DRAFT SF 298

1. Report Date (dd-mm-yy)	2. Report Type	3. Dates covered (from... to)

4. Title & subtitle Adhesion Promotion and Corrosion Prevention from Coatings Based on Sol-Gel Technology Tri-Service Committee on Corrosion Proceedings	5a. Contract or Grant #
	5b. Program Element #

6. Author(s) Dr. Lynn C. Yanyo	5c. Project #
	5d. Task #
	5e. Work Unit #

7. Performing Organization Name & Address	8. Performing Organization Report #

9. Sponsoring/Monitoring Agency Name & Address Tri-Service Committee on Corrosion USAF WRIGHT-PATTERSON Air Force Base, Ohio 45433	10. Monitor Acronym
	11. Monitor Report #

12. Distribution/Availability Statement
Approved for Public Release
Distribution Unlimited

13. Supplementary Notes

14. Abstract

15. Subject Terms
Tri-Service Conference on Corrosion

Security Classification of			19. Limitation of Abstract	20. # of Pages	21. Responsible Person (Name and Telephone #)
16. Report	17. Abstract	18. This Page			

TRI-SERVICE CONFERENCE ON CORROSION

1994 TRI-SERVICE · DEPARTMENT OF DEFENSE · UNITED STATES OF AMERICA · CONFERENCE ON CORROSION

21-23 JUNE 1994

SHERATON PLAZA HOTEL
ORLANDO, FLORIDA

PROCEEDINGS

Adhesion Promotion and Corrosion Prevention from Coatings Based on Sol-Gel Technology

Dr. Lynn C. Yanyo
Staff Scientist
Lord Corporation
405 Gregson Drive
Cary, NC 27511

Using a unique form of sol-gel technology, thin organic/ceramic (ceramer) coatings have been applied to metal surfaces to enhance such surface properties as adhesion promotion and corrosion prevention. Isotropic coatings derived from tetraethoxysilane, for example, have been found to effectively inhibit corrosion while being only 100-1000 Å thick. The formation of anisotropic (functionally gradient) coatings permits greater flexibility over the resulting properties. Using combinations of monomers with appropriate reactivities permits the single-step synthesis of anisotropic coatings that can both promote adhesion and prevent corrosion.

Introduction

Sol-gel processing is a method whereby small molecules can be converted into polymeric or ceramic materials [1-7]. Typically, one starts with molecules of the form MR_4, where the R groups are either organic radicals, such as CH_3CH_2- and CH_3CH_2O- or halogens. The metal (M) is typically silicone but can be many other species such as titanium, zirconium, aluminum, etc. [1]. Representative compounds include tetraethoxysilane, dimethyldichlorosilane, and titanium isopropoxide. These small molecules are mixed in an appropriate solvent with water and a catalyst. After a period of time the monomers condense into a matrix that can later be dried and perhaps fired to form solid three-dimensional objects. Depending on the nature of the metal and the R groups, one can form anything from organic polymers such as polydimethylsiloxane to inorganic ceramics such as silicon dioxide.

Sol-gel coatings can be applied to substrates using two different methods. The first, and most widely used, involves making a coating

material from the acid-catalyzed hydrolysis and partial condensation of metal alkoxides. This material is spread, dipped or spun onto the substrate and subsequently cured or hardened. An alternative, patented [8-10] approach reported in this paper is the base-catalyzed growth of coatings directly on the substrate.

In this method, metal alkoxides are mixed with solvent, water, and a basic catalyst in the presence of a substrate (such as aluminum). As the monomers condense, some of them react with the surface of the substrate. As the condensation continues a coating is deposited onto, or more correctly reacted with, the substrate.

If the initial coating solution is formulated such that it contains several metal alkoxides of differing reactivity then the nature of the coating being formed will be a function of time. The lowest layers of the coating will be derived from the most reactive monomers while the upper layers will be made from the least reactive monomers.

The properties of the coating can be optimized so that each part of the coating provides optimum properties. One might choose, for example, for the first layer to interact strongly with the substrate, an intermediate layer to provide some sort of barrier, and a final layer to provide compatibility with a subsequently applied top coat (e.g. paint, primer or adhesive). Properties that can be altered as a function of depth into the coating include elastic modulus, free volume, density, index of refraction, chemical reactivity, barrier properties, electrical and thermal conductivity and extent of crosslinking.

Experimental

The substrates used for corrosion testing were thin films (1000-2000 Å) of aluminum (99.99%) or iron (99+%) that had been evaporated onto glass microscope slides or coupons of 2024-T3 aluminum. Corrosion testing was performed in either 0.1N NaOH or 0.1 N HCl (for aluminum) or pH 3 buffer (for iron, potassium acid phthalate/HCl) by monitoring the presence of the reflective metal surface visually until it disappeared. Corrosion testing of metal coupons was performed by monitoring the rate of weight loss of samples exposed to either 0.1 N NaOH or 0.1 N HCl. The coupons were bonded as lap shears with a 2.5 x 2.5 cm overlap using Tyrite 7520 (Lord Corporation) two part urethane adhesive. The samples were cured for 4 days at room temperature before testing. Selected samples were exposed to boiling water for 24 hours in an all glass apparatus.

The sol gel coating solutions, unless otherwise specified, contained 70 ml of ethanol, 27 ml of water, 3 ml of concentrated ammonium hydroxide and the silane monomers of choice (typically 6 ml). Samples were treated by immersion at room temperature for 10 minutes to 24

hours as indicated, rinsed in ethanol and/or water and allowed to air dry. Some samples for corrosion testing were heated to 100°C for 1 hour prior to testing.

ESCA sputtering was performed with 4keV argon ions. Atomic concentrations were determined from integrated peak areas. Binding energies were corrected for charging by arbitrarily assigning the adventitious carbon peak a binding energy of 284.6 eV. Ellipsometry was performed on a Rudolph Instruments Model 432A42B41 null point ellipsometer using 632.8 nm laser radiation. Thickness values were obtained by computer analysis with the assumption that the index of refraction of the coating was 1.4 [11].
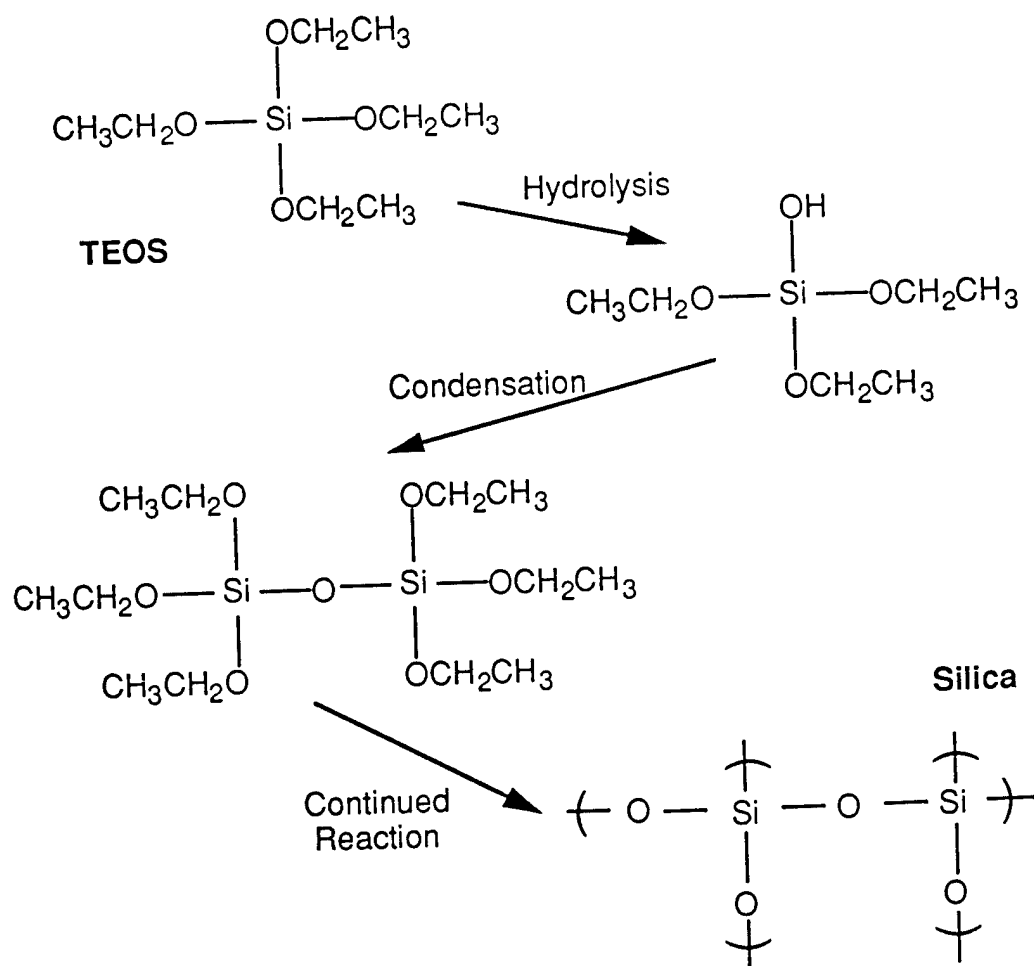
Figure 1. Reactions involved in the hydrolysis and condensation of TEOS to amorphous silica.

Results and Discussion

Isotropic coatings can be made by reacting a single monomer (or multiple monomers with similar reactivity) with an appropriate substrate. The substrates used in this work were films of aluminum or iron that had been evaporated onto glass or aluminum coupons. Isotropic films were made on these substrates by allowing TEOS (tetraethylorthosilicate or tetraethoxysilane) to react with water in a solution containing ethanol and ammonium hydroxide. As the hydrolysis and condensation reactions proceed (Fig. 1) colloids are formed in solution, causing the solution to become blue then milky white. At the same time, the silane species are reacting with active sites on the substrate surface, forming a thin coating consisting of SiO_2 (and aluminosilicates in the case of the aluminum substrate).

Under typical reaction conditions, it takes approximately 20 minutes for the coating to reach its maximum thickness of about 400-700 Å (Fig. 2). This thickness was determined by ellipsometry and was confirmed by several other techniques, including ESCA sputter depth profiling, profilometry, gravimetric analysis, and other techniques. The coating that results from this treatment is invisible to the unaided eye. In scanning electron microscopy at 10,000-100,000X, the coating has few discernible features other than those of the substrate.
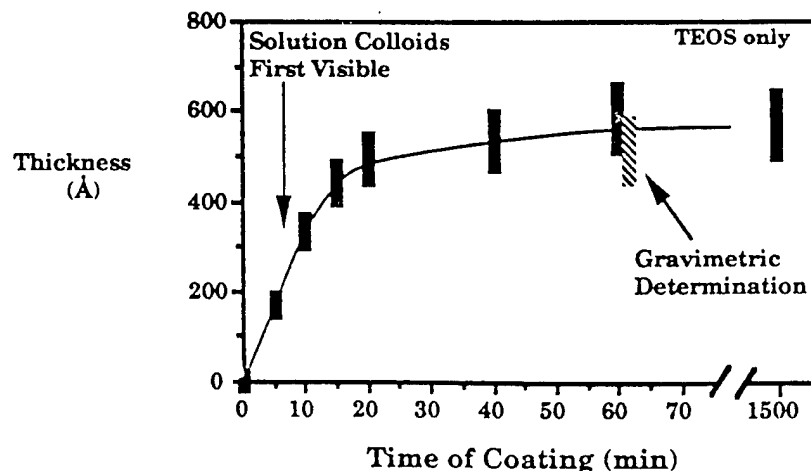
Figure 2. Coating thickness by ellipsometry as a function of the time that aluminum samples (2000Å thick on glass) were immersed in the reacting solution of ethanol, water, concentrated ammonium hydroxide and TEOS.

The corrosion protection afforded by the isotropic coating was quantified in several ways. The simplest method involved analysis of the mirror-like evaporated metal samples described above. The time

4

necessary for 1000Å of aluminum to corrode and become transparent is recorded (Table 1). It is evident from the data that these coatings do provide significant protection to the surfaces of aluminum and iron. In each case, the rate of corrosion has been reduced by a factor of 150-2000. Similar protection can be obtained on steel and aluminum alloy coupons.

**Table 1.** Corrosion protection from sol-gel coatings

Sample	Time (min) to corrode in 0.1 N NaOH	Time (min) to corrode in 0.5 N HCl
Untreated Aluminum (1000 Å)	3	420
Aluminum with 1 coat	1500	74,880
Aluminum with 2 coats	1500-2000	
Aluminum with 20 coats	2200	

Sample	Time (min) to corrode in buffered water, pH 3
Untreated iron (200Å)	2
Iron with 1 coat	1000-4000

The properties of the coating can be changed by varying the amounts and types of ingredients used and the reaction conditions. Figure 3 shows a plot of the thickness of the resulting coating as a function of the amount of TEOS present. As the amount of TEOS increases, the thickness of the coating increases in a straightforward manner. This result is consistent with the theory that the coating is limited in thickness by the availability of silane monomers in the solutions. These monomers are used up by the reaction with the substrate and by reaction to form colloids in solution. If the number of nucleation sites in solution is relatively unaffected by the TEOS concentration, the thickness of the surface coating and the diameter of the solution colloids should increase as the amount of TEOS increases.

This hypothesis is also consistent with the effect observed when the colloids are allowed to form partially before immersing the sample in the solution. In this case most of the monomers are no longer available for reaction with the surface; only pre-colloids, and these would be less likely to attach to the surface in a well-packed manner to form an integral coating. As the length of time between formulation of the solution and the

immersion of the substrate increases, the thickness of the coating decreases (Fig. 4).
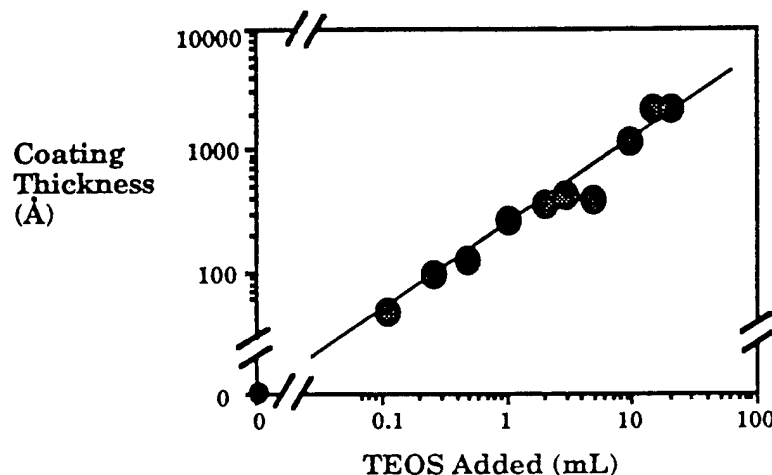
Figure 3. Coating thickness by ellipsometry as a function of the amount of TEOS added to the reacting solution. Aluminum samples (2000Å) were coated for 24 hours and baked dry at 100 °C for 60 minutes prior to testing.

Remarkably, the ability of the coatings to prevent corrosion of the underlying substrate does not seem to be directly related to the thickness of the coating. Figure 5 shows a plot of the time necessary to corrode 2000Å of aluminum in aqueous base after being treated with coating solutions containing various levels of TEOS. Protection increases slightly as the level of TEOS is increased from 0 to 0.003 ml. Between 0.003 and 0.01 ml of TEOS, the corrosion protection increases by a factor of nearly 100. Additional TEOS seems to do little to further increase the corrosion protection. In fact the maximum corrosion protection is reached while the coating is significantly less than 100Å thick.

It is thought that the corrosion protection of aluminum is actually being provided by a layer of aluminosilicate formed by reaction of TEOS with the native oxide on the aluminum. Further coating material (SiO₂) that builds up above the aluminosilicate layer provides little additional protection. This hypothesis is supported by data obtained by corrosion testing of samples with multiple coatings and ESCA.

The application of multiple coats does not significantly increase the corrosion protection over that offered by one coat. (Table 1) Even a sample with 20 coats that is thick enough (1 mm) to offer significant scratch and wear resistance has a corrosion resistance similar to that of a sample with one coat. If the entire coating had been acting as a barrier, one would expect that 20 coats would be significantly more effective than

one coat. If it is a layer of aluminosilicate at the metal surface that is actually providing the protection, it is not surprising that additional silicon dioxide above it does not improve the protection.
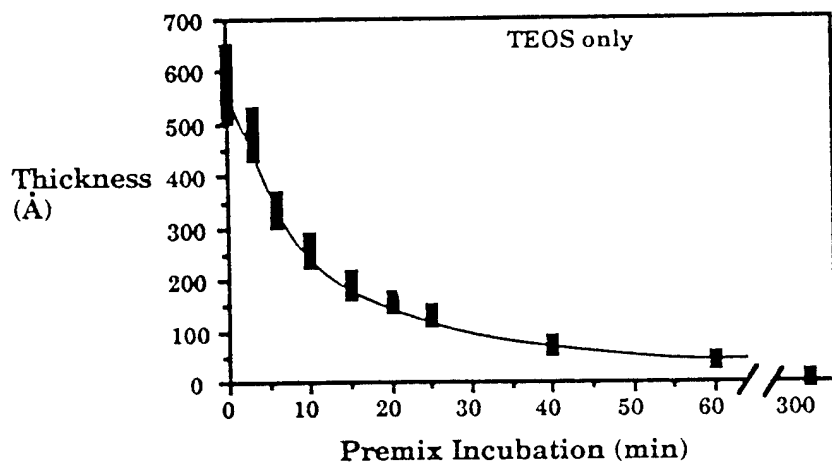
Figure 4. Coating thickness (by ellipsometry) as a function of the time between mixing the solution and the immersion of the substrate. Aluminum samples (2000Å on glass) were coated for 24 hours and baked dry at 100°C for 1 hour prior to testing.
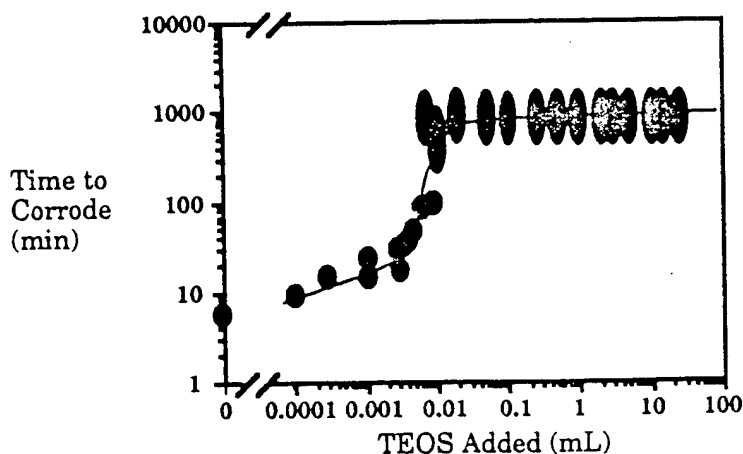
Figure 5. Corrosion protection as a function of the amount of TEOS added to the reaction solution. Aluminum samples (2000Å on glass) were coated for 24 hours and baked at 100°C for 1 hour prior to corrosion testing in 0.1 N NaOH.

ESCA analysis also supports the contention that corrosion protection is provided by the aluminosilicate layer. Figure 6 shows the ESCA analysis of the coated surfaces used in the corrosion testing of Figure 5. When very thin SiO2 coatings are applied, the binding energies of the silicone atoms on the surface are similar to those obtained for the

7

aluminosilicate materials but not to those for silica gel [12]. As the amount of TEOS is increased, the average binding energy gradually shifts toward that of silica gel. The corrosion protection is essentially at its maximum when the surface begins to look like silica gel.
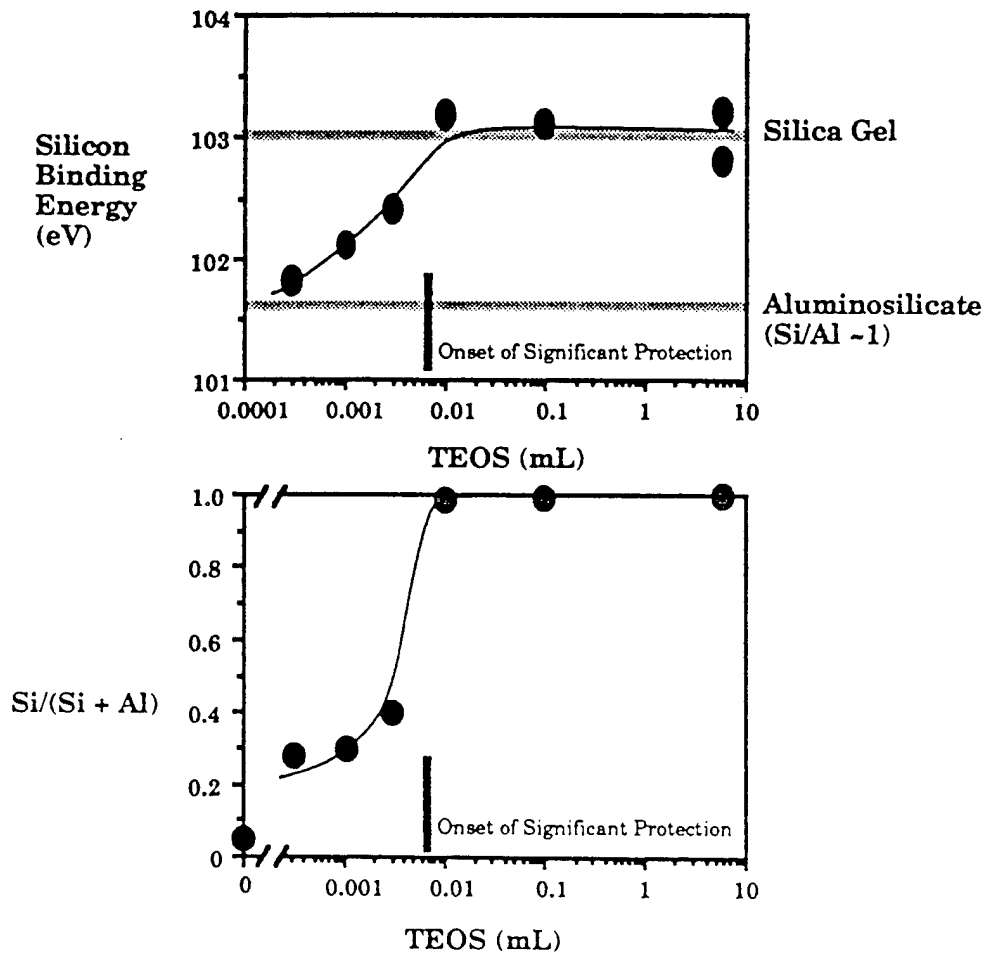
Figure 6. ESCA analysis of aluminum surfaces coated with various amounts of TEOS as in Figure 5. Top: Silicon binding energy corrected for charging by assigning the adventitious carbon peak a value of 284.6 eV. The binding energies obtained for a typical aluminosilicate and for silica gel are shown for reference. Bottom: The atomic proportion of silicon to the total of aluminum and silicon.

Likewise, Figure 6 shows the relative abundance of silicon on the aluminum surface as the coating is applied. In this case, the maximum corrosion protection has been reached in samples where the aluminum is just covered by the silica. Again, significant quantities of silica on top of the aluminosilicate do not contribute to corrosion protection. The mechanism by which this aluminosilicate layer provides protection may

be similar to that afforded by traditional silicate coatings that have been used in anodic protection of aluminum surfaces [13].

The addition of certain organic moieties to the ceramer coating might be expected to lead to better adhesion between organic adhesives and the coating, just as traditional adhesion promoters function. One drawback, however, is that the addition of many organic species leads to a decrease in the corrosion protection of the coating. If one could design coatings where little or no organics were incorporated until an effective barrier had fully formed, one might avoid the problem of the presence of organics within the coating, reducing the corrosion protection. Obviously such layered structures can be formed in multiple steps, but from an engineering or processing perspective, this would be much less desirable than producing a layered effect in one step.

The key to formation of functionally gradient coatings in a single step is controlling the reactivity of the various components in the reaction. The silanes that react more quickly coat the substrate first and as time proceeds the coating forms from less and less reactive materials. One then only needs to control the reactivity to such an extent that the desired materials end up in the desired places in the coating.

There are three methods of controlling the reactivity of metal alkoxides in solution. The first is to change the metal. Titanium alkoxides are, for example, much more reactive than silicon alkoxides. A second method is to influence the reactivity of the metal alkoxide through the nature of the non-alkoxy groups attached to the metal. Methyltriethoxysilane is less reactive than tetraethoxysilane by a factor of more than 100. This method of reducing reactivity is limited because of the usual reason for the incorporation of organic groups is to effect the physical properties of the coating not just the process.

The final way of controlling the reactivity of these materials is through the alkoxy group itself. Larger alkoxy groups are less reactive, both for steric and electronic reasons. One can order the reactivity of alkoxy groups as follows:

methoxy > ethoxy > isopropoxy > s-butoxy

In practice one can gain a measure of the reactivity of various silanes by mixing them into a reaction solution and observing how long it takes for colloids to form. Using this information, one could, for example, control the relative reactivity of a vinyl silane to a methyl silane by having different alkoxy groups on them. To form a coatings with methyl silane in the lower regions of the coating and vinyl silanes near the surface, one could use methyltrimethoxysilane and vinyltriethoxysilane.

In addition to the ability to use various simple alkoxy structures, one can obtain further control by using other ligands attached to the metal atom such as acetoxy, phenoxy, halides, hydrides and hydroxyls.

Applications

There are, of course, a wide range of potential applications for such anisotropic coatings. Combination of corrosion protection and adhesion promotion is a case where a single isotropic coating cannot provide the same benefits as anisotropic or layered coating. Adhesion promotion by aminosilanes is a widely practiced technology, and 3-aminopropyl-triethoxysilane is an effective adhesion promoter for bonding aluminum substrates with a urethane adhesive (while TEOS alone is not).

Conversely, coatings derived from TEOS provide significant corrosion protection while those derived from aminosilane do not. In fact, in mixed coatings of TEOS and aminosilane, it is most important for the N/Si atomic ratio to be low (<0.05) for optimum corrosion protection and high (>0.1) for optimum adhesion promotion. If one makes coatings where the lower regions are primarily derived from TEOS (forming a corrosion resistant barrier) and the upper regions are primarily aminosilane (promoting adhesion) then one can get both properties optimized at once, a feat not possible with a single isotropic coating.

Table 2 illustrates the dramatic effect of silane reactivity and its distribution within the coating on adhesion and corrosion. TEOS is more reactive than 3-aminopropyltriethoxysilane which is more reactive than TBOS (tetrabutoxysilane). In formulations where the aminosilane is not at the surface of the coating, adhesion in poor. In formulations where the aminosilane forms the base of the coating, corrosion protection is poor. In the formulation of TEOS and 3-aminopropyltriethoxysilane, corrosion protection is conferred by the TEOS and the aminosilane is at the surface to provide adhesion promotion.

Conclusions

Anisotropic, multilayered coatings can be formed by taking advantage of the relative reactivity of monomers present in sol-gel reactions. These anisotropic coatings permit the properties of different regions of a coating to be independently optimized for different functions. Anisotropic coatings can, for example, provide corrosion protection as effectively as silicate only coatings and provide adhesion promotion as effectively as organically modified coatings. There are instances where underbond corrosion must be prevented in order to attain maximum environmental resistance in bonding to metal. In these cases, both

adhesion promotion and corrosion prevention must be simultaneously optimized, as is obtained from anisotropic coatings.

Table 2. Bond strengths of joints made from aluminum alloy coupons with various coatings using a two part commercial urethane adhesive, Tyrite 7520. The joints were exposed to boiling water for 2 hours prior to testing. The table also shows corrosion rates for evaporated aluminum samples with similar coatings in aqueous base. Highlighted formulation shows both properties optimized.

Coating Ingredients	Bond Strength (kg/in^2)	Corrosion Rate
None	15	1 (by definition)
TEOS only	0	0.002
Aminosilane only	475	0.6
TEOS + Aminosilane	**620**	**0.002**
TBOS + Aminosilane	75	0.01
TEOS + Aminosilane + TBOS	30	0.003
Two step coatings		
TEOS, then Aminosilane	580	0.002
Aminosilane, then TEOS	0	0.3

References

1 R. Roy, *Science*, **238**, 1664 (1987)
2 H. Schmidt, H. Scholze and A. Kaiser, *J. Non-Cryst. Solids*, 63, 1, (1984)
3 H. Schmidt and H. Scholze, in *Glass - Current Issues*, A. F. Wright and J. Dupuy (eds.) p. 263, Martinus Nijhoff, Boston (1985).
4 H. -H. Huang and G. L. Wilkes, *Polym. Bull.*, **18**, 455 (1987); H. - H. Huang, B. Orler and G. L. Wilkes, *ibid.* , **14**, 557 (1985); H. -H. Huang, B. Orler and G. L. Wilkes, *Macromolecules*, **20**, 1322 (1987).
5 B. Seiferling and H. Schmidt, *Mater. res. Soc. Symp. Proc.*, **73**, 739 (1986).
6 D. Ravaine, A. Seminel, Y. Charbouillot and M. Vincens, *J. Non-Cryst. Solids*, **82**, 210 (1986).
7 D. R. Ulrich, *Chemtech*, 242 (1988).
8 S. R. Holmes-Farley and L. C. Yanyo, *Ultra-Thin, Uniform Sol-Gel Coatings*, U.S. Patent 5,175,027, Dec. 29, 1992.
9 S. R. Holmes-Farley, L. C. Yanyo and Anna M. Thuer, *Method for Metal Bonding,* U.S. Patent 5,139,601, Aug. 18, 1992.
10 S. R. Holmes-Farley and L. C. Yanyo, *Layered Sol-Gel Coatings*, U.S. Patent 5,182,143, Jan. 26, 1993.
11 F. L. McCrackin, E. Passaglia, R. R. Stromberg and H. L. Steinberg, *J. Res.* (NBS), **67A**, 363 (1963).
12 C. D. Wagner, W. W. Riggs, L. E. Davis, J. R. Moulder and G. E. Muilenberg, *Handbook of X-ray Photoelecron Spectroscopy*, Perkin Elmer, Eden Prarie, MN (1979).
13 G. Wranglen, *An Introduciton to Corrosion and Protection of Metals*, p. 169, Chapman and Hall, New York, (1985).