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The role of iron(III) and tartrate in the zincate immersion process for plating aluminium

S. G. ROBERTSON, I. M. RITCHIE*

A.J. Parker Cooperative Research Centre for Hydrometallurgy, Murdoch University, Western Australia 6150

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The zincate immersion process is a commercial process used to treat aluminium prior to electroplating. Superior zinc coatings are obtained through modifications to the original process. One such modification involves the addition of ferric chloride, complexed with potassium sodium tartrate, to the plating baths. This paper describes a detailed investigation into the function of these additives. It was found that the addition of tartrate alone did not significantly affect the rate of zinc deposition, the deposit morphology or the position of the aluminium or zinc polarization curves. This suggests that the role of tartrate is solely as a complexing agent to maintain iron (III) in solution. In contrast to this, the addition of iron(III)/tartrate had a marked effect on the reaction. It was found that iron(III) functioned primarily by reducing the size of the zinc crystals as they formed. This produces a thinner and more compact zinc immersion coating.

1. Introduction

The zincate immersion process is a commercial process used to treat aluminium prior to electroplating. The aluminium is immersed into an alkaline zincate solution where the oxide layer is dissolved. An intermediate zinc coating is then formed on the surface through displacement. A variety of metals including copper, nickel, silver and chromium may then be electroplated onto this coating [1, 2].

Despite having been used for many decades, the zincate immersion process still experiences a number of problems. The two of most concern are alloy sensitivity, which refers to the difficulty encountered with plating different alloy types, and the limited corrosion resistance of the final product. In a previous paper [3], it was shown that the displacement of zinc by aluminium is chemically controlled, meaning that the reaction is sensitive to the surface condition of the aluminium. This, therefore, highlights the cause of alloy sensitivity. The limited corrosion resistance of the final product has largely been attributed to the immersion coating itself. In 1950, Keller and Zelley [4] reported that the thinnest possible zinc coatings produced the best corrosion resistance. Thus considerable research activity has been directed towards limiting the amount of zinc deposited. Improvement in the coating characteristics has largely been achieved through modifications to the zincate immersion process. One of the earliest modifications was double dipping, in which the first immersion coating is stripped in acid and a second coating of superior quality is applied. Another is the addition to the plating baths of ferric chloride complexed with potassium sodium tartrate. A third is the use of 'modified alloy zincate' (MAZ) solutions (also known as the Bondal process). MAZ solutions contain a variety of cations and complexing agents, including ferric chloride and tartrate [5]. Of the three modifications, only the function of the double dip is understood. The role of the various additives in the ferric chloride/tartrate and MAZ modifications has been studied in detail, but no consensus has yet been reached. This paper describes an investigation into the role of ferric chloride and potassium sodium tartrate in the zincate immersion process.

The addition of ferric chloride/tartrate to the plating baths is reported [1] to improve the corrosion resistance for the majority of electroplated alloys, give more uniform coverage in subsequent electroplating baths and allow a greater operating range for the double dip technique. The use of the ferric chloride/tartrate modified solution has been studied quite extensively by a number of authors, particularly Zelley [6], Lashmore [7, 8] and Zipperian [9]. It has been found that the iron(III) added to the zincate bath is predominantly reduced to iron(II), with very little metallic iron being deposited in the immersion coating [10]. Zelley [6] reported that the addition of ferric chloride/tartrate to dilute zincate baths reduced the amount of zinc deposited. Although the benefits of the ferric chloride/tartrate addition are known, how ferric chloride affects the mechanism of zinc deposition is not well understood. Wyszynski [5] referred to ferric chloride as a 'grain refining substance' which inhibited the formation of needle-like zinc crystals, resulting in the formation of a smooth uniform coating. However, Zipperian *et al.* [10] reported that the zinc coatings were more crystalline in the presence of ferric chloride. There is, therefore, a need to determine how the addition of ferric chloride/tartrate affects the deposition of zinc.

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* Author to whom correspondence should be sent.

In a previous paper [3], the results from a study of the zincate immersion process, without any modifications, was presented. The reaction was studied utilizing the large body of knowledge that exists for cementation, or metal displacement, reactions. It was found that for the particular case of 0.1 M zincate, 3.0 M sodium hydroxide and at a disc rotation rate of 262 rpm, the cementation of zinc onto aluminium was chemically controlled with an activation energy of $35 \pm 7\,\mathrm{kJ\,mol^{-1}}$. In this paper, the results from an investigation into the effect of ferric chloride/tartrate on the cementation of zinc by aluminium are presented.

2. Experimental details

Reagents of analytical grade and deionized water obtained from a Millipore Milli-Q system were used in preparing the solutions. All electrodes were constructed from metals of 99.999% purity. The aluminium metal used in the kinetic measurements was supplied by Boyne Smelters Ltd, while the zinc and aluminium metals used in construction of the rotating disc electrodes were from the Aldrich Chemical Company. The zincate solutions were prepared from a concentrated stock solution of 1.0 M zincate and 15.0 M sodium hydroxide. The stock solutions were tightly sealed to minimize contamination by carbon dioxide. All solutions were deaerated with high purity nitrogen before the experiment commenced, and a nitrogen atmosphere was maintained for the duration of the experiment. A thermostated water bath was used to keep the experiments at the selected temperatures ± 1 °C. The addition of tartrate only and ferric chloride/tartrate was performed using a 60% (w/v) ferric chloride solution and followed the method outlined by the ASTM standard B 253–87 [1].

In the kinetic experiments, 250 mL of test solution was used. This was placed in an electrochemical cell and the 3.5 cm diameter aluminium disc mounted on the rotating disc apparatus described by Power *et al.* [11]. The disc was operated at the open circuit potential. The aluminium surface was pretreated by cleaning on various grades of silicon carbide paper and dipping in warm 1.2 M sodium hydroxide for 30 s. It was then rinsed with copious amounts of deionized water and immediately used in the experiment. At timed intervals, 1.0 mL samples were withdrawn and analysed using atomic absorption spectrophotometry.

Errors in the rate constants correspond to the 95% confidence interval.

For all electrochemical measurements, a saturated calomel electrode (SCE) was used as the reference electrode and all potentials reported are expressed with respect to this. The rotating disc electrodes were pretreated by cleaning with silicon carbide paper and rinsing with deionized water. For the mixed potential measurements, it was necessary to dip the electrode in warm 1.2 M sodium hydroxide followed by rinsing with deionized water to obtain reproducible results. The polarization experiments were carried out using a PAR 273 potentiostat. A scan rate of $1\ \mathrm{mV\ s^{-1}}$ was employed.

The morphology of the cementation deposits was studied using a Philips XL 20 scanning electron microscope. The effect of ferric chloride/tartrate additions on the electrolytic deposition of zinc was performed by immersing a rotating zinc electrode in 0.1 M zincate, 3.0 M sodium hydroxide and applying a potential of –1.80 V for a period of 4.5 min. The electrode was rotated at 270 rpm. The morphology of the zinc deposits formed in the presence and absence of ferric chloride/tartrate was compared.

3. Results and discussion

3.1. *Kinetic studies*

The effect of ferric chloride/tartrate on the cementation reaction was investigated by studying first the addition of tartrate only, and secondly the addition of varying concentrations of ferric chloride complexed with a given amount of tartrate. The kinetics of the reaction in the presence and absence of the various additives was monitored. Provided the volume change due to sampling is negligible, cementation reactions usually obey a first order rate equation of the type [12]

$$\ln\left(\frac{C_0}{C}\right) = \frac{kAt}{V} \tag{1}$$

where C_0 is the initial concentration of the precipitating metal (zinc), C is the concentration at time t, k is the rate constant for the reaction, A is the area of the reactant metal surface and V is the volume of the solution. For each of the kinetic runs, the fit of the experimental data to Equation 1 was tested. It was found that for all experiments conducted in the presence of tartrate and ferric chloride/tartrate, a linear relationship between $\ln(C_0/C)$ and time was observed, with the correlation coefficients for these lines lying in the range 0.991 to 0.997. Thus the cementation of zinc from an alkaline solution by aluminium is a first order process even when tartrate and ferric chloride/tartrate have been added to the solution.

The effect of the additives on the cementation reaction is reflected in the values of the first order rate constant. Figure 1 shows the plot of the rate constant as a function of the concentration of ferric chloride added. It can be seen that the rate constant determined in the presence of tartrate only is not significantly different to that obtained in the absence of all additives (▲). Thus the addition of 48 mM tartrate did not alter the kinetics of zinc cementation. Zelley [6] reported that the addition of ferric chloride/tartrate to dilute zincate solutions reduced the amount of zinc deposited. It can be concluded from Fig. 1 that the addition of tartrate alone is not responsible for this change.

By contrast, the presence of ferric chloride/tartrate significantly decreased the value of the experimental

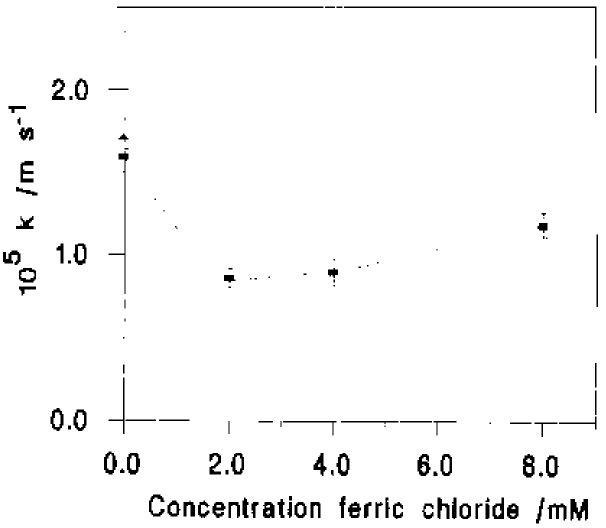

Fig. 1. First order rate constant, k, as a function of the concentration of ferric chloride. Experimental conditions: 0.1 M zincate, 3.0 M sodium hydroxide, 22 °C, $\omega = 262$ rpm. All solutions contain 48 mM tartrate, except (▲) = 0 mM tartrate.

rate constant. Therefore it is ferric chloride, even when present at low concentrations such as 2 mM, which is responsible for the changes in the cementation reaction. Interestingly, Fig. 1 shows that there is a small increase in the value of the rate constant as the concentration of ferric chloride is progressively increased from 2 mM. It was not possible to determine experimentally if this represented a trend as ferric chloride could not be maintained in solution, at the given concentration of tartrate, above 8 mM. However, the results reported by Zipperian [9] indicate that there is no trend.

3.2. *Deposit structure*

The cementation deposit formed in the absence of tartrate and ferric chloride/tartrate was dark grey, spongy, nonadhesive and non-cohesive. In the presence of 48 mM tartrate, no significant change in the deposit morphology was observed. In contrast to this, the zinc coating formed in the presence of ferric chloride/tartrate was quite thin and a fine grained, and not spongy. The deposit was not however, coherent or adherent. The improvement in morphology observed in the presence of ferric chloride is consistent with the kinetic measurements. It should be noted that the cementation deposit formed in 0.1 M zincate, 3.0 M sodium hydroxide and 3.0 M sodium chloride was spongy. nonadhesive and noncohesive. Therefore the beneficial effect of ferric chloride on the morphology is due to the presence of the iron(III) ion and not the chloride ion.

3.3. *Mixed potential measurements*

The change in the mixed potential of an aluminium electrode with time has been shown to assist with determining the mechanism of zinc cementation on aluminium [13]. Appropriately, the changes in the mixed potential recorded in the presence of tartrate and iron (III)/tartrate were compared with the results obtained in the absence of these additives. Interestingly, there was no significant difference between any of the mixed potential traces recorded, indicating that the effect of iron(III) could not be determined in this manner.

3.4. *Evans' diagrams*

An Evans' diagram for a cementation reaction consists of the superposition of the cathodic polarization curve of the precipitant metal (zinc) and the anodic polarization curve of the substrate metal (aluminium). As shown in the previous paper [3], Evans' diagrams are useful for interpreting the effect of changing experimental conditions on the cementation of zinc by aluminium. Consequently they were again constructed to study the effect of tartrate and iron(III)/tartrate additions.

It was found that the addition of 48 mM tartrate did not alter the position of either the zinc or aluminium polarization curves. This implies that the sole purpose of tartrate is as a complexing agent to maintain iron(III) in the alkaline solution. The result contradicts the finding of Zipperian [9], who reported that tartrate enhanced the rate of aluminium dissolution at sodium hydroxide concentrations greater than 2.5 M, but it is consistent with the results obtained from the kinetic and morphological studies. Thus the addition of tartrate alone does not affect the cementation of zinc.

The effect of iron(III)/tartrate on the zinc and aluminium polarization curves is shown in Fig. 2. Lines z_1 and z_2 show the zincate reduction polarization curves recorded in the presence of tartrate and iron(III)/tartrate respectively. Likewise, lines a_1 and a_2 show the aluminium oxidation polarization curves obtained with the addition of tartrate and iron(III)/ tartrate respectively. It will be noted from Fig. 2 that in the absence of iron(III), the intersection of the zinc (z_1) and aluminium (a_1) polarization curves occurs in the diffusion limited region of the former. This suggests that the cementation reaction is diffusion controlled when in fact the reaction has been shown to be under chemical control [3]. The reason for this inconsistency is believed to be due to difficulties with simulating the cementation reaction. Specifically, the polarization curves were recorded using clean, flat electrodes. In the cementation reaction, the zinc deposit blocks part of the substrate and thus aluminium dissolution occurs from a reduced area. This will depress the aluminium curve to lower currents. A further problem is that the anodic polarization curve does not solely represent the dissolution of aluminium as hydrogen evolution occurred concurrently in this potential range.

Despite these limitations, the Evans' diagram shown in Fig. 2 is useful for interpreting the effect of iron(III) on the cementation reaction. It can be seen that while the position of the zincate reduction polarization curve is not greatly altered, the alumi-

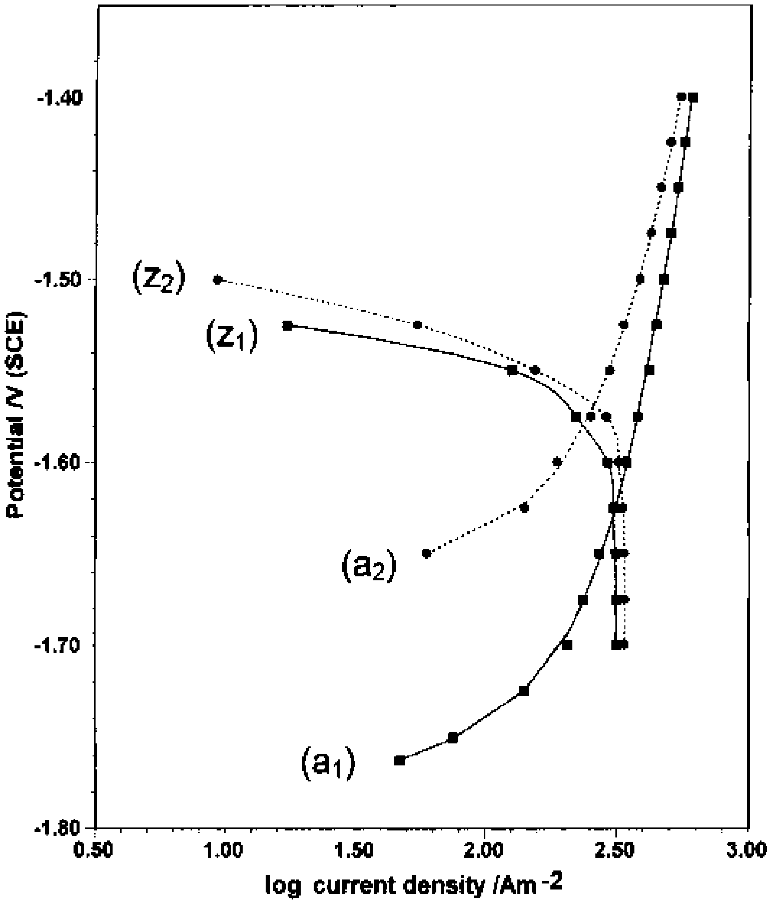

Fig. 2. Evan's diagram showing polarization curves for zinc and aluminium recorded in the presence of tartrate (z_1 and a_1, respectively) and ferric chloride/tartrate (z_2 and a_2, respectively). Experimental conditions: 3.0 M sodium hydroxide, 25 °C, ω = 270 rpm, 48 mM tartrate and for the zinc polarization curves, 0.1 M zincate. Curves z_2 and a_2 obtained in the presence of 4 mM ferric chloride.

nium curve has been shifted to higher potentials in the presence of iron(III). This is with the exception of very high anodic overpotentials where the polarization plots are similar. It can be seen that one consequence of the shift in the position of the aluminium oxidation polarization curve is that the intersection of the zincate reduction and aluminium oxidation polarization curves now occurs closer to the Tafel region of the former. Since the reaction is already under chemical control, for reasons as discussed previously, Fig. 2 can be interpreted as indicating that the presence of iron(III) forces the intersection of the two curves further into the chemically controlled region. Consequently the current density at which the two polarization curves intersect (i_{reaction}) is less and the rate of zinc deposition is reduced. This is consistent with the results obtained from the kinetic studies. The fact that the cementation reaction is chemically controlled, both in the presence and absence of iron(III), means that the mixed potential will be relatively insensitive to the reaction conditions, as found experimentally.

3.5. *Effect of iron(III) on the electrolytic deposition of zinc*

The results presented in the previous Sections show how the cementation reaction is affected by the addition of iron(III)/tartrate. It has been established that the rate of zinc deposition is significantly decreased and that the zinc coating produced is thin, reasonably smooth and fine grained. It was also observed that the zinc deposits formed on aluminium in the presence of iron(III) were smaller and more irregularly shaped than those deposited in the absence of iron(III). This suggested that iron(III) might be directly affecting the zinc electrocrystallization reaction. Accordingly, it was decided to investigate the effect of iron(III) on zinc electrodeposition in the absence of aluminium.

The effect of iron(III) on the deposition of zinc was studied using a simplified system. The zinc was deposited electrolytically at –1.80 V on a zinc electrode. This meant that no aluminate ions would be present and the amount of hydrogen gas evolved would be reduced as zinc has a higher hydrogen overpotential than aluminium in alkaline solutions [14]. A potential of –1.80 V was chosen as the mixed potential of an aluminium electrode when first immersed into a zincate solution containing iron(III) was approximately –1.80 to –1.90 V, and the initial stages of the cementation reaction have been shown [13] to play an important role in influencing the final deposit morphology. As deposition was effected using a high overpotential for an extended period of time

(4.5 min), the resulting zinc deposit was dendritic. It was found that the maximum size of the dendrites, their density and their shape when examined at higher magnifications, were useful criteria for determining the effect of iron(III).

The zinc coating formed in the absence of additives was found to consist of dendrites as large as 100 μm in length. The dendrite density was high. Examination of the deposit at higher magnifications (740× and above) showed that the tips of the dendrites were quite pointed and the edges of each side branch well detailed and defined (see Fig. 3). The arrows on the image indicate the regions of particular interest on the dendrite. In the presence of iron(III)/tartrate, the dendrites formed were found to be quite different, as illustrated by Fig. 4.

It should be noted that Fig. 4 was recorded at a magnification approximately 2.5 times that for Fig. 3. Significantly fewer dendrites were formed in the presence of iron(III)/tartrate and the maximum length of these was approximately 30 to 40 μm. Additionally, the dendrites were different in shape. As highlighted by the arrows in Fig. 4, the tips of the dendrites were more rounded and the edges of the side branches were smooth and not detailed. There are two possible explanations for the effect of iron(III) on the deposit morphology. The first is that the iron(III) adsorbed on the growing edges of the zinc dendrites, curtailing further growth. The second is that the iron(III) oxidized the most active zinc regions, i.e. where the crystals were growing most rapidly at the dendrite tips and edges. It is known [10] that iron(III) is predominantly reduced to iron(II) and so some oxidation reaction involving iron(III) is taking place.

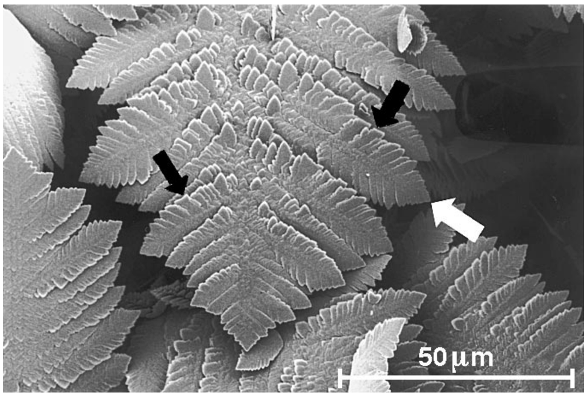

Fig. 3. SEM image of a zinc deposit formed electrolytically in the absence of ferric chloride/tartrate, at 740 × magnification. Experimental conditions: 0.1 M zincate, 3.0 M sodium hydroxide, 25 °C, $\omega = 270$ rpm, $E_{\text{applied}} = -1.80$ V for 4.5 min.

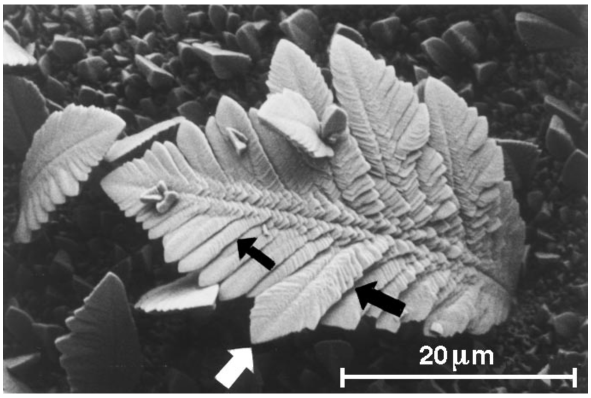

Fig. 4. SEM image of a zinc deposit formed electrolytically in the presence of 4 mM ferric chloride/ 48 mM tartrate, at 1993 × magnification. Experimental conditions: 0.1 M zincate, 3.0 M sodium hydroxide, 25 °C, $\omega = 270$ rpm, $E_{\text{applied}} = -1.80$ V for 4.5 min.

To discriminate between the two possibilities, zinc dendrites were grown in an unmodified zincate solution and either returned to the same solution or immersed in a solution containing iron(III). A potential of –1.80 V was applied in all cases. The characteristics of the dendrites formed in the absence and presence of iron(III) were then compared. It was found that the interruption to the applied voltage altered the shape of the dendrites formed in the absence of iron(III). However, the tips of the dendrites remained pointed and the edges of the sides branches were well detailed. In contrast to this, the dendrites formed in the presence of iron(III) were quite rounded and the edges of the side branches were smooth and not detailed. Thus the zinc dendrites have undergone chemical attack in the iron(III) solution. Although an adsorption effect cannot be ruled out, it would appear that iron(III) acts by oxidizing the edges of the dendrites, resulting in smaller dendrites. In addition, the presence of iron(III) would mean that the growth of new dendrites would be inhibited. Iron(III) would be expected to act in a similar manner on the spongy cementation deposits since these were found to have a degree of crystallinity [13]. Thus the addition of ferric chloride, complexed with potassium sodium tartrate, functions by reducing the size and growth of the deposited zinc crystals. In other words, as Wyszynski [5] correctly surmised, ferric chloride is a grain refining agent. It should be noted that the addition of 4 mM aluminate, the concentration present after 20 min immersion during the kinetic studies, did not affect the manner in which iron(III) altered the morphology of the dendrites.

4. Conclusions

The following conclusions can now be made:

(i) The addition of 48 mM potassium sodium tartrate to 0.1 M zincate, 3.0 M sodium hydroxide did not significantly affect the cementation kinetics, deposit morphology, mixed potentials or the position of the aluminium or zinc polarization curves. It appears that the role of tartrate is solely as a complexing agent to maintain iron(III) in the alkaline solution.

(ii) The addition of low concentrations (2–8 mM) of ferric chloride, complexed with tartrate, decreased the value of the first order rate constant by a factor of 1.5 to 2.0. The zinc deposit obtained was reasonably compact and smooth, brittle and nonadhesive. The mixed potentials recorded with time and the zincate reduction polarization curves were, within an experimental error of 20 mV, unaffected by the addition of iron(III). However the aluminium polarization curves were shifted to more positive potentials.

(iii) Iron(III) acts by oxidizing the edges of the zinc crystals deposited during the cementation reaction. This inhibits the growth and formation of the crystals, thus producing a more compact deposit. Adsorption of iron(III) may also play a role in restricting crystal growth.

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