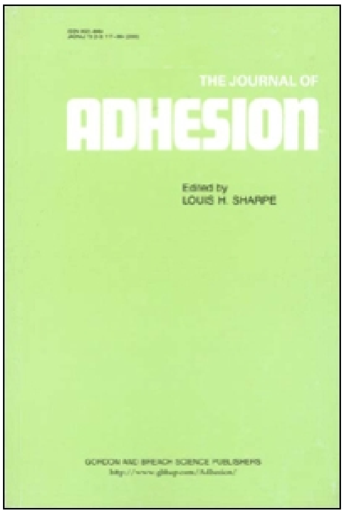

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C. M. Reddy[a]; C. M. Weikart[a]; H. K. Yasuda[a]
[a] Surface Science and Plasma Technology Center and Department of Chemical Engineering, University of Missouri, Columbia, MO, USA

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The Effect of Interfacial Tension on the Adhesion of Cathodic E-coat to Aluminum Alloys

C. M. REDDY, C. M. WEIKART and H. K. YASUDA*

Surface Science and Plasma Technology Center
and Department of Chemical Engineering, University of Missouri,
Columbia, MO 65211, USA

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Adhesion of a cathodically electrodeposited paint (E-coat) to aluminum alloys, Alclad 2024-T3, AA 2024-T3 and AA 7075-T6, was investigated to examine the influence of interfacial tension at the paint/metal interface. The surface energy of an aluminum plate was modified by depositing a plasma polymer of a mixture of trimethyl silane (TMS) and one of three diatomic gases (O_2, N_2, and H_2) by cathodic plasma polymerization. The contact angle (θ) of water on a modified surface changes as a function of the mole fraction of the diatomic gas. The plot of $\cos\theta_{PP}$ of a plasma polymer as a function of the mole fraction of the gas crosses the plot of $\cos\theta_{EC}$ of the E-coat. The difference, $\Delta\mathrm{Cos}\,\theta = \cos\theta_{PP} - \cos\theta_{EC}$, is a parameter which indicates the level of interfacial tension at the paint/metal interface. $\Delta\mathrm{Cos}\,\theta = 0$ represents the minimum interfacial tension. The adhesion of a cured E-coat on a panel was evaluated by the *N*-methyl pyrrolidinone (NMP) paint delamination time test. The maximum peak of adhesion test values plotted as a function of $\Delta\mathrm{Cos}\,\theta$ occurred around the zero point, $\Delta\mathrm{Cos}\,\theta = 0$, indicating that maximum adhesion is obtained with minimum interfacial tension. Mixtures of TMS and N_2 on all three aluminum alloys studied consistently displayed longer delamination times in the NMP test than mixtures of TMS and O_2 or H_2.

Keywords: Interfacial tension; plasma polymers; cathodic E-coat adhesion; aluminum alloys

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*Corresponding author. Tel.: 573-882-3563, Fax: 573-882-1831, e-mail: yasudah@missouri.edu

1. INTRODUCTION

Good adhesion of polymer films to metal surfaces is an important parameter in the protection of metal from corrosion and mechanical stress. Improvement in the adhesion of metal-polymer bonds has been a topic of research for the past several years [1 – 4]. There have been several pretreatment methods developed to improve the adhesion of paint to metal surfaces [2]. The adhesion of polymer films depends on characteristics of the metal surfaces, such as surface roughness, surface contaminants, and the nature of chemical bonds on the surface [3, 4], which exist prior to polymer film application. Mechanical interlocking of a polymer to porous surfaces was one focus of studies on improvement of the adhesion at metal-polymer film interfaces [5]. Over the course of several years, many pretreatments have been investigated in an attempt to improve the adhesion of polymer films to metal surfaces. The pretreatment processes developed range from surface cleaning to surface conversion into different oxides [1]. Because of their porous column structure, anodized surfaces of aluminum alloys were found to result in better adhesion performance of polymer film-metal bonds.

Glow discharge plasma techniques have been used in several areas, such as semiconductors and biological applications, to modify surfaces by non-reacting gas plasma treatment or plasma polymer deposition [6]. Plasma polymers from DC glow discharge have been used for corrosion protection of metal surfaces because of their superior barrier properties, good adhesion to substrates and chemical inertness [7].

Cathodic electrocoating has been widely used as a primary layer coating or top coat in corrosion protection systems employed in the automotive, industrial and appliance areas for years [8]. The chemistry of cathodic electrocoatings and electrodeposition parameters have been the subject of several investigations [9 – 13]. Cathodic electrocoating has a number of advantages which make it an attractive coating system: these include high throwing power, superior corrosion protection, high coating utilization (> 95%), a low level of resulting pollution (aqueous system), and easy automation. Recently, the cathodic electrocoating process has been used for painting in the automobile, mechanical, engineering and domestic appliance industries. Cathodic electrocoating is a fairly simple process and can be used on various scales. High throwing power makes the cathodic electrocoating process attractive in the automobile industry, as it ensures that the electrocoat penetrates into cavities and pores of curved parts.

Aluminum alloys AA 2024-T3, Alclad 2024-T3 and AA 7075-T6 have been used in the aircraft industry because of their high mechanical strengths. Pure aluminum, which has high corrosion resistance properties, has limited application due to its low mechanical strengths [14]. With the addition of small quantities of alloying elements, the mechanical strengths of aluminum are increased significantly. However, the addition of such alloying elements drastically reduces the corrosion resistance of these metals. For the past several years, this has been overcome with the chromate conversion coating process, which provides excellent corrosion protection for such alloys [15]. Because of their health hazards, the use of chromates has come under severe Environmental Protection Agency restrictions necessitating the development of an environmentally benign corrosion protection process [16].

Electrodeposition is an excellent alternative process due to its environmentally benign nature. In this technique, the E-coat polymer-metal bond is an important factor in the protection of metal from corrosion. In the present study we have looked into the improvement of adhesion strengths of electrodeposited films to the aluminum alloys Alclad 2024-T3, AA 2024-T3 and AA 7075-T6 with the application of cathodic plasma polymers. The cathodic electrocoating technique is being investigated for use in the preparation of airplane construction materials, as it has several advantages which can be exploited to our benefit. The objective of this study is to investigate the adhesion strengths of cathodic electrocoat to different plasma polymer surfaces on aluminum alloys to determine a suitable composition of TMS/diatomic gas mixture which maximizes adhesion strengths. Although good adhesion of paint films to a metal surface is an important factor in the corrosion protection of the metal, corrosion performance was not evaluated in this study. The adhesion phenomenon was studied to examine the effect of the composition of the monomer feed gas in plasma polymerization on the adhesion of cathodic E-coat.

2. EXPERIMENTAL

2.1. Materials

Aluminum alloy panels of Alclad 2024-T3 [2A], AA 2024-T3 [2B] and AA 7075-T6 [7B], each 3″ × 6″× 0.034″ (7.6 × 15.2 × 0.086 cm) in size, were procured from Q-Panel Lab Products for use in the present study. The polyurethane-based cathodic electrocoat used was a mixture of 44 wt% resin emulsion (BASF U32CD033A), 8 wt% paste (BASF U32AD290), 48 wt% deionized (DI) water ($< 10\,\mu$mhos conductivity) and 4 vol% additive (BASF 20CD0043). Turco 4215S$^{\mathrm{TM}}$ was utilized as an alkaline cleaner for chemical cleaning of substrate 7B surfaces. Amchem 7$^{\mathrm{TM}}$ in combination with nitric acid was employed as a deoxidizing agent. The solvents acetone and *N*-methyl pyrrolidinone were procured from Fisher Scientific, Inc. Trimethylsilane (TMS) with 97% minimum purity was procured from PCR, Inc. and Gelest, Inc. The diatomic gases used were hydrogen (99%), oxygen (99.9%) and nitrogen (99.99%); these were procured from Airgas. All the gases and the monomer were used as received without any further purification.

2.2. Experimental Procedures

2.2.1. Reactor System and Sample Preparation Procedure

A low temperature DC plasma technique was used in this study to treat the surface and to deposit plasma polymer films on the aluminum alloy surfaces. The bell jar reactor system (Fig. 1) utilized in this study consisted of six major components: (i) the reactor chamber (about 75 liters), (ii) the anode magnetron electrode setup (25.4 cm × 25.4 cm × 0.16 cm stainless steel plates with 8 bar magnets placed equidistantly on the back), (iii) the monomer/gas feeding system, (iv) the pressure and flow rate control systems, (v) the vacuum pump system (Edward Booster with mechanical pump, capacity 240 m^3/h at 0.3 mbar), and (vi) the DC power source. An MDX-1K Magnetron Drive (Advanced Energy Industries, Inc.) was used as the DC power source and was controlled in power mode. The flow and pressure controllers (made by MKS) were used to monitor flow rates of the monomer/gas and reactor chamber pressure.

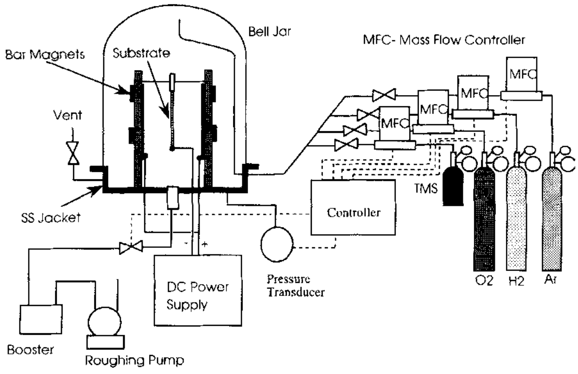

FIGURE 1 Schematic of the DC bell jar reactor system.

TABLE I Surface treatment processes investigated in this study

Code	*Chemical pretreatment*	*Plasma pretreatment*[1]	*Plasma polymer deposition*[2]
(Ace/O_2)/TMS + O_2	Acetone wipe	O_2	TMS + O_2
(Ace/O_2)/TMS + H_2	Acetone wipe	O_2	TMS + H_2
(Ace/O_2)/TMS + N_2	Acetone wipe	O_2	TMS + N_2
(Alk/Dox/O_2)/TMS + O_2	Alkaline clean/ Deoxidization	O_2	TMS + O_2
(Alk/Dox/O_2)/TMS + N_2	Alkaline clean/ Deoxidization	O_2	TMS + N_2

[1] O_2 plasma pretreatment was carried out at 100 mTorr pressure, 40 watts DC power, 2 sccm O_2 flow rate for 10 minutes.

[2] Plasma polymer deposition was carried at 1 sccm TMS + 1 sccm diatomic gas (O_2/N_2/H_2) flow rate, 50 mTorr pressure, 5 watts DC power for 1 minute.

Three diatomic gases, O_2, H_2 and N_2, were mixed with TMS to create the plasma polymer forming monomer/gas mixtures. Two different initial cleaning processes, acetone wiping and alkaline cleaning followed by deoxidization (in the case of substrate 7B), were used to examine the effect of chemical cleaning on the adhesion of cathodic electrocoat to plasma polymers. The processes examined in this study are shown in Table I.

Two substrate panels clipped together with alligator clips were placed between two anode magnetrons used as a cathode. The reactor chamber was evacuated to 1–2 mTorr vacuum after the panels were installed. Once desired pressure was achieved, the pretreatment gas oxygen (O_2) was introduced with a 2 $\mathrm{cm}^3_{\mathrm{STP}}$/min flow rate, and pressure was set to 100 mTorr. O_2 plasma pretreatment was carried out for 10 minutes at 100 mTorr and 40 watts DC power. Following the pretreatment, the reactor was evacuated to 1–2 mTorr pressure before the monomer/gas mixture was introduced into the reactor chamber. Introduction of the specific monomer/gas mixtures was then started at a fixed flow rate maintained by the flow controllers. Pressure was set to 50 mTorr for all the mixture combinations. Plasma polymerization was carried out at 50 mTorr pressure and 5 watts DC power for one minute in the case of each TMS/diatomic gas mixture. Panels were removed from the reactor after evacuation to 1–2 mTorr pressure. Cathodic E-coat was then applied on the plasma polymer coated panels within 10 minutes after the samples were taken out of the plasma chamber. This time was controlled in all cases to eliminate any possible influence of time-dependent change in adhesion performance. In a previous experiment not reported here, the adhesion performance of E-coat on plasma polymer films was found to be independent of time up to 5 days before adhesion performance started to decline.

For the purpose of thickness and refractive index measurement, silicon wafers of the size 1 cm × 1 cm were placed on the substrate at different locations before the substrates were installed in the bell jar reactor. The thickness and refractive indices of plasma polymer films were then measured on these silicon wafers by an AutoEL-II Automatic Ellipsometer (Rudolph Research Corporation), which is a null-seeking type with a 632.8 nm helium-neon laser light source.

Within 2 hours after each sample was taken out of the plasma chamber, contact angles of all plasma polymer surfaces were measured using the sessile drop contact angle measurement method with the help of a computerized contact angle measurement system, the VCA 2500XE (AST Products, Billerica, MA). The VCA 2500XE system allows measurement of water contact angles within a short time, thus avoiding changes in contact angle due to surface dynamics. The contact angles of plasma polymers and E-coat surfaces were measured by placing a 3 μl DI water ($<$ 10 μmhos conductivity) droplet on each surface and capturing the droplet image within a few seconds. Then, using each captured image, contact angles were calculated by means of VCA 2500XE software. To eliminate local variation of contact angles, the average of four contact angles, measured at four different locations on each surface, was figured.

In cases involving acetone wiping, panels were wiped with acetone using tissue paper (Kimwipes®, Fisher Scientific, Inc.) to clean the ink marks and loose organic matter off their surfaces. In the cases involving deoxidization, panels were first alkaline cleaned by immersion in the alkaline bath (approximately 4 liters of solution) for about 25 minutes until each panel became water-break-free when rinsed with DI water. Following this, the panels were immersed in deoxidizer (approximately 4 liters of solution) for 10 minutes and then rinsed with DI water for 5 minutes. The purpose of alkaline cleaning and deoxidization was to remove the native oxide which is contaminated with milling oil when the alloy is made. The composition of the alkaline cleaning solution was maintained such that a water-break-free surface would be obtained while rinsing with DI water after immersion in the alkaline bath for a specific amount of time. Water contact angles of all the plasma polymer surfaces were measured by the sessile drop method before electrodeposition. Electrodeposition was carried out in a one-gallon electrocoat bath using the substrate as the cathode and a stainless steel strip (1.5″ × 10″) (3.8 × 25.4 cm) as the anode. A Darrah Digital® DC power source with variable voltage facility was used for the electrodeposition.

Electrodeposition on each panel was carried out in galvano-potentiostatic mode as described below. The panel was immersed in the electrocoat bath using a paper clip, and the DC power source was switched on. The current was controlled to be under one ampere during the initial stages, and the voltage was slowly increased to maintain the current at one ampere as electrodeposition proceeded. As the current decreased (within one minute), the voltage was increased to 250 V and maintained throughout the remaining 2 minutes. Electrocoating duration was controlled by an automatic function of the DC power supply. The electrocoated panels were then rinsed with DI water to remove any loose electrocoat from the surface. Panels were allowed to dry in air for 30 minutes and were then cured in an oven for 30 minutes at 300°F (150°C).

Contact angle measurements were carried out on the cured electrodeposited polymer surfaces for comparison with those obtained for the plasma polymer surfaces before E-coating. Adhesion strengths of the electrodeposited polymers to the plasma polymers were evaluated using the NMP test as described below.

2.2.2. The NMP Test

Test specimens 0.5″ (1.27 cm) in diameter were punched out of the cured panels and used for the *N*-methyl pyrrolidinone (NMP) test. The NMP test, developed by van Ooij *et al.* [17], is a good method for distinguishing the adhesion strengths of E-coated polymer films on metal surfaces and it was used to distinguish the adhesion strength of electrocoats to substrate surfaces coated with plasma polymer. The NMP test was performed as described below. First, three specimens were punched out of each cured electrocoated panel. These were placed in NMP that had been preheated to 60°C, and a stop watch was started. The 60°C temperature of the NMP was maintained while the specimens were closely observed for signs of delamination. If the entire electrocoated film lifted off of the specimen, the time was noted as the NMP time, otherwise the specimen was left in the NMP for 120 minutes. Percent adhesion of E-coat film was noted by visual observation for the specimens that lasted 120 minutes in the NMP without total delamination of the E-coat film. The average NMP time for each set of three specimens was calculated.

3. RESULTS AND DISCUSSION

3.1. Plasma Polymer Thickness and Refractive Index

Plasma polymer deposition rate depends on the composition of the monomer-gas mixture. Increases in the concentration of non-polymerizing gas will decrease the deposition rate considerably when other parameters are kept constant. To examine this relationship, the thickness of plasma polymer developed during a fixed time of deposition was measured at different places on each panel. The average thickness was figured, and this average has been plotted against the mole fraction of diatomic gas. Figure 2 shows plasma polymer thickness variation plotted against the mole fraction of diatomic gas. Plasma polymer thickness developed during 1 minute of operation at different mole fractions lies in the expected range of 200 to 650 Å. Plasma polymer growth does not seem to depend on the substrate material, but thickness developed in $TMS + H_2$ and $TMS + N_2$ systems is slightly higher than that in the $TMS + O_2$ system (Fig. 2). This could be due to

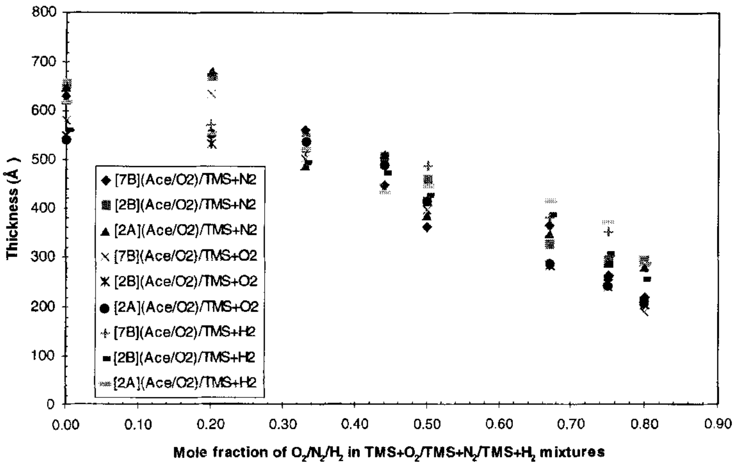

FIGURE 2 DC plasma polymer thickness variation with mole fraction of O_2, N_2 and H_2 in TMS + O_2, TMS + N_2 and TMS + H_2 mixtures, respectively, on three substrates: 2B (AA 2024-T3), 7B (AA 7075-T6) and 2A (Alclad 2024-T3), with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

SiO_x-type films formed in TMS + O_2 systems by the elimination of methyl groups.

Refractive indices of all the plasma polymer films were measured; these are shown in Figure 3. Increases in diatomic gas concentration decrease the refractive indices of TMS plasma polymers. Refractive indices of TMS + H_2 and TMS + N_2 plasma polymers were found to be higher than those of TMS + O_2 plasma polymers (Fig. 3).

3.2. Minimizing Interfacial Tension

The following working hypothesis has been investigated in this study: ***minimization of the interfacial tension at the E-coat/metal interface can maximize E-coat adhesion***. However, there is no way to measure the interfacial tension between a polymer layer and a metal surface directly. The term surface energy is generally used to describe the interfacial energy between a solid surface and ambient air. Therefore, an attempt to estimate such a surface energy for two contiguous surfaces in an effort to estimate the interfacial energy is not warranted.

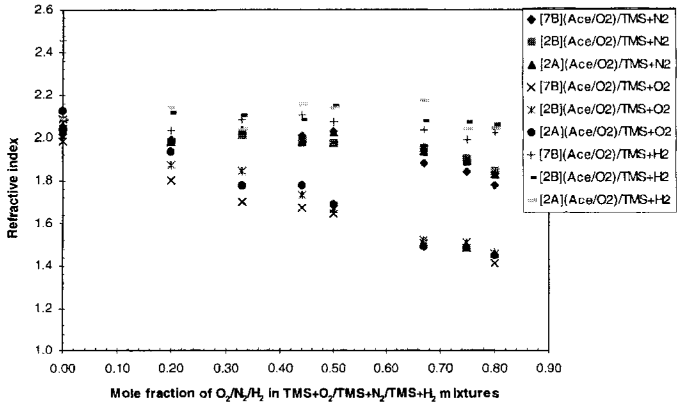

FIGURE 3 DC plasma polymer refractive index variation with mole fraction of O_2, N_2 and H_2 in $TMS + O_2$, $TMS + N_2$ and $TMS + H_2$ mixtures, respectively, on three substrates: 2B (AA 2024-T3), 7B (AA 7075-T6) and 2A (Alclad 2024-T3), with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

In other words, air is not a common constituent of the interface under consideration.

Because water is a common constituent material when an E-coat is applied to a metal surface, a more realistic approach is to compare the contact angles of water on both surfaces to estimate the level of interfacial tension. The value of $\gamma \cos\theta$ is a measurable thermodynamic quantity introduced by Guastalla [18, 19], which is applicable to the situation under consideration. Since the contact angle measurements were made under identical conditions with water, for which γ (the surface tension) is a constant, the change in $\cos\theta$ rather than $\gamma \cos\theta$ was taken to be indicative of the level of interfacial tension for all cases investigated in this study.

The empirical approach works well to show the influence of the interfacial tension on the adhesion of E-coat as is evident in the following sections. The plot of $\cos\theta_{PP}$ of a plasma polymer as a function of the mole fraction of the gas crosses the plot of $\cos\theta_{EC}$ of the E-coat. The difference, $\Delta\text{Cos}\,\theta$, is a parameter which indicates the level of interfacial tension at the paint/metal interface. In the scale of mole fraction of a gas, where $\Delta\text{Cos}\,\theta = 0$ it is assumed that the minimum interfacial tension is attained.

The water contact angles of plasma polymer surfaces are compared with those of a cured E-coat in Figure 4. The values of $\cos\theta$ of $TMS + N_2$, $TMS + H_2$ and $TMS + O_2$ plasma polymer surfaces are plotted against diatomic gas concentration. As evinced by Figure 4, $\cos\theta$ variation is significant with the increase of diatomic gas concentration. Water contact angles of a cured E-coat surface with a corresponding composition of monomer/gas mixture are also shown in Figure 4; these do not depend on the contact angle of the underlying substrate.

The difference between $\cos\theta$ of plasma polymer (PP) surfaces and cured E-coat (EC) surfaces is calculated as follows:

$$\Delta\mathrm{Cos}\,\theta = \cos\theta_{\mathrm{PP}} - \cos\theta_{\mathrm{EC}}$$

$\Delta\mathrm{Cos}\,\theta$ variation according to the composition of monomer/diatomic gas mixture is shown in Figure 5. As anticipated, $TMS + O_2$ plasma polymers have more hydrophilic surfaces than $TMS + N_2$ and $TMS + H_2$ plasma polymers. This figure demonstrates that, for $TMS + O_2$ and $TMS + N_2$ plasma polymer surfaces, there exists an interfacial tension minimizing point for the composition range studied. The

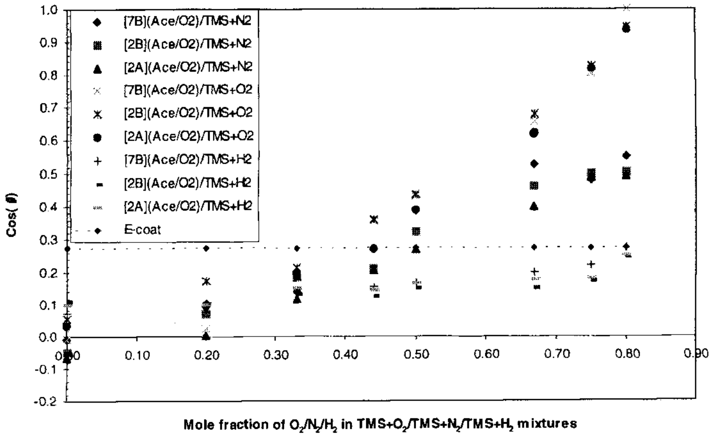

FIGURE 4 DC plasma polymer contact angle variation with mole fraction of O_2, N_2 and H_2 in $TMS + O_2$, $TMS + N_2$ and $TMS + H_2$ mixtures, respectively, on three substrates: 2B (AA 2024-T3), 7B (AA 7075-T6) and 2A (Alclad 2024-T3), with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

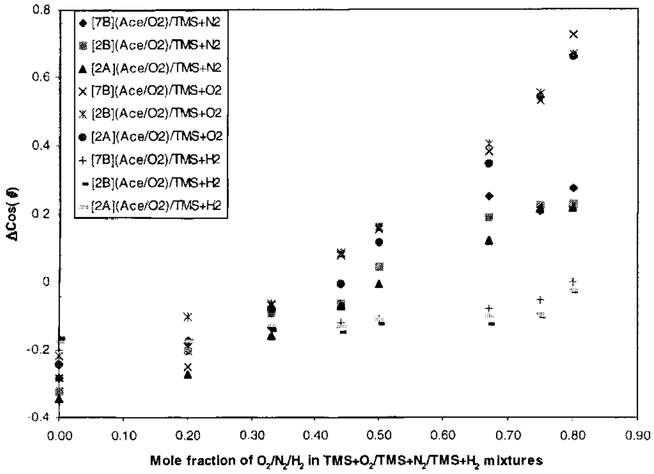

FIGURE 5 DC plasma polymer ΔCos(θ) variation with mole fraction of O_2, N_2 and H_2 in TMS + O_2, TMS + N_2 and TMS + H_2 mixtures, respectively, on three substrates: 2B (AA 2024-T3), 7B (AA 7075-T6) and 2A (Alclad 2024-T3), with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

TMS + H_2 system has a wide composition range in which the interfacial tension between the plasma polymer and the E-coat is minimized, while the value of $\cos\theta_{PP}$ remains only below that of $\cos\theta_{EC}$. This minimum interfacial tension exists for all the diatomic gas mixtures which were studied: TMS with H_2, N_2 and O_2. This approach predicts that, if we measure the adhesion strengths of E-coat film to the plasma polymer surfaces, we will be able to see maximum adhesion strengths existing at this minimum interfacial tension.

3.3. Adhesion of E-coat to Modified AA 2024-T3 Alloy Surfaces

Adhesion strengths of cathodic E-coat films on metals or modified surfaces of metals are best evaluated by the NMP solution swelling method [17]. The conventional tape test could not be used to distinguish the adhesion strengths of E-coat to the plasma polymer coated metal surfaces in this study, as all the surfaces passed the maximum possible rating available with this method. The NMP solution method is based on the solvent swelling force exerted on the E-coat films in delamination from the surfaces. Film delamination depends on the strengths of the E-coat-substrate bonds. The NMP method was used to differentiate the adhesion performance of the E-coat films on the plasma polymer coated surfaces.

The NMP times for substrate 2B coated with the three monomer/diatomic gas mixture systems are shown in Figure 6. A comparison of the adhesion of E-coat film to the plasma polymers of the different TMS/diatomic gas mixtures deposited on 2B shows that NMP times for all compositions of TMS + N_2 mixtures are the best among all the combinations of the various mixtures. TMS + H_2 mixtures show poor adhesion times in the NMP test as compared with TMS + N_2 mixtures. All three systems show improved adhesion at the interfacial tension minimizing point, which depends on the specific system. The NMP times of E-coat delamination observed on plasma polymers deposited on substrate 2B are far superior to those observed for E-coat deposited on substrate wiped with acetone (the maximum NMP times for E-coat on acetone-wiped 2B surfaces is 2.0 minutes). Even though plasma polymers of all concentrations show longer NMP times than bare surfaces

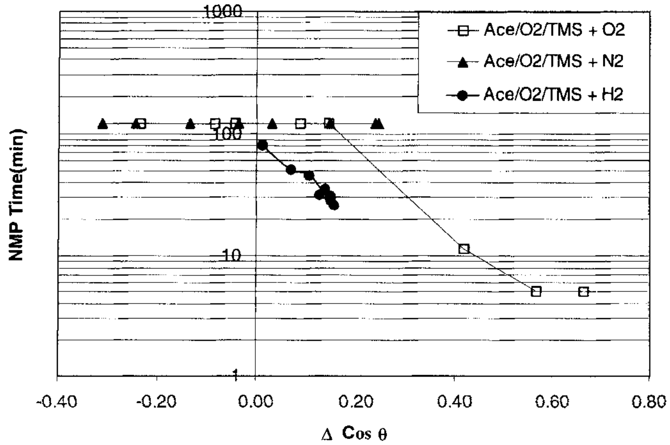

FIGURE 6 NMP time *versus* ΔCos(θ) for three plasma polymer systems, TMS + O_2, TMS + H_2 and TMS + N_2, on substrate 2B (AA 2024-T3) with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

wiped with acetone, the maximum adhesion achievable with each system is different.

Percent adhesion of the specimen which surpassed 120 minutes of the NMP test without total delamination was recorded by visual observation. Figure 7 depicts percent adhesion of E-coat to plasma polymer surfaces on substrate 2B plotted against $\Delta\text{Cos}(\theta)$. From this figure, it can be seen that adhesion of E-coat to $\text{TMS}+\text{N}_2$ plasma polymer surfaces is better than to the other two plasma polymer mixtures. Since E-coat films on $\text{TMS}+\text{H}_2$ plasma polymer surfaces were completely delaminated within 120 minutes of testing time, this system does not appear in Figure 7. The maximum E-coat adhesion was found at 0.5 mole fraction of N_2 in the $\text{TMS}+\text{N}_2$ mixture, 0.5 mole fraction of O_2 in the $\text{TMS}+\text{O}_2$ mixture and 0.67 mole fraction of H_2 in the $\text{TMS}+\text{H}_2$ mixture.

The maximum adhesion of E-coat to the plasma polymer surfaces does not show dependence on the film thickness or refractive index variation. Plasma polymer film thickness and refractive indices show gradual change over the diatomic gas mole fraction range (see Figs. 2 and 3) while the NMP delamination times show abrupt change, on either side, near the interfacial tension minimization point, $\Delta\text{Cos}\,\theta = 0$.

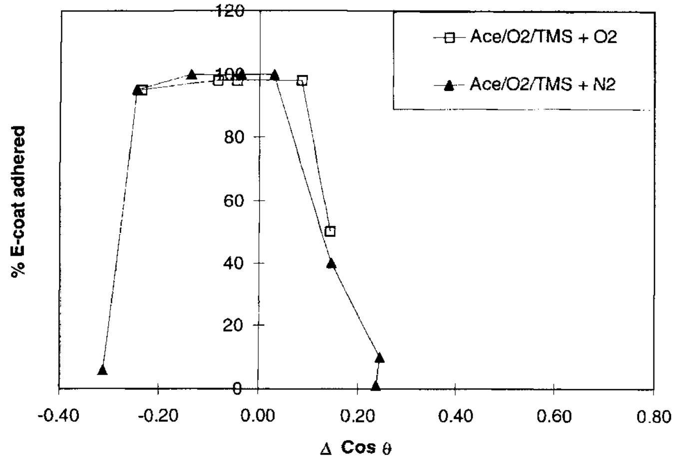

FIGURE 7 Percent E-coat adhered *versus* $\Delta\text{Cos}(\theta)$ for two plasma polymer systems, $\text{TMS}+\text{O}_2$ and $\text{TMS}+\text{N}_2$, on substrate 2B (AA 2024-T3) with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

3.4. Adhesion of E-coat to Modified AA 7075-T6 Alloy Surfaces

NMP paint delamination times for E-coat on different TMS + O_2, TMS + H_2 and TMS + N_2 plasma polymer surfaces on substrate 7B are plotted in Figure 8. It can be seen from this figure that NMP delamination times for TMS + H_2 and TMS + N_2 plasma polymer surfaces are longer than those for different TMS + O_2 plasma polymer surfaces. Additionally, it is evident that TMS + H_2 plasma polymer surfaces show longer adhesion times than TMS + N_2 plasma polymer surfaces. However, it should be noted that significantly longer NMP delamination times were found for all three systems near the interfacial tension minimizing point.

Average percent adhesion of E-coat to three specimens of TMS + O_2, TMS + H_2 and TMS + N_2 plasma polymer surfaces on substrate 7B is plotted against $\Delta\text{Cos}\,\theta$ in Figure 9. The percent adhesion of E-coat on TMS + O_2 and TMS + N_2 plasma polymers on 7B surfaces is slightly lower than on the corresponding 2B surfaces, but TMS + H_2 surfaces show higher percent adhesion on the 7B surfaces.

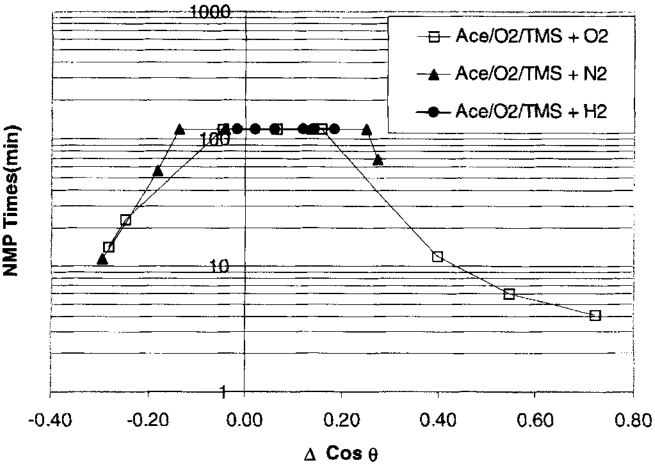

FIGURE 8 NMP time *versus* $\Delta\text{Cos}(\theta)$ for three plasma polymer systems, TMS + O_2, TMS + H_2 and TMS + N_2, on substrate 7B (AA 7075-T6) with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

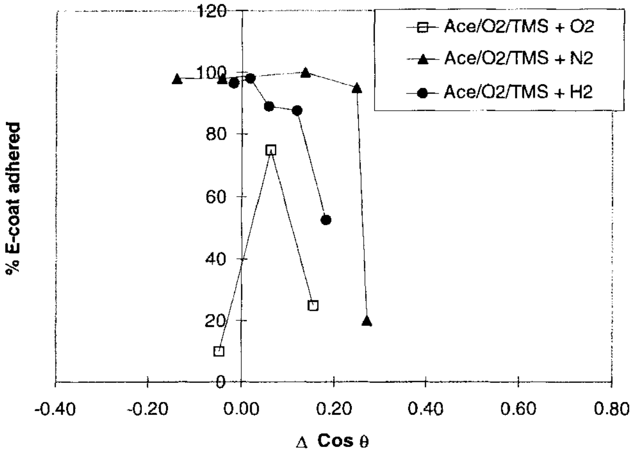

FIGURE 9 Percent E-coat adhered *versus* $\Delta\mathrm{Cos}(\theta)$ for three plasma polymer systems, $TMS + O_2$, $TMS + H_2$ and $TMS + N_2$, on substrate 7B (AA 7075-T6) with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

Among all three systems, $TMS + N_2$ plasma polymer systems have superior percent adhesion of E-coat. Again, as seen on 2B plasma polymer surfaces, there are maximum adhesion points for all three systems of TMS and diatomic gas. Plasma polymer coated AA 7075-T6 surfaces show maximum E-coat adhesion at 0.5 mole fraction of N_2 in the $TMS + N_2$ mixture, 0.5 mole fraction of O_2 in the $TMS + O_2$ mixture, and 0.67 mole fraction of H_2 in the $TMS + H_2$ mixture.

3.5. The Effect of Chemical Cleaning on the Adhesion of E-Coat to Modified AA 7075-T6 Alloy Surfaces

Adhesion performance of polymers on bare metal surfaces improves when the surface is cleaned by a chemical process such as alkaline cleaning [20,21]. Chemical alkaline cleaning with Turco 4215S^{TM} followed by deoxidization with Amchem 7^{TM} deoxidizer solution is a common industry practice for cleaning an alloy surface before subjecting it to further processes. To examine the effect of chemical cleaning of the aluminum alloys on the NMP paint delamination times for E-coat on different $TMS + O_2$ and $TMS + N_2$ plasma polymer surfaces on substrate 7B, alkaline cleaning followed by deoxidization was employed. NMP paint delamination times for these systems are plotted in Figure 10. NMP delamination times for TMS + N_2 plasma polymers are longer than those for TMS + O_2 plasma polymer surfaces. Although NMP delamination times have improved slightly from those obtained for acetone-cleaned TMS + N_2 plasma polymer surfaces, this improved adhesion performance is not significant, because the acetone-wiped surfaces also show long NMP delamination times. This could be due to the fact that chemical cleaning has little effect on top layer plasma polymer.

Average percent adhesion of E-coat to TMS + N_2 plasma polymer surfaces on (Alk/Dox) substrate 7B is plotted again ΔCos θ in Figure 11. The adhesion performance of E-coat on all these surfaces is superior to that on acetone-cleaned 7B surfaces. TMS + N_2 plasma polymer systems have superior percent adhesion of E-coat to that of TMS + O_2 plasma polymer systems on chemically-cleaned 7B surfaces. Since NMP paint delamination times for TMS + O_2 plasma polymer surfaces are below 120 minutes, this system does not appear in Figure 11.

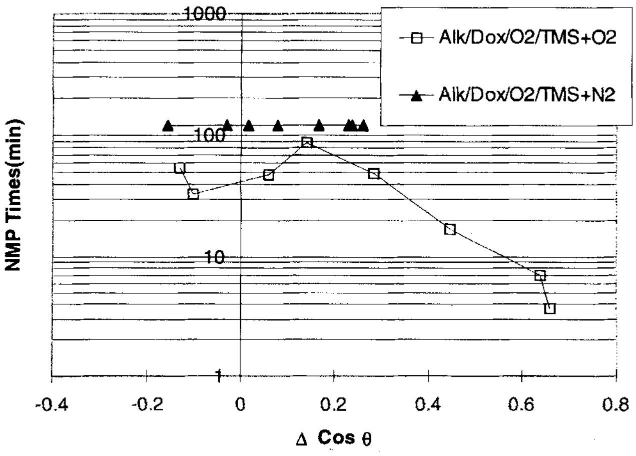

FIGURE 10 NMP time *versus* ΔCos(θ) plot of two plasma polymer systems, TMS + O_2 and TMS + N_2, on deoxidized substrate 7B (AA 7075-T6) with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

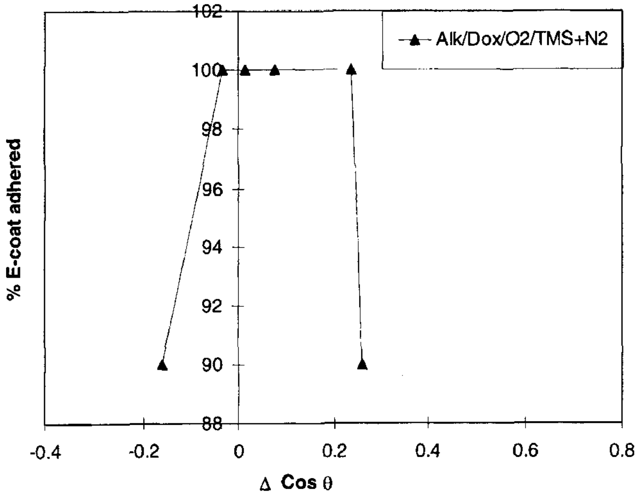

FIGURE 11 Percent E-coat adhered *versus* $\Delta\mathrm{Cos}(\theta)$ for the plasma polymer system $TMS + N_2$ on deoxidized substrate 7B (AA 7075-T6) with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

3.6. Adhesion of E-Coat to Modified Alclad 2024-T3 Alloy Surfaces

NMP paint delamination times for E-coat on different $TMS + O_2$, $TMS + H_2$ and $TMS + N_2$ plasma polymer surfaces on substrate 2A are plotted in Figure 12. From this figure, it can be seen that NMP delamination times for $TMS + O_2$ and $TMS + N_2$ plasma polymers are longer than those of plasma polymer surfaces of $TMS + H_2$. Also, $TMS + N_2$ plasma polymers show longer delamination times than $TMS + O_2$ plasma polymers. It is interesting to note that the longer NMP delamination times occur at the minimum interfacial tension point for all three systems on substrate 2A.

Average percent adhesion of three specimens of $TMS + O_2$, $TMS + H_2$ and $TMS + N_2$ plasma polymer surfaces on substrate 2A is plotted against $\Delta\mathrm{Cos}\,\theta$ in Figure 13. This figure clearly shows that maximum percent adhesion occurs at the minimum interfacial tension point. As compared with results for substrates 2B and 7B, the percent

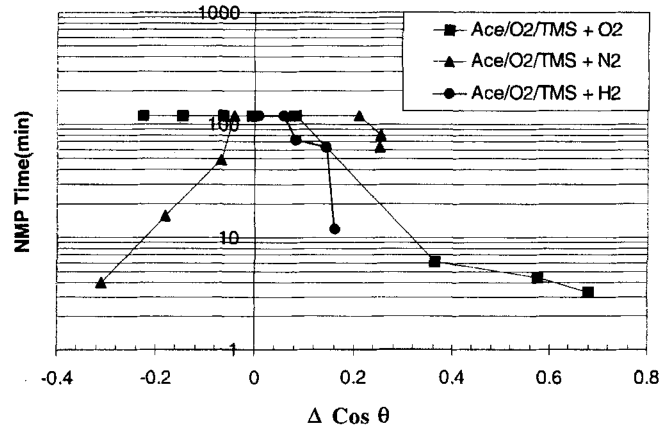

FIGURE 12 NMP time *versus* ΔCos(θ) for three plasma polymer systems, TMS + O_2, TMS + H_2 and TMS + N_2, on substrate 2A (Alclad 2024-T3) with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

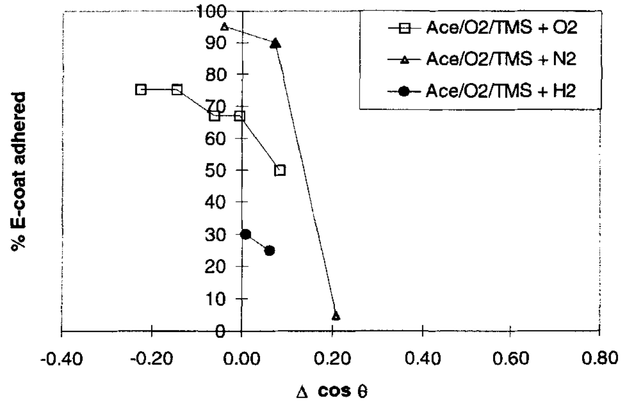

FIGURE 13 Percent E-coat adhered *versus* ΔCos(θ) for three plasma polymer systems, TMS + O_2, TMS + H_2 and TMS + N_2, on substrate 2A (Alclad 2024-T3) with other treatment conditions fixed. Deposition conditions for all concentrations were 5 watts DC power, 50 mTorr pressure and 1 minute deposition time.

adhesion of E-coat on substrate 2A is lower for all three systems. Of all three systems, the TMS + N_2 plasma polymer system displays superior E-coat adhesion times on substrate 2A.

3.7. SEM Analysis of Substrate Surfaces 2B, 7B and 2A

The adhesion improvement provided by plasma polymer surfaces as compared with untreated substrate surfaces (NMP paint delamination times are about 2–5 minutes maximum) is explained by interfacial tension minimization. Surface roughness enhances the adhesion of polymers to metal surfaces by means of mechanical interlocking. To examine the effect of plasma polymer deposition on surface morphology, scanning electron microscopy (SEM) studies were conducted for the surfaces of all three alloys without treatment and with typical plasma treatment and plasma polymer deposition. SEM showed that plasma treatment and plasma polymer deposition made the surfaces smoother than the untreated ones. This indicates that surface roughness of the panels was not a significant factor in the adhesion improvement accomplished in this study. The panels, which were cut from larger sheets, were not polished prior to use in the plasma reactor; therefore, they did not contribute to the smoothness observed with SEM. Thus, the dramatic improvements in the adhesion performance of plasma polymer deposited surfaces achieved in this study are due to changes in surface state.

4. CONCLUSIONS

1. The results of this study indicate that minimizing the interfacial tension between the metal/polymer interface maximizes the adhesion of paint.
2. Composition of the plasma polymer gas used in deposition changes $\cos\theta$ of plasma polymer coated metal surfaces.
3. Maximum adhesion for three systems studied, $TMS + O_2$, $TMS + H_2$ and $TMS + N_2$, was obtained when there was minimum interfacial tension between plasma polymer and E-coat film.
4. On all three substrates, AA 2024-T3, Alclad 2024-T3 and AA 7075-T6, the $TMS + N_2$ system showed better adhesion performance than the $TMS + O_2$ and $TMS + H_2$ systems.

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