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Surface energy and chemical characteristics of interfaces of adhesively bonded aluminium joints

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The deleterious effects of water on the physico-chemical aspects of the durability of adhesively bonded aluminium joints has been investigated. Emphasis was placed on analytical techniques that lead to the better understanding of changes induced at the metal/epoxy interface by the presence of water. Analytical techniques such as contact angle measurements, X-ray photoelectron spectroscopy and X-ray diffraction were practical in obtaining information on the chemical composition and structure of the samples. Chemical conversion-coated samples were found to be much more stable in wet conditions compared to samples without conversion coating. The surface structure on the adherend, after extensive immersion times, was found to consist of a compact layer of bayerite with traces of gibbsite. The calculations of interfacial energy, γ_{sl}, and work of adhesion in dry and wet conditions, W_A and W_{Al}, were carried out to evaluate the maximum bond strength. It was found that the durability of the bond in the presence of water was quite high for the XD4300/6061-T6 joint systems.

1. Introduction

One of the most important characteristics of structural adhesives is the ability to retain a significant proportion of its load-bearing capability for long periods under the wide variety of environmental conditions encountered during its service life. Water, a commonly encountered environment, is considered to be one of the most hostile for structural adhesive joints.

To protect the structural aluminium components from the effects of water, an "artificially thickened" oxide layer is formed at the surface. Examples of widely used preparation procedures are the Forest Products Laboratory (FPL) process [2], the Boeing phosphoric acid anodize (PAA) process [3] and the chromic acid anodize (CAA) process [4].

The chemical conversion-coating method is most commonly used. Chemical conversion coating is an amorphous phosphatization process where the aluminium is treated with a solution containing phosphoric acid, chromic acid and fluorides. The chemical conversion coating is normally used as a primer for improved paint adhesion. The present study was undertaken to look further into the effects of water penetration on the epoxy, the treated aluminium surface and the metal/epoxy interface. In the hopes of contributing to the further understanding of the complex range of factors effecting the durability of aluminium joints exposed to water environments, several modern analytical techniques and conventional laboratory tests were performed on the individual components (adhesive and adherend) and joint systems. Analytical techniques such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction spectroscopy (XRD) and contact angle measurements were used to characterize the sample surfaces and interfaces.

2. Experimental procedure

The adherend material employed was Al–Mg–Si alloy, 6061-T6. The surface pretreatment steps included vapour degreasing, acid etching and chemical conversion coating.

Cured XD4300 adhesive film samples were prepared by gently spreading a controlled thickness of slightly heated epoxy on to commercial Alcan aluminium foil. The spread epoxy and foil were then placed in a convection oven to cure at 180 °C for 40 min. Immersing the cured samples in 10 M NaOH solution for 60 s to dissolve the foil backings resulted in free adhesive film samples.

The sessile drop method was used for determining the surface energy of each of the samples where the contact angles of calibrated fluids were measued with a Rame-Hart A-100 goniometer. The surface composition of each of the samples was determined by XPS analysis using a Surface Science M probe. Finally, the composition of the product of the surface treatments of the adherend were also determined by X-ray diffraction using a Philips PW1730 diffractometer.

3. Results and discussion

3.1. Surface energy measurements

The Kaelble plot method was used in determining the surface energy values for the solid samples [5, 6]. The

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equation used for the Kaelble plot is

$$\frac{W_A}{2\alpha_l} = \alpha_s + \beta_s\left(\frac{\beta_l}{\alpha_l}\right) \qquad (1)$$

where $\alpha = (\gamma^d)^{1/2}$ is the square root of the dispersive component of the surface energy, $\beta = (\gamma^p)^{1/2}$ is the square root of the polar component of the surface energy, W_A is the work of adhesion, and s, l are subscripts indicating solid and liquid. Because β_l, α_l were known and W_A experimentally obtainable, α_s and β_s were easily determined when $W_A/2\alpha_l$ was plotted against β_l/α_l for several known liquids.

These results were used to calculate the interfacial free energy, (γ_{SL}), which has been considered as an important factor in determining the strength of the joint. Levine *et al.* [7], Mittal [8] and Dyckerhoff and Steel [9] have claimed that the maximum strength of the joint is achieved when the interfacial free energy is at its minimum value (zero). The interfacial free energy can be calculated by the equation

$$\gamma_{sl} = \gamma_s + \gamma_l - W_A \qquad (2)$$

The thermodynamic work of adhesion under dry and wet conditions is represented as W_A and W_{Al}, respectively. Depending on whether these values are negative or positive, the stability of the interface may be predicted under each condition [10]. W_A and W_{Al} can be calculated as

$$W_A = 2[(\gamma_x^d\gamma_y^d)^{1/2} + (\gamma_x^p\gamma_y^p)^{1/2}] \qquad (3)$$

$$W_{Al} = 2[\gamma_L - (\gamma_x^d\gamma_l^d)^{1/2} - (\gamma_x^p\gamma_l^p)^{1/2} - (\gamma_y^d\gamma_l^d)^{1/2} - (\gamma_y^p\gamma_l^p)^{1/2} + (\gamma_x^d\gamma_y^d)^{1/2} + (\gamma_x^p\gamma_y^p)^{1/2}] \qquad (4)$$

where x and y are two different solid surfaces.

The results of the Kaelble plots were used to determine the surface energies of the solid surfaces with respect to a proposal which are found in Tables I and II. The surface energies of the pretreated 6061-T6 extrusion samples (Table I) seem quite low when compared with metal alloys. This is obvious when compared to the surface energy values of pure aluminium oxide [11].

Carre and Schultz [12] have assumed that the blue–green film, formed on the surface of the aluminium substrate after conversion coating (cc), has a chemical composition consisting of Al_2O_3, $2CrPO_4$, $8H_2O$. When dried, the coating consists of Cr_2O_3 and $AlPO_4$. Their results are also shown in Table I and indicate that the surface energy is somewhat lower than that of the Al_2O_3 but is high enough to adsorb many contaminants when exposed to the atmosphere.

The measurements of the surface energies of the samples with three different conversion coating times were quite consistent. The dispersive and polar components averaged around 27.5 and 4.2 dyn cm^{-1} (1dyn cm^{-1} = 10^{-3} N m^{-1}), respectively. Good dry adhesion and high water resistance are obtained when the dispersive component, γ_s^d, is high and the polar component, γ_s^p, is low.

After 188 days immersion at room temperature, all 6061-T6 samples, except for the case of vapour degreased only, showed increases in surface energy. It was interesting to note that the increase was only within the polar component of the surface energy equation.

The surface energy of the dry XD4300 free film is found in Table II. These results have similar values as the epoxy studied by Gledhill and Kinloch [10] also shown in the table. Like the substrate samples, the epoxy samples showed an increase in polar component of the surface energy after 203 days water immersion. It was previously mentioned that the interfacial energy, γ_{sl}, could be used as an indicator of the bond

TABLE I Surface energies of 6061-T6 extrusions after various surface treatments

Surface treatment(s)	Wet time (day)	γ_{sv}^d (dyn cm^{-1})	γ_{sv}^p (dyn cm^{-1})	γ_{sv} (dyn cm^{-1})
Vapour-degreased (VD)	0	15.4	31.7	47.1
	188	27.3	24.6	51.9
VD + acid-etched (AE)	0	26.9	2.3	29.2
	188	19.9	43.5	63.4
VD + AE + 10s (CC)	0	27.5	4.9	32.4
	188	24.5	31.0	55.5
VD + AE + 25s CC	0	26.0	4.8	30.8
	188	22.2	34.5	56.7
VD + AE + 40s CC	0	29.2	3.1	32.3
	188	24.8	30.7	55.5
Pure Al_2O_3 [11]		100	538	638
Conversion coating [12]		150	1.5	151.5

TABLE II Surface energies of XD4300 free film samples

Surface treatment(s)	Wet time (day)	γ_{sv}^d (dyn cm^{-1})	γ_{sv}^p (dyn cm^{-1})	γ_{sv} (dyn cm^{-1})
Free-side	0	27.5	2.5	30.0
	203	26.3	14.1	40.4
Gledhill and Kinloch [10]	–	41.2	5.0	46.2

strength. Dyckerhoff and Steel [9] made the following claims.

(a) The maximum strength of the joint is to be expected for systems in which the surface energies of the adhesive and substrate are equal.

(b) When the surface energies of the components are not equal, the decrease in strength is less for those systems in which the surface energy of the substrate is higher than the surface energy of the liquid. The decrease in strength is greater for those systems in which the surface energy of the solid is lower than the surface energy of the liquid. Table III shows the values of the γ_{sl} calculated from Equation 2 for the XD4300/6061-T6 system before and after immersion. All three conversion-coated joints would result in good dry bond strength because the values of γ_{sl} for each case are close to zero (maximum bond strength). The values of γ_{sl} for the immersed samples show a slight increase, which means that some decrease in bond strength should be expected. This decrease is due to the inequality of the surface energy between the substrate and adhesive. The magnitude of the drop in strength, however, is somewhat minimized because the surface energy of the substrate is higher than that of the adhesive as explained by Dyckerhoff and Steel (see (a)).

The joint durability or its stability in liquid environments can also be evaluated thermodynamically by calculating the work of adhesion. Table IV shows the calculated thermodynamic work, W_A and W_{Al}, of adhesion using Equations 3 and 4 for both dry and wet conditions, respectively. The results are similar for all three surface conversion coating times except for a slight decrease for the samples immersed in water. Because W_A and W_{Al} are both positive, the joint is stable under dry and wet conditions.

3.2. X-ray photoelectron spectroscopy

The atomic concentrations of each element found in the low-energy resolution spectrum of the 6061-T6 samples were plotted against the type of surface pretreatment applied on the adherends. The survey spectrum of 6061-T6 sample showed peaks of carbon, oxygen, aluminium, chromium and phosphorus. The results of these spectra of 6061-T6 samples are shown in Fig. 1. In the case of the vapour degreased (VD) surface, the significant amount of carbon (≈ 65%) on the surface indicates a large presence of contamination. This level of contamination on an aluminium alloy arises because a clean pure aluminium surface has a very high surface free energy and thus will adsorb contaminants such as hydrocarbons and nitrogen from the atmosphere.

TABLE III Interfacial energy calculations of XD4300/6061-T6 joint systems

Surface treatment	Wet time (day)	γ_{sl} (dyn cm^{-1})
VD + AE +	0	0.4
10s CC	188	3.3
VD + AE +	0	0.4
25s CC	188	4.7
VD + AE +	0	0.1
40s CC	188	3.3

TABLE IV Thermodynamic work of adhesion calculations of XD4300/6061-T6 joint systems with and without the presence of water

Surface treatment	Conditions	W_A (dyn cm^{-1})	W_{Al} (dyn cm^{-1})
VD + AE +	Dry	62.0	
10s CC	Wet		55.4
VD + AE +	Dry	60.4	
25s CC	Wet		55.4
VD + AE +	Dry	62.2	
40s CC	Wet		60.6

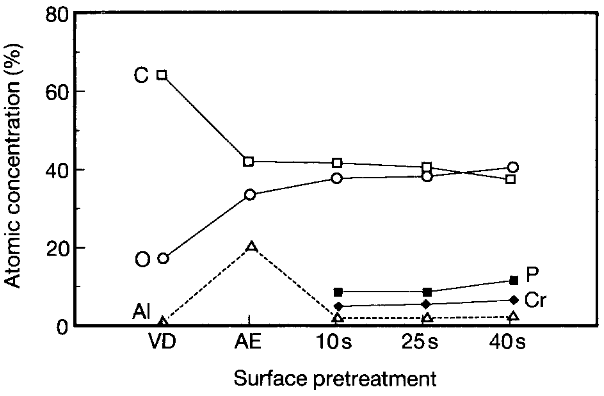

Figure 1 XPS results: atomic concentration for various surface pretreatments of 6061-T6 (dry).

Fig. 1 of the XPS analysis on dry substrate samples show the large relative quantity of contaminants such as carbon and oxygen present at the surface. These contaminants were probably adsorbed when the samples were exposed to the atmosphere during the drying period and during the time of contact angle measurement. Although the samples were contained in a vacuum desiccator during storage, exposure to atmosphere at certain times was inevitable. Therefore, part of the low surface energy results for the dry 6061-T6 samples may be attributed to surface contamination. The vapour degreased + acid etched surface has a lower amount of carbon and a higher amount of aluminium and oxygen, compared to the vapour degreased surface. This is to be expected because the contaminants have been dissolved and a new oxide film formed upon exposure to the atmosphere. The resulting oxide film consists of aluminium oxide which is less susceptible to atmospheric contamination.

The results for the three conversion coating times following degreasing and acid etching are very similar for the unexposed samples (Fig. 1). The atomic percentages of the various elements are ≈ 40% for oxygen and carbon, ≈ 10% for phosphorus, ≈ 5% for chromium, and ≈ 2% for aluminium. The phosphorus, in the form of $AlPO_4$, and the chromium, in the form of Cr_2O_3, are formed after conversion coating in alodine. Results in Fig. 2 were obtained after immersing all the adherend samples in distilled water

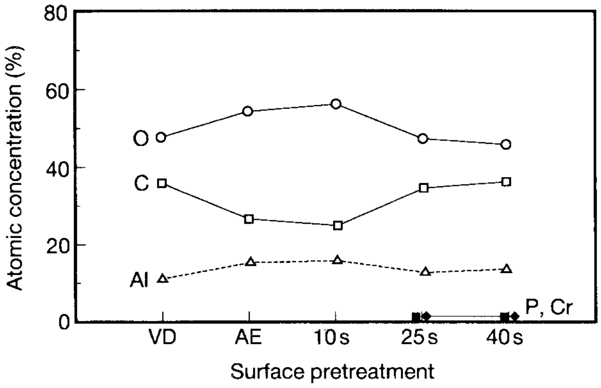

Figure 2 XPS results: atomic concentration for various surface pretreatments of 6061-T6 (77 days immersion).

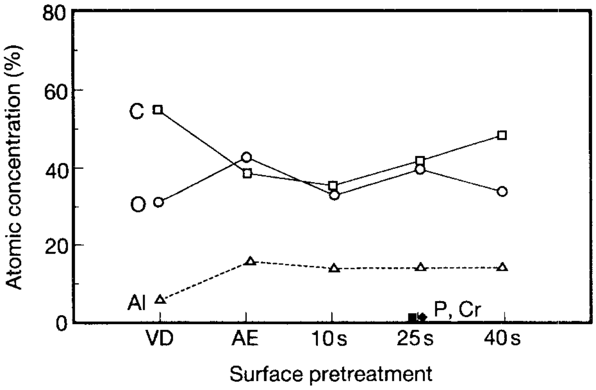

Figure 3 XPS results: atomic concentration for various surface pretreatments of 6061-T6 (188 days immersion).

for 77 days. In all cases, except for the vapour degreased sample followed by acid etching, an increase in oxygen and aluminium was observed with a decrease in carbon, phosphorus and chromium. These results are very similar to those found by Kinloch and Smart [13] for samples of aluminium alloy NE4 that were chromic-acid etched. After immersion in water, they also noted an increase in oxygen and aluminium and a decrease in carbon. The increase in oxygen may be related to the hydration of the $AlPO_4$ to $AlP \cdot nH_2O$ followed by the hydration of Al_2O_3 to $Al(OH)_3$.

Fig. 3 shows the XPS results of the 6061-T6 samples after 188 days immersion. The results indicate an increase in carbon and a decrease in oxygen, phosphorus and chromium as compared to the 77 days samples. Only the 25 s conversion-coated sample had traces of phosphorus and chromium. The decrease in phosphorus is probably due to the dissolution of the $AlPO_4$ by the presence of water. (Therefore, this local area of the 25 s conversion-coated sample may still show signs of water inhibition.) The atomic concentration of aluminium remains around 15% for the samples of increasing conversion coating times. This is similar to the results found after 77 days of immersion.

The XPS results of the XD4300 epoxy film sample are given in Fig. 4. There is very little change in atomic concentration increasing immersion times. There seems to be only a slight decrease in carbon and a slight increase in oxygen after 99 days immersion but the reverse is observed after 203 days immersion. The fluctuation of carbon and oxygen resembles those observed in the 6061-T6 samples.

Table V shows the oxygen and aluminium XPS spectra results at high-energy resolution for the 6061-T6 samples. Except for the vapour degreased + acid etched sample, there is very little aluminium detected for the dry samples. This probably reflects the high level of contamination which masks the presence of aluminium. It can be assumed, therefore, that the oxygen present on the suface is probably in the form of contaminants. The vapour degreased + acid etched sample would most likely possess an oxide thickness around 5 nm which is normally found on aluminium exposed to air. Because the depth of analysis using XPS is typically around 5–7 nm, aluminium both as oxide and from the substrate may have been detected. The spectra of aluminium and oxygen for all samples, after 77 and 188 days immersion, show the presence of aluminium mainly in oxide form. This correlates well with the XRD results.

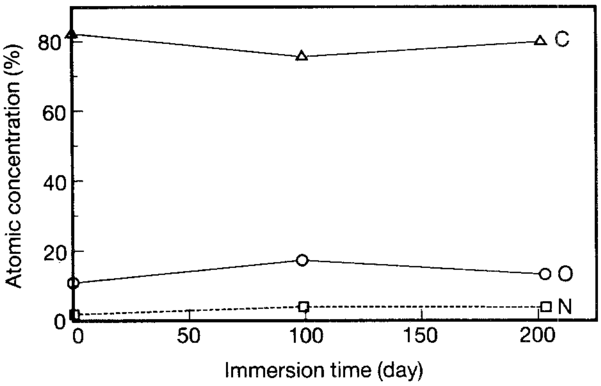

Figure 4 XPS results: atomic concentration of XD4300 for phase immersion times.

The carbon and oxygen spectra for the XD4300 epoxy film are shown in Table VI. Although there was very little change in atomic percentages of each element before and after immersion, the results indicate a change in chemical composition. This is evident from the difference in the number of carbon–oxygen bonds between the dry and wet samples. The dry sample shows the presence of only C–C and C–O bonds, but the immersed samples show an additional C=O bond. This seems to indicate that the interaction between water and adhesive results in the formation of a double bond of carbon and oxygen within the adhesive. This was expected because the water uptake for the XD4300 did not reach equilibirum after the long immersion time.

3.3. X-ray diffraction spectroscopy

The identification of the surface film on the dry 6061-T6 untreated extrusion samples was difficult to achieve due to the very small thickness of the surface film. The pretreatment steps of vapour degreasing and acid etching may likely form boehmite (AlOOH) and the conversion coating in alodine solution normally

TABLE V Multiplex spectra results of oxygen and aluminium for 6061-T6 samples

Surface treatment	Conditions	Peak Type			
		O^-	O^{2-}	Al (metal)	Al (ox ide)
VD	Dry	×			
	77 days	×	×	×	×
	188 days	×			×
VD + AE	Dry	×	×	×	×
	77days	×	×	×	×
	188 days	×	×	×	
VD + AE + 10s CC	Dry	×			
	77 days	×		×	×
	188 days	×			×
VD + AE + 25s CC	Dry	×			
	77 days	×	×		×
	188 days	×			×
VD + AE + 40s CC	Dry	×			
	77 days	×	×		×
	188 days	×	×		×

TABLE VI Multiplex spectra results of oxygen and carbon for XD4300 samples

Conditions	Peak type			
	O^-	C–C	C–O	C=O
Dry	×	×	×	
99 days	×	×	×	×
203 days	×	×	×	×

TABLE VII XRD analysis on 6061-T6 extrusion samples after 77 days immersion

Surface treatment	Signal intensity (net c.p.s.)	
	Gibbsite	Bayerite
VD	Not detected	2500
VD + AE	Not detected	2000
VD + AE + 10s CC	300	1800
VD + AE + 25s CC	150	850
VD + AE + 40s CC	100	600

TABLE VIII XRD analysis on 6061-T6 extrusion samples after 188 days immersion

Surface treatment	Gibbsite	Bayerite
VD	traces	bulk
VD + AE	traces	bulk
VD + AE + 10s CC	minor	bulk
VD + AE + 25s CC	minor	bulk
VD + AE + 40s CC	minor	bulk

forms a chromate (Cr_2O_3) and phosphate ($AlPO_4$) surface film.

The results in Table VII identified the surface layer of the adherend samples after 77 days immersion in water. The results indicate that bayerite is the major component of the oxide film for all surface treatments. There are also minor amounts of gibbsite for the samples that have been conversion coated. This agrees with the findings of Davis *et al.* [14] where the dissolution of $AlPO_4$ is followed by the hydration of exposed Al_2O_3 and results in the formation of bayerite. Raupach [15] has also reported that an aluminium sample developed a crystal structure of bayerite after extensive ageing in water at 25 °C.

The structure of $Al(OH)_3$ depends on pH, temperature, reagent concentration and other possible experimental factors. Brosset [16] has pointed out that an "α-gel" (a least stable substance formed on the aluminium) in a neutral or basic environment will convert to a "β-gel" (pseudo-boehmite) on ageing, and will eventually form boehmite (AlOOH). Raupach [15] reported that bayerite and gibbsite were the most stable substances formed in alkaline solutions while amorphous $Al(OH)_3$ and Al_2O_3 were the most stable in acid solution. Hem and Roberson [17] have found that bayerite was the most stable form of solid precipitate in the pH range 7.5–9.5. It is therefore not surprising to obtain XRD results which show that the majority of the surface precipitates consisted of bayerite.

The sequence of degradation on phosphated aluminium surfaces seems to follow the three steps proposed by Davis *et al.* [14]:

(i) adsorption of water by the surface $AlPO_4$ layer without change in morphology;

(ii) slow dissolution of the inhibitive phosphate followed by the rapid hydration of the freshly exposed Al_2O_3 to AlOOH with drastic change in morphology;

(iii) nucleation and growth of the bayerite phase. Although studies have indicated a formation of bayerite crystallites on top of the boehmite, it is not known whether the bayerite is converted from the boehmite via dissolution and redeposition or if it simply nucleates in the presence of boehmite.

Table VIII gives the XRD results on the same samples after 188 days immersion. These results are similar to those after 77 days immersion indicating the continued presence of bayerite at the sample surface. Hem and Roberson [17] have found that aluminium in natural water of pH 7.5–9.5 resulted in the formation of bayerite after 10 days. This explains why boehmite was not detected for our samples. The standard free energies of formation for boehmite, gibbsite and bayerite are 217.5, 272.3 and 274.0 kcal mol^{-1}, respectively. This shows that the bayerite phase is thermodynamically slightly more stable but these differences are small and can account for the variation of results that have been reported.

4. Conclusions

1. The sessile drop method of measuring the contact angle is a practical method for the selection of the adherend and adhesive to obtain the optimum bonding condition. Contact angles of known liquids were used to calculate the surface energies of the solid surfaces using the Kaelble plot method. The surface energy measurements allowed for the calculation, of the interfacial energy, γ_{sl}, and the work of adhesion in dry and wet conditions, W_A and W_{Al}, respectively. These calculations revealed that the maximum bond strength and good joint durability was achieved for the XD4300/6061-T6 joint system, where the adherend was conversion coated. There was no statistical difference between the values found for different conversion coating times. The surface energy calculations (Table III) show an increase in only the polar component of the surface energy upon exposure to room-temperature water.

2. The XPS analysis was useful in identifying the chemical composition, the oxidation state of elements and the types of chemical bonds present at the surface ($<$ 7 nm) of the material. Its high sensitivity in detecting surface elements contributed to the identification of the minor elements such as phosphorus and chromium near the surface. The analysis also revealed the presence of a high level of surface contamination on the conversion-coated 6061-T6 samples. This is due to the adsorption of low surface energy contaminants on to the high surface energy solid upon exposure to the atmosphere. The high-energy resolution spectra of carbon, oxygen and aluminium showed the changes in the type of bonding in the XD4300 and the oxidation state of the aluminium in the adherend. The conversion-coated 6061-T6 samples had an aluminium peak in the oxide binding energy region for both dry and wet samples. The XD4300 epoxy film showed the presence of C=O bonds after 99 and 203 days immersion as well as C–C and C–O bonds found in the dry samples.

3. The XRD analysis was significant in the identification of the surface films or the adherend. Although the discrimitation of the signals in the dry 6061-T6 samples was difficult, the identification of the surface film after 77 days and 188 days of immersion was found to be bayerite with traces of gibbsite. The difficulty found in the identification of the surface layer of the dry samples is due to the very thin surface layer resulting a very weak X-ray signal. The formation of bayerite after an extended immersion time confirm the findings of Hem and Roberson [17].

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