

Significance of Limiting Current Density by Influence of the Process Parameter for the Electrodeposition System

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Abstract

In this investigation, the process parameters for the electrodeposition of zinc has been carried out using direct current. Cathode current efficiency (CCE%) and deposit thickness were determined by weight measurement method. Manipulation of current density on the deposition process was also investigated. Effect of temperature on the deposition process and deposit morphology was also studied. Cathodic polarisation and Bath agitation measurements were used to study the mass transport conditions of the electrolytic bath. Field Emission Scanning Electron Microscopes were utilised to study the morphologies of the deposits. Temperature and pH changes had marked influence on the morphology of the deposits. It was observed that cathode current efficiency was dependent on the current density and bath temperature, while deposit thickness was dependent on current density, bath agitation and time. Cathodic polarisation studies revealed that bath agitation and composition had significant effect on the limiting current density and hence mass transport of the bath.

Keywords: Cathode current efficiency, morphology, cathode polarisation, mass transport, limiting current density.

Introduction

A wide variety of plating bath composition has been employed in electrogalvanizing to control the growth of cathode deposits, inhibiting the formation of dendrites and to produce fine-grained, smoother deposits. Electrode position yields grain sizes in the nanometer range when variables such as bath composition, pH, temperature, current density, etc are chosen such that nucleation of new grains is favoured rather than growth of existing grains. As the basis of a whole range of sacrificial coatings, Zinc has found widespread use for ferrous substrates. The corrosion characteristics are strongly determined by the texture and microstructure obtained, which in turn depends on the specific deposition procedure employed. It can be applied by a variety of techniques, including hot-dipping, metal spraying,

cementation, cladding and electrode position and it is the most commonly used sacrificial coating¹. The role of electroplating parameters on the formation of different textures and microstructures is well established by several researchers²⁻⁴ using various approaches, which has effectively lead to the preparation of coatings that differ in their macro and micro-structure, texture density, uniformity and corrosion resistance. The main disadvantages of the acid type baths are that they are corrosive so care has to be taken to protect operators and equipment and these baths generally exhibit poor current efficiency. Electroplating normally takes place under a DC regime, however, improved smoothness by means of pulse plating, a periodically interrupted process in which a certain duty cycle of cathodic potential/current is employed⁵⁻⁹. Venkatesha T V¹⁰ found that in the zinc electrocrystallization process two types of inhibition occur, primary and secondary inhibition. He reported that the conditions for cathode deposit formation and consequently crystallite orientation are significantly altered by hydrogen codischarge. According to the authors, the increasing zinc concentration, increased the current efficiency in a non-linear fashion and that the highest rate of increase occurred when the zinc concentration was increased from 20 to 50 gpl. Both of these factors improve the current efficiency. Indicators of an excellent electrode position bath includes; good current efficiency and throwing power, longevity of the bath, minimal hydrogen evolution, etc. This works consequently hunt for the study process parameters suitable for the bath in question to produced zinc electrodeposits with good sacrificial defensive properties.

Experimental Methods

Preparation of Bath

The optimized composition of the bath formulation used for this study is as follows:

Electrolyte constituents concentration (gpl):	Operating condition
ZnSO ₄ .7H ₂ O- 0.28M Na ₂ SO ₄ .7H ₂ O	-Alloy plating bath
Sodiumhydroxide(2N KOH)/con H ₂ SO ₄ acid (4N H ₂ SO ₄)	- to enhance the specific conductance, to improve the bath stability
pH	2.0 to 4.0



Fig.1.Top views of Experimental Electrochemical Cell

The whole process was carried out at room temperature. Cathode current density was varied by DC regulated power supply (Aplab L3230 model, India make). Measurements of pH were carried out and adjusted accordingly using sodium hydroxide (2N KOH) or concentrated sulphuric acid (4N H₂SO₄). Deionised water was poured into a beaker and the reagent was added gradually with mild agitation initially and then more vigorously, to enhance¹¹⁻¹² dissolution. The solution was finally made up to 1 litre by adding more water. Zinc was electrodeposited from additive-free, aqueous solutions composed of standard AR-grade (Merck India) laboratory chemicals.

Gravimetric Determination of Cathode Current Efficiency and Deposit Thickness

Pre-weighed samples after plating were first rinsed immediately in running tap water, immersed in acetone, dried in a stream of warm air and then weighed again to determine the weight gain. Cathode current efficiency and deposit thickness were measured, consequently calculated using the formulae:

$$\text{Cathode current efficiency (CCE)} = \frac{\Delta W}{W_T} \times 100\% \quad [1]$$

Where (CCE) – Cathode current efficiency (%)

ΔW – Change in weight after plating (g)

W_T – Theoretical weight of deposit (g)

$$\text{Whereas } W_T = \frac{I \times t \times M_{Zn}}{n \times F} \quad [2]$$

Where I – Current (Amp)

t – Time (second)

M_{Zn} – Molecular weight of Zinc (g/mol)

F – Faraday constant (96500 C/mol)

n – number of electrons involved in the reaction

Computer Controlled Potentiostatic Studies of Cathodic Polarisation for Zinc

The volume of electrolyte was 500 ml. Two bath compositions were utilized to investigate the mass transport behaviour of zinc electrodeposition and are given below:

Bath 1	100 gpl ZnSO ₄ + 7H ₂ O
Bath 2	200 gpl ZnSO ₄ + 7H ₂ O

Each test was carried out with Glassy carbon electrode of an area of 0.25 cm^2 (Tokai Carbon Company, Japan make) was used as the working electrode. Platinum foil of $2.5 \text{ cm} \times 2.5 \text{ cm}$ area was used as the counter electrode and saturated calomel electrode was used as the reference electrode. Cathodic polarisation studies were conducted for zinc using an Auto Lab PGSTAT 30 electrochemical analyser (The Netherlands make). To eliminate the interference of oxygen, bath was purged by passing pure nitrogen for one hour. Each of these different sets of polarisation studies was conducted in order to obtain data for metal deposition. Cathodic overpotential was measured at every 30 seconds at a given cathodic current density with reference to saturated calomel electrode (SCE) through a Luggin probe assembly¹³.

Results and Discussion

To improve the Mass transport by use of Bath Agitation

Figure 2 shows that current efficiency of the bath was better without or at lower rates of solution agitation at a constant current density of 5 Adm^{-2} . The zinc ion concentration near the cathode is quickly depleted and the cathode reaction shifts from zinc deposition to hydrogen evolution. Since the main reactions at the cathode during electrode position is a competition between zinc reduction and hydrogen evolution, as the limiting current density is approached during zinc deposition. To improve the mass transport in the electrolyte and therefore enhance the rate of deposition, the use of bath agitation is intended. However, in terms of cathode current efficiency, bath agitation was found to reduce the current efficiency with increase in agitation.

Generally, due to the fact that an improvement in cathode current efficiency with agitation, agitation helps to prevent the adsorption of evolved hydrogen, thereby preventing zinc reduction. As the hydrogen bubbles are swept away, it should lead to improved zinc deposition and hence current efficiency. This means, agitation may have been detrimental to the zinc nucleation process in the prevalent conditions. This may well in the deposition of a mixture of zinc and zinc hydroxide or zinc oxides due to pH increase in the locality of the cathode. However, this does not appear to be the case in the present investigations. Additionally, the applied current is shared between two processes: zinc deposition and [HER]. This could be unfavourable to zinc deposition as adsorbed hydrogen on the surface of the cathode could obstruct zinc nucleation. This could mean a higher current density may be needed to drive zinc deposition. But then, at higher current densities, a larger driving force is required to effect zinc deposition due to possible rise in both anode and cathode potentials with increase in current density.

To Optimise Conditional Effect of Current Density and Time on Deposit Thickness

Visually acceptable coatings were obtained within the current density range of $1.0\text{-}5.0 \text{ Adm}^{-2}$. In an effort to optimise conditions for the production of thick zinc electrodeposits, a range of current densities were investigated. In each case, maintaining a constant quantity of electricity supplied was crucial to obtain uniform deposit thickness in all the samples.

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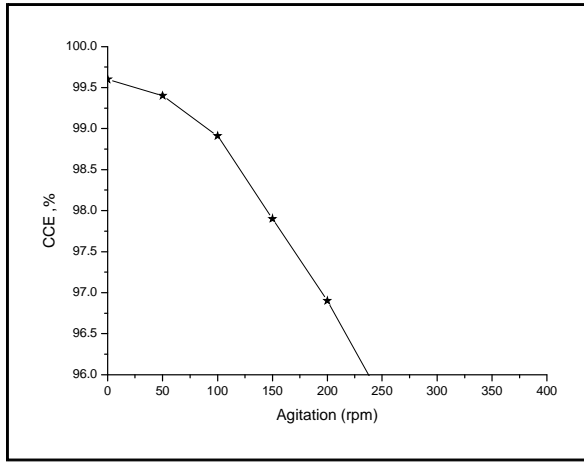


Fig. 2

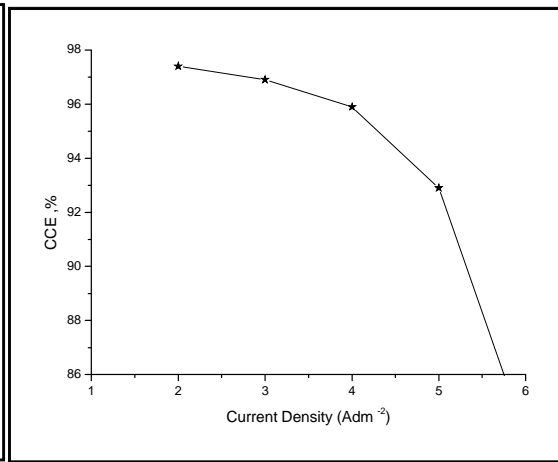


Fig. 3

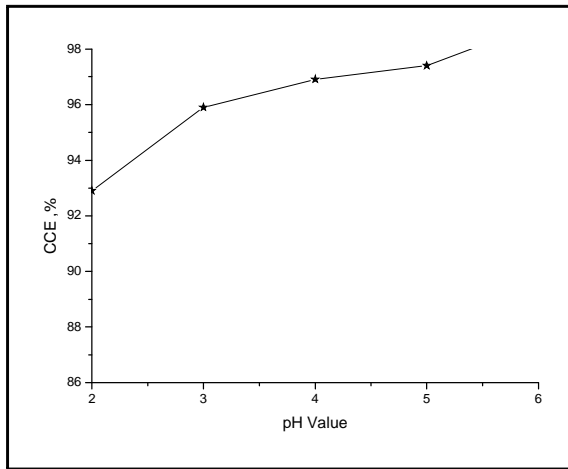


Fig. 4

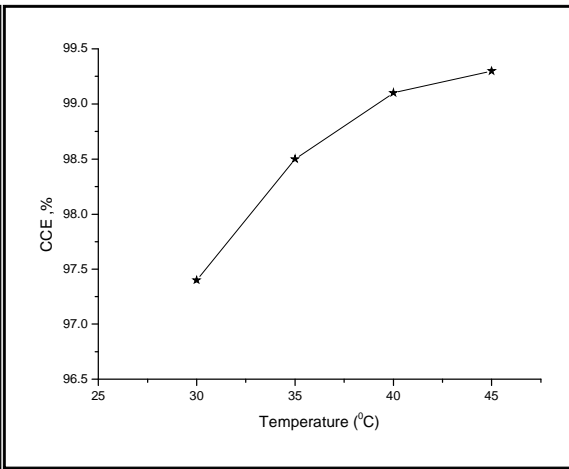


Fig. 5

Fig.2. Effect of Bath Agitation on the CCE of the Bath at 5 Adm⁻², pH 2.5 and T= 32 °C.

Fig.3. Effect of Current Density on the CCE of the Bath at pH 2.5, Deposition Time 15 min, T= 32 °C

Fig.4. Effect of pH on the CCE of the Bath at 5 Adm⁻², Deposition time 10 min., T = 32 °C

Fig.5. Influence of Bath Temperature on the CCE of the Bath at 5 Adm⁻²

The experimental results show that current density is inversely proportional to time to obtain the same deposit thickness. At higher current densities, this is reliable rate of deposit and deposition faster. On the low deposition current densities are associated with small rates of thickness has to cover the whole surface of the substrate. This means that lower current densities require longer durations to deposit thickness. For each current density, there is corresponding time duration for the

production of thick electrodeposits. Either the bath chemistry or other electrodeposition parameters are modified to either enhance or reduce the deposition rate or reduce reactions in the area of the cathode that are critical to metal deposition.

Effect of current density on cathode current efficiency (CCE)

Analogous observations were reported by Rakhshen *et al*¹⁴. In case, the effect of current density on cathode current efficiency (CCE) is offered in Fig. 3. This is a suggestion that there was trifling mass transfer resistance or concentration over potential for the range of current densities. Changes in current efficiency of the bath appear to be trivial over a range of current densities between 1.5-5.0 Adm^{-2} . On the other hand, with additional increase in current density, the current efficiency decreased noticeably. This is pointed to increase in HER. This is attributed to increase in hydrogen evolution. Still, with further increase in current density, the current efficiency decreased significantly.

Analogous observation Effect of pH

The possibility of excellent deposition conditions in the bath, the formation and successive codeposition of zinc oxide and hydroxide. Also in agreement with Jiricny *et al*¹⁵, it can be seen from Fig.2.and 3 that majority of current efficiency results produced at $\text{pH} < 3$ shows current efficiencies of less than 100%. Analogous observations have been reported by other investigators¹⁶⁻¹⁷ that a decrease of the pH leads to a decrease of the current efficiency. Fig.4. shows that for the range of pH from 2.0-2.5, the cathode current efficiency increased with increase in pH. At $\text{pH} > 3$ almost all current efficiencies were greater than 100% (Fig. 3.). It appears, at higher pH values, the formation and consequent codeposition of ZnO and $\text{Zn}(\text{OH})_2$ probably occurred due to HER with a resultant increase in pH within the area of the cathode.

Influence of temperature Effect on CCE

Rakhshen *et al*¹⁴. reported that current efficiency increased with increase in temperature from 94.0% at 30°C to 97.7% at 35°C with a resultant decrease in energy utilization. It was meaningful that the decrease in energy spending is to increase in current efficiency and a decrease in cell voltage as the temperature rises. Control of temperature on CCE shows an increasing linear relationship from Fig.5. as increase in bath temperature from 32 °C to 35°C with corresponding increase in the CCE from 97.6% to 98.7%. At higher temperatures the rate constants of both cathodic reactions increase hence a lower driving force is required. The conductivity of an electrolyte increases with increase in temperature and this is often more pronounced at higher acid concentrations.

Morphological characteristics changes

A field emission scanning electron microscope (FESEM) (JEOL- JSM 6701F) was used to examine the grain size ($>1\mu\text{m}$) of the coated surface and cross-sectional morphologies of the nanocrystalline zinc deposits. Thorough systematic studies of the mechanisms of electrical transport,

and the effect of the interaction between defects and dopants on these mechanisms, are scarce. The physics of defects in Zn electrodeposition is quite complex and to a large extent unknown, and the understanding of doping and conduction mechanisms in this material are still incomplete and challenging. Deposit properties of zinc are largely dependent on the texture and surface morphology of the electrodeposits. zinc occurs in (hexagonal) crystalline form, the morphological features usually sponge, platelets, boulders originate from different arrangements of hexagonal units ⁸. The predominant crystallographic orientations reported on zinc electrodeposits produced from acid sulphate baths without additives are usually the randomly preferred orientations. These morphologies can be tailored with changes in electrodeposition parameters such as current density, temperature, pH, catholyte flow, impurities and the presence of certain additives.

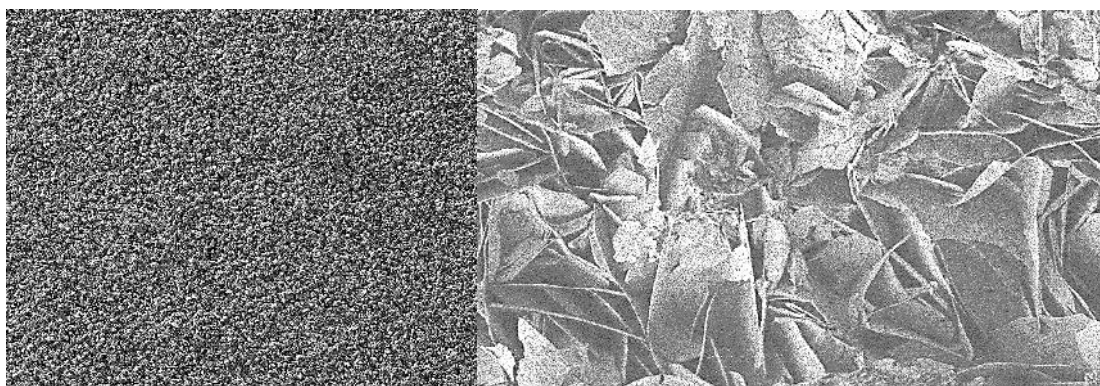


Fig. 6.(a)

Fig.6.(b)

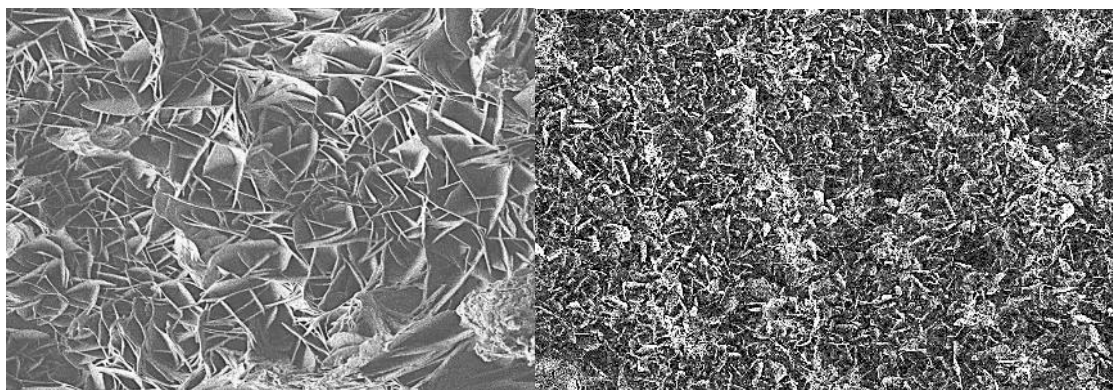


Fig.6.(c)

Fig.6.(d)

Fig.6.(a)FESEM Micrograph of Zinc Electrodeposits from the Bath at 2 Adm^{-2} and pH 2.5.

Fig.6.(b) FESEM Micrograph of Zn Electrodeposits from the Bath at 3 Adm^{-2} and pH 3

Fig.6.(c) FESEM Micrograph of Zn Electrodeposits Produced at 4 Adm^{-2} and pH 2.5, T = 30°C.

Fig.6.(d) FESEM Micrograph of Zn Electrodeposits Produced at 3 Adm^{-2} and pH 3 , T = 35°C.

During further deposition, these surface protrusions continue to grow keeping characteristic sponge shapes. After longer deposition times, assimilation of the separate growing sponge groups occurs and the whole electrode area becomes covered with a disperse zinc sponge deposit. From FESEM images [Fig. 6.(a) to (d)], it was observed that the deposit morphology was influenced by the alloy composition in zinc electrodeposits.

Morphological changes with pH

The observed improvement in cathode current efficiency with increase in temperature as earlier mentioned and shown in Fig.5. is probably as a result of such growths and consequent incorporation in the electrodeposits thereby increasing the weight gain and hence cathode current efficiency values. As the temperature increased to 35°C, the white patches became conspicuous on the surface of the deposit as obvious in Figure 6.(b). In addition, at about 32°C, on deposit of white patches was noticed as particles on the edges of zinc crystal (see Fig.6.(c)). With increasing temperature, the tangential stacking sequence of crystal orientation appears to have transformed from the usually messy orientations (see Fig.6.(b)) to that with the edges of the crystals perpendicular to the surface of the substrate (see Fig.6.(c) and Fig.6.(d)).

Morphological changes with temperature

Increase in temperature was observed to have some effect on the crystal orientation of the deposit. With increasing temperature, the lateral stacking sequence of crystal orientation appears to have transformed from the usually random orientations (see Figure 6.(a)) to that with the edges of the crystals perpendicular to the surface of the substrate (see Figures 6.(a) and 6.(b)). Also, at about 35°C, onset of white patches was noticed as particles on the edges of zinc crystal (see Figure 6.(d)). As the temperature increased to 40°C, the white patches became conspicuous on the surface of the deposit as obvious in Figure 6.(c). The observed improvement in cathode current efficiency with increase in temperature as earlier mentioned and shown in Figure 6.(d) is probably as a result of such growths and consequent incorporation in the electrodeposits thereby increasing the weight gain and hence cathode current efficiency values.

Gradual studies on Cathodic polarisation of Zinc Electrodeposits

Fig. 7. plots a pair of cathodic polarization of Zinc Electrodeposits curves from the dilute bath and another pair from the concentrated bath both with and without agitation. It is observable from this figures that current density increased for all the investigations carried out in the presence of bath agitation. Similar improvements in mass transport and hence zinc deposition current densities have previously been reported¹⁹. It appears zinc deposition did not occur until the potential gradually increases, depending on the concentration of Zn^{2+} , with steep activation.

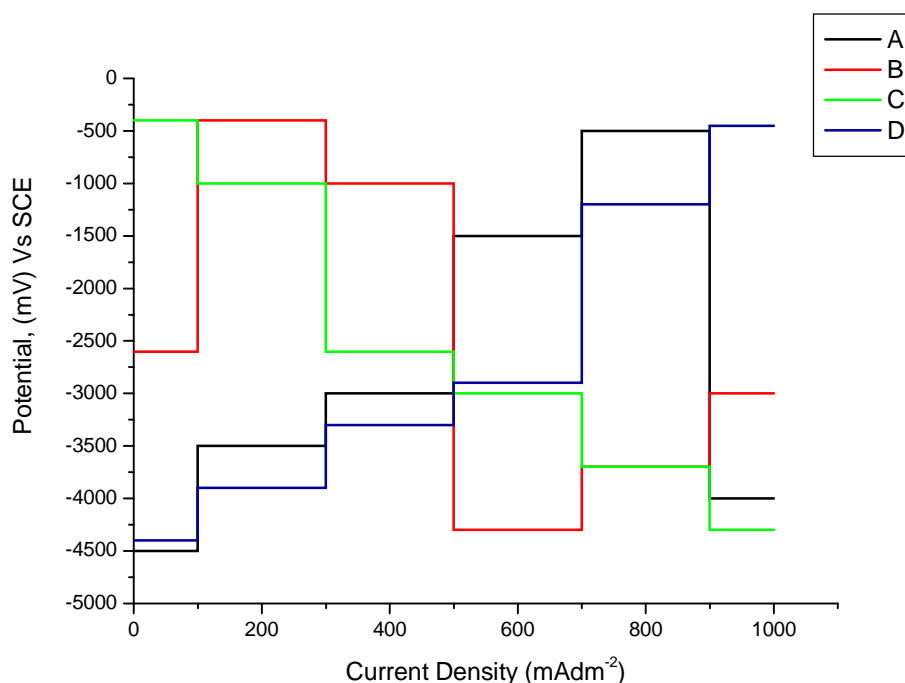


Fig.7. Cathodic polarisation of zinc (i) baths containing 200 gpl $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (A) With agitation (B) Without agitation. (ii) baths containing 100 gpl $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (C) With agitation (D) without agitation

Deposition was also carried out simultaneously, over mechanically polished and electrocleaned stainless steel panels of size $5.0 \text{ cm} \times 2.5 \text{ cm} \times 0.05 \text{ cm}$, under the given conditions in order to achieve well-defined deposition behaviour in the polarisation curves as opposed to solutions with high zinc levels where metal reduction peaks are less clear²⁰. For the investigations without agitation, the zinc deposition current appears to be very low, that indicates that the bath compositions and deposition conditions were favourable for the zinc deposition reaction due to enhanced mass transport. After that observed short range of potential and diffusion control appears to take over at higher potential values.

Conclusion

For comparable deposit thicknesses, plating time was inversely proportional to current density. At higher temperatures, patches of white deposits thought to be oxides of zinc were observed. In general, Cathode current efficiency and deposit thickness were dependent on current density, agitation and bath temperature. Temperature and pH had spot influence on the deposition process.

Cathodic polarisation studies divulged that bath agitation had momentous effect on the limiting current density and consequently mass transport of the bath. Electrolyte Solution agitation was somewhat unhelpful to the current efficiency of the bath.

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