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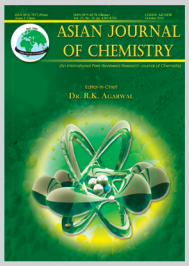

Study of the Preparation of γ-Glycidoxypropyltrimethoxysilane Film on Metallic Surface

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Silylation is the process of surface treatment for metal or non-metal using solution of organic silicane. In this paper, the process of surface pretreatment with γ-glycidoxypropyltrimethoxysilane (KH560) for stainless steel was studied. The results indicate that different process conditions (*i.e.*, the type of hydrolytic reagent, the concentration of silane, hydrolysis time, aging temperature and time) all have effect on the properties of silane film. The optimum operation conditions using water/methanol/glycerin as hydrolytic reagent are the following: the concentration of silane is about 2 %, the hydrolysis time is 10 h, aging temperature is 120 ºC and aging time is 20 min. The time of corrosion resistance is more than 1 h in pitting corrosion test of $CuSO_4$, which indicates good properties of silane film.

Key Words: γ-Glycidoxypropyltrimethoxysilane, Process conditions, Surface treatment, Silane film, Corrosion resistance.

INTRODUCTION

Surface pretreatment of metal can improve its corrosion resistance and its bonding strength with coating. The traditional methods of surface treatment include phosphating, chromate passivation, and so on. However, the energy consumption of these processes is high and environmental pollution is serious. Therefore, the development of new and non-polluting metal surface treatment technology attracts much attention[1,2].

Silicon coupling agent includes two different reactive groups and its chemical structure is Y-R-SiX_3, where X is group that can hydrolyze to form silanol group (Si-OH) that can link with some metal, Y group can react with polymer to improve the reactivity and compatibility between silicon coupling agent and polymer. The X group may be alkoxy, acetyl oxygen, halogens, *etc.*; the Y group may be vinyl, amino, epoxy, *etc.*[3-5].

Therefore, silicon coupling agent can be used as molecular bridge between coating and metal, thereby enhancing chemical binding between the metal and organic coating[6]. Compared with phosphating, the process has many advantages, such as simple, non-toxic, non-polluting, widely applicable, low cost and good anti-corrosion effect, which indicates it is a surface treatment technology with good prospect[7-9].

Wang *et al.*[10-12] researched the preparation of γ-glycidoxypropyltrimethoxysilane (KH560) film, using water/methanol as hydrolytic reagent. Moreover, factors influencing the bonding strength of silane film and bonding mechanism were studied.

In order to improve the stability of the silane solution, in this paper water/methanol/glycerin was chosen as hydrolytic reagent, the process conditions and anti-corrosion performance of KH560 silane film were studied.

EXPERIMENTAL

All the chemicals used were analytical grade. KH560 was purchased from Nanjing Capatue Chemical Co., Ltd. Methanol and acetic acid was from Chongqing Chuandong Chemical Co., Ltd. Glycerine was purchased from Zhengzhou Chemical reagent factory and used as surfactant. The concentration of NaOH (Chongqing Chemical reagent factory) solution used for cleaning the surface of metal was 5 % (m/m). The concentration of $CuSO_4$ (Chongqing Chemical reagent factory) solution for pitting corrosion test was 40 % (m/m).

The hydrolytic degree of KH560 was analyzed by the variation of conductivity of solution monitoring with digital conductivity apparatus[13]. The pH was measured by a standard pH-meter (Shanghai Precision & Scientific Instrument Co., Ltd). 85-2 Constant temperature magnetic stirrer (Shanghai S & P instrument Co. Ltd.) was used for controlling temperature and accelerating hydrolysis. The aging process of the silane film was achieved in the 101-2 Electric blast drying oven.

General procedure: The process of surface treatment of metal using KH560 silane was shown in Fig. 1.

Distilled water and methanol were added into flask, the pH was adjusted to 4 using acetic acid solution. Then, 2 % (v/v) KH560 and 1 % (v/v) glycerin were added to flask. The hydrolysis of silane was at 20 ºC with stirring by 85-2 constant temperature magnetic stirrer.

The size of the low carbon plate is 20 mm × 5 mm, dipping time is 5 s. The corrosion resistance of silica coatings is tested using 3 % $CuSO_4$.

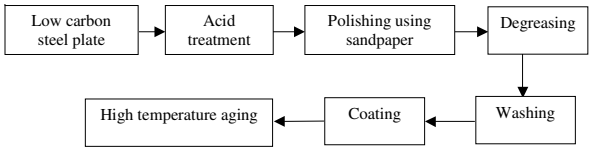


Fig. 1. The process of surface treatment of metal using KH560 silane

RESULTS AND DISCUSSION

Factors influencing the stability of silane solution: The stability of hydrolyzate of KH560 can be influenced by solvent type and pH of solution. In neutral medium, the hydrolysis rate of silane is slow, which can be accelerated in acidic and alkali mediums. The results show that the hydrolysis of KH560 can occur in acidic system and the electrical conductivity keeps relatively stable at pH = 3.5-4.5, which indicates that the stability of system is good. In this study, the effect of different hydrolysis system on the hydrolysis of KH560 is studied at pH = 4.

Fig. 2 displays the curves of electrical conductivity of two hydrolysis systems (*i.e.*, water/methanol and water/methanol/glycerin). It is seen that electrical conductivity of two hydrolysis system increases with the prolongation of hydrolysis time within 10 h Furthermore, electrical conductivity of water/methanol system is higher than that of water/methanol /glycerin system. It indicates that degree of hydrolysis increases gradually in two system and hydrolysis rate of the former is higher than the later. Electrical conductivity of water/methanol system decreases gradually, while electrical conductivity of water/methanol/glycerin system almost keeps steady, when the hydrolysis time is longer than 10 h. It suggests the crosslinking reaction occurs between different silanol generated during hydrolysis of silane in water/methanol system. The existence of glycerin can effectively decrease the rate of hydrolysis by restraining the hydrolytic equilibrium shift to right. A large number of hydrogen bonds also form because of the existence of glycerin, which can restrain the crosslinking reaction between different silanol to ensure the stable existence of silanol in solution. Therefore, the best hydrolysis time of silane solution is 10 h in this study.

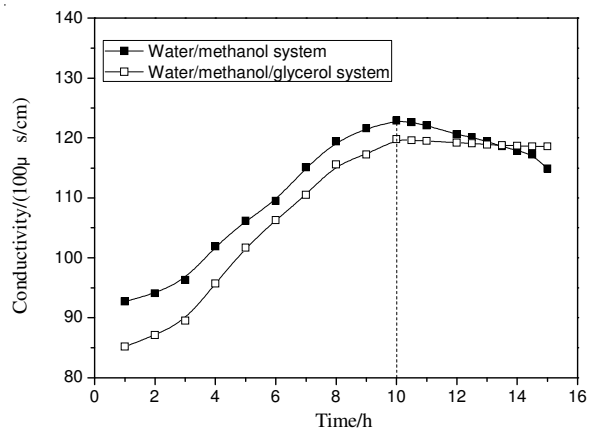


Fig. 2. Curves of electrical conductivity of KH560 in water/methanol and water/methanol/glycerin system (KH560: v/v = 2 %)

Effect of concentration of KH560 on the performance of silane film: From Fig. 2, with the increasing of the concentration of silane in solution, the concentration of silanol generated during hydrolysis increases. However, the crosslinking reaction between different silanol results in the decrease of the stability of solution. Therefore, the concentration of silane is one of the significant factors influencing the stability of solution and the performance of silane film.

Fig. 3, displays the relationship curve of the time of corrosion resistance and concentration of KH560 The experimental conditions are as following: pH = 4.0, hydrolysis temperature is 20 ºC, hydrolysis time is 10 h, aging temperature is 120 ºC and aging time is 20 min. It can be seen that the time of corrosion resistance of silane film increases with the increases of the concentration of KH560 solution. When the concentration of KH560 reaches 2 %, the time of corrosion resistance of silane film is about 1 h, and increases slowly with the continue increasing of concentration of reaches The results[14] show that the thickness of silane film mainly depends on the concentration of silane. The concentration is higher, the film is thicker. Meanwhile, with the increasing of the concentration of KH560, the content of silanol rises, and the compactness of silane film formed by the crosslinking reaction in aging process is good. When the concentration of KH560 exceeds 2 %, the time of corrosion resistance remains stable.

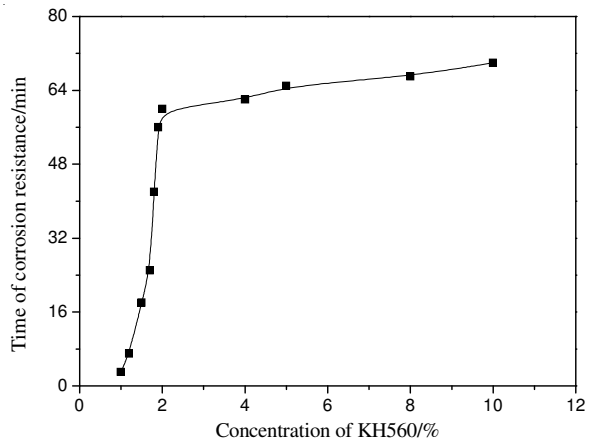


Fig. 3. The relationship curve of concentration of KH560 and the time of corrosion resistance in water/methanol/glycerin system

Effect of the hydrolysis temperature on the performance of silane film: The hydrolysis temperature is also a significant factor in the preparation of silane film except the concentration of silane, hydrolysis time and the pH of solution. Fig. 4, shows the relationship curve of the time of corrosion resistance and the hydrolysis temperature. The experimental conditions as following: pH = 4, concentration of KH560 is 2 %, hydrolysis time is 10 h, aging temperature is 120 ºC and aging time is 20 min. Higher hydrolysis temperature can accelerate the rate of hydrolysis[15]. The amount of silanol generated in the same time increases, which is beneficial to the formation of silane film with certain thickness in the aging process. Therefore, the time of corrosion resistance increases from 5 min at 10 ºC to 65 min at 25 ºC (Fig. 4). With continuous increasing of hydrolysis temperature, a large amount of silanol generates, which promotes the crosslinking reaction of silanol. It can explain the

reason that the time of corrosion resistance decreases to 20 min at 45 ºC. The experimental results under different temperatures indicate that the optimum hydrolysis temperature is 25 ºC.

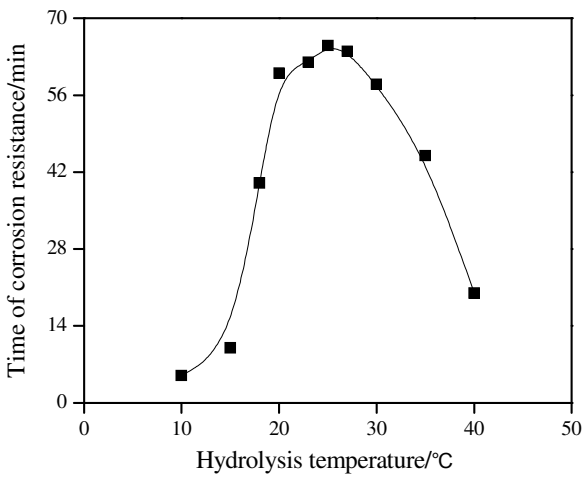
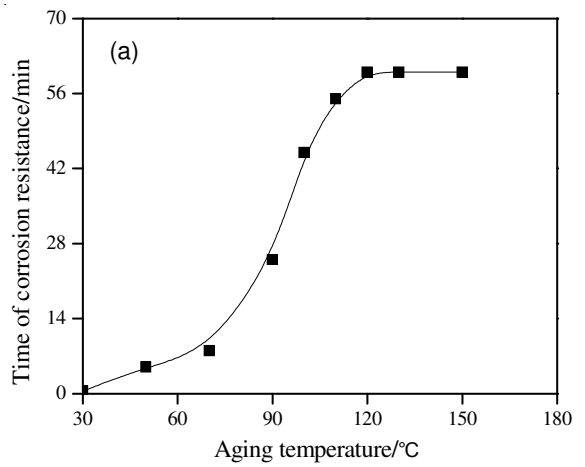


Fig. 4. The relationship of the corrosion resistance time and the hydrolysis temperature in water/methanol/glycerin system

The effect of aging temperature and time on the performance of silane film: Figs. 5 (a) and (b) shows the relationship curves of the time of corrosion resistance with the aging temperature and time, respectively. The experimental conditions are as following: pH = 4, the concentration of KH560 is 2 %, hydrolysis time is 10 h and hydrolysis temperature is 25 ºC. Meanwhile, in Fig. 5(a), the aging time is 20 min and in Fig. 5 (b) the aging temperature is the optimum temperature obtained. From Fig. 5 (a) and (b), it can be seen that the time of corrosion resistance both increase obviously with the increasing of the aging temperature and the prolonging of the aging time. When the aging temperature is higher than 120 ºC and the aging time is more than 20 min, the time of corrosion resistance almost maintains stable.

In the aging process, the main reactions occurring are the formation of chemical bond of Si-O-metal, the crosslinking reaction and condensation between different silane and silanol[16]. The reactivity of silanol and the motility of chain increase with the increasing of aging temperature, which accelerates the dehydration between different silanol. On the other hand, the degree of crosslinking is higher and the compactness of silane film is increases.



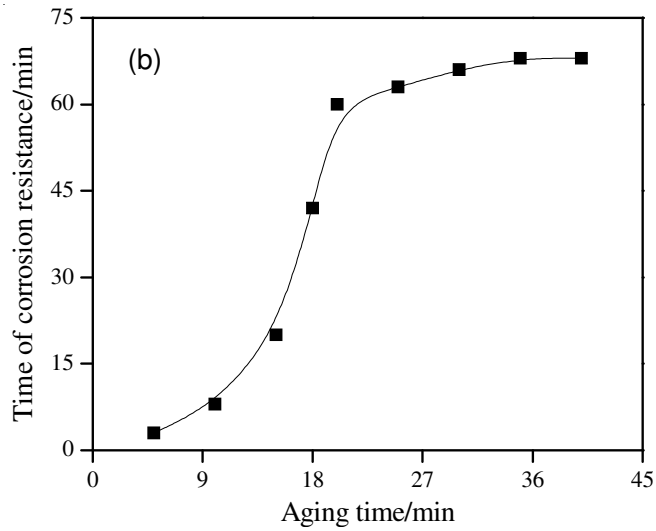


Fig. 5. The relationship curves of the time of corrosion resistance with (a) the aging temperature and (b) the aging time in water/methanol/glycerin system

Morphology of silane film: Fig. 6 shows the pictures of stainless steel plate with and without silane film. The silyanization is carried out under the optimum conditions mentioned above. It can be seen that the surface of stainless steel plate with silane film is very smooth. The area of corrosion after pitting corrosion test does not increase after 1 h.

Fig. 6. Comparison pictures of treated and untreated stainless steel plate by silane solution

Conclusion

In this work, preparation conditions influencing the performance of silane film was studied using γ-glycidoxypropyltrimethoxysilane (KH560) as silane reagent. The results show that the addition of glycerin slowdown the hydrolysis rate of silane, meanwhile, a large amount of hydrogen bonds form which restrains the occurring of the crosslinking reaction between different silanol and enhances the stability of the solution. The process parameters in the preparation of silane film all affect the concentration of silanol and stability of solution. The optimum process conditions are as following: pH = 4, concentration of KH560 is 2 %, hydrolysis time is 10 h, hydrolysis temperature is 25 ºC, aging time is 20 min and aging temperature is 120 ºC. The time of corrosion resistance

of silane film exceeds 1 h under the optimum conditions, which indicates the performance of corrosion resistance is good.

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