The determination of the optimum hydrolysis time for silane films deposition

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ABSTRACT

There is an increased controversy regarding when the actual silane deposition process takes place, whether or not the silane solution should be left for a longer time before the silanization, so that a maximum concentration of hydroxil groups is achieved. The proposed method uses a specifically designed electrochemical cell to monitor the behaviour of the silane solution during hydrolisation process versus time. The main characteristic parameters are reunited into a goal function (the temperature influence is also taken into account) used for supplying the maximum coordinates, graphical method or from the first derivative. The results may be used further for the silane deposition process, so that the best possible coating is obtained.

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1. Introduction

Silane films have been used lately as environmental friendly pre-treatment for metallic surfaces such as aluminium, copper, steel, magnesium and their alloys, in order to achieve an increased adhesion of some organic coatings [1–14].

The silane films are chemically stable, homogeneous layers, therefore an effective protective barrier against oxygen diffusion [4] and chemical attack [1], [6] which confer a higher corrosion resistance to the new product [2], [3], [5].

The final properties of the silane films are influenced by the characteristics of the silane solution from which the deposition takes place and by the curing treatment of the deposited film [15]. Usually, silanes used as adhesion promoters are applied from a water–alcohol solution [8,10,16–18]. Since the very beginning of the solution preparation, the silane solutions undergo two reactions, namely the hydrolysis of the alkoxy groups and the condensation of the silanol groups [19].

During the hydrolysis reaction, the alkoxy groups of the silane are converted to silanol groups (Si-OH) as follows [9,11,13,15,20–23]:

$$R - Si - OR' + H_2O \rightarrow R - Si - OH + R' - OH \qquad (1)$$
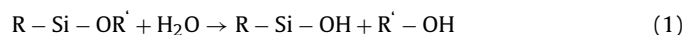
where R is an organofunctional group and R'is a hydrolysable group

From the chemical point of view, the optimum time for deposition on metallic substrates may be considered to be the point when a sufficient number of silanol groups are generated in solution, i.e. when the maximum hydrolization of the silane is reached [15]. The actual deposition of the silane is the reaction of the silanol groups with the metal hydroxide (Me-OH) when the metallo-siloxane bonds are formed according to Eq. (2) [9,11,15,20,21,23]:

$$Me - OH + R - Si - OH \rightarrow Me - O - Si - R + H_2O \qquad (2)$$
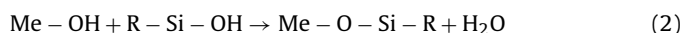
The silane molecules that do not react with the metallic substrate undergo a condensation reaction with each other and form a siloxane network (Si-O-Si) [9,11,15,21–23,24]:

$$R - Si - OH + HO - Si - R - Si - OH \rightarrow R - Si - O - Si - R + H_2O \quad (3)$$
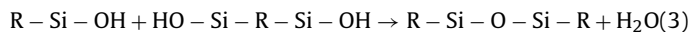
In a silane solution, both hydrolysis and condensation reactions occur simultaneously in the presence of water, but their reaction rates depend on several factors [11,18], such as concentration, pH and temperature [10,18,19,22,25,26,27].

Therefore, if one may find a solution for determining the actual time or the time interval when the concentration of silanol reaches the maximum point that will solve the above presented problem. The solution envisaged here would be to monitor the conductivity of silane solutions versus time as the conductivity increases with increasing the silanol concentration, as a result of silanol ionization reaction, the range of the conductivity for n-octyltriethoxysilane being between 10 and $25\,\mu\mathrm{S\,cm^{-1}}$ [28]. Once the maximum

Nomenclature

BTSE	Bis-1,2-(triethoxysilyl) ethane
BTESPT	Bis(3-triethoxysilylpropyl) tetrasulfide silane
DTMS	*N*-decyltrimethoxysilane
GF	Goal function
MA	Moving average
Me-OH	Metal hydroxide
R	Organofunctional group
R'	Hydrolysable group
Si-OH	Silanol groups
Si-O-Si	Siloxane network
TEOS	Tetraethyl orthosilicate
TI	Tolerance interval (minutes)
TOG	Optimum time taken from the graphical representation (minutes)
TPO	Practical optimum time (minutes)
λ	Conductivity (μS/cm)
λ_{max}	Maximum value of conductivity (μS/cm)
$\bar{\lambda}$	Normalised conductivity
pH_{max}	Maximum value of *p*H
$\bar{pH}$	Normalised value of *p*H
n	Number of measured points
v.v	Volume:volume
x	Independent variable used for the purpose of establishing the optimum hydrolysis time
f(x)	Goal function used for the purpose of establishing the optimum hydrolysis time
$f'_{(x)} = 0$	Derivative of the mathematical expression of the goal function

concentration of silanol is reached, one could easily determine now the optimum time for hydrolysis. This would be a convenient way to do it if it were not for the influence of pH during the hydrolysis of silanes [18,19]. To be more specific, the *p*H of the silane solutions is one parameter that strongly influences and provides information about the evolution of the hydrolysis and condensation reactions. Usually, under acidic conditions, the hydrolysis rate is higher than the condensation rate. At a neutral *p*H value, both reaction rates are slow [18], while under basic conditions the condensation rate is favoured [18,19].

The kinetics of these reactions have a paramount importance for the properties of the final silane film because if the film is not deposited at the optimum hydrolysis time, the solution will condense and the attained film will be a jellified one [18,28].

The aim of this study is to establish the optimum time or time interval for certain silane films deposition and to characterize the behaviour of the silane solutions by simultaneously monitoring the conductivity, pH and temperature of solutions.

2. Material and methods

2.1. Material

The silanes used in this study were bis-1,2-(triethoxysilyl) ethane (BTSE), bis(3-triethoxysilylpropyl) tetrasulfide silane (BTE-SPT), *n*-decyltrimethoxysilane (DTMS), tetraethyl orthosilicate (TEOS), purchased from Fluorochem Ltd, Hadfield, U.K.

The tested solutions were 2% and 5% silane solutions prepared in a mixture of distilled water and an organic solvent (using either ethanol or methanol, depending on the solubility of the silane, each particular solution being fully described in terms of composition and concentrations). BTSE and DTMS solutions were prepared by adding the silane in a 50:50 (v:v) mixture of ethanol and distilled water. TEOS solutions were prepared in an ethanol-distilled water mixture, in volume ratios of silane/distilled water/ethanol = 2:2:96, respectively 5:5:90, while BTESPT solutions were prepared similarly with TEOS, but using methanol as organic solvent, due to its increased solubilization power, since one has observed that BTESPT forms an emulsion with ethanol.

In order to adjust *p*H of DTMS 2% solution one has used glacial acetic acid (Sigma Aldrich, concentration >99.7%). All solutions were prepared from analytical grade reagents.

2.2. Methods

The conductivity, *p*H and temperature of the above mentioned solutions were monitored continuously, starting from the initial time, corresponding to the preparation of the solutions, up to 48 h, depending on the type of silanes. The reason for having a variable monitoring time is that once the maximum is reached, there is no point in prolonging the monitoring too much, as the point of interest is the maximum point, after that the condensation reaction takes over and the conductivity decreases [28]. The monitoring was carried out using a Phywe Cobra 3 pH-conductivity meter, interfaced with a computer controlled data acquisition system, using a sampling rate of 3 measurements per hour.

The experimental electrochemical cell setup consists in a three in one *p*H-conductivity-temperature cell, based on two parallel stainless steel electrodes for measuring conductivity (Millipore), an industrial *p*H electrode (Sensorex, make 2416) and a temperature sensor (Mc Btechnik, make type K). The temperature sensor was used to assure the information needed for the automatic
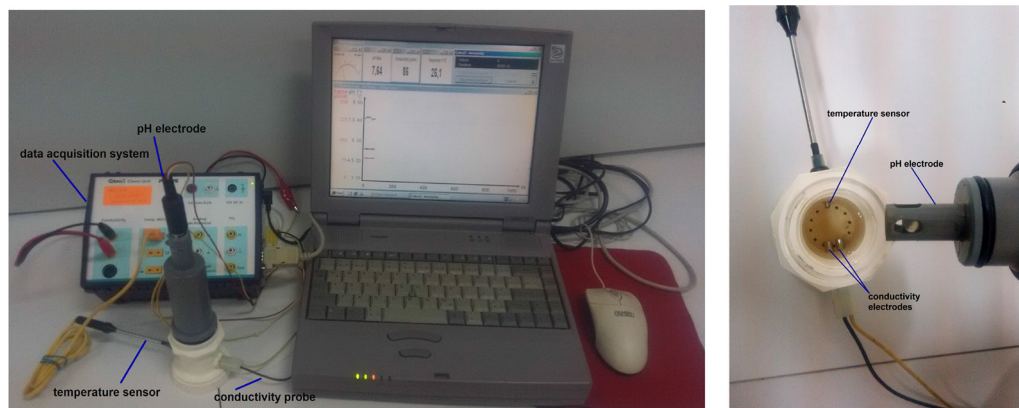

Fig. 1. (a) A depiction of the experimental layout and (b) view from above of the electrochemical cell with the *p*H electrode removed.