EFFECT OF SUBSTRATE CHEMICAL SURFACE TREATMENT ON SURFACE ENERGY AND THE INFLUENCE TOWARDS COATING ADHESION

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ABSTRACT: Surface energy is a characteristic factor which affects the surface properties and interfacial interactions such as wetting and adhesion. A high adhesion is achieved on substrates with high surface energies, in particular high polar shares. Substrate surface treatments prior to the coating deposition process are carried out using 2 categories of solution which are A (sodium hydroxide) and B (sodium hydroxide, distilled water, acid, distilled water, alcohol). The surface treatment was carried out using ultrasonic cleaner by varying the solution, time and wiping process. The main aim of this study is to determine the effect substrate surface treatments on the surface energy of the tungsten carbide (WC) substrate. The surface energy of the substrate was measured using two liquids with dominant polar and dominant dispersion components which was distilled water and methylene iodide. Owens-Wendt method carried out to calculate the surface energy of the substrate. The WC substrate was titanium nitride (TiN) coated using PVD coating machine. The adhesion test was employed using Rockwell indenter. The result showed that cleaning process using solution B for 20 minutes without the wiping process lead to the highest surface energy of 0.1263 N/m with the polar share of 0.0805 N/m which lead to the best coating adhesion. Wiping process reduce the surface energy of the substrate due to carbon residue left on the substrate surface. Finding from this research suggested that solution, time, interaction between solution and time, interaction between solution and wiping, interaction between time and wiping, and interaction between all factors significantly influence the surface energy of the substrate.

KEYWORDS: *Surface energy, Coating adhesion, TiN, Wetting, PVD coating*

1.0 INTRODUCTION

Coatings are used to improve surface properties of components in great number of applications including die casting tools, cutting tools, and others [1]. The most important element in the application of coated elements is the adhesion between coating and substrate. Coating adhesion is mainly affected by the surface treatment of the substrate [2]. Surface treatment is the key factor in determining the success on the deposition of coating layer [1]. Surface treatments can be divided into mechanical and chemical treatment. There have been lot of researches done on the effect of mechanical treatment on coating adhesion. However, there is lack of studies on the effect of chemical treatment parameters on the coating adhesion. The main objective of surface treatment is to create proper adhesion of a coating over an underlying substrate by removing the foreign materials (grease, oil, dust) and modification of the surface layer (roughness, morphology). Proper surface treatment is vital to the service life and overall effectiveness of a coating for protection of the substrate. The improved performance of surface treated cutting tools has been proven and documented [3, 4, 5]. Surface energy is often used as a measure of adhesive properties [6]. Adhesion of coatings to the substrate depends on surface energy of the coating and substrate, and also the interfacial energy between them [7]. The surface energy plays an important role in the wettability of the PVD coated surfaces. The forces of attraction and repulsion acting at the phase boundary are attributed to van der Waals interactions which could be divided into dispersed and polar components [8]. The bonding energy of the polar forces is up to a factor of 10 greater than the dispersion forces [9]. Therefore, polar interactions have a significantly greater influence on adhesion mechanisms. High adhesion is achieved on substrates with high surface energies, in particular high polar shares [6]. In this study, the effect of substrate chemical surface treatment on the coating adhesion was investigated.

II. EXPERIMENTAL SETUP

A. Sample Preparation

Tungsten carbide rectangular block was used as substrate; fixed size was 12.7 mm x 12.7mm x 4.76mm. Substrates were treated using ultrasonic cleaner with 3 different parameters including solution, time and wiping process. These parameters were selected based on the previous works conducted by those researchers. The wiping process is carried out using cotton gauze for each respective solvent before the undergoes the treatment process using ultrasonic cleaner. Table 1 shows

the surface treatments of the substrates in details. The composition of etching solution using acid is tabulated in Table 2.

Table 1. Factors and levels selected for the experiments.

Factor	Level	
	Low	High
Solution	A (Sodium hydroxide)	B (Sodium hydroxide , distilled water, acid, distilled water, alcohol)
Time (min)	10	20 for each solvent
Wiping	No	Yes

Table 2. Composition of etching solution for tungsten [4].

Solution Component	Parts by Weight
Nitric acid, specific gravity 1.41	30
Sulfuric acid, specific gravity 1.84	50
Hydrofluoric acid, 60% wt. concentration	5
Deionized water	15

B. Contact Angle Measurement

The contact angles between the substrate and the deposited liquids are measured using the sessile drop technique [10] as depicted in Figure 1. A liquid droplet is applied to the surface using a syringe to provide a constant volume of fluid. The droplet is recorded with a camera and the images were then processed by a computer and stored. In the investigations carried out, the contact angles measurement is measured by a digital 800k USB 2.0 CCD DCAM and VIS ver7 software. Through the contact angle measurement, the surface energy of the substrate was calculated by using Owens-Wendt equation.
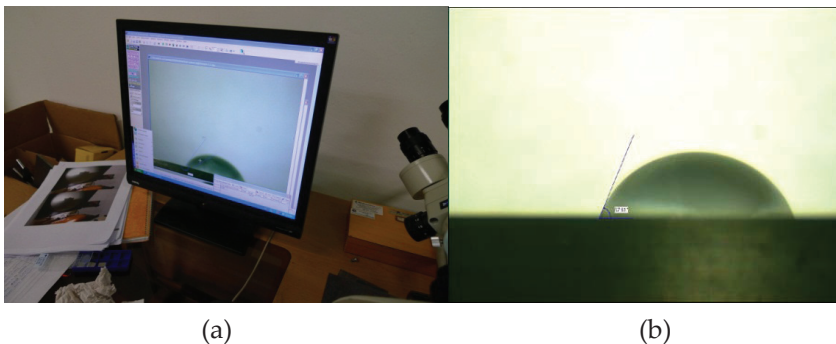

(a)   (b)

Fig 1. Contact angle of deposited liquid (a) projected image of deposited liquid, (b) contact angle measurement using VIS ver7 software.

C. Calculation of Surface Energy

Owens-Wendt method is one of the common methods used to calculate the surface energy of solid after the surface treatment, prior to the PVD coating deposition [6, 11, 12]. In the Owens-Wendt method, there has been extension in the proposed equation by Fowkes [9] by considering polar forces in addition to dispersive forces [4]. According to Owens and Wendt [13], the interfacial tension of each phase can be spilt into polar and dispersion components. Two measured liquids (polar and dispersion) with known surface energy are used to determine the surface energy. The liquids with dominant polar and dominant dispersion components were selected [9]. Basically, water was a highly polar liquid while methylene iodide was a highly dispersion liquid. The surface energy components of water and methylene iodide were shown in Table 2.

Table 2. Surface energy components for water and methylene iodide [14].

Liquid	Surface Energy, N/m		
	Disperse (γ^d)	Polar (γ^p)	$\gamma = \gamma^d + \gamma^p$
Water	0.0218	0.051	0.0728
Methylene iodide	0.0495	0.0013	0.0508

The surface energy of the solid (γ_s) is calculated by measuring the contact angle (θ) of two liquids using (1). The unknown values for γ^d and γ^p can be calculated by substituting the calculation for either water or methylene iodide into either one of the calculation for the liquids. Equation 2 is used to calculate the total surface energy of the solid.

$$\gamma_L \left(1 + \cos\theta\right) = 2\left(\sqrt{\gamma^d{}_S \gamma^d{}_L} + \sqrt{\gamma^p{}_S \gamma^p{}_L}\right) \tag{1}$$

$$\gamma_S = \gamma^d{}_S + \gamma^p{}_S \tag{2}$$

D. Physical Vapour Deposition (PVD) Coating

The TiN coating was deposited by VTC PVD-1000 unbalanced magnetron sputtering system for 3 hours. The deposition temperature was 400oc and substrate bias was -200V. The coating process consisted of three stages including ion cleaning, interlayer coating and TiN deposition. All substrates were sputtered-cleaned by using argon ion to remove impurity from the substrate surface. Ti interlayer was pre-deposited between TiN film and tungsten carbide substrate in order to improve adhesion between the TiN and WC substrate.

E.   Characterization of Adhesion

Rockwell-C indentation testing was performed to determine the film adhesion using Rockwell indentation tester (Mitutoyo HR 500) with a Brale diamond indenter at applied load of 60, 100 and 150 kgf. The adhesion properties were determined by analysis of the cracks formation after the indentation using optical microscope as tabulated in Table 3. The lateral crack diameter of indentation is plotted on three different applied loads as shown in Figure 2. The slopes of the indentation load versus the lateral crack diameter was used to determine the adhesion of the coatings, because they reflect the lateral cracks propagated and are proportional to the load applied [15]. The slope of the indentation load versus lateral crack diameter provides a good measure on the adhesion of coatings on substrates and was found to be more accurate than the approximate measurement of the crack initiation load [16]. Higher slopes indicate poorer coating adhesion, while lower slopes indicate better coating adhesion [16].

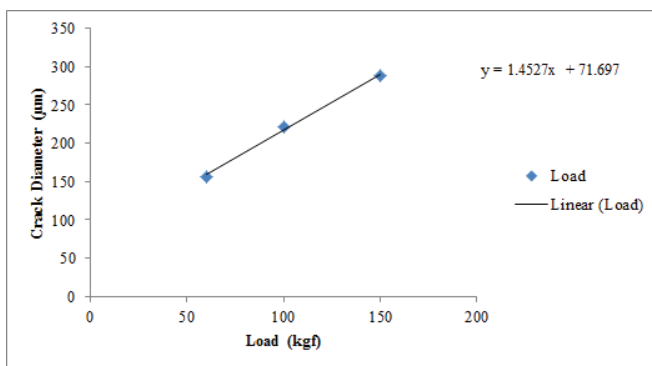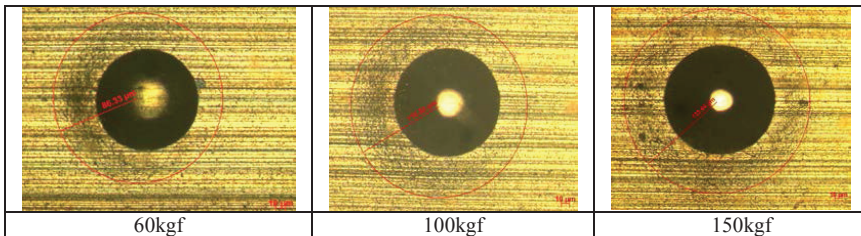Table 3. Crack diameter for substrate (run 5) treated using alkaline solution for 10 minutes with wiping.

| 60kgf | 100kgf | 150kgf |

Fig 2. Adhesion slope measurement for substrate (run 5) treated using alkaline solution for 10 minutes with wiping.

III.   RESULTS AND DISCUSSION

A.   Experimental Results

There are total of 16 experimental runs generated through the general factorial method carried out using Minitab 16 statistical software. The results of the output responses investigated are tabulated in Table 4. The surface energy data was measured using the contact angle data gathered through the contact angle measurement using Owens-Wendt method.

Table 4. Experimental results.

Run	Factors			Output Responses		
	A: Solution	B: Time (min)	C: Wiping	Surface energy (N/m)	Surface energy (Polar) (N/m)	Adhesion slope (µm/kgf)
1	A	20	No	0.119	0.0719	1.2587
2	B	20	Yes	0.1219	0.0781	0.81
3	B	20	No	0.1263	0.0805	0.3354
4	B	10	Yes	0.1221	0.0772	0.8321
5	A	10	Yes	0.1094	0.0660	1.4527
6	A	20	Yes	0.0988	0.0578	1.7287
7	A	20	Yes	0.1000	0.0572	1.6841
8	A	10	No	0.1090	0.0648	1.4929
9	A	10	No	0.1106	0.0651	1.4381
10	B	10	No	0.1246	0.0787	0.7442
11	B	20	Yes	0.1204	0.0771	1.0155
12	A	10	Yes	0.1115	0.0689	1.3526
13	B	10	No	0.1242	0.0789	0.6618
14	A	20	No	0.1188	0.0725	1.2492
15	B	20	No	0.1259	0.0793	0.3504
16	B	10	Yes	0.1196	0.0758	1.0111

B.   Analysis of Variance (ANOVA)

The determination of significant factors influencing the output responses investigated was done using analysis of variance (ANOVA). In this design, the factors with p-value less than 0.05 are considering significant factors. The main effect and interaction plots were obtained to examine the effects of factors on output responses. The main effect plot can be used to compare the relative strength of the effects across factors. It is important to know how the system behaves when variation is brought upon by varying only one parameter keeping the others constant. This gives the dependence of the system over the varied parameter. A main effect occurs when the mean response changes across the levels of a factor. For the interaction plot, this plot is used to interpret significant interactions between the process parameters.

Interaction is present when the response at a factor level depends upon the levels of other factors. Since they can magnify or diminish the main effects of the parameters, evaluating interactions is extremely important. Based on the p-value, the significant factors are solution, wiping, interaction between solution and wiping, interaction between time and wiping and interaction of all factors as depicted in Table 5.

Table 5. ANOVA for surface energy.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Solution	1	0.0007277	0.0007277	0.0007277	674.14	0.000
Time	1	0.0000000	0.0000000	0.0000000	0.00	0.981
Wiping	1	0.0001870	0.0001870	0.0001870	173.25	0.000
Solution*Time	1	0.0000039	0.0000039	0.0000039	3.61	0.094
Solution*Wiping	1	0.0000268	0.0000268	0.0000268	24.81	0.001
Time*Wiping	1	0.0001161	0.0001161	0.0001161	107.56	0.000
Solution*Time*Wiping	1	0.0000879	0.0000879	0.0000879	81.43	0.000
Error	8	0.0000086	0.0000086	0.0000011		
Total	15	0.0011580				

As indicated in ANOVA analysis in Table 5, there is no interaction between time and solution because the lines in solution versus time plot are approximately parallel, indicating a lack of interaction between the two factors. It suggests that mutual interaction between solution and time has neglible effect on the surface energy.
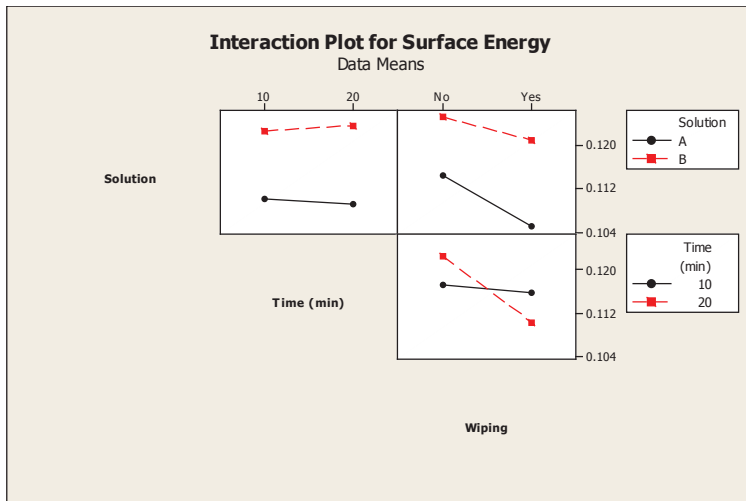

Fig 3. Interaction plot for surface energy.

The second plot depicts synergic interaction between solution and wiping. Although the lines on the plot do not cross each other, but lack of parallelism of the lines exhibit significant interaction. The greater the departure of the lines from the parallel state, the higher the degree

of interaction. Based on the interaction plot, substrate treated without the wiping process exhibits better surface energy compared to wiped substrate for both solution A and B. Wiping process using cotton gauze worsen the surface energy of the substrate due to the carbon residue left from the cotton gauze. The energy dispersive X-ray (EDX) pattern for sample treated using solution B with and without the wiping process is depicted in Figure 4. Sonoda et al.[17] reported the same finding that carbon residue worsen the coating adhesion. According to the analysis carried out using EDX for every sample, a larger amount of carbon was detected on the surface after the wiping process as tabulated in Table 6. According to Simpson and Crawshaw [18], there was about 52% of carbon element contain in the cotton gauze. Therefore, the wiping process left traces of carbon on the substrate surfaces which lead to poor wettability and resulting to the reduction of surface energy.
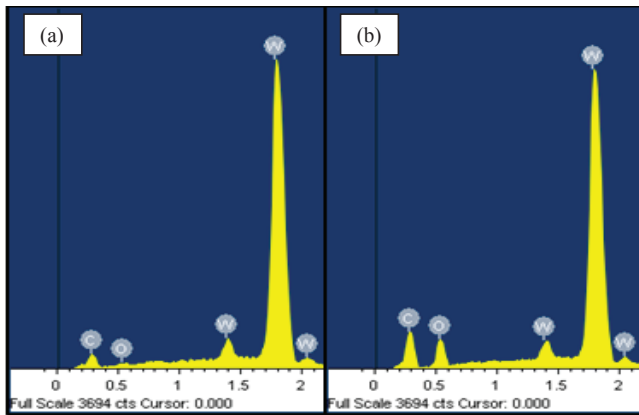

Fig. 4: EDX pattern for sample treated using solution B for 20 min (a) no wipe, (b) wipe.

Table 6: EDX analysis on the amount of carbon content before and after wiping.

Types of solution	Carbon content (wt%)			
	No wipe		Wipe	
	10 min	20 min	10 min	20 min
Solution A	6.42	6.96	7.07	7.13
Solution B	6.91	6.71	10.37	14.41

In the third plot, there exists antagonistic interaction between the time and wiping as the lines of the graph cross each other. It shows that the higher value of surface energy can be obtained at time of 20 minutes and without the wiping process. Based on the AFM image presented in Figure 4.13, substrates treated at longer time (20 minutes) have uniform surface compared to substrates treated at shorter time (10 minutes) for

both alkaline and acid solutions. The uniformity of the substrate surface resulting in better surface energy compared to irregular substrate surface. Hence, the wettability of the substrate surface is affected by surface morphology of the treated substrate. Nevertheless, the surface energy when the wiping process is carried out for both low and high level time, due to the carbon contamination left from the cotton gauze after the wiping process.
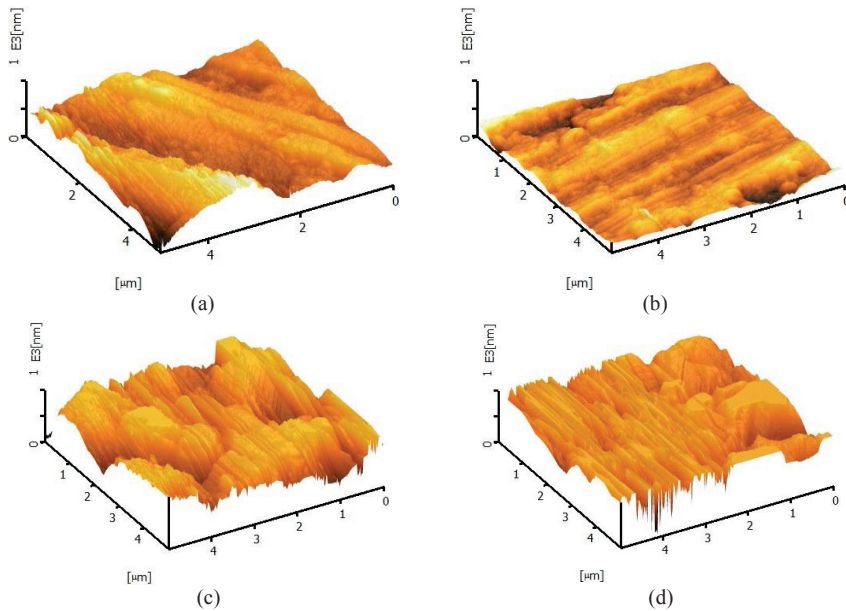

Fig. 5: AFM image for sample treated without wiping using (a) solution A for 10 minutes, (b) solution A for 20 minutes, (c) solution B for 10 minutes, (d) solution B for 20 minutes.

It is also important to know how the system behaves when variation is brought upon varying only one parameter keeping the others constant. This gives the dependence of the system over the varied parameter. A main effect occurs when the mean response changes across the levels of a factor. The main effect plot shown in Figure 6 can be used to compare the relative strength of the effects across factors. It can be asserted from the graph that the solution has positive effects while the wiping has negative effect on surface energy. Time does not have effect on the surface energy.
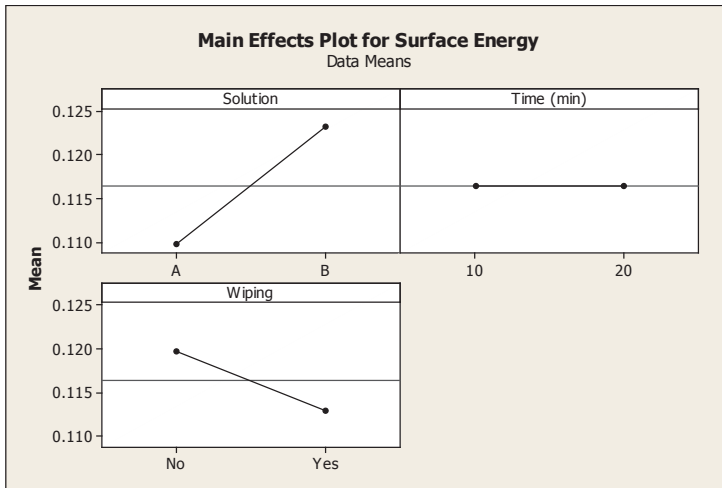
Fig 6. Main effect plot for surface energy.

C.   Correlation Study

This study is carried out to determine the relationship between surface energy and adhesion slope. The method selected to accomplish this is by calculating the coefficient of determination, R^2. The R^2 value indicates how well a regression line represents the data. If the regression line passes through every point on the scatter plot, the relationship between both output responses are well correlated. The R^2 value of 1 means there is strong positive correlation between both responses, if the R^2 value of -1 means the correlation is perfectly negative. The R^2 value of 0 represents that there is no correlation between the two responses being investigated.
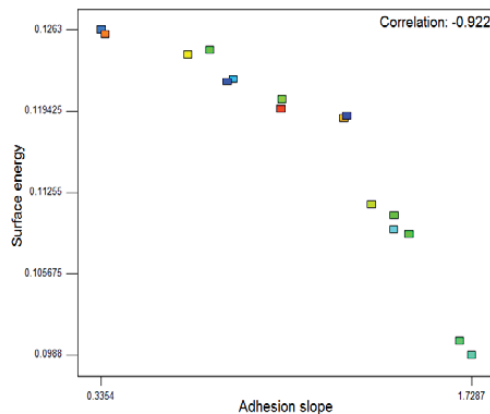

Fig 7. Correlation between adhesion slope and surface energy.

Data in Table 4 indicates that the adhesion slope has the strong linear correlation with the surface energy, with the R^2 value of -0.922 as shown in Figure 7. The strong correlation between adhesion slope and the surface energy was expected due to many reports and publication supporting the fact [6, 19]. Based on the researchers [6, 19], the increase in surface energy of the substrate lead to better adhesion between the deposited coatings and the substrate surface.
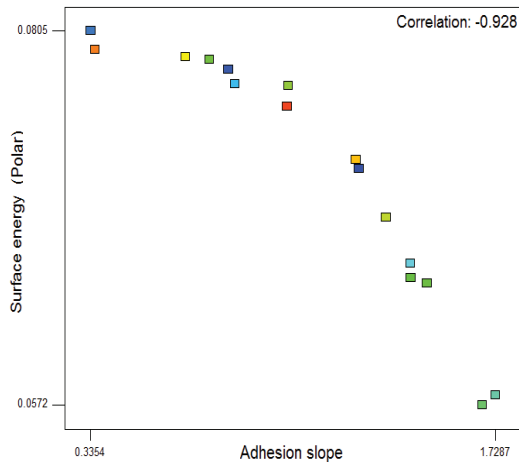

Fig 8. Correlation between adhesion slope and surface energy (polar).

The R^2 value between adhesion slope and surface energy (polar share) is -0.928 as shown in Figure 8. It shows that the polar share of the surface energy had more influence on the adhesion slope. The finding found in this study is same to the results reported by the other authors where the wettability properties of the solid surface are influenced by high surface energy, especially by the polar share [6, 11].

IV. CONCLUSION

The surface energy of substrate can be determined by measuring the contact angle between the deposited liquid and the substrate surface. A high surface energy with high polar shares influenced towards the best coating adhesion. The highest surface energy was obtained by the substrate cleaned using solution B for 20 minutes without the wiping process, with the surface energy of 0.1263 N/m, with polar share of 0.0805 N/m. The coating adhesion increases as the surface energy increases, especially in polar share. Wiping process using cotton gauze worsens the surface energy of the substrate due to the left over of the carbon residues which reduce the coating adhesion. Through the correlation

study, the polar share of the surface energy had more influence towards the coating adhesion with the coefficient of determination, R2 of -0.928. Thus, the surface energy could be an indicator to determine the coating adhesion.

ACKNOWLEDGMENT

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