Polysilazane Anti-corrosion Coating that Can Replace Hot-dip Galvanizing

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Abstract. In response to the problems of high energy consumption and pollution and insufficient anti-corrosion performance in the preparation process of hot-dip galvanized anti-corrosion materials, a polysilicon nitride anti-corrosion coating was developed. Using vinyl polysilazane as the base resin and adding zinc powder antirust pigment to the resin, a polysilazane zinc-rich anticorrosion coating was developed. The performance of the coating was characterized, and the results showed that the coating had a hardness of 6 H after heat treatment at 250°C and a salt spray resistance better than that of hot-dip zinc samples. 2000 h of salt spray resistance after heat treatment at 600°C, which is twice that of hot-dip galvanized materials, and the scratches are self-healing. The coating is a good substitute for hot-dip galvanized material.

Keywords: Anticorrosive coating; polysilazane; silicone resin.

1. Introduction

Steel materials are widely used in human production and construction activities. Steel fails due to corrosion in complex service environments. Hot-dip galvanizing of steel with high corrosion resistance, controlled thickness and surface morphology of zinc plating with low process cost has become an effective method for corrosion protection of steel. [1] [2] However, the environmental performance of the process is very limited: (1) acid contamination in the steel pretreatment process (2) high energy consumption in the heating facilities for maintaining the 500 °C zinc pot for a long time (3) zinc and zinc oxide vapors cause "zinc fever" and dust lung in the production line workers. [3]

Polysilazane is an organic-inorganic hybrid polymer with Si-N as the repeating unit. [4] Since polysilazane coatings can be directly coated, they have good adhesion to metal substrates and excellent thermal stability, and can be used as reinforcing fillers for organic polymers to enhance the heat resistance of polymerization products. In recent years, the research of polysilazane coatings has become a hot spot and has applications in metal protection, semiconductor devices, space materials, fireproof materials, corrosion protection, etc. [5] [6] [7] Since Si-N bonds can react with metal surfaces to form Si-O-Me bonds similar to those in silane surface treatment technology, and the films formed by such polymers are dense and have good barrier properties, [8] [9] polysilazane can be used as the base resin to prepare polysilazane anti-corrosion coatings.

In this paper, a polysilazane anti-corrosion coating was prepared using vinyl silazane as the base resin. The coatings have good adhesion to metal substrates, excellent salt spray resistance and high hardness. Compared with traditional zinc-rich coatings, the coating has high hardness and excellent scratch resistance, and compared with hot-dip zinc, the coating process has low energy consumption, good anti-corrosion performance and is more environmentally friendly.

2. Experimental section

2.1 Materials

Vinyl polysilazane: industrial grade, Institute of Chemistry, Chinese Academy of Sciences; Zinc powder: 500 mesh, Hunan Xinwei Ling New Material Co.Dimethyl nylonate: industrial grade Jinan Xinsun Chemical Co., Ltd; Defoamer 066N: industrial grade, Bick Chemical; Di-tert-butyl hydrogen peroxide, chemically pure, Shanghai Aladdin Biochemical Technology Co.

2.2 Preparation of coating

Weighed 35g of vinyl polysilazane, 45g of zinc powder, and 20g of dimethyl nylonate, mixed well and then ground well in a three-roller mill to obtain vinyl polysilazane dispersion. Then add 0.5g of Deco 410, 0.2g of 066N defoamer and 1g of di-tert-butyl hydrogen peroxide into the dispersion and disperse with a high-speed disperser, stirring for 30min to produce vinyl polysilazane anti-corrosion coating.

2.3 Sample preparation

The Q235 sandblasted steel plate (150mm×70mm×0.8mm) is wiped clean with cotton dipped in alcohol to confirm that the surface is free of dirt. The wiped steel plate to dry, spraying vinyl polysilazane anti-corrosion coating on the surface of the steel plate, room temperature curing 10 min after curing at 125 ℃ for 30 min, heat treatment 250 ℃ or 600 ℃ baking 10 min, the production of silazane anti-corrosion coating samples.

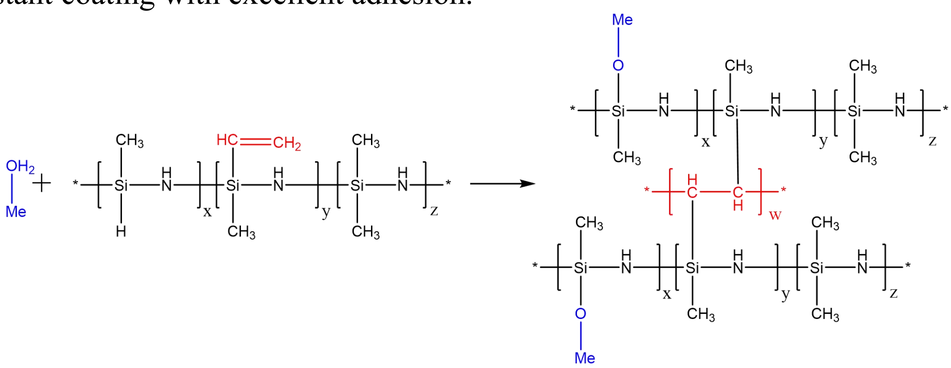
2.4 Characterization methods

Testing adhesion according to GB/T 9286-1998; testing impact resistance according to GB/T1732-1993; testing salt spray resistance according to GB/T 1771-2007; testing pencil hardness according to GB/T6739-2022; testing fineness according to GB/T1724-1989; testing solid content according to GB/T1725-2007; testing viscosity according to GB/T1723-1993.

3. Results and Discussion

3.1 Principles and Basic Properties of Coating Curing

As shown in equation (1), di-tert-butyl hydrogen peroxide in the coating is decomposed by heat to form free radicals, which can trigger the polymerization of vinyl in the vinyl silazane resin, thus forming a network structure with high cross-linkage and increasing the denseness of the coating. Vinyl silazane contains Si-H, which can react with the hydroxyl groups on the surface of the substrate and zinc powder to form Si-O-Me bonds after high temperature. The silazane resin can form a covalent bond with the zinc powder in the coating and the steel plate substrate, resulting in a corrosion-resistant coating with excellent adhesion.



(1)

The basic properties of the polysilazane anti-corrosion coating were characterized, and the characterization results are shown in Table 1 so. The adhesion of polysilicon nitrogen anticorrosive coating is 0 level, and the adhesion is superior. The hardness of traditional organic anticorrosive coating is 3-4H, and the hardness of silicone nitrogen anticorrosive coating is 6H without scratch, which is higher, so the coating has excellent wear resistance and scratch resistance. The solid content of this polysilazane anti-corrosion coating is 80%, and the solvent used is a high boiling point environmentally friendly solvent.

Table 1. Basic properties of polysilicon nitrogen anti-corrosion coatings

Name	Value	Reference standards
State in container	Uniform and free from lumps	GB/T9755-2001 5.3
Fineness/ μm	70	GB/T1724-1989
Adhesion/Grade	0	GB/T 9286-1998
Impact resisitance/kg cm	50	GB/T1732-1993
Solid content/%	80	GB/T1725-2007
Viscosity/s	35	GB/T1723-1993
Hardness	7H	GB/T6739-2022

3.2 The Effect of Heat Treatment Temperature on Salt Spray Resistance

After curing at 125 ℃, the samples of polysiloxane anti-corrosion coating were subjected to heat treatment for 10 minutes in ovens at 250 ℃ and 600 ℃, respectively. Then, the samples treated at different temperatures were placed together in a neutral salt spray box, and the samples were taken out for 72 hours, 456 hours, 1000 hours, and 2000 hours respectively for observation and photography. The results are shown in Figure 1.

From Figure 1, it can be seen that after 72 hours of salt spray testing, the scratch on the surface of the sample treated at 600 ℃ is no longer obvious, and zinc powder reacts to form zinc oxide to fill the scratch site, playing a "self-healing" role. With the extension of salt spray time, there was no obvious rust or blistering on the surface of the paint film, and no rust expansion occurred at the scratches. After 456 hours of salt spray testing at 250 ℃, a small amount of red rust appeared at the scratched area of the sample. After 1000 hours of salt spray testing, the rust gradually became apparent at the scratched area. After 2000 hours of salt spray testing, rust marks began to expand at the scratched area, but the non scratched area remained relatively flat without bulging or rust spots.

During the curing process of the sample at 125 ℃, di-tert-butyl hydrogen peroxide decomposes to produce free radicals, triggering the instantaneous polymerization of vinyl groups in vinyl silazane, forming a cross-linked network structure. At this point, Si-H in the paint film does not react with the hydroxyl groups on the metal surface, and the adhesion and cohesion energy of the paint film are relatively low. After treatment at 250 ℃, the zinc powder did not melt, the Si-H in silazane reacted with the hydroxyl group on the metal surface, and the coating formed Covalent bond with the substrate and zinc powder, which improved the compactness of the coating. After treatment at 600 ℃, the temperature is higher than the melting point of zinc powder. The Covalent bond is not only formed between silazane, substrate and zinc powder, but also the compactness of the paint film is relatively increased after zinc powder melting, so its salt spray resistance is also better.

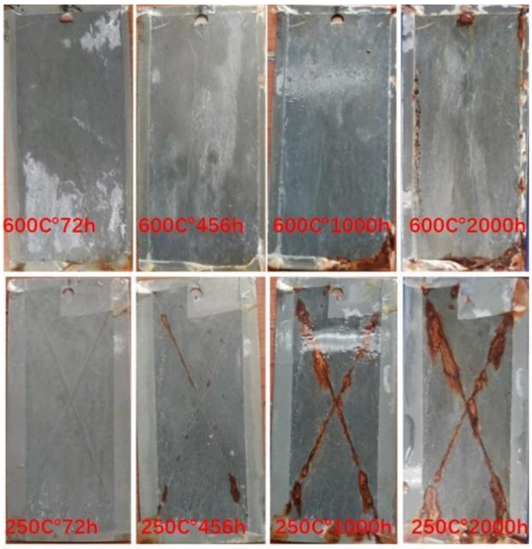


Fig. 1 Effects of 250 ℃ and 600 ℃ heat treatments on the anti-corrosion performance of coatings

3.3 Comparison of salt spray resistance between polymer silicon nitrogen coating and zinc plating

Due to the relatively high energy consumption of the 600 ℃ heat treatment process, the salt spray resistance of the samples prepared by the 250 ℃ heat treatment process was compared with that of hot-dip galvanizing. Place the polysiloxane anti-corrosion coating and hot-dip galvanized sheet simultaneously in a neutral salt spray box, and after 1000 hours of salt spray test, take out the sample to check its status and take photos. From Figure 2, it can be seen that after 1000 hours of salt spray test, a large amount of red rust has appeared on the surface of hot-dip galvanizing (Figure 2c), and the hot-dip galvanizing layer has completely lost its corrosion protection ability. After 1000 hours of salt spray test, there was no significant change on the surface of the polysilazane anti-corrosion sample without scratch treatment (Figure 2b). The scratched polysilazane anti-corrosion sample showed obvious rust at the scratch area, and there were no rust spots or bulges in the non scratched area (Figure 2a). The anti-corrosion performance of polysilazane samples treated at 250 ℃ is significantly better than that of hot-dip zinc samples. The heat treatment temperature is half of the hot-dip galvanizing temperature, and there is no need for processes such as acid washing and water washing. Compared to the hot-dip galvanizing process, it has lower energy consumption and is more environmentally friendly. Hot dip galvanizing requires maintaining the zinc pot at 500 ℃ for a long time, making it difficult to start and stop, while polysilazane anti-corrosion can be started and stopped at any time.

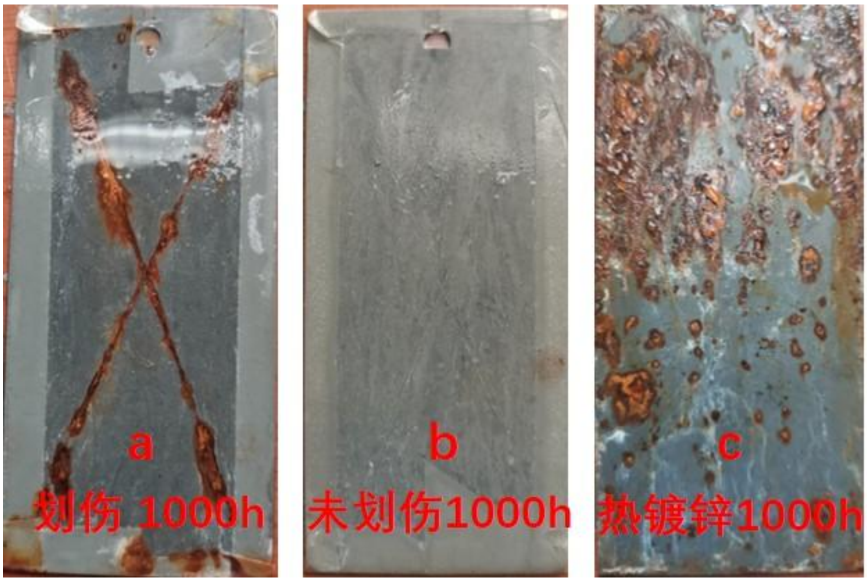


Fig. 2 Comparison of salt spray resistance between polysilazane anti-corrosion coating and hot-dip galvanizing

4. Summary

A polysiloxane anti-corrosion coating was prepared, which has a hardness of up to 7H after high-temperature treatment at 250 ℃, and its anti-corrosion performance is better than that of hot-dip galvanized anti-corrosion samples. The construction process of this coating has lower energy consumption compared to the hot-dip galvanizing process, and the process is simple and environmentally friendly. After heat treatment at 600 ℃, the anti-corrosion performance of this coating is better, and after 2000 hours of neutral salt spray test, there is no significant corrosion. This anti-corrosion coating is a good choice to replace hot-dip galvanizing anti-corrosion.

References

[1] SHAO Dawei, HE Zhirong, ZHANG Yonghong, et al. Research progress of hot-dip galvanizing technology [J]. Hot Working Technology, 2012, 41(6): 100-103

[2] YAO Xiongting, KONG Gang, CHE Chunshan, et al. Current research status and progress of the flux for Hot-Dip galvanizing [J]. Materials Protection, 2023, 56(01): 121-126.

[3] YANG Zhenbo, QU Shuai, SHI Hua, et al. VCI sheet zinc technology that can replace hot dip galvanizing process [J]. Coating and Protection, 2018, 39(02): 55-58.

[4] ZHANF Zongbo, ZENG Fan, LUO Yongming, et al. Progress in Application of Polysilazane [J]. Silicone Material, 2013, 27(03): 216-22.

[5] GARDELLE B, DUQUESNE S, VU C, et al. Thermal degradation and fire performance of polysilazane-based coatings [J]. Thermochimica Acta, 2011, 519(1-2): 28-37.

[6] ROSSI S, DEFLORIAN F, FEDEL M. Polysilazane-based coatings: corrosion protection and anti-graffiti properties [J]. Surface Engineering, 2018, 35(4) :343-350

[7] CHEN Xiaolei Measurement of surface contact angle and study on surface energy of solid polymer [D]; Central South University, 2012.

[8] ZOUMing, ZHOU Xiaolong, HUANG Wenwen, et al. Polysilazane conversion film for metal surface pretreatment [J]. Paint & Coatings Industry, 2020, 50(04): 19-25.

[9] HUANG Y D, CAO H L, GONG] G F. Effects of ambient-temperature curing agents on the thermal stability of poly(methylphenylsiloxane) [J]. Polymer Degradation and Stability, 2004.80(1),725-731