Advanced Materials Research *Online: 2012-02-10*
ISSN: 1662-8985, Vol. 460, pp 94-97
doi:10.4028/www.scientific.net/AMR.460.94

Initial Exploitation of Corrosion Resistance and Adhesion of 10 Kinds of Silane on A3 Steel

Qi Zhou[a], Guangxia Sun, Bo Hu, Ping Zhao[b]

School of Environmental and Chemical Engineering, Shenyang Ligong University, No.6 Nanping Middle Road, Hunnan New District, Shenyang, Liaoning, 110159, P.R. China

[a]zhouqi2469@163.com, [b]pingzhao2000@126.com

Keywords: Silane; Painting; pretreatment; adhesion; Corrosion Resistance.

Abstract. Silane coupling agent is gradually concerns as a substitute for phosphate pre-treatment of painting. Ten kinds of silane solution such as the KH-450, KH-460, KH-470, KH-550, KH-560, KH-567, KH-578, 5501, 9810, BTSE were chosen as research objects in this paper. Corrosion resistance and adhesion of film were studied after silane treatment on A3 steel surface by copper sulfate drop test, alternate immersion in salt solution and adhesion experiments. These silane films were compared with uncoated A3 steel specimens. The results show that: silane treatment can improve the corrosion resistance of A3 steel in acid solution. KH-560, KH-5501 and KH-470 were ranked the top three in the corrosion resistance. KH-550, KH-560, KH-567 were fourth, fifth and sixth, respectively. Silane treatment can improve the corrosion resistance of A3 steel in neutral salt solution. KH-460, KH-560 and KH-567 have the best salt water corrosion resistance. KH-560 has better adhesion with paint film, following by KH-550 and KH460. When using ethanol and water as the hydrolysis solvent of silane, KH-450, KH-460, KH-470, KH-550, KH-560, KH-567, KH-578, 5501 have the better stability, but stability of 9810, BTSE are poor.

Introduction

Several studies have shown how some silane compounds can be used as adhesion promoters between an organic coating and a metallic substrate [1–5]. These silane-based compounds used as primers of adhesion are organo-functional silanes, of general formula: $(R_1O)_3–Si–(CH_2)_n–R_2$. The principle of the adhesion of organo-silane on mineral substrates is based on the reactivity of the siloxane function ($Si–OR_1$) [1]. This group is hydrolysed to silanol and reacts with the metal hydroxide groups on the surface. The latter reaction is currently called “silanization” and it occurs in competition with the silanol/silanol condensation reaction. When the rate of hydrolysis is sufficiently high compared to the silanol/silanol condensation, many Si–O–M bonds can be formed between small-sized silanols and the metal. In the opposite case, few Si–O–M bonds are formed between largesized hindered silanols and the substrate [6]. The R_2 group is an organo-functional group (vinyl, amine, epoxy, mercapto, etc.) whose role is to establish a chemical bond with the organic coating.

Experimental section

Process follows. 50mm×30mm A3 steel→Polished by sandpaper→Rinsing→Alkaline cleaning→Hot water rinsing→Cold water rinsing→Mixed pickling→Cold water rinsing→Blowing with cold wind→ immersed into the silane solution for 2min at room temperature→ take out→ cold wind blow dry→ placed in the baking oven at 100 ℃ for 50min-60min→take out→ cooled to room temperature and test.

Corrosion resistances of steel parts are evaluated according to GB/T 6807-1986 (copper sulfate technical standards) and ISO 11130:1999 standard (Corrosion of metals and alloys - Alternate immersion test in salt solution) before painting. The testing of painting adhesion carry out according to standard GB1720-89.

Results and discussion

Composition and appearance of silane solution. At room temperature the ten kinds of silane solution placed in a cool ventilated dry place for four months, observing and recording the appearance of the silane solution, the results are shown in Table 1. The silane solution content of each component is also recorded in Table 1. The results of table 1 are as follows: KH-460 and KH-5501 is a yellowish solution, other models are colorless and transparent solution. Two kinds of silane solution 9810/1 and BTSE become muddy and appear a few floc after four months. BTSE silane has been gelatinous since six months; the other solutions are still colorless and transparent. That indicates two kinds of silane 9810/1 and BTSE are less stable, the rest silane solution have good stability.

Table 1 Composition and appearance of silane solution

Type	Silane:ethanol:water	pH	colour	whether turbid
KH-450	3:22:75	6	Colorless	no
KH-460	20:48:32	5	Yellowish	no
KH-470	1:3:1	6	Colorless	no
KH-550	3:22:75	5	Colorless	no
KH-560	1:4:2	6	Colorless	no
KH-567	1:3:1	6	Colorless	no
KH-578	3:22:75	5	Colorless	no
KH-5501	5:20:75	5	Yellowish	no
9810	2:5:3	5	Colorless	yes
BTSE	1:4:1	4.5	Colorless	yes

Alternate immersion test in salt solution. Table 2 is the results of evaluation taking out all specimens from the salt solution after four days. Table 2 is corrosion results record of the silane film soaked in salt water for a certain time at a certain pH value. KH-460, KH-560, KH-567 are the best corrosion resistance, KH-550, KH-578, KH-450 followed, KH-9810 / 1, BTSE, KH-470 are the worst corrosion resistance.

KH-5501, 9810/1 have rust after drying surface, KH-470 form flaking at a large area, the others have no other special phenomena. The reason is KH470 silane treatment did not fully wet specimen, it has no good hydrophilic properties, leading to the specimen serious corrosive.

Two hours later alternate immersion test results show that KH-578 \ 450 \ 560 \ 567 \ 470 \ 5501 \460 did not change, 9810\1 and BTSE appear small bubbles. That is to say the silane film began to dissolve; its corrosion resistance goes down because hydrophobic silane on the iron substrate is difficult to form a dense solid anti-corrosion film.

After 3 hours corrosion of 9810\1, KH-5501, KH-450, BTSE films occur severely; KH-470 film peel off from the substrate, KH-550, KH-567 was locally eroded; KH-460 and KH-560 have little corrosion.

Table 2 Results of alternate immersion in salt solution and $CuSO_4$ drop test

silane type	*pH of silane solution*	*Appearance of film after cossion in NaCl solution*	Time of appearing yellow rust/day	*Destruction degree of NaCl solution*	*Grade for immersion in NaCl solution*	*Time of appearing red dots in $CuSO_4$ solution*
KH-450	6	Rust in local	3	5%	4	23
KH-460	5	Argentate black film	2	0.25%	8	30
KH-470	6	Argentate black film, flaking in local	2	2.5%	5	110
KH-550	5	Gray, transparence, rusty free	3	0.5%	7	109
KH-560	6	colorless, transparence, rusty free	4	0.25%	8	1380
KH-567	5	slight rusty	2	0.2%	8	60
KH-578	5	Gray, transparence, rusty free	3	0.5%	7	25
KH-5501	5	colorless, transparence, rust free	1	5%	4	215
9810	5	All is rusty	1	5%	4	12
BTSE	4.5	rusty	1	5%	4	78
uncoated			12h			5

***$CuSO_4$* drop test.** Table 2 shows the data results of $CuSO_4$ drop test. Corrosion resistances of ten kinds of silane film from strong to weak are as follows: KH-560> KH-5501> KH-470> KH-550> BTSE> KH-567> KH-460> KH-578> KH-450> 9810 / 1> blank. Table 2 data results indicate that the silane treates specimens can increase corrosion resistance. Because the infiltration properties of various types of silane on A3 substrate are different, the one hand the corrosion resistance of specimens is relational with silane itself (silane structure, the amount of silane), on the other hand it is relational with pH of the silane solution, silane type, silane treatment time, solvent type and the amount, baking temperature and time of silane films.

The results of copper sulfate drop experiments and immersion in salt solution experiment show that KH-560 has the best corrosion resistance, the conditions are pH = 6.0, silane soak for 2min, silane coupling agents: ethanol: water = 1:4: 2 (volume ratio), film-forming temperature of 100 ℃, time is 1h. Followed are the KH-550, KH-460, and KH-567 silane solution. KH-470 film is locally peeled off immediately as forming the film.

Adhesion with paint film. KH-560 has better film adhesion from Table 4 the film adhesion test results, followed by KH-550, KH-460. Paint film thickness is roughly 26μm.

Table 3 Comparison table of general score for each properties of silane solution

Points	Time of $CuSO_4$ drop(second)	Adhesion/grade	Immersion in salt solution /grade
1	0~5	7	3
2	6~10	6	4
3	11~20	5	5
4	21~40	4	6
5	41~80	3	7
6	81~160	2	8
7	over 160	1	9

Table 4 Adhesion test result of paint film

Type	Thickness of paint film /μm	Adhesion of paint film /grade	General properties points
KH-450	26	5	2.9
KH-460	26	3	5.1
KH-470	32	7	2.6
KH-550	26	3	5.2
KH-560	28	2	6.2
KH-567	25	5	4.3
KH-578	24	4	4.3
KH-5501	22	6	3.0
9810	23	6	2.2
BTSE	36	6	2.6

The properties of each silane have different advantages and disadvantages for these 10 kinds of silane solution, which need a comprehensive properties analysis. For the all properties of the film adhesion accounts for 50% of the overall performance, salt solution immersion test 30%, drop test 20%. The film adhesion points are set as seven levels, the highest rating (1 grade) is awarded 7 points, 7 grade is the lowest rated awarded 1 point. The worst effects of immersion in salt solution is grade 3, so the lowest grade 3 rated 1 point, nine is the highest awarded 7 points. According to Table 4, the general properties of KH-550, KH-560, KH-460, KH-567, and KH-578 are excellent. KH-560 is the best. KH-567, KH-578 is relatively poor.

Conclusions

(1) When ethanol and water are used as the hydrolysis solvent of silane, KH-450, KH-460, KH-470, KH-550, KH-560, KH-567, KH-578, 5501 have the better stability, but 9810, BTSE are poor stability.
(2) Silane treatment can improve the corrosion resistance of A3 steel in acid solution. KH-560, KH-5501 and KH-470 were ranked the top three in the corrosion resistance.
(3) Silane treatment can improve the corrosion resistance of A3 steel in neutral salt solution. KH-460, KH-560 and KH-567 have the best salt water corrosion resistance.
(4) KH-560 has better adhesion with paint film, following by KH-550 and KH460.

Acknowledgments

This work was supported by the doctoral starting-up specialized foundation of Shenyang Ligong University (No.2011BS-07-10), China.

References

[1] E.P. Plueddemann, Silane Coupling Agents, Plenum Press, New York, 1991
[2] K.L. Mittal, Silane and Other Coupling Agents, VSP, Utrecht, 1992
[3] R.P. Digby, S.J. Shaw, Int. J. Adhes. Adhes. 18 (1998) 261.
[4] A. Rattana, J.D. Hermes, M.L. Abel, J.F. Watts, Int. J. Adhes. Adhes. 22 (2002) 205.
[5] A.N. Rider, Int. J. Adhes. Adhes. 26 (2006) 67.
[6] J.M. Chovelon, L.E.L. Aarch, M. Charbonnier, M. Romand, J. Adhes. 50 (1995) 43.