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EVALUATION OF PLASMA POLYMERS OF SILANES AS ADHESION PROMOTERS FOR ORGANIC PAINT*

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Plasma-polymerized coatings were prepared in a bell-jar-type reactor equipped with a magnetron system behind parallel aluminum electrodes using an a.c. source of frequency 10 kHz. Tetramethoxysilane, dimethyldimethoxysilane and hexamethyldisilane were used as monomers. Alkyd paint was coated on titanium plates onto which plasma polymer films had been deposited, to investigate the characteristics of the plasma-deposited films as adhesion promoters. The relationship between the adhesion strength for the paint and the conditions for the plasma polymerization was studied. The properties of the plasma polymers are dependent on the conditions of plasma polymerization manifested by two domains, namely the energy-deficient and the monomer-deficient regions. In the energy-deficient region, the differences due to the monomer structure can be clearly observed; however, in this region the adhesion of the plasma polymer film to the substrate metal is poor, and the plasma polymer does not serve as a good primer for the paint. In the monomer-deficient region (for this study a power input per unit mass of starting material of $W/FM \geqslant 1.7 \times 10^9$ J kg^{-1}) improved adhesion of the paint is obtained; however, in this region the difference due to the monomer structure is found to be minimal.

1. INTRODUCTION

Adhesion failure of paints is one of the problems in the coatings industry. The purposes of primers are to protect substrates from corrosion and to give a base for finishes. They form secondary bondings with metal surfaces and adhere well to such substrates. However, if the characteristics of the surfaces are changed by water or other corrosive chemicals in the environment, through pinholes or other defects in the paints, these bondings are easily broken and adhesion failure will occur.

Many efforts have been made to reduce this problem[1]. Very thin primer coatings are used for this purpose, *e.g.* wash primers, phosphate coatings and

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conversion coatings. Basically, their mechanisms of adherence to the substrates are very similar, *e.g.* a substrate is etched in phosphoric acid to yield a very thin phosphate coating in the first stage of the coating. These treatments improve the corrosion resistance of the substrate and form a porous base for good paint adhesion[1]. Another technique developed as a coating system uses reactive silanes, which form primary organic bonds with vehicles and primary inorganic bonds with metal substrates, to give good paint adhesion. This type of primer is called an adhesion promoter. Walker has shown that organosilanes could be used as adhesion promoters for organic coatings[2]. However, adhesion failure which results from pinholes in the coating is still an unavoidable problem because of the difficulty in completely removing organic contamination from the surface[3].

Plasma polymerization is known as a technique for depositing uniform and ultrathin films onto many materials[4]. This technique makes it possible to obtain pinhole-free coatings in one step, while conventional methods require several steps. Williams and Edwards[5] reported that plasma-deposited films of styrene protected steel sheets from corrosion because of the pinhole-free coatings. Schreiber *et al.*[6] showed that corrosion was inhibited when plasma-polymerized films of organo-silicons, which had high densities and were pinhole free, were applied on metal substrates. By the use of an inert gas plasma to remove organic contamination on the substrates, complete cleaning of the surface could be achieved[5]. Furthermore, Yasuda *et al.*[7] showed that this technique enhanced the water-resistant adhesion of polymers to metal substrates.

The actual glow discharge is controlled by maintaining the glow discharge current at a constant level. However, it is difficult to compare glow discharge polymerizations if the starting materials are different because of the complexity of the reactions. Yasuda and Hirotsu[8] introduced the composite parameter W/FM, where W is the power input, F is the flow rate and M is the molecular weight of the monomer, to describe the glow discharge polymerization conditions. The parameter W/FM represents the power input per unit mass of the starting material.

Plasma-deposited films would be very useful as primers if they were to adhere well to the substrate and could be used as a base for organic coatings. The present authors investigated plasma-deposited films of silanes as adhesion promoters for alkyd paint applied to titanium plates and also the correlation between the surface properties of plasma-deposited films, the adhesion strength for the paint and the parameter W/FM of the plasma polymerization.

2. EXPERIMENTAL DETAILS

Ti–6Al–4V plates (Meta Spec. Co., TX, U.S.A.) were used as substrates to investigate the characteristics of the plasma-deposited films as adhesion promoters.

Plasma polymerization was carried out in a bell-jar-type reactor equipped with a magnetron system behind parallel aluminum electrodes[9]. The substrates, cleaned with a xylene rinse, were placed on a stainless steel disc which was rotated around its center axis between the electrodes. The monomers used for the glow discharge were tetramethoxysilane, dimethyldimethoxysilane and hexamethyldisilane (Silar Laboratories, Inc.). The monomers were fed into the reactor at pressures from 10 to 50 mTorr. In order to determine the effect of the plasma-deposited films on the

adhesion strength for the paint on the substrates, the plasma polymerization was carried out at monomer flow rates of 0.25–4.9 cm³ (standard temperature and pressure (STP)) min⁻¹ and discharge powers of 7–160 W using an a.c. source of frequency 10 kHz. The deposition rate during the glow discharge and the total thickness of the plasma-deposited films were monitored by using a quartz crystal thickness monitor (Kronos, Inc.) placed between the electrodes. The coating thicknesses were varied from 125 to 2500 Å to investigate the effect of the thickness on their characteristics as adhesion promoters.

The paint used in this investigation was Dry Swift enamel, sun yellow (alkyd-type paint, Dutch Boy). The paint was coated onto the plasma-treated surface to a wet thickness of 150 μm. The adhesion strengths, in the vertical direction, of the paint were measured by the adhesion tester of Elcometer Instruments, Ltd., in order to evaluate the characteristics as adhesion promoters of the plasma-deposited films on the titanium surfaces. Since the drying conditions for the paint were not controlled during this study, an uncoated substrate was always tested with the plasma-coated substrates, *i.e.* an uncoated sample was painted at the same time as each series of coated samples was painted. The variation in adhesive strength due to differences in the drying, conditioning etc. of the paint is accounted for by the differences in the adhesion strength between the standard (uncoated) samples.

In order to study the properties of the plasma-deposited films, the surface energies of the plasma-deposited polymers were determined according to the methods reported by Owens[10]. Samples for the surface energy studies were prepared by depositing the plasma polymer films onto pre-cleaned microscope slides and measuring the contact angles of water and methylene iodide on them. Glass slides were used, instead of the titanium substrates, because the smoother surfaces of the slides allowed for more precise determination of the surface energies of the plasma-deposited films.

Electron spectroscopy for chemical analysis (ESCA) was used to study the surface layers of these plasma-deposited polymers. The polymer samples used for this purpose were prepared by depositing the films onto aluminum foil under the same polymerization conditions used during the coating of the titanium substrates.

Scanning electron microscopy (SEM) was also used to examine the morphology of the surface of the plasma-deposited films.

3. RESULTS AND DISCUSSION

3.1. Conditions of plasma polymerization

Tetramethoxysilane was chosen from among many materials for plasma polymerization because of the good adherence of plasma-deposited polymers of silanes to substrates[6,11]. Also, it has a sufficient vapor pressure to obtain an adequate monomer flow rate in a low pressure system. Furthermore, the structure is very similar to organofunctional silanes which are used in a conventional method to improve the adhesion strength of organic coatings[2].

As shown in Fig. 1, the deposition rates of the plasma polymer of tetramethoxysilane increased with increasing power input and also increasing flow rate up to 1.00 cm³ (STP) min⁻¹. The deposition rates were lower when monomer flow rates of 1.85 and 4.45 cm³ (STP) min⁻¹ were used for plasma polymerization. The power input W
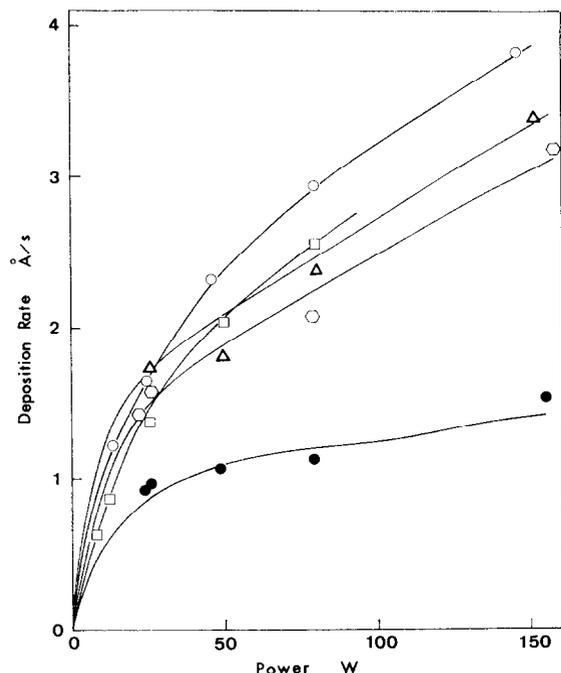
Fig. 1. Relationship between the glow discharge power and the deposition rate for the following monomer flow rates (monomer, tetramethoxysilane): ●, 0.26 cm^3 (STP) min^{-1}; □, 0.50 cm^3 (STP) min^{-1}; ○, 1.00 cm^3 (STP) min^{-1}; △, 1.85 cm^3 (STP) min^{-1}; ◇, 4.45 cm^3 (STP) min^{-1}.

and monomer flow rate F are important factors since they control the deposition rate and the polymer characteristics. However, W or F cannot be discussed as an independent variable in plasma polymerization. To discuss the effect of these factors, the composite parameter W/FM is very useful, i.e. as can be seen in Fig. 2 there is a better correlation between the deposition rate and the parameter W/FM than between the deposition rate and the power as observed in Fig. 1. At each monomer flow rate the deposition rate increases with increasing W/FM. Also, the deposition rate increases with increasing flow rate at each value of W/FM. However, these results are still not enough to understand the plasma polymerization because deposition rates are still dependent on flow rates. In order to make clear the role of the parameter W/FM in plasma polymerization, the conversion ratio DR/FM was used instead of the deposition rate, where DR is the deposition rate of the plasma polymer, F is the monomer flow rate and M is the molecular weight of the monomer. The factor DR/FM represents the conversion ratio of the monomer to polymer per unit area and may be considered as the specific deposition rate at a given plasma polymerization condition. As shown in Fig. 3, the conversion ratio of the monomer is almost uniquely related to the parameter W/FM. The wide variation observed in the curves of Fig. 2 is narrowed significantly.

In addition, two regions can be clearly seen from this figure; these are an energy-deficient (monomer-sufficient) region and a monomer-deficient (energy-sufficient) region. In the energy-deficient (monomer-sufficient) region, the yield of the polymer increased when the plasma polymerization was carried out at higher
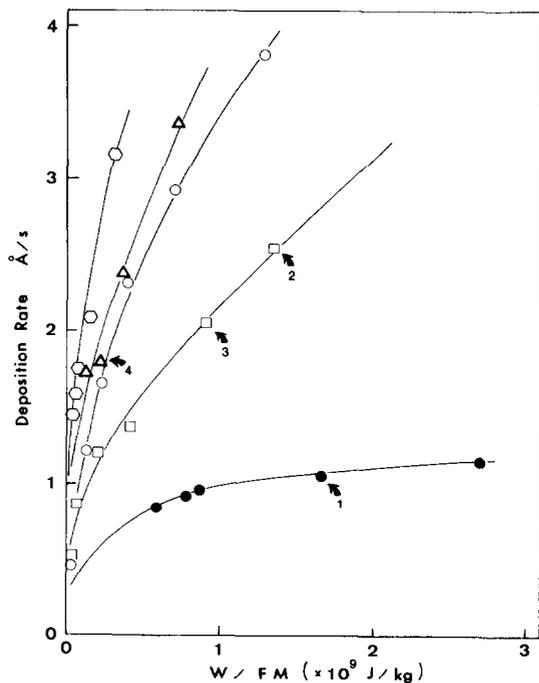
Fig. 2. Correlation between the deposition rate and the composite parameter W/FM for the following monomer flow rates (monomer, tetramethoxysilane): ●, 0.26 cm^3 (STP) min^{-1}; □, 0.50 cm^3 (STP) min^{-1}; ○, 1.00 cm^3 (STP) min^{-1}; △, 1.85 cm^3 (STP) min^{-1}; ◇, 4.45 cm^3 (STP) min^{-1}.
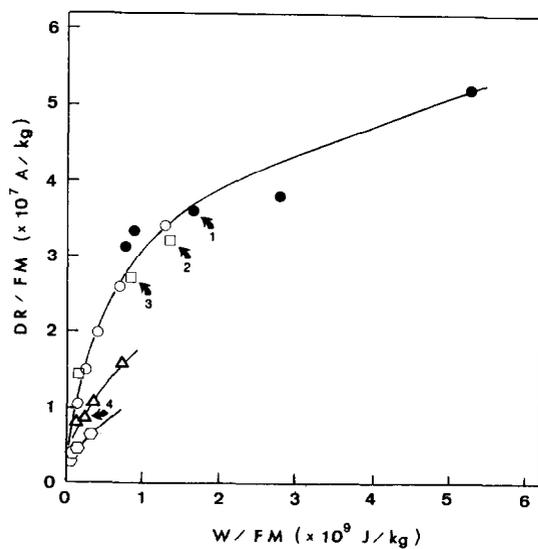

Fig. 3. Correlation between the conversion ratio DR/FM and the composite parameter W/FM for the following monomer flow rates (monomer, tetramethoxysilane): ●, 0.26 cm^3 (STP) min^{-1}; □, 0.50 cm^3 (STP) min^{-1}; ○, 1.00 cm^3 (STP) min^{-1}; △, 1.85 cm^3 (STP) min^{-1}; ◇, 4.45 cm^3 (STP) min^{-1}.

W/FM values because the monomer input was sufficient for polymerization. In contrast, in the monomer-deficient region, the supply of monomer becomes the rate-determining factor and the conversion ratio of the monomer reached a plateau even when W/FM was increased.

ESCA and SEM were carried out to investigate the effect of the parameter W/FM on the properties of the surface layers. The estimated elemental compositions of the plasma-deposited films as determined by ESCA were different, as shown in Table I. At low values of W/FM, a significant deficiency of oxygen and carbon is observed. However, an increase in the carbon-to-silicon ratio, beyond the original atomic ratio of the monomer, and an appreciable increase in the ratio of oxygen to silicon are observed as W/FM is increased. These trends may be explained by the following two phenomena which are associated with plasma polymerization: the detachment of oxygen-containing ligands and the post-plasma oxidation of trapped free radicals. Since oxygen is one of the most electronegative elements, oxygen-containing organic compounds tend to be detached preferentially in the glow discharge. This detachment of the oxygen-containing ligand, i.e. —O—CH$_3$, evidently occurs appreciably even at low W/FM values which leads to the loss of both oxygen and carbon in the film compared with the composition of monomer. At higher W/FM values, where plasma polymerization becomes more atomic than molecular, non-discriminatory fragmentation of monomer molecules takes place and consequently the effect of preferential loss of oxygen-containing ligands becomes less pronounced. The increase in oxygen content is mainly due to the incorporation of oxygen by trapped free radicals, which is evident from the oxygen contents observed for plasma polymers of hexamethyldisilane. The morphologies of the film surfaces observed by means of SEM were very similar and no cracks were observed (Fig. 4).

TABLE I

ESTIMATED ELEMENTAL COMPOSITION[a] OF THE PLASMA-DEPOSITED POLYMERS[b] BY MEANS OF ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

Monomer	Monomer flow rate (cm^3 (STP) min^{-1})	Power input (W)	Composite parameter W/FM (J kg^{-1})	Estimated composition of polymer
Tetramethoxysilane	0.26	50	1.70×10^9	$SiO_{3.2}C_{4.1}$
(SiO$_4$C$_4$)	0.50	50	0.88×10^9	$SiO_{3.1}C_{4.1}$
	1.85	50	0.24×10^9	$SiO_{2.6}C_{1.9}$
Dimethyldimethoxysilane	0.25	50	1.81×10^9	$SiO_{2.9}C_{5.4}$
(SiO$_2$C$_4$)	0.54	50	0.71×10^9	$SiO_{2.6}C_{4.5}$
	2.15	50	0.22×10^9	$SiO_{2.0}C_{2.9}$
Hexamethyldisilane	0.28	50	1.64×10^9	$SiO_{1.0}C_{3.1}$
(SiC$_3$)	0.54	50	0.85×10^9	$SiO_{1.0}C_{3.3}$
	2.06	50	0.22×10^9	$SiO_{0.6}C_{3.3}$

[a] Hydrogen content is neglected.
[b] Thickness of plasma-deposited polymer, 500 Å.

3.2. Adhesion strength for organic paint

Because of the results discussed in the previous section, in which wide variations were observed in deposition rates and elemental compositions, experi-
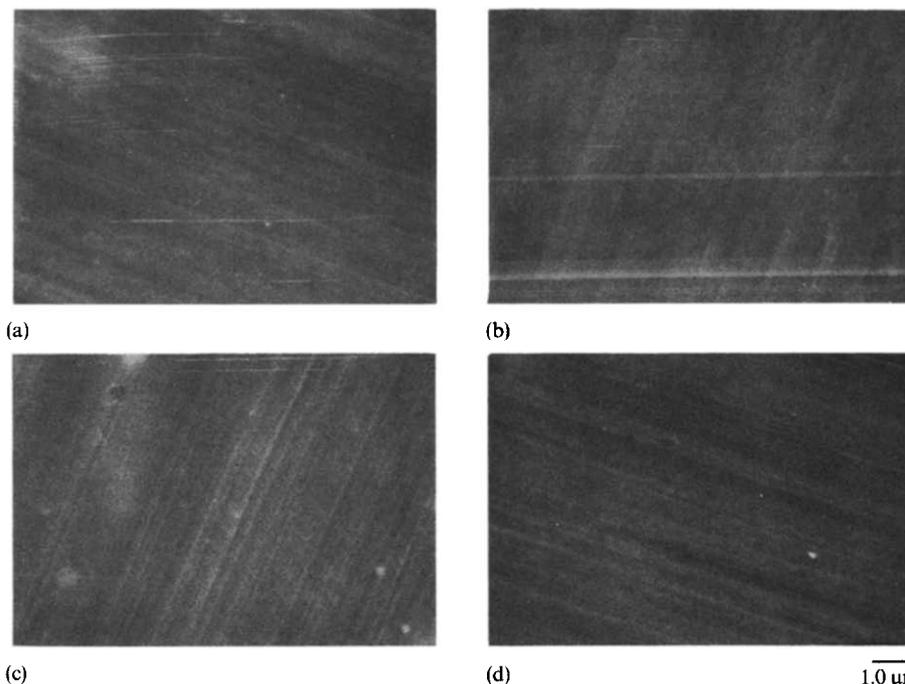
Fig. 4. Scanning electron micrographs of plasma-deposited films (thickness, 500 Å) of tetramethoxy-silane on aluminum foil: (a) standard; (b) run 1 $(W/FM = 1.70 \times 10^9 \ \mathrm{J\,kg^{-1}})$; (c) run 3 $(W/FM = 0.88 \times 10^9 \ \mathrm{J\,kg^{-1}})$; (d) run 4 $(W/FM = 0.24 \times 10^9 \ \mathrm{J\,kg^{-1}})$. Each condition corresponds to Table III and Fig. 3.

ments were carried out to determine which parameters of the plasma polymerization process have the greatest effect on the improvement of the adhesion of the paint to the titanium substrates.

It is important to note the failure mode of the coatings before discussing the results. Four failure modes were considered: (1) adhesive failure from the titanium surface (T); (2) cohesive failure of the plasma-deposited films (A); (3) adhesive failure of the paint from the plasma-deposited films (S); (4) cohesive failure of the paint (P). The failure mode A was not easily observed because of the very low thickness of the plasma-deposited films. If the failure mode is T, the plasma-deposited films cannot be used as adhesion promoters.

The effect of the thickness of the plasma-deposited films on the adhesive strength of the paint to the titanium substrates is shown in Table II. The plasma films were deposited under the same conditions $(F = 0.5 \ \mathrm{cm^3} \ (\mathrm{STP}) \ \mathrm{min^{-1}}; \ W = 50 \ \mathrm{W}; \ W/FM = 1.7 \times 10^9 \ \mathrm{J\,kg^{-1}})$ using tetramethoxysilane as the monomer. The failure modes observed for the plasma-coated samples are P and S indicating that the plasma-deposited films adhere well to the substrates. Since the failure modes are the same for all the samples it is possible to compare the adhesive strength of the paint in the different cases.

The adhesive strength of the paint was improved, compared with the value which was measured on the control surface, when the plasma-deposited films were used as adhesion promoters at thicknesses of up to 1000 Å. However, it was less than

TABLE II

EFFECT OF THICKNESS OF PLASMA-DEPOSITED FILMS ON ADHESION STRENGTH FOR THE PAINT

Thickness of plasma-deposited films[a] (Å)	Adhesion strength for the paint[b] (kgf cm^{-2})	Failure mode[c]
0 (standard)	6.5	P, T
125	8.9	P, S
250	8.1	P, S
500	10.3	P, S
1000	7.8	P, S
2500	6.0	P, S

[a] Conditions for plasma polymerization: monomer flow rate, 0.50 cm^3 (STP) min^{-1}; power input, 50 W; frequency of a.c. source, 10 kHz.
[b] Wet paint thickness, 150 μm.
[c] Failure mode is indicated as follows: P, cohesive failure of the paint; S, adhesive failure of the paint from plasma-deposited films; T, adhesive failure of plasma-deposited films from the titanium surface.

that of the standard sample at a plasma polymer thickness of 2500 Å. In this case, adhesion failure from the titanium surface also occurred. This result was considered to be caused by the brittleness of the plasma-deposited film because of too great a thickness.

In order to compare the effect of the conditions used during the plasma polymerization of tetramethoxysilane, a coating thickness of 500 Å was chosen from the above results. Table III shows the effects of the conditions of plasma polymerization of tetramethoxysilane on the adhesion strength for the paint when the deposited films were used as primers. The values given in Table III correspond to those in Figs. 2 and 3. Several conventional primers employed in the coating industry were applied to the paint–metal system of this study to compare conventional methods with the use of plasma-deposited films. Bonderizing, Parkerizing and organofunctional silane treatments, however, did not yield films that were adherent to the titanium surfaces. Only a wash primer treatment could be used to do so. The failure mode was P and S for this sample. As can be seen in Table III, the higher adhesion strengths for the paint were obtained when lower monomer flow rates and higher W/FM values were used as the conditions for plasma polymerization. The highest value which was obtained in the series of experiments was 15.1 kgf cm^{-2}. It was higher than measurements on the titanium plate treated with wash primer.

The surface energies γ_s^d and γ_s^h of plasma polymers of tetramethoxysilane are also shown in Table III, where γ_s^d and γ_s^h represent the dispersion force component and the polar component respectively. The values of γ_s^d were similar on each plasma-deposited surface. A higher adhesion strength for the paint seemed to be obtained on the surfaces which have a higher polar component for the films prepared from the tetramethoxysilane.

Other types of silanes were also applied as monomers to study the effect of monomer structure on the adhesion strength for the paint. Dimethyldimethoxysilane and hexamethyldisilane were chosen because of similarities in structure with tetramethoxysilane. The correlations between the conversion ratio DR/FM and the composite parameter W/FM for both silanes, shown in Fig. 5 and Fig. 6 respectively,

TABLE III

EFFECT OF CONDITIONS OF PLASMA POLYMERIZATION[a] ON ADHESION STRENGTH FOR THE PAINT

Run[b]	Monomer flow rate (cm³ (STP) min⁻¹)	Power input (W)	Composite parameter W/FM (J kg⁻¹)	Adhesion strength for the paint[c] (kgf cm⁻²)	Failure mode[c]	Surface energies on plasma-deposited films (dyn cm⁻¹)	
						γ_s^d	γ_s^h
Standard[d]	—	—	—	9.8	P, T	—	—
Standard[e]	—	—	—	12.1	P, S	—	30.8
1	0.26	50	1.7×10^9	15.1	P, S	31.5	26.8
2	0.50	80	1.41×10^9	12.3	P, S	30.0	25.2
3	0.50	50	0.88×10^9	13.1	P, S	31.6	23.2
4	1.85	50	0.24×10^9	8.4	P, S, T	29.4	

[a] Monomer, tetramethoxysilane; thickness of plasma-deposited films, 500 Å.

[b] The numbers correspond to those in Figs. 2 and 3.

[c] Wet thickness of the paint and failure mode as given in Table II.

[d] No treatment.

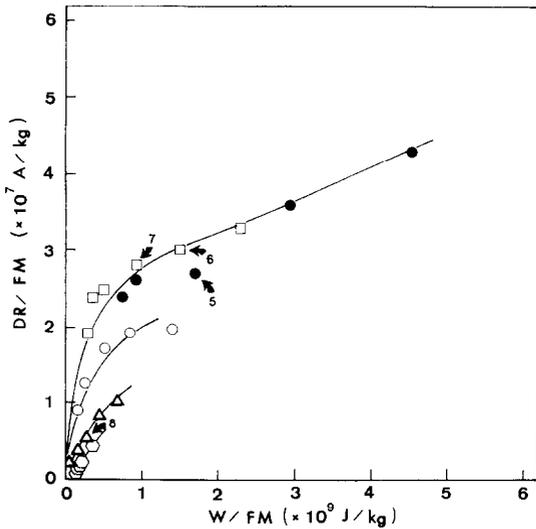[e] Wash primer was applied on the titanium surface.

Fig. 5. Correlation between the conversion ratio DR/FM and the composite parameter W/FM (monomer, dimethyldimethoxysilane).
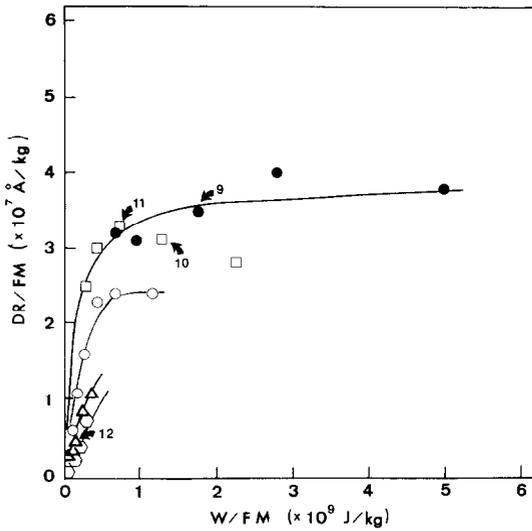

Fig. 6. Correlation between the conversion ratio DR/FM and the composite parameter W/FM (monomer, hexamethyldisilane).

were very similar to that for tetramethoxysilane. Therefore, values of W/FM which were similar to those used for tetramethoxysilane were chosen as conditions for plasma polymerization to compare the different starting monomers. The values from the measurements of adhesion strength for the paint are shown in Tables IV and V. Once again failure modes were P and S.

Improvement of the adhesion strength for the paint was observed in both cases. The higher adhesion strengths were obtained when higher values of W/FM were

TABLE IV

EFFECT OF CONDITIONS OF PLASMA POLYMERIZATION[a] ON ADHESION STRENGTH FOR THE PAINT

Run[b]	Monomer flow rate (cm³ (STP) min⁻¹)	Power input (W)	Composite parameter W/FM (J kg⁻¹)	Adhesion strength for the paint[c] (kgf cm⁻²)	Failure mode[c]	Surface energies on plasma-deposited films (dyn cm⁻¹)	
						γ_s^d	γ_s^h
Standard[d]	—	—	—	7.8	P, T	—	—
5	0.25	50	1.81×10^9	9.5	P, S	31.0	13.0
6	0.64	80	1.34×10^9	8.3	P, S	35.0	8.8
7	0.54	50	0.71×10^9	8.7	P, S	35.5	7.7
8	2.15	50	0.22×10^9	8.1	P, S	35.2	3.7

[a] Monomer, dimethyldimethoxysilane; thickness of plasma-deposited films, 500 Å.

[b] The numbers correspond to those in Fig. 5.

[c] Wet thickness of the paint and failure mode as given in Table II.

[d] No treatment.

TABLE V

EFFECT OF CONDITIONS OF PLASMA POLYMERIZATION[a] ON ADHESION STRENGTH FOR THE PAINT

Run[b]	Monomer flow rate (cm³ (STP) min⁻¹)	Power input (W)	Composite parameter W/FM (J kg⁻¹)	Adhesion strength for the paint[c] (kgf cm⁻²)	Failure mode[c]	Surface energies on plasma-deposited films (dyn cm⁻¹)	
						γ_s^d	γ_s^h
Standard[d]	—	—	—	6.3	P, T	—	
9	0.28	50	1.64×10^9	10.0	P, S	39.6	0.8
10	0.56	80	1.31×10^9	8.6	P, S	37.5	1.4
11	0.54	50	0.85×10^9	8.5	P, S	37.5	1.4
12	2.06	50	0.22×10^9	9.0	P, S	32.7	1.0

[a] Monomer, hexamethyldisilane; thickness of plasma-deposited films, 500 Å.
[b] The numbers correspond to those in Fig. 6.
[c] Wet thickness of the paint and failure mode as given in Table II.
[d] No treatment.

used during the plasma polymerization process. Surface energies were also determined to examine the surface properties of the polymer films from these monomers. The γ_s^d values were similar for each monomer, while the γ_s^h values increased with increasing W/FM; however, the γ_s^h values were much lower than those of the films from tetramethoxysilane. When hexamethyldisilane was used as the monomer for the plasma polymerization, the γ_s^d value was highest while the γ_s^h value was lowest. When dimethyldimethoxysilane was applied for the plasma polymerization, both component values were intermediate between those of tetramethoxysilane and hexamethyldisilane. In the case of tetramethoxysilane, the γ_s^d value was lowest and the γ_s^h value was highest. The adhesion strengths for the paint on the polymers were very similar and were slightly improved compared with that of the standard sample in each case.

These results indicated that the surface energies of plasma polymers of silane derivatives used in this study vary depending on both the chemical structure of the monomers and the conditions of plasma polymerization. However, these parameters, *i.e.* γ_s^d and γ_s^h, of the plasma polymer surfaces cannot be uniquely correlated to the improvement of adhesion of the paint. The more important factor found in this study is that the best adhesion strength (for each monomer) was obtained when the plasma polymerization was carried out at a W/FM value of approximately 1.7×10^9 J kg^{-1}. In other words, if the plasma polymerization is carried out near or in the monomer-deficient region, similar results for adhesion improvement were obtained regardless of γ_s^d and γ_s^h values. This observation may reflect that the adhesion of a plasma polymer to the substrate metal surface is still the key factor in the use of plasma polymer primers.

Since the overall adhesion of a paint to a metal surface is dependent on the nature of both the paint and the metal, the best choice of primer should also depend on the combination. This study was aimed at obtaining information on parameters of plasma polymerization which might influence the primer characteristics of plasma polymers. The substrate and the paint were arbitrarily chosen; nevertheless, the trends found in this study for the improvement in adhesion of organic paint to titanium surfaces are in the same general direction found for the improvement in adhesion of Parylene polymers to platinum surfaces discussed in ref. 7. Further studies to explore the atomic interfacial mixing principle by plasma polymerization seem to be needed in order to utilize fully the advantages of plasma polymerization for the primer applications.

REFERENCES

1   W. M. Morgans and J. R. Taylor, *Introduction to Paint Technology*, Oil and Colour Chemists'
     Association, Wembley, 1976.
2   P. Walker, *J. Coatings Technol.*, *52* (670) (1980) 49.
3   C. H. Hare, *Corrosion and the Preparation of Metallic Surfaces for Painting*, Federation Series on
     Coatings Technology, Unit 26, Federation of Societies for Paint Technology, Philadelphia, PA,
     1978.
4   H. Yasuda, *J. Polym. Sci.*, *16* (1981) 199.
5   T. Williams and J. H. Edwards, *Trans. Inst. Met. Finish.*, *44* (1966) 199.
6   H. P. Schreiber, M. R. Wertheimer and A. M. Wrobel, *Thin Solid Films*, *72* (1980) 487.
7   H. K. Yasuda, A. K. Sharma, E. B. Hale and W. J. James, *J. Adhes.*, *13* (1982) 269.
8   H. Yasuda and T. Hirotsu, *J. Polym. Sci., Polym. Chem. Edn.*, *16* (1978) 743.
9   N. Inagaki and H. Yasuda, *J. Appl. Polym. Sci.*, *26* (1981) 3425.
10   D. K. Owens, *J. Appl. Polym. Sci.*, *13* (1969) 1741.
11   A. M. Wrobel, J. Kowalski, J. Grebowicz and M. Kryszewski, *J. Macromol. Sci. Chem.*, *17* (3)
     (1982) 433.