Hybrid Epoxy-Polyurethane Coatings for Improved Corrosion Protection of Aluminium

Zhafran Asyran Zainal Alam, Ammar Shafaamri, Iling Aema Wonnie Ma, Ramesh Kasi and Ramesh T. Subramaniam

Centre for Ionics, Department of Physics, University of Malaya, Kuala Lumpur 50603 Malaysia

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Abstract. A polymeric matrix consisting of epoxy resin and epoxidized soy bean oil (ESO) was prepared at the ratio of 90:10 to increase the anti-corrosion properties of epoxy. Water based epoxy and solvent based epoxy were used in this study for comparative study. Acrylic polyol was blended with the prepared epoxy/ESO and it was cured by using aliphatic polyisocyanate (NCO) to produce a hybrid of epoxy-polyurethane. The hybrid coating systems were prepared in different weight ratios of epoxy and polyurethane and were applied on aluminium panels. The thicknesses of the coatings were maintained around 90 to 110 µm. After curing, the coatings were characterized by using electrochemical impedance spectroscopy (EIS) to study its barrier characteristics and its performance against corrosion. Further test such as pencil hardness test, cross hatch test and pull-off test was run to study the adhesion of the coatings.

Keywords: Water based epoxy, solvent based epoxy, polyurethane, aluminium panels, EIS

I. INTRODUCTION

Aluminium is widely used as a component for aircrafts, ships, automobiles and railway carriages. A thin layer of aluminium oxide can be formed naturally on the metal surface which in turn makes it more stable compared to the metal itself against corrosion. However, reliable solutions are needed to prolong the lifespan of aluminium since the thin layer of oxide is unable to prevent corrosion in extreme corrosive environment which causes the metal to lose its structural, physical and chemical characteristics. In this regard, coatings are used to improve the corrosion protection of aluminium by forming a physical barrier thus isolating aluminium from the corrosive surrounding [1].

Epoxy resins are considered as premier selection in organic coating industry where the resins are used to formulate protective coatings for concrete and steel surfaces. Epoxy can be used to provide corrosion protection for aluminium since it has excellent electrical insulation, high adhesion, good scratch resistance and moderate water absorption [2]. Some drawbacks of an epoxy are low flexibility and poor resistance to crack propagation that may facilitate transfer of corrosive agents such as oxygen and ions to the surface of aluminium metals thus promoting the corrosion process [3]. Therefore, it is wise to modify epoxy or formulate it with other type of resins first.

Polyurethane resins (PU) are considered one of the newest material used in coating industry and have garnered significant attention for the past several years. In most commercial applications, polyurethanes are prepared from acrylic polyols and are known to have exceptional outdoor stability, fast curing speed and optimal balance of flexibility and hardness. PU can be formulated to produce coatings with high gloss finish and good mechanical properties. However, they have mediocre thermal properties thus limiting their applications [4]. Some work has been carried out where hybrid of epoxy and polyurethane resins (EPU) was shown to be able to produce a new coating system with significant increase in anti-corrosion properties [5].

Nowadays, interest in using eco-friendly materials in coating is growing due to increase in awareness of environmental problems, disposal of waste and deficiency of non-renewable resources. One example of an eco-friendly material suitable for coating is soy bean oil which is cheap, renewable plant-based natural oil and provides an excellent platform for functionalization [6]. Soy bean oil (ESO) used as modifier for epoxy resin has proven to produce a tough epoxy-based material at a lower cost. The formulated epoxy/ESO at weight ratio of 90:10 indicates superior mechanical characteristics and enhanced hydrophobic properties [7, 8]. Thus, this study aimed to produce a hybrid of polyurethane and epoxy which is modified with ESO to produce a high quality coating suitable for corrosion protection of aluminium metals.

II. EXPERIMENTAL

2.1 Materials

All chemicals in this research work were used as received without any additional purification. Water based epoxy resin (EPIKOTE 3520-WY-55A) with weight per epoxide of 485-555 and viscosity of 7,000-17,000 cP was supplied by Asachem (Malaysia). Solvent based epoxy resin (EPIKOTE 828) derived from bisphenol A and epichlorohydrin with weight per epoxide of 185-192 and viscosity of 11,000-15,000 cP at 25° C was obtained from Asachem (Malaysia). Acrylic resin (Setalux A 870 BA) with equivalent weight of 575 and viscosity of 3500 cP at 23° C was supplied by Nuplex (Malaysia). Polyisocyanate (Desmodur N 75 MPA/X) with 17% NCO content and viscosity of 250 cP at 23° C was supplied by Bayer Material Science (Malaysia). Epoxidized soy-bean oil (ESO) was obtained from East West Global Sdn Bhd (Malaysia). Dibutyltin dilaurate provided by Sigma-Aldrich (Malaysia) was used as catalyst and xylene (C8H10) from Evergreen Engineering & Resources (Malaysia) was used as a solvent.

2.2 Preparation of sample and coatings application

Aluminium substrates with dimensions of 75.0 mm (width) x 0.5 mm (thickness) x 50.0 mm (length) are cleaned using suitable amount of acetone to remove any grease, oil and stain. The cleaned aluminium substrates were then sandblasted. The prepared coating systems are applied subsequently on both sides of the sandblasted aluminium substrates. Residual of the prepared coating is poured on Teflon plates. All samples were left to dry at room temperature for 5 days.

2.3 Preparation of hybrid paint system

Water based resin and solvent based epoxy resin were blended separately with ESO at weight ratio of 90:10. Studies have proved that addition of ESO by 10% to 20% wt. increases the anti-corrosion properties of the epoxy [9]. Dibutyltin dilaurate catalyst and calculated amount of acrylic resin were added and then the mixture was subjected to magnetic stirring at a rotation rate of 350 rpm for 15 min followed by 700 rpm for 45 min. Stoichiometric amount of NCO was added into the mixture and stirred manually using glass rod for 5 min. 4 systems with different weight ratios were prepared as tabulated in Table 1:

TABLE 1. Composition of coating systems.

System	Epoxy type	ESO (wt. %)	Epoxy (wt. %)	Polyurethane (wt. %)
100P	-	0	0	100
90P10W	Water based	1	10	90
80P20W		2	20	80
70P30W		3	30	70
90P10S	Solvent based	1	10	90
80P20S		2	20	80
70P30S		3	30	70

2.4 Characterization techniques:

2.4.1 Dry Film Thickness

The dry film thickness of all the developed coating systems was determined via using digital Elcometer 456 Thickness Gauge. Five readings were taken for each sample and the average thickness was reported.

2.4.2 Electrochemical Impedance Spectroscopy (EIS)

EIS was used to study the barrier characteristics and performance of the developed coatings against corrosion. 3% NaCl solution was used at room temperature with frequency range of 0.1 Hz to 100 kHz and the test was carried out for 30 days by using Gamry PC14G300 potentiostat with faraday's cage to minimize noise.

2.4.3 Pencil Hardness Test

Pencil Hardness Test provides swift information on hardness of the developed coatings and its scratch resistance. Elcometer 501 Pencil Hardness Tester was utilized at room temperature by using pencils with varying hardness level, 6H (very hard) to 6B (very soft). The hardness of the developed coating was recorded as the grade of the pencil that did not leave any clear marking on the surface of the film.

2.4.4 Cross Hatch Test

Cross Hatch Test method was used to determine the adhesion of coating systems and the resistance of the coating systems to separation from substrates. Elcometer 107 Cross Hatch Cutter was utilized following ASTM D3359-B standards to produce two cuts at an angle of 90° to each other on the surface of the coating. Comparison was made between the crossed cut samples and the given ASTM Standards, at which 5B indicates high adhesion and 0B signifies poor adhesion.

2.4.5 Glossiness Test

Glossiness Test was used to measure the degree of specular reflection gloss for the developed coating systems. Novo-Gloss Lite Instrument was used to determine glossiness by measuring the reflected light after a light was incident onto its surface.

2.4.6 Pull-off Test

This test was designed to measure the adhesion of developed coatings quantitatively by fixing a loading fixture to each coating. Loading fixtures (dollies) were glued on the surface of the coating using Regular Araldite adhesive which was left to cure at room temperature for 24 hours. Elcometer 106 Adhesion Tester was used to pull-off the dolly to determine the force needed to pull an area of coating away from the substrate.

III RESULTS AND DISCUSSION

3.1 Dry Film Thickness

In order to investigate the dry film thickness of the all developed coating systems, Electrometer 456 was utilized and five different readings were recorded at different points of each sample. In Figure 1, the average values for the thickness of the coatings were illustrated. The results of dry film thickness test showed that the thickness of all prepared coating systems were in the range of 80 - 110 µm.

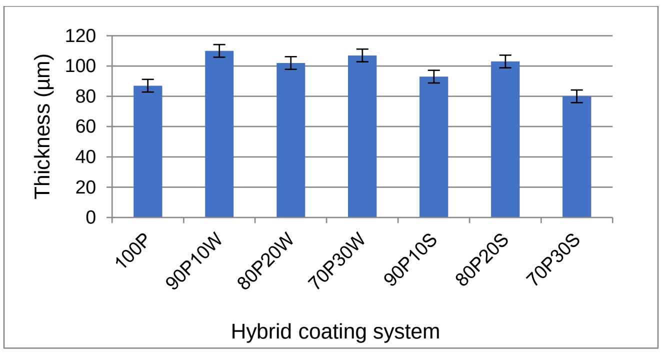

FIGURE 1. Thickness of coating systems developed.

3.2 Electrochemical Impedance Spectroscopy (EIS)

EIS studies were conducted to investigate the electrochemical behaviour of all the coatings. Nyquist plots in Figure 2 and 3 were drawn after the coatings have been immersed in 3% NaCl solution for 1 and 15 days. In order to attain the best numerical fit of the EIS data, two models of equivalent circuits were used as in Figure 4.

After 24 hours of immersion, Nyquist plots for 100P and 70P30S have one capacitive loop which is a confirmation that the coatings mentioned have superior barrier performance. Therefore, model A of equivalent circuit in Figure 4 was employed to describe the electrochemical behaviour of these coatings. However, the other solvent based coating systems namely, 90P10S and 80P20S, as well as, all prepared water-based coating systems demonstrated Nyquist plots with full semicircle. That, in turn, means that electrolyte has penetrated the coating layer and reached coating – substrate interface, therefore, the corrosion reaction was initiated [10]. Thus, model B of equivalent circuit was employed to explain the behaviour of these coatings at this stage of immersion time. It is worth to be mentioned that the correct selection of the equivalent circuit model is very important to obtain the best numerical fitting of the collected EIS data and to represent the level of the protection that has been offered by the coating film at any specific time. In this study, differentiate among the capacitive behaviour of the coating layer, represented by model A, and the mixed capacitive - resistive behaviour of the coating film, represented by Model B, the shape of the Nyquist plot and whether it intersects with the X-axis or not have been considered [11].

80P20S system fails abruptly due to brittleness after being exposed to 3%NaCl for more than 24 hours. However, it is compelling that all coating systems except for 80P20S, showed to have one capacitive loop after 15 days of immersion as in Figure 3. These coating systems have superior barrier performance at this stage of immersion. It was deduced that after initial corrosion has taken place in 24 hours, aluminium undergoes oxidation:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

Aluminium oxide that was formed at the coating-substrate interface provides additional barrier protection by inhibits corrosion due to its highly capacitive behaviour [12]. As the result, the Nyquist plots after 15 days showed to have an arc shape. Model A of equivalent circuit was employed to obtain the numerical fit. Coating resistance for all coating systems for 1 and 15 days are tabulated in Table 2.

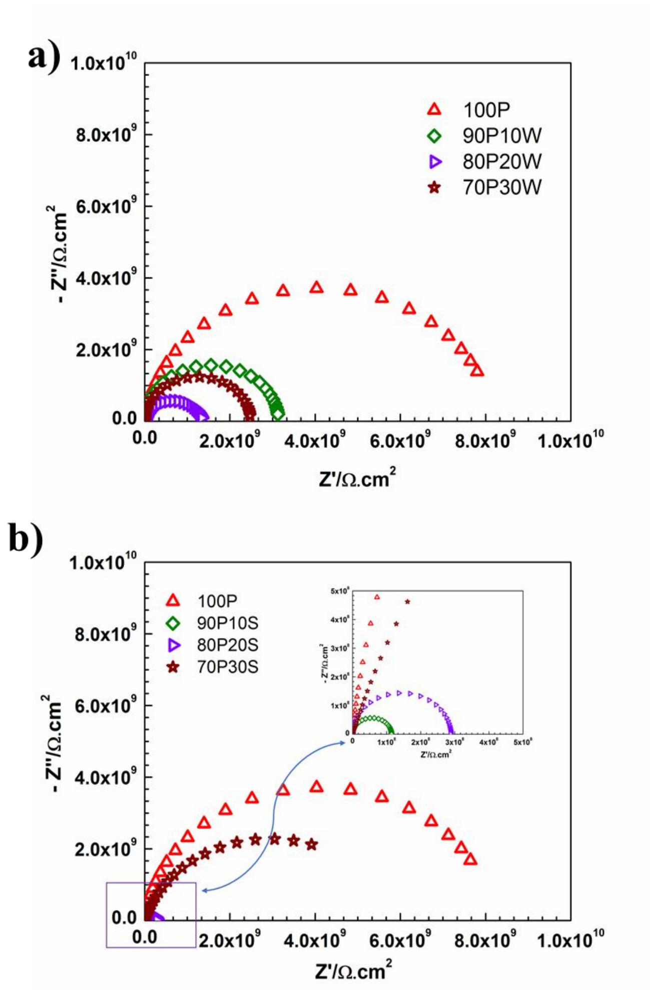

FIGURE 2. Nyquist plot for (a) water-based system and (b) solvent-based system after 1 day of immersion

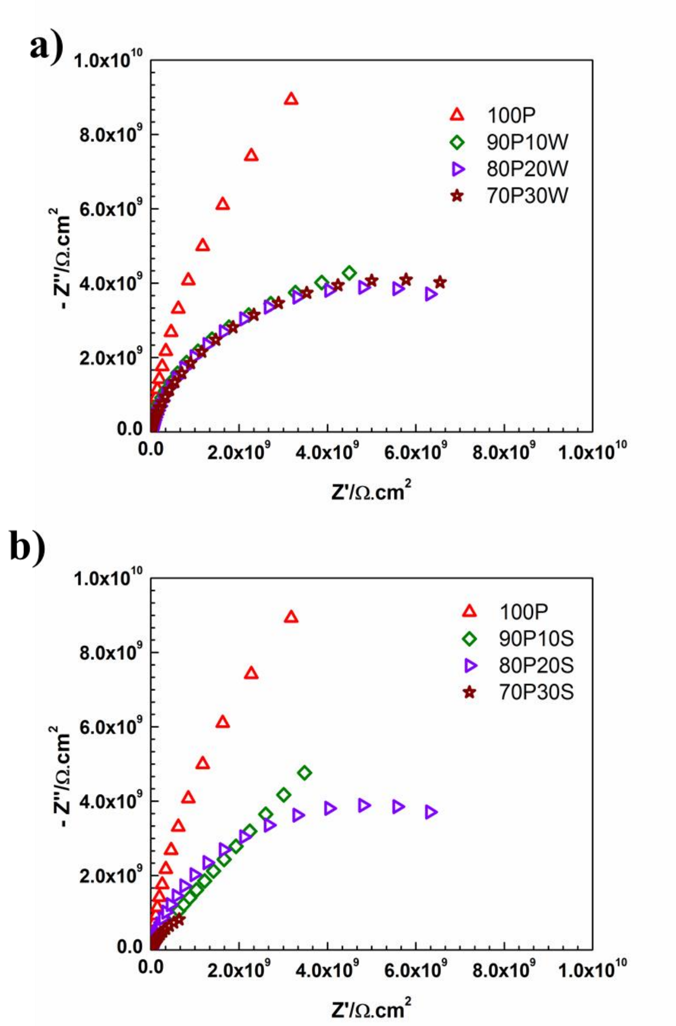

FIGURE 3. Nyquist plot for (a) water-based system and (b) solvent based system after 15 days of immersion

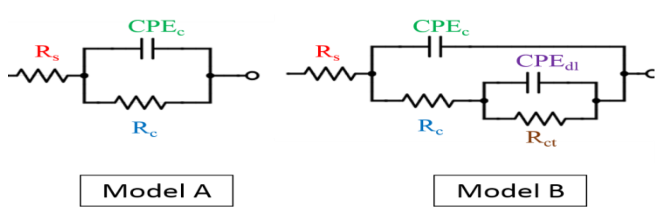

FIGURE 4. Electrical equivalent circuit

TABLE 2. Coating resistance for all coating systems.

System	Coating resistance, R_c (Ω cm^2)			
	Immersion days			
	1	Model used	15	Model used
100P	(8.0 ± 0.2) ×10^9	A	(3.0 ± 0.1)×10^{10}	A
90P10W	(2.0 ± 0.2) ×10^9	B	(9.0 ± 0.1)×10^9	A
80P20W	(6.0 ± 0.1) ×10^8	B	(7.0 ± 0.1)×10^9	A
70P30W	(2.0 ± 0.7)×10^9	B	(8.0 ± 0.1) ×10^9	A
90P10S	(4.0 ± 0.2) ×10^8	B	(4.0 ± 0.1) ×10^9	A
80P20S	(3.0 ± 0.3) ×10^8	B	-	A
70P30S	(5.9 ± 0.1) ×10^9	A	(3.0 ± 0.1) ×10^9	A

3.3 Pencil Hardness Test

The hardness of a surface of a developed coating is directly related to its adhesion [10]; thus pencil hardness test was run. The results of this test were recorded as the grade of the pencil that did not leave any clear marking on the surface of the film. The hardness was in the following order: 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H where 6H is the hardest and 6B is the softest. Addition of epoxy to polyurethane system should improve the adhesion because epoxy resin can contribute additional carboxylic and hydroxyl functional groups that increase the cross-linking and network density of the developed coating [13].

For solvent based system, it can be noticed that lower hardness of the coating film was observed compared to pure polyurethane. As ratio of solvent based epoxy was increased, the hardness of the coating system was reduced. 10% wt. of solvent based epoxy has a hardness of HB, 20% wt. has a hardness of 2B and 30% wt. has a hardness of 3B. The hardness of the coating decreased as amount of solvent based epoxy was increased. In contrast, addition of water-based epoxy to polyurethane by 10% increases the hardness by one grade to 3H as demonstrated by 90P10W system. Further increment of water-based epoxy causes the hardness to reduce and maintain at grade F as shown by 80P20W and 70P30W system. From the obtained results it can be conclude that the addition of the epoxy resin (solvent or water based) at its lowest ratio specifically, 10% wt., did not significantly affected the hardness of the resultant coating films. However, increasing the loading ratio of the epoxy resin significantly soften the coating layers which could be attributed due to the additional free volume within the hybrid polymeric matrix due to the insufficient amount of the curing agent that is able to crosslinking the additional connotations of epoxy resins [14].

TABLE 3. Results of pencil hardness test.

Coating systems	Pencil Hardness
100P	2H
90P10W	3H
80P20W	F
70P30W	F
90P10S	HB
80P20S	2B
70P30S	3B

3.4 Cross Hatch Test

From cross hatch test, it was shown that 100P and 90P10W systems can be classified as 5B according to ASTM D3359 standards where the edges of the cuts made are smooth and the squares of the lattices are intact. 80P20W system and 70P30 W system were classified as 4B, where detachment that occurred was less than 5% of the cross cut area. For solvent based system, 90P10S and 80P20S were graded as 4B where detachment was still at minimum. However, solvent based 70P30S showed ordinary adhesion with some peel off at the intersection of the cuts and the affected cross cut area was in between 5% to 15% and its adhesion was graded as 3B. These observations was in complete agreement with the results pencil hardness tests were the addition of more loading ratios of ESO - epoxy led to an obvious degradation in the curing performance of the coating films. This could be explained also by the fact that the soybean oil is characterized with lower viscosity comparing to the epoxy and polyurethane resins, thus, the increment of ESO loading ratios is directly responsible for the production of lower crosslinking density of the coating films, therefore, poor adhesion properties [15, 16].

TABLE 4. Results of cross cut test.

Coating systems	Cross cut results
100P	5B
90P10W	5B
80P20W	4B
70P30W	4B
90P10S	4B
80P20S	4B
70P30S	3B

3.5 Glossiness Test

High gloss values were observed for solvent based coating systems comparing to the water based coating systems. Among all epoxy modified polyurethane coating systems, 90P10S system demonstrated the highest glossiness value at 83.2. Whereas, the lowest glossiness was at 81.3 for 70P30S system. Meanwhile, gloss values observed for water based systems were mediocre with 90P10W had glossiness at 71.5 and the lowest glossiness was at 56.5 by 70P30W system. Important to note that pure polyurethane had the highest glossiness recorded at 84.9. It can be deduced that as epoxy content increases in hybrid epoxy-polyurethane, the glossiness decreases due to reduced availability of polyurethane chains in the developed coatings [17]. However, solvent based epoxy up to 30% wt. can still be used with polyurethane to produce a coating with high gloss finish. The close glossiness values between the pure polyurethane coating systems and the solvent based epoxy modified coating systems could be attributed due to the nearly matched reflective indexes of polyurethane and epoxy resins at 1.4 and 1.5, respectively. While, on contrary, the reduction of the glossiness values with the application of water based epoxy modified coating systems is believed to be due to the lower reflective indexes of water, at approximately 1, comparing the to the reflective index of the xylene which is the solvent of the epoxy resin and holding a reflective index around 1.5 [18].

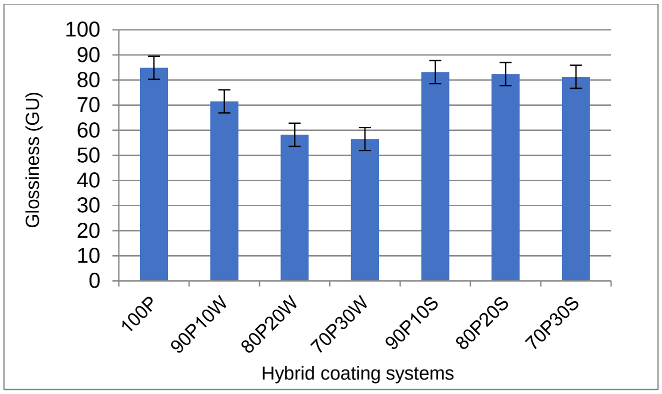

FIGURE 5. Glossiness of coating systems developed.

3.6 Pull-off Test

To obtain accurate results, the tested areas of the coated substrates were checked to ensure the privation any moisture, oil and dust. The test was conducted in a dry environment, at room temperature, due to fact that the states of the coating films may have an effect on the resultant adhesion strengths [19]. Pure polyurethane (100P) coating system recorded high adhesion strength at a magnitude of 0.8 MPa. Solvent based system showed reduced adhesion strength of the hybrid coating except for 70P30S system which had the same adhesion strength as pure polyurethane. Water based system showed promising results as 90P10W and 80P20W have adhesion strength of approximately 1 MPa. Meanwhile, 0.8 MPa was recorded for 70P30W system. Overall, the differences in the adhesion strengths were found to be insignificant due to the small changes in the recorded values which could be affected by the thickness of the coating films of the test conditions. Therefore, it can be concluded that the modification of the polyurethane polymeric matrix with different loading ratio of epoxy resin (solvent or water based) did not significantly alter the adhesion strengths of the coating films [20].

TABLE 5. Results of pull-off test.

Coating systems	Adhesion strength (MPa)
100P	0.8
90P10W	1.0
80P20W	1.0
70P30W	0.8
90P10S	0.6
80P20S	0.5
70P30S	0.8

IV. CONCLUSION

A polymeric matrix consisting of epoxy resin and epoxidized soy bean oil (ESO) was prepared at the ratio of 90:10. Water based epoxy and solvent based epoxy were blended separately with ESO before added to polyurethane. Comparison study was made to determine which has better properties as a coating for aluminium metals. EIS studies discovered that performance of the coating systems improved after 24 hours of immersion. Water based system; 90P10W had the highest coating resistance after 15 days of immersion at $9.0\times10^{9}\ \Omega$. Pencil hardness test, pull-off test and cross hatch test showed that addition of water based epoxy by 10% wt. to the polyurethane increases the adhesion of the coating. Further increment in weight ratio of water based epoxy will reduce the adhesion performance of the coating. On the other hand, any addition of solvent based epoxy to polyurethane will reduces the adhesion of the developed coating. Glossiness test showed outstanding results for solvent based system with average glossiness of 82.3.

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