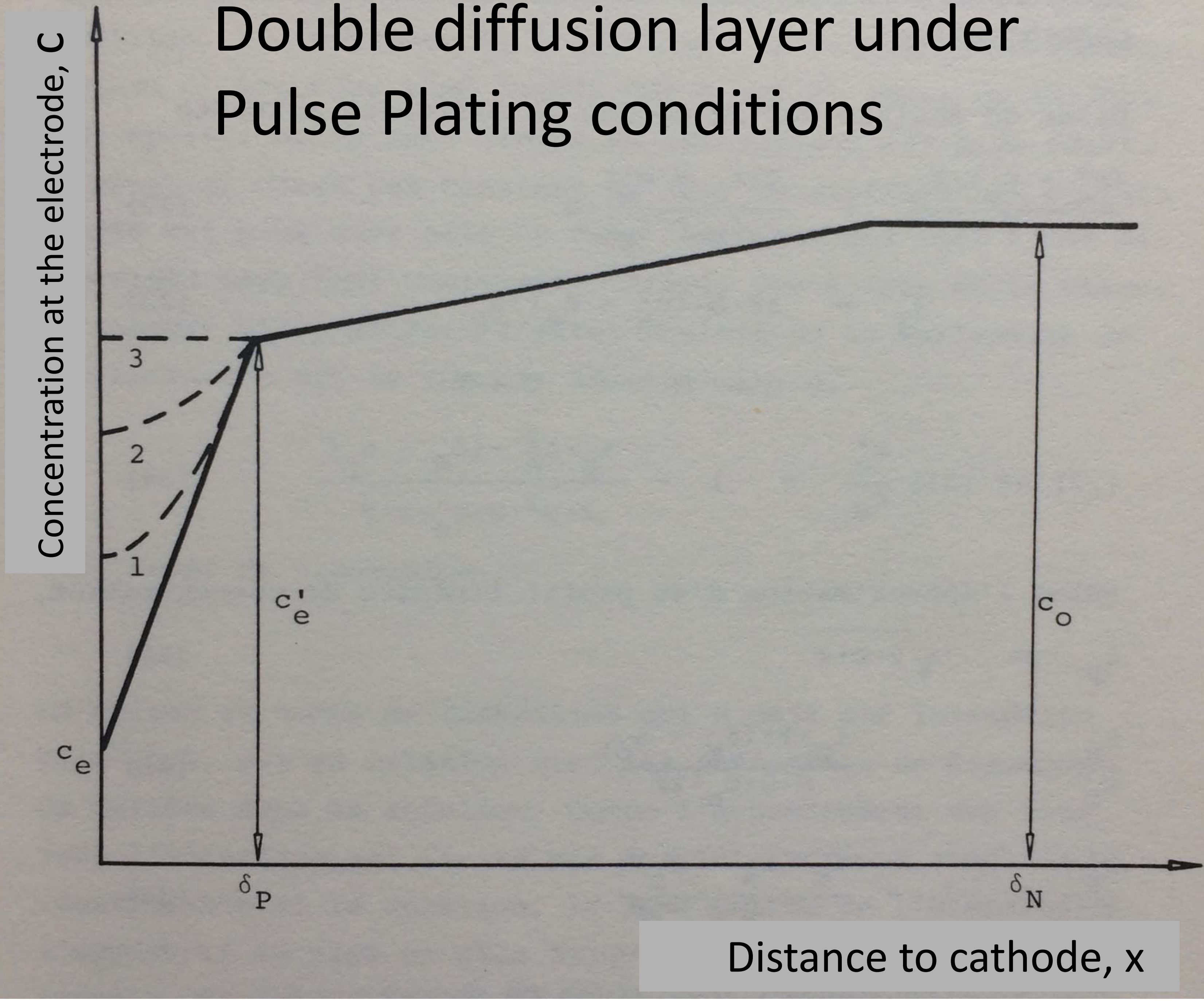
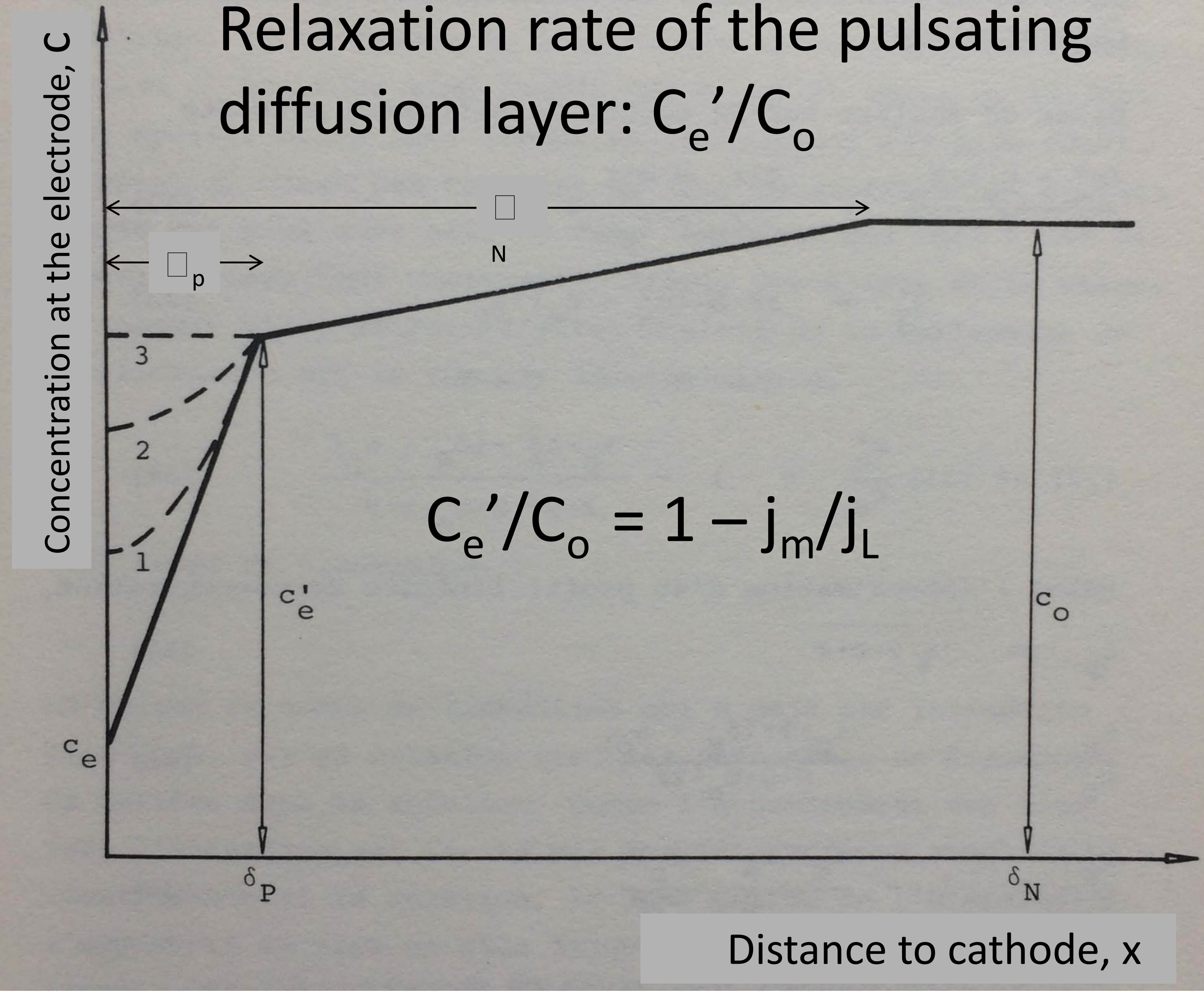
Diffusion layer under DC conditions



Double diffusion layer under Pulse Plating conditions

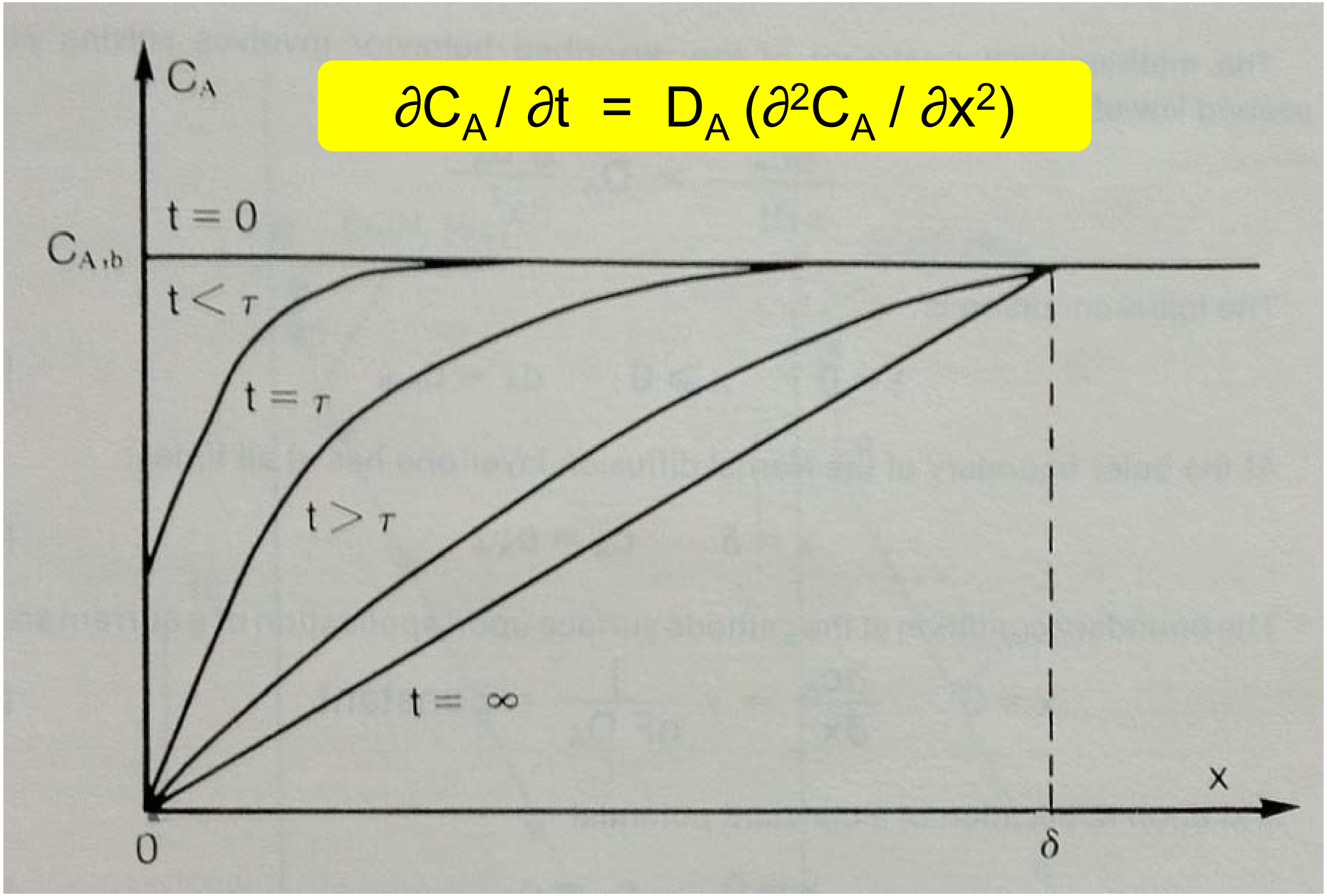


Relaxation rate of the pulsating diffusion layer: C_e'/C_o



$$C_e'/C_o = 1 - j_m/j_L$$

Concentration profile in transient state according to the 2^{nd} Fick law



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Particular solutions Fick II equation

Under potentiostatic conditions:

$$\delta = \sqrt{\pi D t}$$

Under galvanostatic conditions:

$$\delta = 2 \sqrt{D t / \pi}$$

Transition time for galvanostatic pulses

$$\tau = \pi D C_e'^2 (n F)^2 / 4 j_p^2$$

Upper limit of the on time T_{on}

The upper limit of T_{on} is dictated by the transition time τ . In order to stay away from the mass transport control, to avoid hydrogen evolution and therefore a strong drop of current efficiency, T_{on} has to be set bellow τ

$$T_{on} < \tau$$

It should however be enhanced that in some cases, as for instance in alloy deposition, it may be necessary to reach the transition time of one species in order to promote the deposition of other species.

Mass transport limitations of the off time T_{off}

Considering mass transport limitations, T_{off} has no upper limit but a lower limit in order to allow the pulsating diffusion layer to reach a high relaxion rate.

The concentration at the electrode C_e' at the beginning of each pulse should be close to the bulk concentration C_o

For $\delta_N >> \delta_p$, the relaxation rate $Ce'/Co = 1 - j_m/j_L$

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Excel table of «allowed» pulse parameters

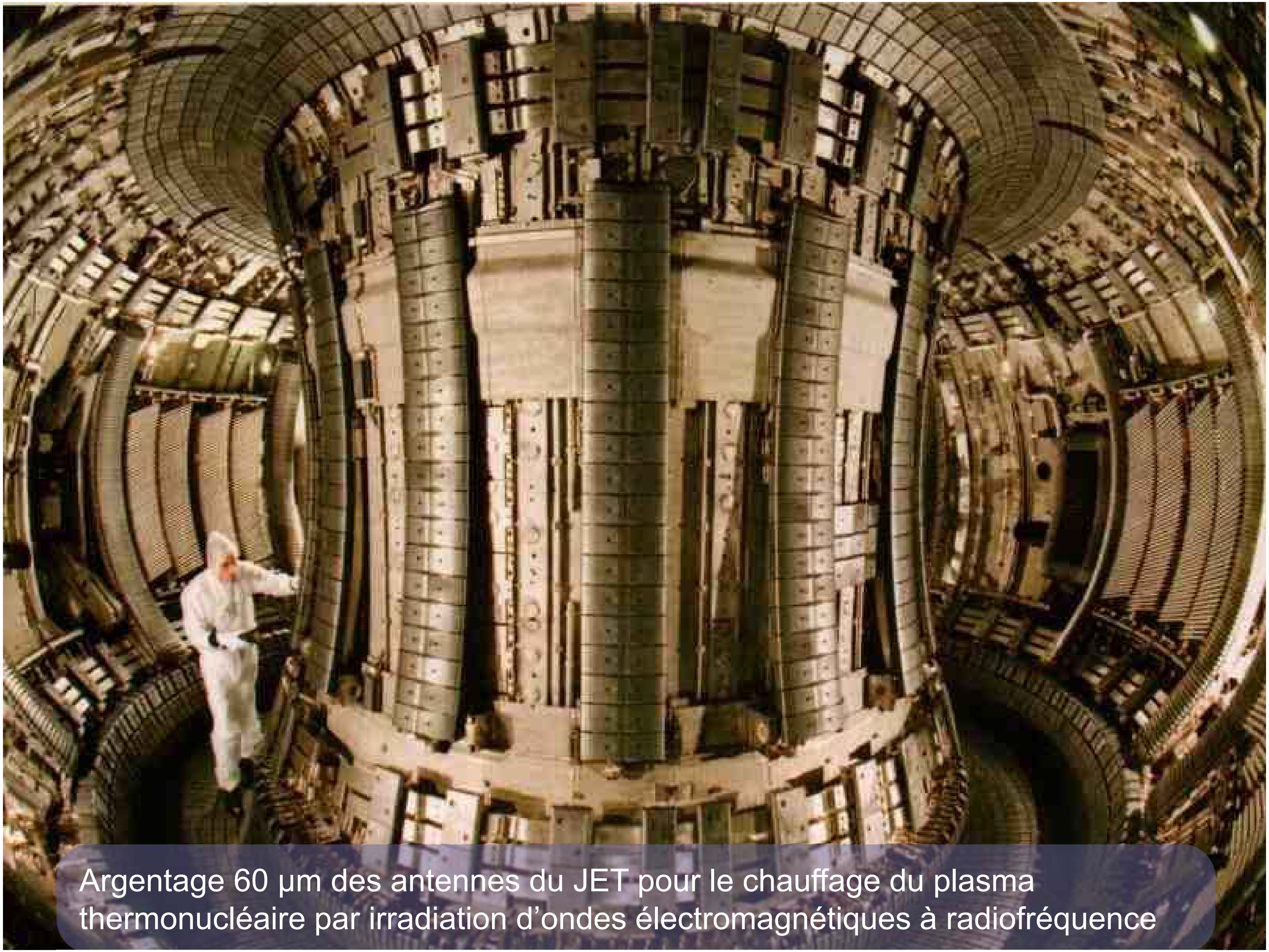
Examples of Pulse Plating aplications in the experimental physics

Requirements for the experimental physics:

- High conductivity : RRR > 250
- High purity of cooating for non degasing
- Low roughness even for high thicknesses above 100 µm

the only way to obtain the requested specifications is to apply Pulse Plating

Cuivrage intérieur de 416 dipôles de 9.58 m et 214 quadripôles de 3 m
pour le ring de l’accélérateur HERA (6.3 km) du DESY à Hamburg



Argentage 60 µm des antennes du JET pour le chauffage du plasma thermonucléaire par irradiation d'ondes électromagnétiques à radiofréquence

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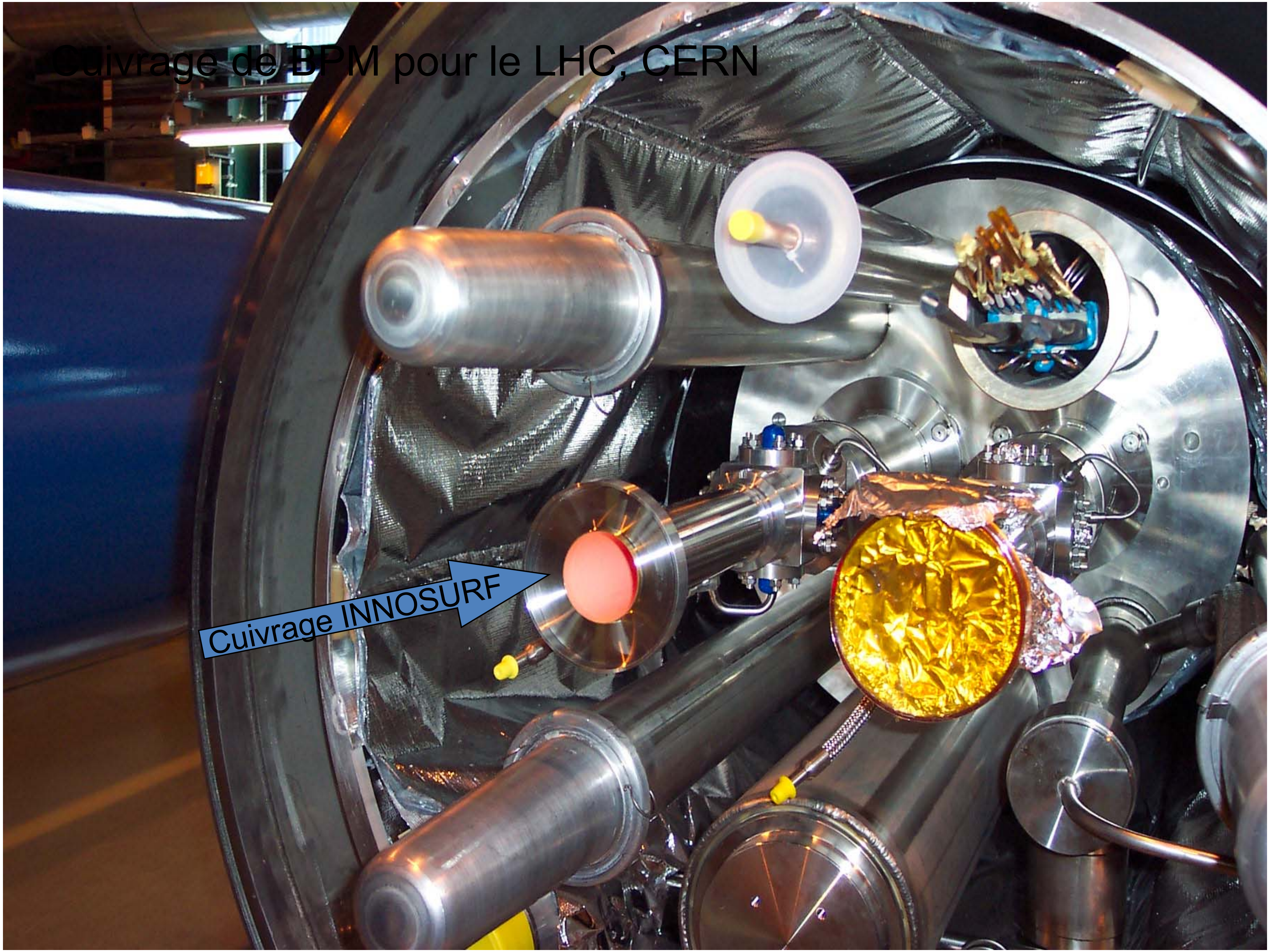
100 µm Copper plating of 900 BPM components for the LHC at CERN

Cuivrage de BPM pour le LHC, CERN



IN MEMORIAM our Passed President Prof Pietro Cavalotti and our regretted collegues Prof Chris Raub, Prof Nicolas Spyrellis, Prof V.N. Kudryavtsev, Prof M. Froment, Prof Jan Przyluski, Prof St. Rashkov, Prof E. Budevski, Prof A. Despic

Thank you for your attention