



Acid Zinc Plating Process: A review and experiment of the effect of various bath parameters and additives (i.e. brighteners, carriers, levelers) on throwing power

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ABSTRACT

This review comprises of the chemical formulations, fundamental and technical aspects of the complete acid zinc plating process. The review discusses the effect of physical and chemical plating parameters, brighteners, carriers and levelers on the throwing power of the plated product. In practice, there are several additives that are added to make an acid zinc plating process efficient. In this article, we talk about their influence solely on the throwing power. The effect of Tiron and SiO₂ nanoparticles on the throwing power of acid zinc bath is also investigated in the article.

Keywords: Electroplating, acid zinc plating, throwing power, nanoparticles, colloidal silica, tiron, additives

1. INTRODUCTION

Zinc is one of the most prominent metals that is used as a depositing metal in the electroplating industry. The sacrificial protection offered by the zinc metal at a low cost is one of the reasons which make the plating process highly relevant. The advantage of acid zinc process is high current efficiency and a superior covering power. The characteristic throwing power of the acid zinc bath is not extraordinary, for which the use of leveling agents and additives comes into action (1). The aim of this study is to investigate the influence of plating parameters and the influence of p-anisidine, sodium dodecylbenzenesulfonate, tiron and nanoparticles of SiO₂ on the throwing power. At the end, we compare our results of acid zinc plating to the Zn-Ni alloy plating and Zn-Co alloy plating.

The plating process can be performed in two ways- Rack Plating and Barrel Plating.

Barrel Plating means placing the parts to be plated inside a barrel usually made up of polypropylene. The electrical current is conducted via the barrel's central bars. While submerged in the electrolytic plating solution, the barrel spins slowly. The pieces tumble or "cascade" as a result, resulting in an even, homogeneous coating application.

Rack plating varies from barrel plating in that the components are screwed, wired, or spring-loaded to metal racks. As a result, when the metal rack is immersed in the plating solution, the pieces remain fixed. Therefore, metal platers choose rack plating for fragile components that may not be able to survive barrel plating's tumbling or cascading motion. Rack plating also works well for large or complex components (2).

The bath parameters like metal ion concentration, current density, chloride content in the solution differ in both the systems, which we will see later in our review.

1.1 TERMINOLOGIES

Corrosion is a process in which a material is oxidised by environmental chemicals, resulting in the loss of electrons. Corrosion resistance refers to a metal's ability to retain its binding energy and survive the degradation and chemical breakdown that would otherwise occur if it were exposed to such an environment. (4)

Salt spray testing is an accelerated corrosion test that exposes coated samples to corrosive assault in order to determine the coating's appropriateness for use as a protective finish (6)

Sacrificial protection is a corrosion-prevention technique in which a more electrochemically active metal (in this example, zinc) is electrically connected to a less electrochemically active metal (substrate). Zinc will corrode or be sacrificed to preserve the underlying substrate since it is more electrochemically active. When a zinc coating is applied to a substrate, it will not corrode as rapidly, even if it is scratched or damaged. The zinc coating will always tarnish and corrode first (3).

Throwing Power- The ability of an electroplating solution to plate a consistent thickness over an unevenly shaped cathode is measured by throwing power. If the whole surface of the unevenly shaped cathode is coated to a consistent thickness, the solution possesses perfect throwing power. If it is just plated near the anodes, on the other hand, the solution has a low throwing power. (4)

The route of least resistance is followed by electricity. As a result, protruding portions, edges, and components near to the anode will get the highest current. The deposit in these locations is usually the thickest. A consistent deposit thickness throughout the whole component is usually preferred. The thinnest deposits will be seen in recesses or places farthest from the anode. The components should be arranged such that all regions are around the same distance from the anode to maximize current distribution and provide a uniform deposit. (4)

Micro and Macro are the two types of throwing power.

The capacity of a bath to plate into microscopic surface imperfections and fill them with deposit is known as microthrowing power. Surface defects will be even off and the surface will be smoother using a solution with excellent microthrowing power. Polarization has an impact on microthrowing. Metal will tend to deposit into surface defects when polarization is enhanced by the application of addition agents, resulting in a higher quality deposit.

The ratio of deposit distribution to distance from anode to cathode is known as macrothrowing power. The area of a cathode that is closest to the anode receives the thickest deposit, while the area furthest from the anode receives the thinnest deposit. Regardless of anode to cathode spacing, an electrolyte with 100 percent throwing power will deposit a uniform thickness. Polarization, as before, is in charge of controlling this macrothrowing power. (16)

Some of the ambiguities associated with the use of the concept of throwing power can be resolved, according to Jelinek and David (20), by using the "throwing index," which is calculated by plotting the metal distribution ratio M versus the linear current distribution ratio L on arithmetic co-ordinates. The throwing index is the reciprocal of the line's slope and gives a direct approximation of the bath throwing force. At $M = 1$, a solution with ideal throwing characteristics will produce a horizontal line, whereas a bath with poor throwing power will produce a very steep line in this plot.

Thomas (7) defines **leveling** as an electroplating solution's ability to produce deposits that are relatively thicker in small recesses and thinner on small protrusions, resulting in a reduction in the depth or height of small surface irregularities. There are three types of leveling- (i) poor micro throwing power, (ii) geometric leveling and (iii) true leveling.

Covering power is the degree to which a coating obscures the underlying material i.e. the ability of the bath to produce a coating at the lower current density area. (5)

Brightening is defined as an electroplating solution's ability to produce fine deposits with crystallites smaller than visible light wavelengths, i.e. less than $0.4/\mu\text{m}$ (8)(9) and an oriented grain structure (10). A small grain size is required for brightness, but it is not sufficient; similarly, not all fine-grained deposits are bright. The brightness of electrodeposits is found to be dependent on the degree to which morphological components of the surface are in the same plane. (11).

Carriers are plating inhibitors or suppressors. They create and maintain a defined diffusion layer at the anode, which regulates the flow of metal ions from the anode into the electrolyte and ultimately at the cathode.

1.2 BATH PARAMETERS

Metal ion concentration is one of the critical bath variables. The source of metal ion is usually the metal salt present in the electrolyte. In the case of a soluble anode, there are two sources of metal ion namely - from the anode through electrolysis and salt present in electrolyte (1). High metal ion concentration causes poor low-current-density deposits, and low concentration causes high-current-density burning (12).

Acid chloride baths used are of 2 types - based on ammonium chloride or potassium chloride. Ammonium based baths can operate at higher current densities with respect to the potassium chloride bath, however the action of ammonium chloride as a complexing agent in waste streams required expensive chlorination before disposing. This led to the development of potassium chloride based baths. (13) Recently, new baths based on sodium chloride have been formulated. These have provided various advantages over traditional baths including reduced operating cost, less corrosive solution, and thicker deposits with good bond strength. However, at higher current densities burning occurs in these baths which limits their use. (14)

Boric acid is added as a **buffer** to maintain pH during the electroplating process. Higher pH leads to formation of precipitates and anode polarization and lower pH shows poor plating quality. Thus, sufficient amount of boric acid ensures larger range of pH to work with (1).

In most aqueous solutions there is a limiting factor on **temperature**. Boiling point, decomposition and breakdown of organic molecules influence the working temperature range of the electroplating bath. (12)

A variety of zinc plating baths based on zinc sulphate and zinc fluoborate have also been developed which provide relatively cheap cost, safety features and pollution control characteristics, but throwing power and inadequate brightness are the drawbacks. (15)

Keeping in view the above factors the following bath formulation was used:

BATH PARAMETERS	RANGE	OPTIMUM VALUE
Zinc Chloride	62 - 85 g/L	71 g/L
Potassium Chloride	186 - 255 g/L	207 g/L
Boric Acid	30 - 38 g/L	34 g/L
Carrier Brightener	-	4%
Primary Brightener	-	0.25%
pH	4.8 - 5.8	5.2
Temperature	21-35 °C	27 °C

2. EXPERIMENTAL DETAILS

The Throwing Power of the Acid Zinc bath was calculated using the Hull Cell testing mechanism. Perspex sheet was used to construct the Open Hull Cell mechanism, with slots to give positive location for the electrodes. The cross-internal section's dimensions were the same as a standard 267 ml cell, with a 2.5-inch gap between the parallel sides, which were 1.35 in and 5 in long. As a result, the cathode plated length was 4 inches, with a 38.7° inclination to the anode. The cell was 3.6 inches deep, with an effective cathode area of 3.6 inches.

The percentage of throwing power was calculated with the help of the Field's Formula (16):

$$TP\% = \frac{L - M}{L + M - 2} \times 100$$

Where L is the current distribution ratio and M is the metal distribution ratio of the near to the far cathodes.

The metal distribution or the thickness of the metal deposit was calculated using the Fischerscope X-Ray XUL machine. The current density at the high current density area was taken to be 33 A/dm² and at low current density area was taken to be 3 A/dm².

Hence, the current density ratio (L) was calculated as 11.

Reagent grade Tiron was used without any further purification.

The nanoparticles of SiO₂ were prepared in the laboratory. Colloidal silica or SiO₂ nanoparticles are produced by Sol-Gel process. The process involves hydrolysis and condensation of silica alkoxides in the presence of acid or base as a catalyst. (21) Various researchers have worked on the effect of concentration reagents on the average particle size. The chemicals used to perform the following experiment include tetraethyl orthosilicate, ethanol, ammonia and distilled water. To produce colloidal silica with average particle size of 20 nm the following concentration was taken: (22)

CHEMICALS	CONCENTRATION
ETHANOL	4 mol/L
TEOS (Tetraethyl orthosilicate)	0.045 mol/L
NH ₄ OH	14 mol/L
H ₂ O	14 mol/L

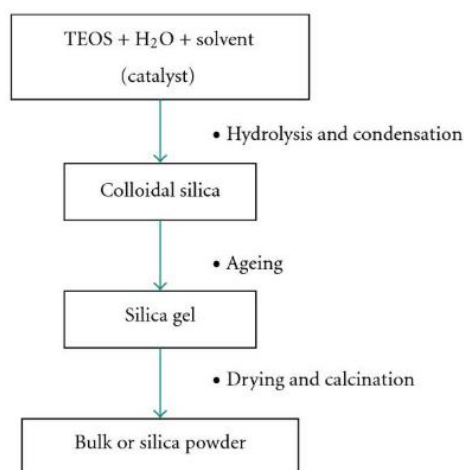


Figure 1- Preparation of SiO₂ nanoparticles. (21)

3. RESULTS AND DISCUSSION

The Hull Cell was used for measuring the throwing power of the acid chloride baths under variable plating conditions. The throwing power values of the acidic zinc plating baths calculated by Field's empirical formula under different plating conditions is shown in Table 1 (17)

3.1 EFFECT OF PLATING PARAMETERS

The throwing power of the solution enhances with an increase in Zn²⁺ ion concentration. This could be justified by the increase in the electrolytic conductivity (see Table 1) of the solution because of the increased Zn²⁺ ion content. Increasing the electrolytic conductivity, results in improved throwing power (18).

The throwing power is increased by an increase in current density. This could be justified by the cathodic polarization increment. Increasing temperature leads to an enhancement in throwing power and this is due to the increase in the electrical conductivity of the solution (see Table 1).

However, according to (39), in the case of Hull Cell the throwing power may not necessarily increase with an increase in average current. This is because in the Hull Cell, the current density values cannot be determined accurately because the cathode is at an angle to the anode, which rapidly changes the value of current density at any two points of the cathode. Therefore, when we increase the current supplied to the cathode, the current density at the High Current Density area increases by a larger amount as compared to the Low Current Density area.

There is no pronounced effect in the throwing power with increase in pH of Zn bath from 1 to 2.5. Increasing the pH to 4.5, on the other hand, improves the throwing power. The fact that electrical conductivity (Table 1) and cathodic polarization are reduced to some extent with higher solution pH contradicts this result. Cobalt electrodeposition from sulphate baths showed a similar effect. (19)

The values of throwing power and throwing index in Table 1 show that the computed values of TI vary in lockstep with the calculated values of TP. Because five experimental points are collected during the measurements of the throwing index, it is beneficial to express the results in the form of throwing index rather than throwing power. This reduces mistakes in measurement of any one point. In addition, a single value is derived that is representative of a variety of linear ratios. (17)

i ($A\text{dm}^{-2}$)	Temp ($^{\circ}\text{C}$)	pH	Time (min)	TP(%)	TI	κ ($\Omega^{-1}\text{cm}^{-1}$)
1.33	25	3.2	10	-14.9	0.76	0.40
1.33 ^a	25		10	15.9	1.37	0.47
1.70	25	3.2	10	14.3	1.33	0.40
2.70	25	3.2	10	24.0	1.57	0.40
1.33	40	3.2	10	1.27	1.04	0.41
1.33	50	3.2	10	19.0	1.41	0.43
1.33	25	2.5	10	-14.9	0.76	0.43
1.33	25	4.5	10	15.9	1.37	0.40
1.33	25	3.2	15	9.6	1.22	0.40

^a This bath contains 0.35M ZnSO₄ and 0.2M Na₂SO₄.

Table 1- Effect of some plating parameters on throwing power (TP) and throwing index (TI) for zinc electrodeposition (17)

3.2 EFFECT OF ADDITIVES

Organic additives play a significant role in electrolysis mechanisms such as grain refinement, crystal growth inhibition, stress reduction and leveling. There are two classes of brighteners - class 1 and class 2 which are also referred to as primary and secondary brighteners.

Surfactants, which comprise wetting agents, levellers, and grain refiners, make up the majority of the primary brighteners utilised. Organic chemicals such as aromatic and aliphatic aldehydes, ketones, sulphur-containing compounds, and alkyl aryl ammonium salts are secondary additives [brighteners] (12). Boric acid, nicotinic acid, and p-benzoquinone enhanced the brightness of the Zn deposit, indicating that they may be used as brighteners; however, they cause a small reduction in the solution's conductivity(23). Addition of dihydric alcohols such as ethylene glycol enhanced the cathodic current efficiency, hence giving a smooth zinc deposit (24). Additives including ethylene diamine, ammonia and acetonitrile have significant brightening effect, and influence the morphology and grain size of the zinc deposit (25-26). Organic additives including dimethylacetamide and DMSO have shown uniform deposit and better corrosion resistance (27).

Furthermore, by establishing a cationic complex with the metal ions, Ionic Liquids as an additive can promote charge transfer to the metal ions. Furthermore, due to the excellent charge transfer processes at the electrodes, ILs adsorption on the surface resulted in a smoother and brighter deposit. Studies have shown that using ILs as appropriate additives can change the character of the deposit in terms of particle size and shape. (28)

Thus, additives play an important role in improving the properties of electrodeposited material and their direct impact of properties like conductivity, and cathode current efficiency impact the throwing power as well. In an attempt to improve the macro-throwing power of acid zinc bath researchers have studied the impact of various additives on the throwing power of the bath.

3.3 EFFECT OF P-ANISIDINE AND DBS

One of the most successful and widely used techniques for improving both the quality of the deposits and the throwing power of electrolytic baths is to add organic chemicals (29)

These organic additions often have a polarizable or charged group that is based on Nitrogen or Sulphur. Surfactants and wetting agents are sometimes used to improve the quality of the bath. (30)

Because it influences the metal distribution over various regions of the cathode, cathodic polarisation is a significant component in determining the bath's throwing power (31)

It has been shown that the presence of DBS causes a significant shift in cathodic polarisation towards higher negative potential values, inhibiting Zn²⁺ ion deposit. The presence of both DBS and PA produces a bigger change in cathodic polarisation than the presence of either additive at the same concentration, indicating that Zn²⁺ ions deposition is hindered more. (32)

Researchers have reported that addition of PA or DBS to acidic zinc bath have resulted in improvement of the throwing power of the bath. When DBS is present, the throwing power rises by more than four times when compared to DBS-free bathing. The presence of PA, on the other hand, increases it by one-and-a-half times. The concentration of the additives used has no bearing on the gain in throwing power. The increase in throwing power might be ascribed to the additives' preferential adsorption on the cathode surface on especially active sites; growth at these places is therefore inhibited for the reduction of Zn²⁺ ions, resulting in an increase in throwing power. (17, 33)

Additives concentration	TP(%)	TI	κ ($\Omega^{-1}cm^{-1}$)
0.00	-14.9	0.76	0.40
$0.1 \times 10^{-3}M$ PA	1.3	1.03	0.40
$2.0 \times 10^{-3}M$ PA	7.4	1.18	0.40
$0.08 \times 10^{-3}M$ DBS	31.2	1.96	0.39
$0.15 \times 10^{-3}M$ DBS	51.0	3.13	0.37
$0.1 \times 10^{-3}M$ PA + $0.08 \times 10^{-3}M$ DBS	40.4	2.27	0.38

Table 2- Effect of PA, DBS and a combination of them on throwing power (TP) and throwing power index (TI) for zinc electrodeposition. Taken from (17)

3.4 EFFECT OF USING ZINC ALLOY PLATING PROCESS

Many Researchers have discussed that zinc alloys containing high amounts of zinc provide good corrosion resistance and protection due to its sufficiently negative potential as compared to steel (34). Usually alloys of Zinc with Nickel and Cobalt are used for electroplating application.

Studies have shown that throwing power was enhanced by 20 % when using a Zn-Co alloy bath in place of pure Zn bath. Further, the combination of additives with Zn-Co alloy bath enhanced the throwing power by 33% as compared to the pure Zn bath. Among different additives used in Zn-Co alloy bath, a combined additive of vanillin and Rochelle salt have enhanced the throwing power by 36%. (35)

For Zn-Ni alloy, current density is known to have a direct impact on the throwing power. For acetate Zn-Ni alloy bath, as the current density increases the throwing power of the bath also increases upto a maximum limit but decreases afterwards owing to the brittleness and non-uniformity of the deposit. As, current density the Zn-Ni alloy bath has shown decrease in the Ni concentration thus impacting the throwing power as well. Thus, increasing the current density from 1 A/dm² to 3 A/dm² the throwing power shows an increase of almost 5% but sharp decrease afterwards (36). Increasing the Ni concentration is known to directly increase the throwing power of Zn-Ni alloy bath (37).

Ni content in the bath, g L ⁻¹	Throwing power, %		
	3 A dm ⁻²	4 A dm ⁻²	5 A dm ⁻²
5-0	60-4	51-5	43-5
7-5	63-9	57-9	46-9

Table 3- Throwing power of alloy plating (37)

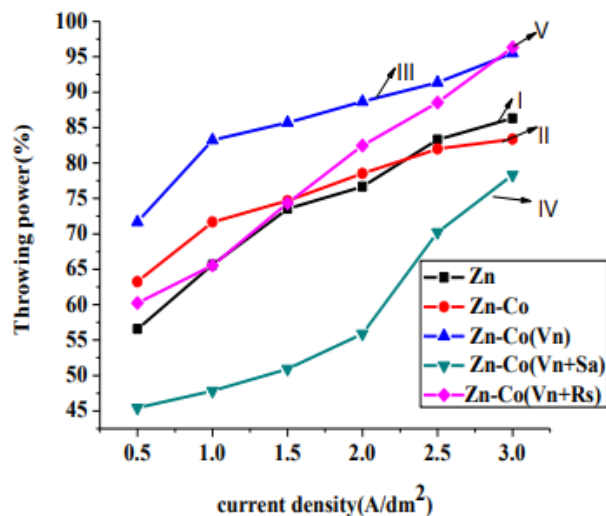


Figure 2- Graph of Throwing power v/s current density for Zinc and Zinc alloys as anodes. (18)

3.5 EFFECT OF USING TIRON AND COLLOIDAL SILICA

The below experiments were performed in the laboratory where different concentrations of tiron and colloidal silica were added in the acid zinc bath at different current readings. Their effect on throwing power of the acid zinc bath was further discovered.

Current (A)	Thickness at High Current Density area (μ)	Thickness at Low Current Density area (μ)	Throwing Power (%)
0.4	3.89	0.54	23 %
0.8	7.72	1.06	22.8 %
1.2	8.85	0.94	8.6 %
1.6	15.60	1.70	10 %

Table 4- Throwing Power % for Simple Acid Zinc plating solution without any additive at different values of current.

Concentration of Tiron (g/L)	Current (A)	Thickness at High Current Density area (μ)	Thickness at Low Current Density area (μ)	Throwing Power (%)
8 g/L	0.8	8.54	0.82	3.03%
16 g/L	0.8	7.71	0.847	10.48%
32 g/L	0.8	6.89	0.44	-18.86%

Table 5- Effect of different concentrations of Tiron at same current density on throwing power.

It can be observed from Table 4 that the highest throwing power % is obtained when the concentration of Tiron in the solution is 16g/L and an adverse effect is observed on further increasing the concentration tiron. Therefore, we fix the concentration of Tiron at 16 g/L for the experiment.

Concentration of Tiron (g/L)	Current (A)	Thickness at High Current Density area (μ)	Thickness at Low Current Density area (μ)	Throwing Power (%)
16 g/L	0.8	7.71	0.847	10.48 %
16 g/L	1.2	7.86	1.16	26.8 %
16 g/L	1.6	12.0	1.76	26.5 %

Table 6- Effect of Tiron (16g/L) at different values of current on throwing power.

Volume of Colloidal SiO ₂ (ml)	Current (A)	Thickness at High Current Density area (μ)	Thickness at Low Current Density area (μ)	Throwing Power (%)
0.5 ml	0.8	6.22	1.01	32 %
0.5 ml	1.2	9.89	1.82	60 %
0.5 ml	1.6	11.7	0.85	-12 %

Table 7- Effect of SiO₂/ Colloidal Silica (0.5 ml) at different values of current on throwing power.

Concentration of Tiron (g/L)	Volume of Colloidal SiO ₂ (ml)	Current (A)	Thickness at High Current Density area (μ)	Thickness at Low Current Density area (μ)	Throwing Power (%)
16 g/L	0.5 ml	0.8	6.60	0.63	27 %
16 g/L	0.5 ml	1.2	6.23	1.51	52 %
16 g/L	0.5 ml	1.6	14.1	2.3	32 %

Table 8- Effect of SiO₂/ Colloidal Silica (0.5 ml) and Tiron (16 g/L) at different values of current on throwing power.

Propriety Additive by a manufacturing company	Current (A)	Thickness at High Current Density area (μ)	Thickness at Low Current Density area (μ)	Throwing Power (%)
As per supplier	0.8	6.20	1.45	50 %
As per supplier	1.2	9.27	2.20	51 %
As per supplier	1.6	13.6	2.28	33 %

Table 9- Effect of propriety additive supplied by a manufacturing company at different values of current on throwing power.

Table (3) shows the throwing power of the simple acid zinc electrolyte without the addition of additives. It can be seen that the values of throwing power are very low which makes the addition of additives necessary. In Tables (5) and (6), it can be observed that the addition of Tiron and SiO₂/ Colloidal Silica significantly increases throwing power % of the acid zinc electrolyte.

On using the combination of Tiron and SiO₂ in table (7), it has been investigated that the values of throwing power reach up to 52 % at 1.2A making it the most suitable condition. These values of table (7) can be compared to the values in Table (8) where the propriety additive by a manufacturer of electroplating chemicals was used. The throwing power values are comparable and thus we infer that the Tiron and Colloidal Silica have a significant effect on the throwing power of the acid zinc solution.

4. CONCLUSIONS

The research article discussed the acid zinc plating process with a major focus on its throwing power. The Acid Zinc Bath is widely used in the plating industry. However, the low throwing power of the bath has forced industrialists to shift to alternative paths. Discussed here are some important plating parameters and additives, which when added can increase the throwing power of acid zinc bath. The throwing power has been observed to strongly depend on zinc ion concentration, pH, current density, temperature, and duration of plating (18). Various additives are being researched to further improve the throwing power of the bath. Additives such as p-anisidine and dodecyl benzenesulfonate have strongly influenced the throwing power and have helped to achieve better results even at lower current densities, which have been talked about in the article.

The effect of Tiron and Colloidal Silica on throwing power was also investigated. The effect of Tiron has slowed down the deposition of Zinc at higher current density areas leading to more uniform deposits. The effect of Tiron is profound. This is because it is divergent from the traditional strategy, where compounds were used such that they were absorbed in high current density areas to slow down the process (39).

Colloidal Silica has been employed in various baths because of its high corrosion resistance. Co-deposition of Silica has been found to increase the throwing power of Zinc-Nickel alloy plating from an acid sulfate bath (40). Similar results have also been achieved when combined with an Acid Zinc bath.

Thus, it can be concluded that the addition of both Tiron and Colloidal SiO₂ positively impact the throwing power of our targeted bath. When combined, the two were able to provide a smooth deposit with throwing power close to that of an acid zinc bath with proprietary additives. However, thorough research on the effect of these additives on surface morphologies, brightness, and long-term corrosion resistance would be vital in future work and their commercialization.

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