EFFECT OF SURFACE ROUGHNESS OF 316L STAINLESS STEEL ON PITTING CORROSION INITIATION AND REPASSIVATION

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الملخص

خشونة السطح (R_a) للحديد المقاوم للصدأ من الخواص السطحية المهمة التي يجب أَن تؤخذ بعين الاعتبار عند إختيار هذا الصنف من الصلب للتطبيقات المختلفة. وترتبط هذه الخاصية بنوع المعالجة السطحية، وهى من بين الخواص السطحية التي لها علاقة بمقاومة التآكل فى الأوساط التآكلية .

وتهدف هذه الدراسة إلى تقييم معامل خشونة السطح أثر عمليات المعالجة السطحية للصلب، وتأثيره على نشوء التآكل النقري للصلب المقاوم للصدأ   (الصنف الأوستنايتى) (AISI316L (UNS 31603) والذي يعد من أكثر أنواع الصلب المقاوم للصدأ استعمالاً في العديد من التطبيقات خصوصا تلك التي تتطلب مقاومة عالية للتآكل بسبب وجود وسط قاس مساعد على التآكل مثل الأوساط الموجودة في الصناعات الكيماوية والصناعات الغذائية وكذلك التطبيقات الطبية. إلا أنه تحت ظروف معينة يكون هذا الصنف من الصلب عرضة للعديد من أنماط التآكل الموضعي مثل التآكل النقري والتصدعي. فى هذه الدراسة جرى إستخدام طريقة الاستقطاب المتغير(potentiodynamic polarization) وقياس معدل تغير جهد التآكل لأجل قياس المعاملات الكهروكيماوية لعينات الاختبار في تركيزين مختلفين من محلول كلوريد الصوديوم . تم تقييم أداء أسطح الصلب المقاوم للصدأ والمعالجة بطرق الكشط والتلميع وكذلك الأسطح المعالجة كيميائيا فى محاليل لكلوريد الصوديوم، عند قيم لمعامل خشونة السطح تتراوح ما بين 0.01 الى 6 ميكرون . وقد أختير هذا النطاق من الخشونة السطحية ليغطي مدى واسع من التشطيب النهائي للعديد من التطبيقات الصناعية

أشارت قياسات جهد التآكل إلى أقل إنحراف في جهد التآكل (E_{corr}) للعينات المعالجة ميكانيكيا إاى إنخفاض مستمر لقيم الجهد عند بدء القياس مما يشير إلى تحلل طبقة الأكسيد المتكونة على السطح. أما بالنسبة للعينات التي عولجت كيميائيا فقد سجلت قياسات الجهد أرتفاع مستمر ينبيء بأستمرار تكوين وتطوير بنية طبقة ألأكسيد.

وقد بينت نتائج الدراسة بأن درجة الخشونة ($R_a = 0.25 \ \mu m$) هى الحد الأدنى لحماية سطح الصلب من استمرار نمو النقور (التآكل النقري) فى محلول الاختبار بتركيز 1000 ppm عند درجة 30 °م وأن القيمة المناظرة عند درجة 50 °م هي ($R_a = 0.20 \ \mu m$) . كما أشارت نتائج الدراسة الى أن الدرجات المختلفة لخشونة السطح لعينات الصلب المقاوم للصدأ الصنف الأوستنايتى AISI 316L لها تأثيرات متفاوتة على مقاومة الصلب للتآكل النقري والخمول السطحي (repassivation). وبصفة عامة أبدت الأسطح الأكثر نعومة مقاومة للتآكل بدرجة أعلى من الأسطح الخشنة .

ABSTRACT

For stainless steel, surface roughness is an important surface property that should not be overlooked during material selection. This property is related to the type of surface treatment applied to metal surface. It is among other surface qualities which affect the stainless steel resistance to corrosive environments.

This study deals with the evaluation of surface roughness parameter, R_a, and its effects on initiation and propagation of pitting corrosion of stainless steel. Austenitic stainless steel, type AISI 316L (UNS S31603), was chosen as the test material due to its wide range of application in food, chemical and pharmaceutical industries. In addition to evaluation under freely corroding conditions, both potentiostatic and potentiodynamic polarization were used for the determination of electrochemical parameters of tested steel in aerated 1000 and 1500 ppm chloride solutions. The corrosion performance was evaluated under ground, polished, passivated and pickled surface finishing conditions. A range of surface roughness between 0.01 and 6 microns has been selected to cover a wide range of industrial finishes that are applied to stainless steel surfaces.

The open circuit potential measurement for mechanically finished steel surface showed an initial dissolution stage, suggesting adsorption of chloride ions on the surface which makes the film less protective. For the rest of tested surface conditions, i.e., passivated, pickled, and as received surface finish, a continuous increase of corrosion potential in the noble direction was noted. This electrochemical behavior suggests an improvement of the properties of surface oxide film formed on steel under these surface treatment conditions. It has been proven that a minimum surface roughness value better than R_a=0.25 micron is required to re-establish passivation on steel surface in 1000 ppm chloride containing water at 30 ºC. Under similar test conditions, except higher testing temperature (50°C), the surface finish must be better than R_a= 0.20 micron.

The data obtained in this work showed that different degrees of surface roughness on finished 316L stainless steel induce differential (not equal) effects on pitting and repassivation potentials. Furthermore, a smoother surface finish has exhibited improved resistance to pitting where nobler breakdown potential values were recorded.

KEYWORDS: Repassivation potential; Pitting potential; Surface roughness; Stainless steel; Surface finish.

INTRODUCTION

During fabrication, the stainless steel is subjected to additional operations such as forming, machining, grinding, welding, etc. All of these processes affect the steel surface properties in various aspects; for instance, surface roughness, geometry, morphology of passive layer and residual stresses are all affected. These surface properties have a determining effect on the stainless steel resistance to pitting corrosion. In welding, Cr/Fe ratio is disturbed and hence the composition of the passive layer is also altered. Thus, in such cases the steel must be passivated in order to restore its surface properties. Besides passivation, stainless steel surface is also pickled, ground or electropolished depending on fabrication process or ultimate usage. The susceptibility of stainless steel to the initiation of localized corrosion in chloride-containing solutions is affected by many parameters: Chloride-ion concentration, temperature, pH, and surface finish are some of the most important of these. In particular, the effect of surface

finish on resistance to pitting corrosion was of considerable interest for many researchers [1-4, 5, 6-8] in the past three decades. Turnbull [9] has introduced the concept of cyclic polarization scan for the determination of pitting corrosion propagation resistance. The results of his study emphasized the importance of surface finish when selecting materials for a particular application. The study has indicated that cold rolled sections had a superior corrosion resistance to other finishes, followed by ground, hot rolled and pickled finishes. Later on, the work carried out by Silverman [10] has dealt with the concept of protection potential or repassivation potential and its relation to the propensity of passive metals to localized attack in the form of pitting or crevice corrosion. Silverman suggested that the value of pitting (E_{pit}) and protection or repassivation potential (E_{prot}) are not intrinsic properties of the alloy alone but are also functions of the experimental variables (scan rate, position of potential reversal, the size of pits formed and surface roughness) and the environment. Nielsen et al [1] have investigated the effect of electropolishing on pitting corrosion resistance of seamless EN 1.4404 stainless steel tubing. They concluded that electropolishing is well able to remove short range irregularities and thus improve corrosion resistance. Honess [4] has pointed out the importance of surface finish in the design of stainless steels. He presented results of an extensive study program carried out by British Stainless Steel to determine the effect of using different polishing grits on corrosion resistance of stainless steel. The consequence of this study was the development of a new surface finish description designated as 2K surface finish in EN10088-2 [11] Standard. Mathiesen and Frantsen [12] reviewed the relationship between the surface condition and corrosion properties of stainless steel used in breweries, dairies and pharmaceutical processing plants. To date, few studies have investigated the effect of surface roughness on the repassivation behavior of 316L stainless steel in chloride- containing waters. Thus, the objective of this study was to investigate the role played by surface roughness in affecting the pitting initiation and repassivation behavior of stainless steel in chloride-bearing waters.

Materials and Methods

AISI 316L stainless steel (UNS S31603) cold rolled and annealed 4.0 mm thick plates were procured from the industrial research center in Tripoli. The steel composition in wt.% was determined by spark emission spectroscopy and is given in Table (1).

Table 1: Chemical composition of tested 316L Stainless Steel, wt.%

Element	C	Cr	Ni	Mn	Si	Mo	S	P	N	Cu	Fe
Wt.%	0.03	17	10.4	1.56	0.33	2.1	0.02	0.025	0.03	0.19	balance

This steel grade was chosen as test material because it is one of the most commonly used stainless steels in chemical, food and pharmaceutical industries. Disc shaped samples 4 mm thick; 15 mm in diameter were cut by electric discharge machining (EDM). The employed sample holder permitted a 1.0 cm^2 exposed area of disc sample during exposure to test solution.

Five types of surface finishes were selected for the investigation of the 316L stainless steel response in chloride-bearing waters under simulated test conditions. The required surface treatment to produce the desired surface finishes are given in Table (2)

Table 2: Type of surface finish produced and the required surface treatment

Surface finish	Required Surface treatment
Ground	finished on grit 80 SiC paper grinding
Polished	Finished with alumina paste
Citric acid passivated	finished on grit 1000 SiC paper, followed by passivation in 10 % citric acid solution, at 60°C for 10 min.
Chemical polish	finished on grit 1000 SiC paper, followed by immersion in 4parts HNO_3,1part HCl,1 part H_3PO_4, 5 parts acetic acid at 70°C for 3 min.
Pickled	finished on grit 1000 SiC paper, followed by pickling in 25% HNO_3 + 8% HF acid solution at 60°C for 30 min.

Roughness Measurement

Cleaned samples of finished stainless steel were analyzed with Taylor Hobson 3^{+} profilometer to determine the surface roughness parameter, R_a. The Stylus was moving in longitudinal and transverse directions over the entire sample surface. Four to five random areas on each sample were analyzed and used to calculate, R_a, the arithmetic average roughness.

Electrochemical Investigations

The electrochemical tests were performed with ACM potentiostat, Model Gill12, V5 PC compatible, using saturated calomel electrode (SCE) as the reference electrode and graphite rod as the counter electrode. The reference electrode was interfaced to the test solution via a salt brige filled with test solution. The bridge was connected to a luggin probe tip of porous glass that terminated about 2 mm from the working disc electrode. The sintered glass tip provides minimal liquid leakage rates and ensures good electrical contact. The Teflon sample holder allowed 1 cm^2 of sample surface area to be exposed to test solution. Corrosion tests were performed in naturally aerated 1000 and 1500 ppm chloride-containing waters at 30, 50 and 70°C. These levels of chloride test solutions were chosen to yield solutions of mild to moderate corrosive environments. Cyclic polarization measurements were carried out on surface finished stainless steel at 1 mV/s scan rate. The voltage of the working electrode with respect to the reference electrode was stepped in the anodic direction from just below the corrosion potential ($E_{corr.}$) till the recorded current density exceeds 2 mA/cm^2 or the potential exceeds 1000 mV (SCE). Then the potential is reversed in the backward direction until the current density drops to or below the recorded passive current density. Open circuit potential measurement was used to determine corrosion potential stabilization in test solutions at various test temperatures for 1800 seconds. All measured potentials are referred to saturated calomel electrode.

RESULTS AND DISCUSSION

Analysis of Surface Roughness data

On finished stainless steel, the average roughness R_a is affected by the grit size number. As given in Table (3) a decrease in measured R_a-value was noted as the grit size number increases. It has been reported [13] that further grinding beyond 600 grit size does not change measured roughness values appreciably. However, finishing the

steel surface on coarse grit size affects both surface roughness and the total depth of disturbed surface layer.

In this research work, average R_a values for the investigated stainless steel samples were in the range of 0.016 to 5.6 microns as shown in Table (3). This range of surface roughness has been selected to cover a wide range of industrial surface finishes which are applied to stainless steel surfaces. As it has been specified in the European standard [14] it can be intuitively deduced that the as received sample has 1D surface finish. This is because test samples were cut from 4mm plate which is usually annealed & hot rolled material. The results for surface roughness measurement were also in agreement with data presented in document 8 [15] of the European Hygienic Engineering and Design Group, EHEDG. For instance, the R_a value for ground sample (grit80) is 1.5 μm.

Table 3: Surface Roughness for finished stainless steel surfaces

Surface Finish	R_a,(micron) [a]	R_a, (micro-inches) [b]	R_z,(micron) [c]
As received sample	5.6	224	28.4
Ground(Grit 80)	1.5	60	6.3
Polished(grit 1000)	0.025	1	0.2
Citric acid passivated	0.065	2.6	0.5
Pickled	0.035	1.4	0.4
Chemical polished	0.016	0.64	0.3

a. Average roughness (R_a) of six measurements in longitudinal and transverse direction.
b. R_a, (micro-inches) $= R_a$ (μm) $\times$ 4o.
c. Mean roughness depth (R_z) of six measurements in longitudinal and transverse direction.

In document 8 of EHEG group the approximate R_a value for abrasive grit number 120 is 1 μm, and for grit size 60 is 3 μm. Also, the R_a value of the surface topography as a result of hot rolling is above four (> 4 μm). In Table (3) the measured surface roughness of as received specimen was 5.6 μm.

Pitting Initiation Resistance:

As shown in Figure (1) the break down potentials (E_b) for chemically polished sample ($R_a = 0.016$ μm) was 705 mV at 30^oC, but for ground finished sample ($R_a = 1.5$ μm) it was only 395 mV. All reported potentials in this work are referred to the saturated calomel electrode (SCE) unless otherwise stated. The corresponding E_b-values at 70^oC were 390 and 185 mV for chemically polished and ground finished samples respectively. These results indicate that the noblest potentials (higher resistance to pitting) were recorded on chemically polished samples.
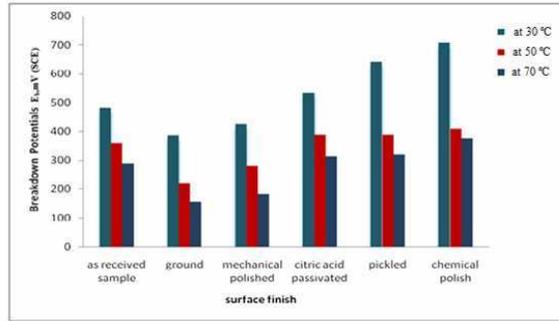
Figure 1: Variation of breakdown potentials in 1000 ppm Cl⁻ solution with finish at different temperatures

In contrast, the least noble pitting potentials were recorded on ground finished samples. Similar observations regarding the correlation between pitting or breakdown potentials and surface finish were noted during testing 316L stainless steel in 1500 ppm chloride solution as shown in Figure (2). The significant difference noted between breakdown potentials of differently finished steel surfaces can be attributed to the difference in surface topography. For instance, it can be inferred that ground surfaces may exhibit deep grooves where chloride ions can accumulate and reach the critical concentration necessary to destroy the passive film and thereby initiating pitting corrosion. On the other hand, chemically polished surfaces exhibited better degree of surface finish; $R_a = 0.016$ µm with eventual smooth surface and less chance for chloride ion accumulation.
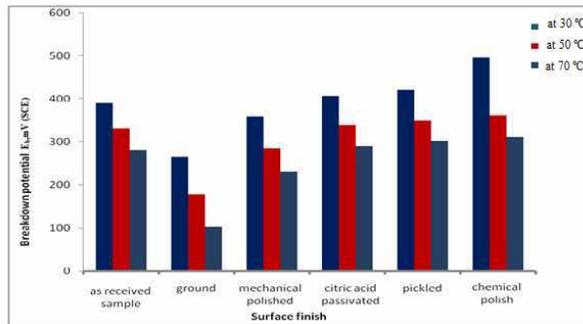

Figure 2: Variation of breakdown potentials in 1500 ppm Cl⁻ solution with finish at different temperatures

It should be noted that the quality of the passive film on stainless steel decides the corrosion resistance of the steel in a given media. For this reason, a semi-quantitative chemical analysis has been carried out, by use of energy dispersive x-ray spectroscopy, for the determination of elemental composition of surface films. The spectral analysis of surface finished samples showed strong peaks of Fe, Cr and oxygen. This is attributed to the formation of iron and chromium oxides in the passive layer. The degree of Cr enrichment in the passive layer of various finished samples is better displayed in Figure (3) after estimation of Cr/Fe ratio. In Figure (3) the highest Cr/Fe ratio of chemically

polished samples is evident. For other differently treated samples, the Cr/Fe ratio decreased in the following order: chemical polish > pickled > citric acid passivated > as received > ground.
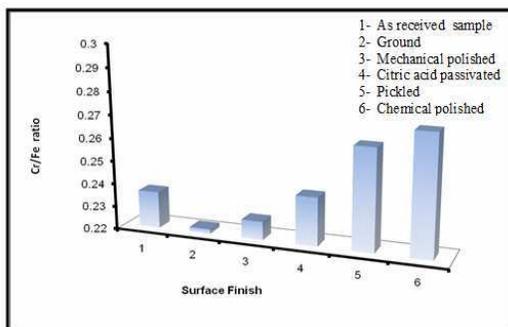

Figure 3: Cr/Fe ratio of the various surface finish treatments on 316 L stainless steel samples.

Correlation between corrosion Potential and repassivation Potential

From the set of potentiodynamic measurements carried out at $30^{o}C$ on various surface finishes of 316L stainless steel samples, corrosion potential (E_{corr}) and repassivation potential (E_{rp}) values were recorded and graphed as shown in Figure (4).
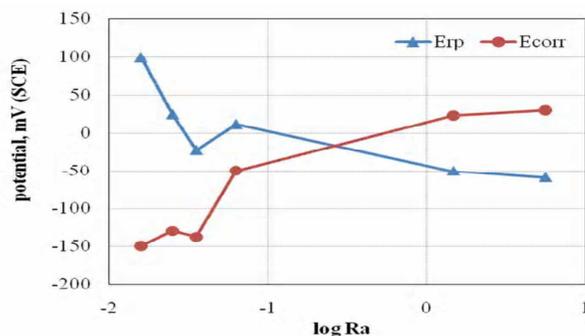

Figure 4: Dependence of repassivation behavior of 316L stainless steel on degree of surface finish at $30^{o}C$

The upper curve in this figure, with data points marked in triangles, represents the variation of repassivation potential as a function of surface roughness. All tested surface finishes have measured R_a- values as was given in Table (3). The lower curve, with data points marked in closed circles, shows the variation of corrosion potential with degree of surface finish. All potential values are reported with reference to saturated calomel electrode (SCE). Similar correlation between the surface roughness and these two electrochemical parameters (E_{corr} & E_{rp}) was obtained during testing at $50^{o}C$. The scattering noted in the measured E_{rp} and E_{corr} potentials was similar to that noted by Yang et al [16] and is considered normal for passive metal alloys, but the general trend is that repassivation potential shifts towards more active potential values, i.e, E_{rp}

decreases with increasing surface roughness. On the other hand, corrosion or open circuit potential (E_{corr}) shifts into the nobler direction, i.e, increases with increasing surface roughness. However, both data sets (curves) intersect at a point. At surface roughness values to the right of the point of intersection, the corrosion potential is nobler than the repassivation potential. This is an indication that the already started pits will not repassivate under these environmental conditions [17]. To the left of the point of intersection, i.e., at successively lower surface roughness values, any formed pits will repassivate.

When pitting does occur on passive metal surface such as stainless steel, there will be a competition between the rate of pit propagation and the rate of passivation. During the course of corrosion process, the bottom of the pit starts to repassivate when the metal potential decreases to the value of repassivation potential. The repassivation potential is important because it indicates whether the metal can passivate its surface again after corrosion initiation where the protective film has been damaged. It can be inferred from the measurement of the repassivation behavior of 316 L stainless steel in the present investigation that a minimum surface roughness value better than $R_a = 0.25$ μm is required to achieve protection against pitting corrosion at 30°C. Similarly, the minimum roughness value for no active pit propagation at 50°C is 0.20 μm. These results explain clearly the role of surface finish on corrosion and repassivation behavior of passive metals such as 316L stainless steel in chloride – bearing waters.

Variation of Corrosion Potential with Time

The open circuit potential (E_{corr}) versus time behavior was recorded for all tested stainless steel surface finishes. For ground surface finished samples, E_{corr} decreased continuously for the first 10 minutes of run to almost -73 mV (SCE) as shown in Figure (5). This suggests adsorption of Cl^- ions on the surface film which makes the film less protective.
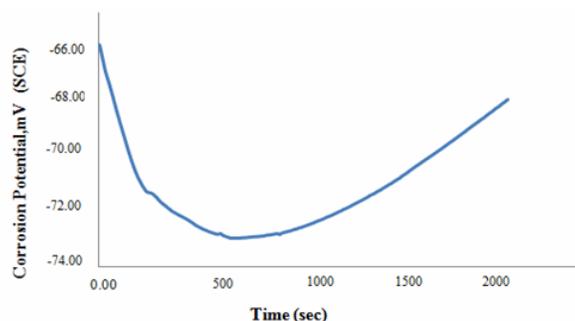

Figure (5) Corrosion potential-time of ground steel in aerated 1000 ppm Cl⁻ solution at 30 °C

For mechanically finished samples (e.g, ground finished sample) surface oxide film has grown in air before exposure to test solution. When chloride concentration reaches the critical value at the adsorbed site, film breakdown takes place and the oxidation reactions such as those shown below take place [8].

$$Fe \rightarrow Fe^{2+} + 2e \tag{1}$$
$$Cr \rightarrow Cr^{3+} + 3e \tag{2}$$

$$Ni \rightarrow Ni^{2+} + 2e \tag{3}$$
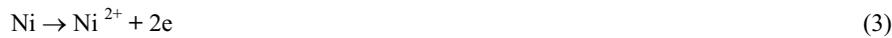
These reactions stimulate the necessary current for the cathodic dissolution of passive film [18] described by equation (4).

$$Cr_2O_3 + 6H+ + 2e \rightarrow 2Cr_2+ + 3H_2O \tag{4}$$

As the surface film is consumed and a new metal surface with normal content of Cr and Ni is exposed to the solution, a new film starts to grow which explains the increase in E_{corr} after the first ten minutes of immersion time. The gradual increase in open circuit potential persisted till the end of test run.

For the rest of tested surface conditions, i.e., passivated, pickled, and as received surface finish, a continuous increase of corrosion potential in the noble direction was noted. This electrochemical behavior suggests an improvement of the properties of surface oxide film formed on steel. The recorded shifts in open circuit potential are given in Table (4)

Table 4: Variation of corrosion potential for surface treated 316L stainless steel, immersion time =1800 seconds

Surface condition	Initial potential mV (SCE)	Final potential mV (SCE)	ΔV, mV
Citric acid passivation	-60.99	-39.25	21.74
Pickled surface	-25.31	-11.42	13.89
Chemically-polished surface	-74.61	-41.74	32.87
As received surface	-108	-92	16

The maximum potential shift (ΔV) was recorded for chemical polished sample. Under all surface conditions given in Table (4) no film dissolution is detected in the initial stage such as that on ground sample. Instead, a gradual increase in E_{corr} was noted suggesting that the film is not growing inside the testing solution.

CONCLUSIONS and RECOMMENDATIONS

The effect of some common surface finishes applied to stainless steel on the corrosion behavior in chloride-bearing solutions has been investigated. The main observations from the electrochemical measurement and surface characterization have led to the following conclusions.

- The repassivation behavior of 316L stainless steel in chloride-bearing waters is a function of the degree of surface finish. It has been deduced that a minimum of $R_a = 0.25$ and 0.20 μm surface roughness values are required to achieve protection against pitting at 30 and 50ºC respectively under the simulated test conditions mentioned in the present work.
- Results of EDS analysis have proven that surface finish has a measurable influence on the degree of Cr-enrichment in the surface film on stainless steel. For the investigated surface finishes, Cr/Fe ratio has increased in the following order: Chemical polished > pickled > citric acid passivated > as received > ground.
- Different levels of surface roughness on finished stainless steel surface induce differential (not equal) effects on pitting and repassivation potentials. Therefore, the steel corrosion resistance is related to surface roughness parameter besides the quality of the surface film.

- Cyclic polarization technique has been used to distinguish differences in the corrosion resistance between various surface finishes applied to a stainless steel. These differences are significant enough to allow ranking of various materials.
- When selecting stainless steel for many important applications such as chemical, food and biomedical applications, engineers are advised to pay attention to specifying the surface state (finish) rather than relying on selecting higher grades for better corrosion resistance. This is recommended for better utilization of the merits of this very important engineering material.
- The surface films grown on stainless steel after chemical surface treatment persist growing under freely corroding conditions with no initial dissolution. In contrast, surface films grown after mechanical treatment show an initial dissolution stage.

ACKNOWLEDGEMENTS

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