

Hydrolysis of trifunctional alkoxysilanes and corrosion resistance of steel sheets coated with alkoxysilane-derived films

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The formation of ceramic coating films for the modification of surface properties of substrates [1-6] is one of the practical applications of the sol-gel method. Ceramic coating on metallic substrates improves the chemical and mechanical properties, such as the corrosion, oxidation and scratch resistances [7-9]. One of the serious problems involved in inorganic oxide films is, however, their poor elasticity: the difference in thermal expansion between coating films and metallic substrates often causes cracking of the films upon heating cycles.

Trifunctional alkoxysilanes, $R'Si(OR)_3$, where R' and R are alkyls, have been used as one of the starting materials to introduce organic groups into the coating films heat-treated at relatively high temperatures [10-12]. These coating films containing organic groups show potential for the preparation of crack-free films even on metallic substrates [13].

The hydrolysis of trifunctional alkoxysilanes, $R'Si(OR)_3$, must depend strongly on R' as well as R , and thus their hydrolysis conditions may affect the corrosion resistance of the resultant coating films on aluminized steel sheets.

In this work various trifunctional alkoxysilanes were used as starting materials for alkyl-containing SiO_2 coating films and their hydrolysis process was investigated for the purpose of obtaining corrosion-resistant and crack-free coatings on steel sheets; trifunctional alkoxysilanes in which R' includes CH_3 and C_6H_5 , and R includes CH_3 , C_2H_5 , C_3H_7 and C_4H_9 are examined.

A variety of reagent grade methyltri-alkoxysilanes, $CH_3Si(OCH_3)_3$ (MTMS), $CH_3Si(OC_2H_5)_3$ (MTES), $CH_3Si(O-n-C_3H_7)_3$ (MTPS) and $CH_3Si(OC_4H_9)_3$ (MTBS), and phenyltriethoxysilane, $C_6H_5Si(OC_2H_5)_3$ (PhTES) were used as starting materials. Initially, 1 mol starting alkoxysilanes was diluted with 4 mol $n-C_4H_9OH$. 4 mol water and a catalyst were diluted with 4 mol C_2H_5OH . These two solutions were mixed and stirred to give homogeneous solutions. The mixed solvents of $n-C_4H_9OH$ and C_2H_5OH were used because the mixed solvents evaporating gradually are likely to provide better coating films than single solvents. HCl or NH_4OH was used as a catalyst. The concentration of these catalysts was adjusted to 0.05 M in the final solutions.

Aluminized steel sheets and stainless steel sheets 0.4 mm thick, which had been degreased ultrasonically in acetone, were used as substrates. Coating was conducted by the dipping-withdrawing method. The withdrawal speed was kept constant at 0.1 m min^{-1} . After being dried the substrates were heat-treated at 400°C for 1 min in an electric furnace. The thickness of the coatings was about 70 nm in the present study.

A gas chromatographer (Shimadzu GC-9A) equipped with a flame ionization detector was used for the analysis of alcohols in the coating solutions. A fused silica capillary column (Ulbon-HR-101, 25 m long and 0.24 mm in diameter) was used and the column temperature was maintained at 60°C . The temperature at injection and detectors was kept at 100°C . About $5 \mu\text{l}$ was sampled at an arbitrary interval from the coating solutions, which were aged at 35°C for various periods. The degree of hydrolysis was determined from the ratio of the peak area of the produced alcohol to that of solvent.

The corrosion resistance of the coated aluminized steel sheets was evaluated by the humidity cabinet test (HCT; JIS K2246, 50°C , 98% relative humidity). For the evaluation of change in gloss caused by rusting at the surface of specimens after the test, the L-value (JIS Z8729) was measured with a colour analyser (Suga type-SM).

For the evaluation of the corrosion resistance of aluminized steel sheets with coating films prepared from trifunctional alkoxysilane solutions aged from 0 to 3 h, the corrosion test was conducted on the as-received and coated aluminized steel sheets. Fig. 1 shows the appearance of specimens after 250 h of HCT. The colour of the as-received aluminized steel sheets was changed to dark by rusting at the surface after the test. On the other hand, the aluminized steel sheets with coating films prepared from the solution aged for 3 h show excellent corrosion resistance. This means that the corrosion resistance of aluminized steel sheets has been remarkably improved by the coatings. It is also clearly shown that these effects are changed with the ageing time of the solutions. Coatings from the solution aged for a longer time were more effective for the improvement of corrosion resistance.

The relationship between the ageing time of the solution and corrosion resistance was examined by using bright annealed stainless steel sheets as shown

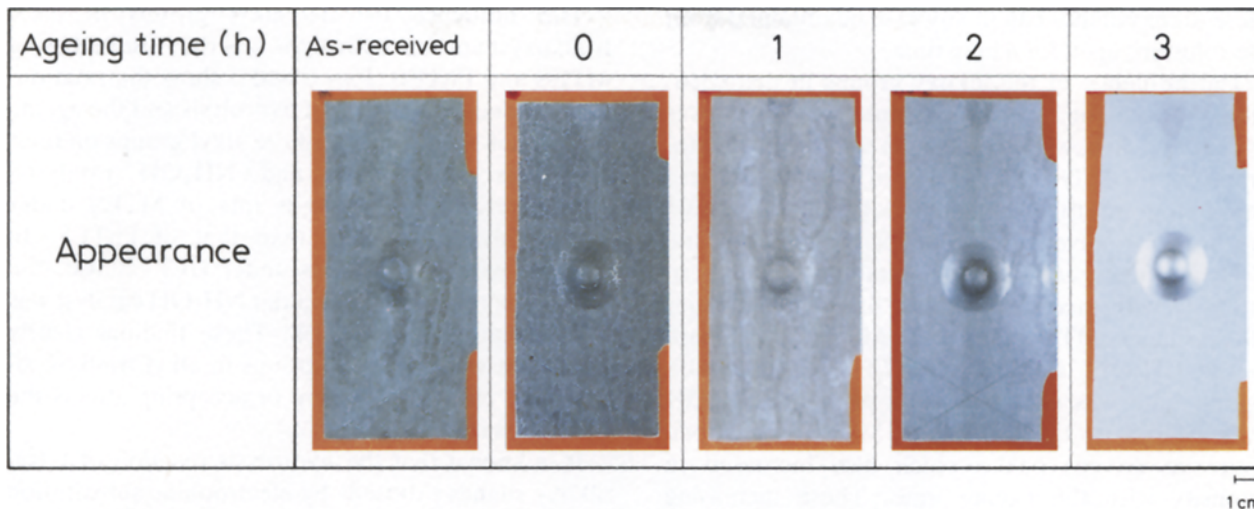


Figure 1 Appearance of aluminized steel sheets coated by differently aged solutions prepared from methyltriopoxysilane after humidity cabinet test at 50 °C in 98% relative humidity for 250 h.

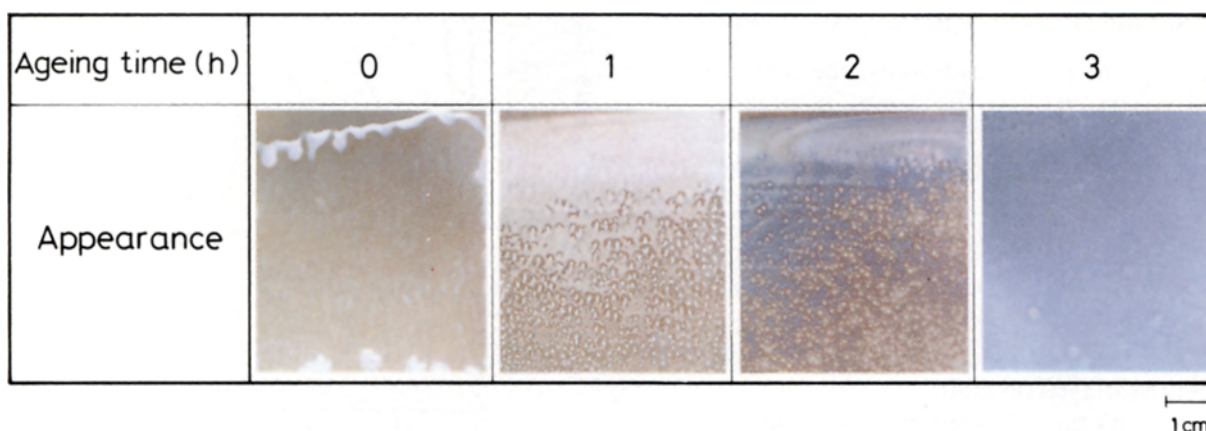


Figure 2 Appearance of stainless steel sheets coated by differently aged solutions prepared from methyltriopoxysilanes.

in Fig. 2. Films from the solution aged for 0–2 h became opaque. Transparent film was obtained from the solution aged for 3 h. The ageing time of the solutions thus strongly affects the properties of the coating films.

The detailed relationship between the ageing time and corrosion resistance was examined using various methyltrialkoxysilanes. In Fig. 3 such a relationship is expressed as the change in gloss (L-value) of the coated aluminized steel sheets after 250 h HCT versus the ageing time. The L-value increased with an increase in the ageing time and was saturated in a certain time. The saturated values are the same as those of the as-received, virgin aluminized steel sheets (about 75%). This means that there was no rusting in the coated aluminized steel sheets coated with alkoxides aged for a sufficient time. The ageing time for obtaining a good corrosion resistance of the films differs by the difference of alkoxy groups in the methyltrialkoxysilanes examined. The coatings prepared from MTMS aged for about 0.5 h showed good corrosion resistance. For MTBS, ageing for >5 h is necessary to obtain the good corrosion resistance. A good corrosion resistance of aluminized steel sheets with coating films prepared from

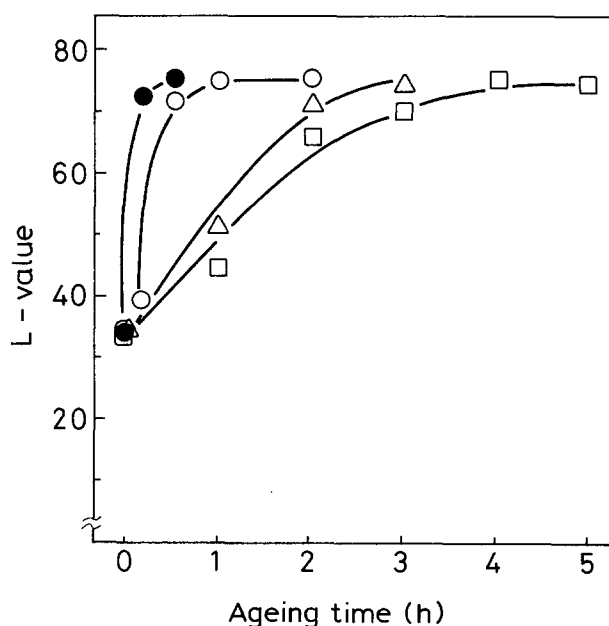
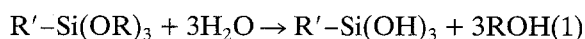


Figure 3 Relationship between the change in gloss (L-value) of coated aluminized steel sheets after humidity cabinet test at 50 °C in 98% relative humidity for 250 h and ageing time of the coating solutions: (●) CH₃Si(OCH₃)₃, (○) CH₃Si(OC₂H₅)₃, (△) CH₃Si(OC₃H₇)₃ and (□) CH₃Si(OC₄H₉)₃.

these alkoxy silanes can in any case be obtained from the solutions aged for a long time.

The influence of the alkoxy groups in methyltri-alkoxysilanes on hydrolysis during ageing was tested. Fig. 4 shows the change in the gas chromatograms for the MTPS solutions aged at 35 °C. In these chromatograms the peaks of C₂H₅OH and C₄H₉OH are both for solvents. Except for these peaks, the C₃H₇OH peak marked B appears and increases in intensity with increasing ageing time. In the other alkoxy silanes, MTMS, MTES or MTBS, an increase in the CH₃OH, C₂H₅OH or C₄H₉OH peak with ageing time was observed. The peak of C₂H₅OH from MTES or C₄H₉OH from MTBS overlapped with the solvent peak, which also increased in intensity with the ageing time. These increasing peaks with ageing time were due to alcohols generated by the hydrolysis reaction [14].

The amounts of alcohols produced when 1 mol trifunctional alkoxy silanes is completely hydrolysed are 3 mol as shown by [15, 16]



In the stage of partial hydrolysis, the amounts of alcohol generated show the degree of progress of hydrolysis during the ageing of the solutions. Accordingly, the degree of hydrolysis can be defined by

$$D = (P/C) \times 100 \quad (2)$$

where D is the degree of hydrolysis (in %), P is the amount of detected alcohol by partial hydrolysis (in mol) and C is the calculated amount of alcohol upon complete hydrolysis (in mol).

Fig. 5 shows the relationship between the ageing time and the degree of hydrolysis. The degree of hydrolysis increases with ageing time for any alkoxy silanes. The rate of hydrolysis, however, is influenced by the difference in alkoxy groups. The ageing time for complete hydrolysis is about 0.5 h for MTMS, about 1 h for MTES and about 3 h for MTPS, whereas >4 h is necessary for MTBS. These results show that methyltri-alkoxysilanes with larger alkoxy groups are hydrolysed more slowly, as already reported for other alkoxy silanes [17, 19]. In combination with these results and the above-mentioned results of the accelerated corrosion test (Fig. 3), it is concluded that good corrosion resistance can be obtained with coatings from completely hydrolysed solutions.

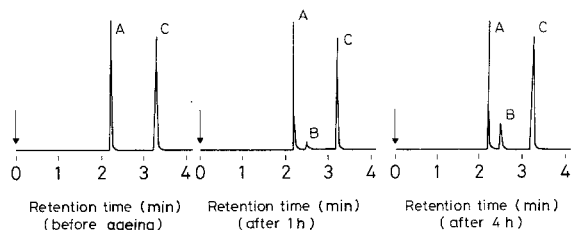


Figure 4 Gas chromatograms of solutions prepared from methyltripropoxysilane and aged at 35 °C: A, ethyl alcohol (solvent); B, n-propyl alcohol; and C, n-butyl alcohol (solvent).

The influence of the alkyl groups in alkyl trialkoxysilanes on hydrolysis was then studied using MTES and PhTES. Figs 6 and 7 show the relationship between the degree of hydrolysis and the ageing time to see the influence of the alkyl groups on their hydrolysis under HCl and NH₄OH catalysts, respectively. The hydrolysis rate of MTES under HCl catalyst was faster than that of PhTES. In contrast with these results under HCl catalyst, the hydrolysis rate of PhTES under NH₄OH catalyst was higher than that of MTES. These findings clearly show that whether alkyl groups in alkyl trialkoxysilanes are electron-donating or accepting affects the hydrolysis rate.

It is known that the hydrolysis reaction of tetra-alkoxy silanes proceeds by electrophilic substitution

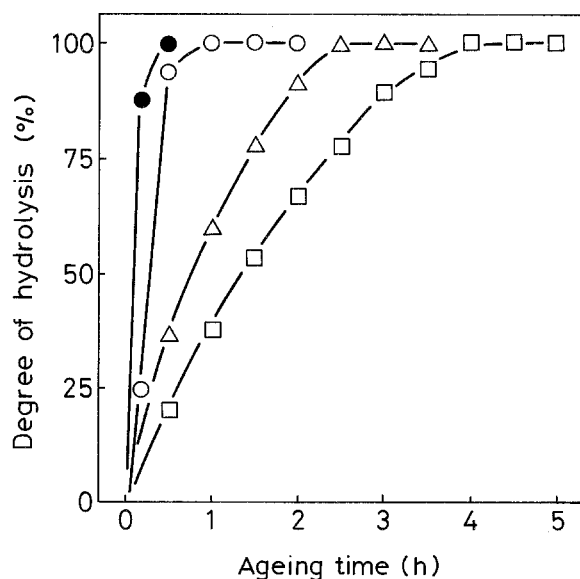


Figure 5 Relationship between the degree of hydrolysis and the ageing time of various methyltri-alkoxysilanes: (●) CH₃Si(OCH₃)₃, (○) CH₃Si(OC₂H₅)₃, (Δ) CH₃Si(OC₃H₇)₃ and (□) CH₃Si(OC₄H₉)₃.

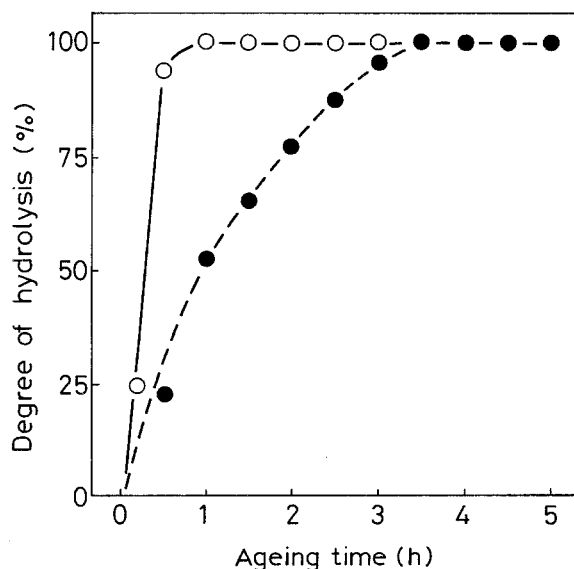


Figure 6 Relationship between the degree of hydrolysis and the ageing time of (○) methyltriethoxysilane and (●) phenyltriethoxysilane under HCl catalyst.

reaction under an acidic catalyst and by second-order nucleophilic substitution reaction (SN2) under a basic catalyst [20–22]. At the beginning of these reactions H_3O^+ attacks the oxygen in alkoxy groups under an acidic catalyst, whereas OH^- attacks Si under a basic catalyst, as summarized in Fig. 8. The electron density on oxygen in alkoxy groups becomes rich by electron donors such as methyl groups, whereas electron acceptors such as phenyl groups show the opposite effect. Accordingly, the increased electron density on O in methyl trialkoxysilane due to the electron-donating group CH_3 increases the rate of hydrolysis in the electrophilic reaction under an acidic catalyst. On the other hand, the presence of the electron accepting C_6H_5 groups decreases the electron density on Si to give rise to the higher hydrolysis rate in the SN2 reaction under a basic catalyst.

In conclusion, the hydrolysis of trifunctional alkoxy silanes and the corrosion resistance of aluminized steel sheets coated with films prepared by these alkoxy silanes were investigated. Coatings from completely hydrolysed solutions were found to give good corrosion resistance for aluminized steel sheets, indicating that complete hydrolysis of alkoxy silanes was of the greatest importance in achieving corrosion-resistant coatings. Alkoxy silanes with larger alkoxy groups showed a lower hydrolysis rate. The hydrolysis rate of MTES was higher than that of PhTES under an acidic catalyst, whereas under a basic catalyst the hydrolysis rate of MTES was lower than that of PhTES. Such a difference was explained in terms of the reaction mechanism of water with the alkoxy silanes.

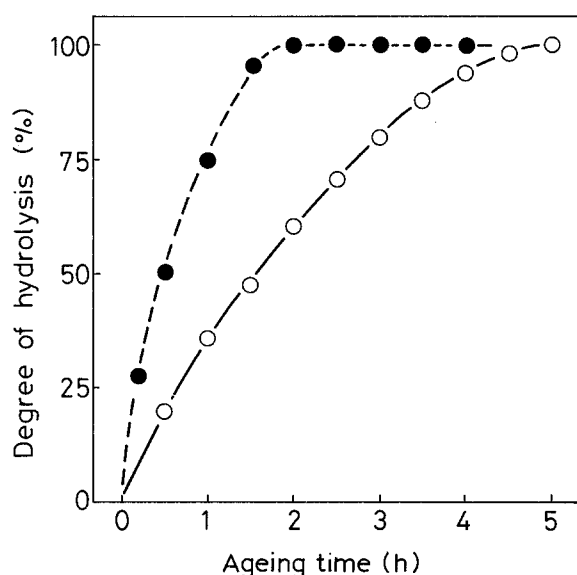


Figure 7 Relationship between the degree of hydrolysis and the ageing time of (○) methyltriethoxysilane and (●) phenyltriethoxysilane under NH_4OH catalyst.

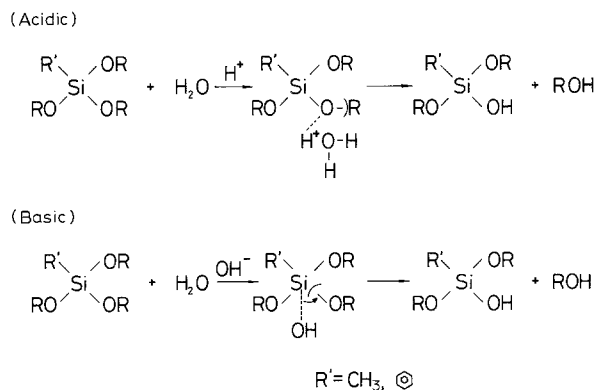


Figure 8 Hydrolysis process of trifunctional alkoxy silane under an acidic or a basic catalyst.

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