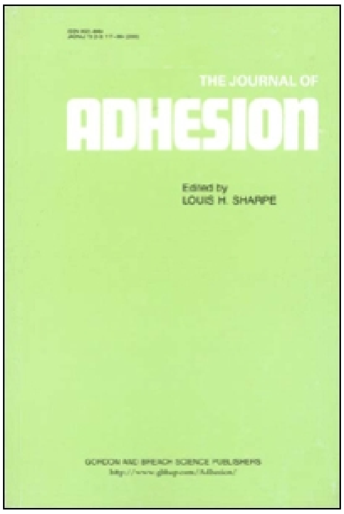

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Surface Modification of Magnesium Particulates with Silanes Presented as Vapour: Inhibition of Atmospheric Corrosion

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We present the use of three silane reagents in the vapour phase to react with the surface of magnesium and compare their performance against uncoated material using an accelerated corrosion test. The influence of atmospheric exposure on the corrosion test was also considered and rationalised based on previous models of the magnesium surface. XPS analysis determined that the silanes coated the surface of the metal; the accelerated gas evolution test showed very good corrosion inhibition properties for triethoxy(1H,1H,2H,2H-perfluoro-1-octyl)silane (FSil) in comparison with 3-aminopropyltriethoxysilane (APTE) and the uncoated material. The surface functionalisation using vapour proves to be an effective solvent free method of engineering oxide surfaces.

Keywords: Magnesium particulates; Surface functionalisation; Vapour phase treatment

1. INTRODUCTION

Magnesium is the lightest of the structural metals and its high strength/weight ratio makes it first choice in many high specification aerospace and automotive applications [1]. The poor corrosion resistance of pure Mg [2,3] is an issue for all applications that involve

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exposure to ambient atmosphere. One strategy to inhibit corrosion is through organic coating where bonding is achieved with the oxide film developed on the metal surface [4–6].

One speciality use of pure Mg is as, flammable metallic material for infrared decoy flares. A typical pyrotechnic flare comprises an oxidising halogenated polymeric material and an organic binder in addition to the metal fuel (*e.g.* Magnesium/Teflon®/Viton®, [MTV]). When ignited the metal undergoes an energetic and vigorous exothermic reaction with halogenated polymers; in this respect Mg has appealing burning characteristics which make it suitable for the heat output and speed of combustion required in such applications [7]. Infrared countermeasures rely upon the large infrared signature heat output from the reaction of the metal with an oxidising halogenated polymeric material (fluoroethylene) to divert heat seeking missiles in military combat situations [7,8]. The surface chemistry of the metal plays a very important role in the performance of the decoy flare. A study on the combustion of Mg/polyfluorethylene propellants determined the oxidation of the pure Mg pellets in this type of mixture occurs from the surface of each Mg particle towards its bulk [9–11] and is largely dependent on the total surface area of the particulates. Consequently, the corrosion of these particles is undesirable.

Magnesium is the tenth in the electromotive series [12], very reactive towards water; the product of its hydrolysis is hydrogen gas. A recent study on ambient storage of pure Mg shows that an oxide/hydroxide forms at the surface with ambient storage time together with organic contamination build up [13]. Both of these would affect ignition through modification of the surface chemistry of the particles and hence, the performance of the flare.

Here, we modify the surface of the Mg particulates by creating a silane barrier against atmospheric moisture attack. This is the first study to assess the performance of the treated surfaces using the novel method of reaction of the silane reagents in the vapour phase at elevated temperature [14]. The reaction of 3-aminopropyltriethoxysilane (APTE), triethoxy(1*H*,1*H*,2*H*,2*H*-perfluoro-1-octyl)silane (FSil), and hexadecyltrimethoxysilane (C16Sil) with the Mg particulate's surface was followed by XPS. The corrosion resistance was determined by using an accelerated ageing test measuring the gases evolved upon the mixing with a highly corrosive paste.

Surface modification using silanes in the vapour phase has been employed previously for silicon by Sugimura *et al.* [15] using fluorosilanes to create self-assembled monolayers (verified by water contact angle [WCA] and XPS), whereas germanium and silicon oxide surfaces have been modified by Hoffmann *et al.* [16] using fluorosilanes and verified by RAIRS and XPS. This technology has potential application for a variety of oxides as atmospheric corrosion protection, as primers for paints, or structural adhesives.

2. EXPERIMENTAL

The magnesium particulates were obtained from the manufacturer (Metal Powder Technology Ltd. [MPT] West Midlands, UK, CAS 7439954, size 2–20 μm, see Fig. 1) and supplied in a sealed container. The container was opened under N_2 (in a glove box) to sample *ca.* 5 g of powder in a glass vial. A very small amount was transferred to the XPS instrument airlock for analysis with minimum exposure to ambient atmosphere (*ca.* 10 min). Approximately 1.2 g of powder were treated with the silane reagents, after which the samples were transferred in glass vials and sealed under N_2 as before. In a separate experiment a large amount of magnesium (70 g) was stored in a dish open to ambient (typical laboratory conditions) for up to 84 days. The amount was spread out in an even layer and samples of 4 g were collected

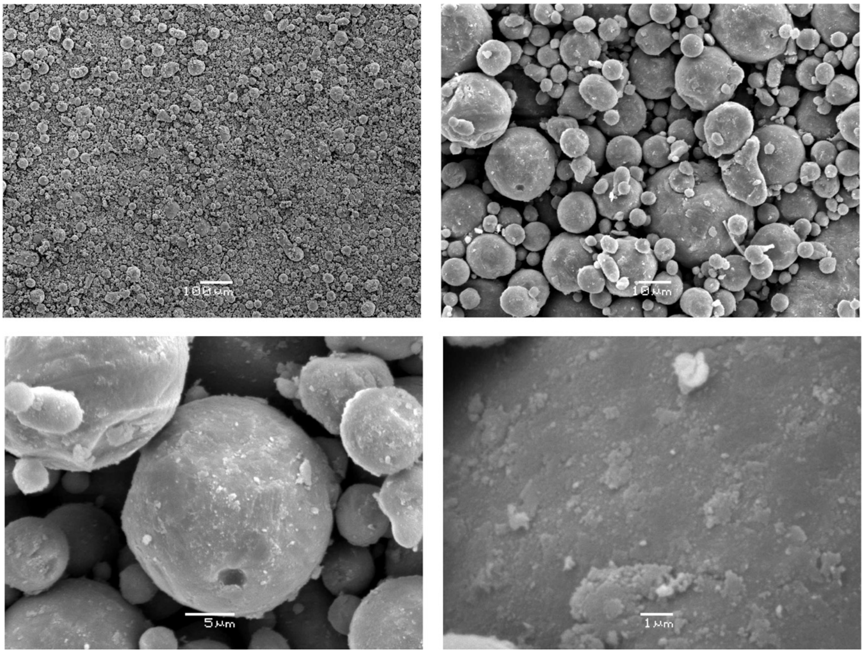


FIGURE 1 SEM micrographs of uncoated Mg particulates (MPT) mounted on adhesive carbon discs.

from the surface at regular intervals and stored in glass vials under N_2 as before.

The silane reagents APTE (99%, bp 217°C), FSil (98%, bp 220°C), and C16Sil (>86%, bp 180°C) were purchased from Sigma-Aldrich, Gillingham, UK and used as-received without further purification. The particulates were placed in a rotating glass drum (spinning at 60 rpm) and open to the atmosphere. The drum with the load was contained in a heated glass bottle [14]. The heating cycle of the assembly was controlled by a temperature regulator which stabilises the reactor at 100°C over the period of exposure. About 1.2 g of Mg particulates were exposed to the silane vapour overnight in the reactor heated at 100°C as described in [14].

The XPS analysis was undertaken with a Kratos Axis Ultra spectrometer (Kratos, Manchester, UK) with a monocromated AlK X-ray beam operating at a chamber pressure of $<5 \times 10^{-8}$ mbar and was run with charge compensation. The photoelectrons emitted from the surface were analysed at a take-off angle of 90°. The elemental composition of the surface was determined using empirically modified relative sensitivity factors supplied by the instrument manufacturer. The functional composition of each core level was determined using the Casa XPS peak-fitting software. The software was allowed to iterate to a best fit in all cases, with appropriate inter-peak constraints, namely, the full width at half maximum (FWHM) for the Mg 2p peak was fixed at 2.0 eV for MgO and 1.9 eV for N 1s. The BE for N 1s and Mg 2p core level peaks were fixed relative to C–C peak positioned at 285.0 eV.

To determine the behaviour of the coated Mg particulates we used an accelerated ageing test employed in the metal powder production industry (proprietary of MPT Ltd.). The Mg particulates are thoroughly mixed with a paste of Magrex 60 salt flux (Foseco Ltd., Tamworth, UK). The paste is formed with 1 ml solution (10% w/w aq) of Magrex 60 added to a 250 ml vessel together with 15 g inert Al_2O_3 particulates (45 μm average size) and mixed thoroughly. 1.0 g of Mg particulates are mixed with this paste and the evolved gases are collected over water in a graduated cylinder at room temperature.

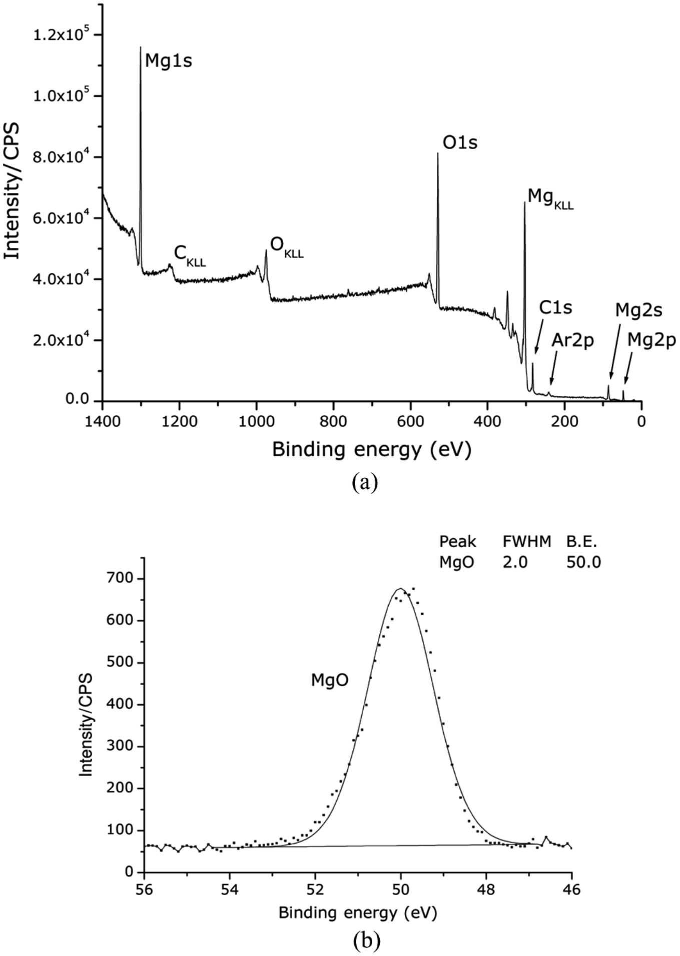
3. RESULTS

Mg particulates were adhered onto conducting double sided tape and analysed by SEM (Fig. 1). They were generally found to be spherical, with an average size of 18 μm and a specific surface area of $3350\,cm^2/cm^3$.

3.1. Surface Analysis by XPS

Particles were mounted on double adhesive tape and introduced in the XPS instrument airlock with minimal exposure to the ambient (*ca.* 10 min).

The survey scan of the as-received Mg particulates presented in Fig. 2 shows the presence of magnesium (Mg 2p, Mg 2s, Mg 1s, Mg_{KLL}), carbon (C 1s, C_{KLL}), oxygen (O 1s, O_{KLL}), and argon from the Ar 2p core level. The liquid metal is blown into an argon atmosphere



(a)

(b)

FIGURE 2 XPS spectra showing: (a) survey scan of as-received (control) Mg particulate and (b) core level of Mg 2p.

during the manufacturing process, leading to the incorporation of argon at the surface. Carbon contamination is common to all oxide surfaces, arising from the adsorption of volatile organic compounds (VOC). Inspection of Fig. 3a (survey scan) indicated the normal carboxyl, carbonate, and ether carbon environments [13] but also carbide, suggesting high temperature exposure to hydrocarbons, most likely in the manufacturing process.

The Mg 2p envelope (Fig. 2b) suggests that a thick oxide layer covers the surface of the particulate (>15 nm). (In this instance the C 1s core level did not offer any new information hence, we omitted it for simplicity.)

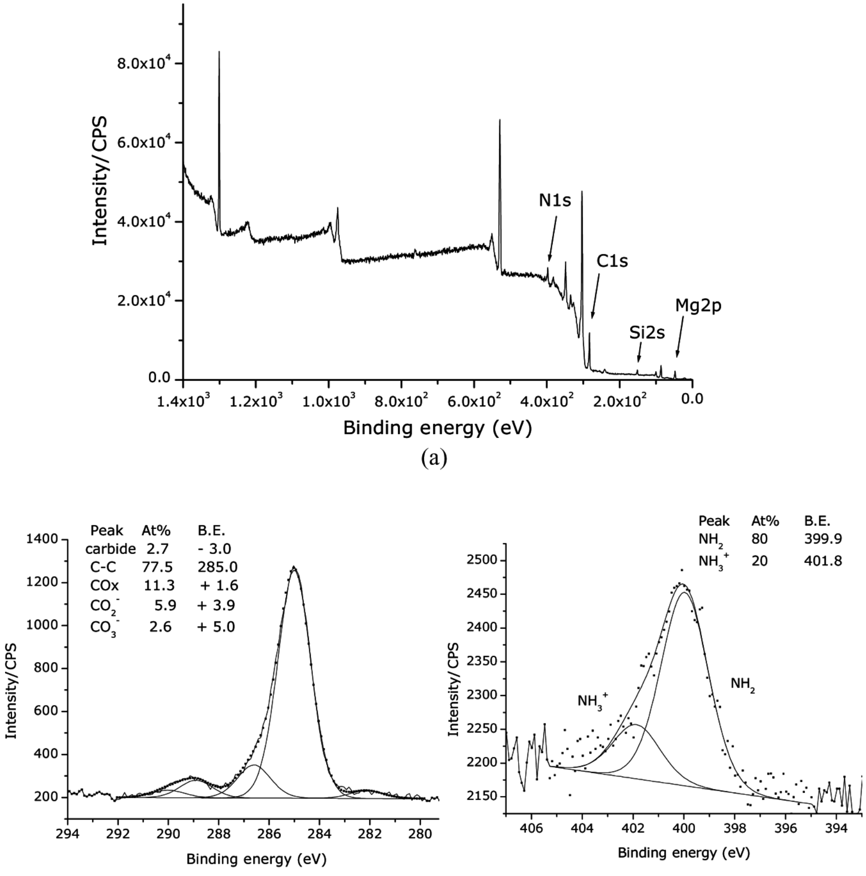


FIGURE 3 XPS spectra showing: (a) survery scan of APTE treated Mg particulate (MPT) and the core levels of (b) C 1s and (c) N 1s.

The position of the broad Mg 2p core level is characteristic of MgO and no narrow metallic component at lower binding energy was observed (Fig. 2b). The analysis depth of the technique is *ca.* 15 nm, suggesting the oxide/hydroxide layer is continuous and $>15\,\text{nm}$ [17].

The exposure of the particulates to the ambient results in an increase in surface carbon to 35% after 84 days. This is accompanied by a decrease in the surface magnesium and oxygen concentrations and is a result in organic material pick-up as an overlayer (see also Table 1). After treatment of the as-received particulates (control) with silane reagents, silicon was detected on the surface of the particulates treated with APTE, FSil, and C16Sil. Nitrogen and fluorine were detected on the APTE and FSil treated particulates, respectively, and are due to the amino and fluorine functionalities of the reagents.

In Fig. 3, the survey scan of the sample treated with APTE shows the presence of Si 2s and N 1s. The envelope of the N 1s core level (Fig. 3b) can be fitted with two peaks. The peak at lower BE has been attributed to NH_2 and the one at higher BE has been assigned to the NH_3^+ [18]. The low concentration of nitrogen (3.5%) in this case affects the signal-to-noise ratio, especially at the low intensity wings of the peaks. The fit parameters correspond to the literature values as described in [17–19].

Although the surface of Mg is very basic ($pH > 10$) [19], these data suggests the silane terminal amino group reacts to some extent with the surface oxide/hydroxide and has been observed previously for APTE on iron, magnesium, and aluminium [20]. (Hydroxide forms very soon on exposure of the oxide surface to atmospheric moisture [18].)

TABLE 1 Surface Composition (Atomic %) as Determined by XPS

Sample	C 1s%	Mg 2p%	O 1s%	Ar 2p%	N 1s%	Si 2s%	F 1s%
Control	28 (0.7)	21 (0.8)	50 (1.4)	1.4 (0.1)	0.0	0.0	0.0
28 days	31 (2.5)	19 (0.5)	47 (2.2)	1.5 (0.1)	0.0	0.0	0.0
42 days	34 (1.4)	18 (0.3)	47 (1.0)	1.0 (0.1)	0.0	0.0	0.0
56 days	30 (2.5)	19 (0.3)	49 (2.4)	1.3 (0.1)	0.0	0.0	0.0
70 days	34 (0.5)	17 (0.4)	48 (0.2)	1.1 (0.2)	0.0	0.0	0.0
84 days	35 (1.1)	17 (0.2)	46 (1.2)	1.1 (0.1)	0.0	0.0	0.0
APTE	31 (0.8)	15 (0.7)	44 (0.7)	1.1 (0.1)	3.5 (0.8)	4.9 (0.3)	0.0
FSil	14 (2.1)	14 (0.8)	35 (0.9)	0.6 (0.1)	0.0	1.7 (0.4)	35 (1.0)
C16Sil	30 (1.6)	18 (1.3)	48 (0.7)	1.1 (0.0)	0.0	2.2 (0.4)	0.0

In brackets are the standard deviation values out of three data points on each sample.

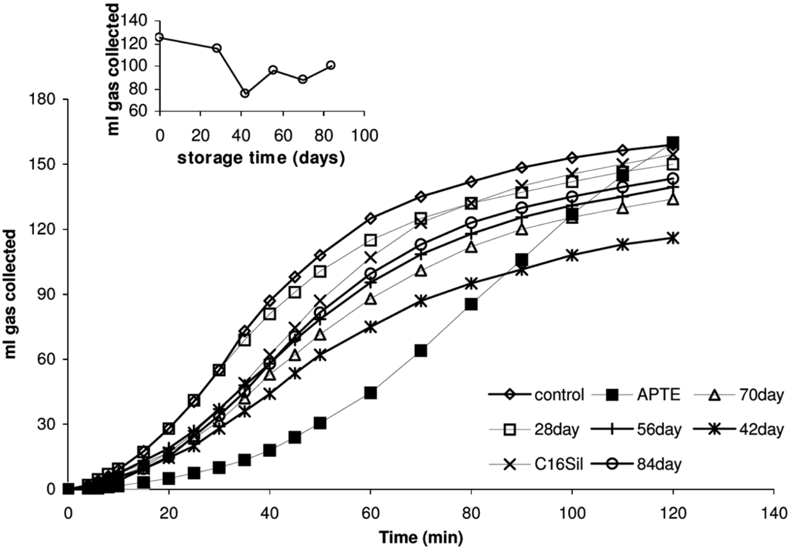


FIGURE 4 Volume of gas collected for 1.0 g Mg particulate as a fuction of treatment.

3.2. Accelerated Corrosion Test

The volume of gas collected as a function of time using the accelerated corrosion test for Mg particulates is presented in Fig. 4. It is apparent

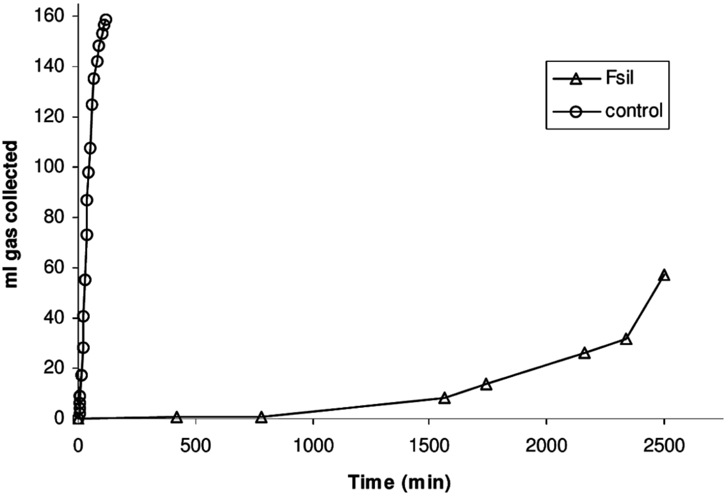


FIGURE 5 Volume of gas collected for 1.0 g Mg particulate treated with FSil.

that the highest volume of gas is generated by the uncoated (control) sample, whereas further exposure to ambient and silane reagents reduces the gas evolution. The insert plot presents the volume of gas collected at the 60 min time point for all samples against storage time, showing that gas production is minimal after 42 days storage.

The volume of the gas collected using the same test for the Mg particulates treated with FSil is compared to the control in Fig. 5. The FSil treated sample is much more stable against the corrosive media, showing no gas evolution for 2 h.

4. DISCUSSION

The gas evolution from Mg powder stored in the ambient atmosphere has been shown to be significantly reduced up to 42 days ambient storage (Fig. 4).

A study on the exposure of Mg plates to the ambient atmosphere has determined the amount of organic contamination deposited on the surface depends on the volume of atmosphere the surface was exposed to; a closed Petri dish produced less contamination at the surface as assessed by WCA, polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS), and XPS [13]. The chemistry of the oxide/hydroxide surface of the Mg metal varied greatly due to its interaction with the ambient, and is a result of the reaction/adsorption of VOC and water vapour. There was, however, no simple relationship between gas evolution and the surface concentration of carbon or oxygen. We postulate that organic adsorbates reduce the corrosion rate.

At increased ambient exposure times beyond 42 days, the corrosion protection decreased. This may relate to the degradation of the protective properties of the surface film due to formation of defects, relating possibly to the formation of crystalline hydroxide at the surface.

This atmospheric contamination layer at the surface of the particulates will interfere with any subsequent surface treatment (*e.g.* adhesion priming or corrosion treatments) and they have been shown to relate to self-assembled monolayers on the Mg [17].

The APTE treatment appears to impart good corrosion resistance to the particulates (Fig. 4); this treatment significantly reduces the amount of gas evolved in our test compared with the control sample. The mechanisms of alkoxysilanes coupling with metallic surfaces have been discussed before [18,21], particular interest being paid to covalent bond formation *versus* adsorption *via* hydrogen [22] bonds. A similar reaction is envisaged to occur here, between the alkoxy group on the silane reagent and the surface oxide/hydroxide (Fig. 6a).

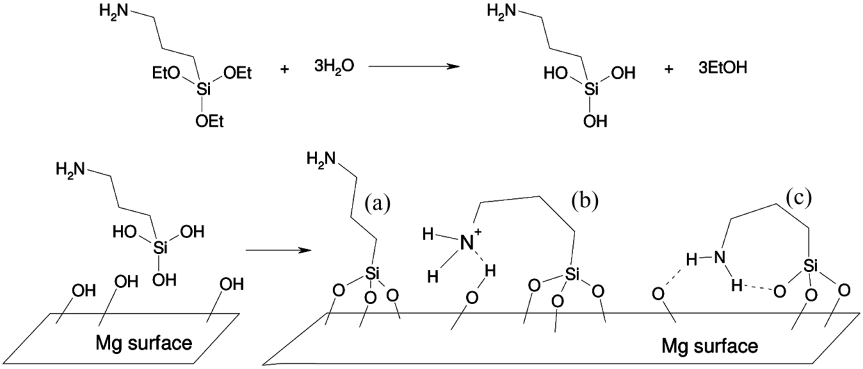


FIGURE 6 Possible coupling scheme of APTE on a hydroxide surface. (a) amino groups oriented up; (b) saturated APTE backbone oriented up with the protonated nitrogen [23,24]; and (c) cyclic compounds formed via hydrogen bonding between the amino group and the silanol with saturated APTE backbone oriented up and protonation.

Three possible coupling configurations of APTE with the Mg oxide/hydroxide are shown in Fig. 6. The presence of protonated nitrogen detected by XPS on the APTE treated surface suggests that a possible cyclic compound forms at the surface in this case (Fig. 6b).

An interesting observation is that, in Fig. 6, the configurations b and c give a more hydrophobic layer, as they present the saturated organic chain outwards. In this particular case, the resultant APTE layer gave an improved performance under the testing conditions.

The FSil treatment gives by far the best corrosion inhibition, showing very low gas evolution for 7 h exposure (1 ml, Fig. 5). The fluorine content on the silane reagent offers good hydrophobic inhibition and, in addition, appears to produce a less reactive surface in comparison with the other treatments. To illustrate, when calculating the surface composition from the XPS data the F has been omitted from the quantification in Table 2 to relate the hydrophobicity of the treated surface to the carbon concentration. This simple calculus will allow

TABLE 2 Surface Composition (Atomic %) as Determined by XPS

Sample	C 1s%	Mg 2p%	O 1s%	Ar 2p%	N 1s%	Si 2s%	F 1s%
FSil	14 (2.1)	14 (0.8)	35 (0.9)	0.6 (0.1)	0.0	1.7 (0.4)	35 (1.0)
FSil (without F)	21	21	54	9.2	0.0	2.6	Omitted
Control	28 (0.7)	21 (0.8)	50 (1.4)	1.4 (0.1)	0.0	0.0	0.0

a direct comparison of the amount of FSil with the hydrocarbon silanes. Using the Mg signal to approximate the overlayer thickness, the FSil sample appears to be of the same thickness as the control (21% C concentration *vs* 28% with the same concentration of Mg, Table 2). Thickness of the overlayer alone does not appear to be the best indicator of corrosion resistance. The impressive performance instead must arise from a combination of good hydrophobicity and chemical resistant properties of the fluorosilanes together with excellent bonding with the oxide surface *via* covalent/hydrogen bonds [15,16,19–21,23,24].

5. CONCLUSIONS

- The vapour phase treatment of Mg particulates with APTE, C16Sil, and FSil produces a silane layer on the surface.
- FSil silane layer offers a considerable corrosion inhibition in comparison with the uncoated and aged Mg powder.
- The change in the Mg particulates' surface chemistry during ambient storage affects its behaviour under testing. It is proposed that adsorption of carbonaceous material from the atmosphere initially reduces the corrosion rate but later disruption of the surface film by hydroxide negates this effect.
- Vapour phase treatment shown for particulates does not require organic solvents and can be easily employed for a variety of substrates and silane reagents, with clear applications in surface priming for adhesion, painting, and corrosion inhibition.

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