

# 氨基硅烷偶联剂对环氧涂层附着力的影响

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**[摘要]** 研究了氨基硅烷偶联剂对提高环氧涂层与钢铁基底材料的附着力的作用。主要对其水解特性和对涂层附着力的影响进行了测试, 并利用反射红外 (RAIR) 对氨基硅烷偶联剂的作用机理进行了分析。结果表明, 氨基硅烷偶联剂在极少量水分的条件下就能够水解形成硅羟基, 添加氨基硅烷偶联剂的涂层与底材之间有化学键作用, 能够显著提高涂层与底材的附着力, 与纯环氧涂层相比, 可以提高 5~6 MPa。

**[关键词]** 氨基硅烷偶联剂; 铁基底材; 水解; 附着力

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## 0 前言

涂层对铁基底材防护效果的好坏, 除了涂层本身的防腐蚀性能, 还取决于涂层与铁基底材之间的附着力, 即它们之间的物理或化学作用力。这种作用力越大, 在腐蚀环境条件下涂层与铁基底材的附着力保持得越久, 涂层可以有效地保护基材, 从而延长基材的使用寿命。国内外专家就涂层的附着机理作了大量的研究, 认为主要包括机械附着和化学附着, 机械附着取决于涂料的润湿性能和底材表面的粗糙度等; 化学附着则是涂料中的极性基团与基材表面的极性基团间的化学作用。一般认为化学附着更为牢固。近些年来对附着力促进剂的研究比较热门, 其中对硅烷偶联剂研究得较多。

硅烷偶联剂是具有特殊结构的物质, 其分子链两端一般都带有活性基团, 其结构为:  $YR_n-Si-X_m$ , X 是烷氧基团, 通常可以水解成极性的硅羟基, 吸附于铁基表面并与其反应<sup>[1]</sup>; Y 是另一种活性基团, 如氨基、环氧基等, 可以与涂料体系中的活性基团反应。这样硅烷偶联剂就能够在涂层和铁基底材之间形成一种连接纽带, 改善涂层与基材的附着力<sup>[2]</sup>。Van Ooij 等<sup>[3~5]</sup>以及徐溢等<sup>[6~8]</sup>对硅烷偶联剂的水解作了深入仔细的研究, 认为用硅烷偶联剂的稀溶液处理金属, 能够达到好的附着及防腐蚀效果。但这种处理工艺比较复杂, 既要控制溶液的浓度、温度以及 pH 值, 还要控制浸泡时间和烘烤时间等参数, 因此实际应用受到了限制。

本工作选择氨基硅烷偶联剂作为附着力促进剂, 直接添加到涂料体系中, 研究了氨基硅烷偶联剂对环

氧涂料与铁基底材之间附着力的影响。

## 1 试验

### 1.1 试验原材料及仪器

试剂: 环氧树脂 CYD-128, 稀释剂 D1217, 氨基硅烷偶联剂, 环氧固化剂 Tz-600, 胶粘剂 EP-10S100, 无水乙醇 (分析纯)。

试片: 普通低碳钢, 规格: 75.0 mm × 50.0 mm × 2.5 mm。

仪器: elcometer 公司产 FA0020 型拉拔仪, 大普仪器有限公司产 DDS-11A 型电导率仪, AVATER 产 DTGS370 型红外光谱仪。

### 1.2 试验内容

(1) 试片处理 将试片除油、清洗干净后烘干水分, 然后用粗砂纸 (180 目) 打磨, 使试片表面处理达到 St<sub>2</sub> 级, 用脱脂棉擦干净表面后放入干燥箱中备用。

(2) 涂料配制 涂料的基本配方如下:

	原料组分	质量 /g
A 组分	CYD127	150
	D1217	50
	铁红	75
	云母	25
	滑石粉	60
	二氧化硅	5
	分散剂 (BYK-163)	4
	流平剂 (BYK-411)	2
	消泡剂 (BYK-060)	2
	氨基硅烷偶联剂	2
B 组分	TZ600	70

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(3)氨基硅烷偶联剂水解性能的测定 水解性能测定就是利用电导仪测定硅烷偶联剂水溶液达到最高的平衡电导率的时间。

(4)涂层附着力的测定 涂层的附着力根据 GB/T 5210—85进行测定。

(5)红外及反射红外分析 根据红外分析试验中烷氧基和硅羟基的吸收峰来分析氨基硅烷偶联剂水解的程度,利用反射红外分析试验来分析添加氨基硅烷偶联剂的涂层与底材之间是否有化学键作用。

## 2 试验结果与讨论

### 2.1 氨基硅烷偶联剂的水解性

将氨基硅烷偶联剂直接添加到环氧涂料中,要使其发挥偶联作用,就必须让硅烷偶联剂快速水解,形成硅羟基。硅烷偶联剂水解速率可以通过水溶液的电导率来反映,水解越快,水溶液就会在越短的时间内达到最高的平衡电导率,也就是说,如果硅烷促进剂达到最大的电导率的时间越短,相应的硅烷偶联剂的水解能力就越强。选用的氨基硅烷偶联剂在稀溶液和高浓度的水解情况见图 1 和图 2。

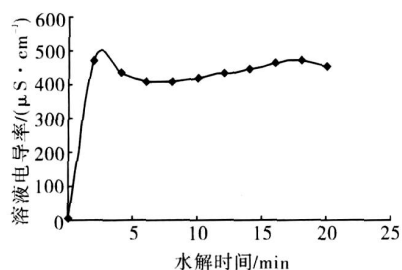


图 1 浓度为 5% 的氨基硅烷偶联剂的水解电导率

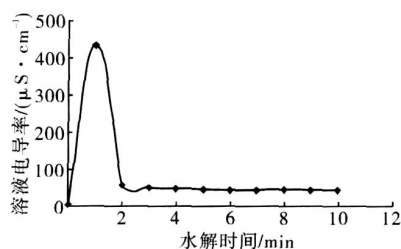


图 2 浓度为 80% 氨基硅烷偶联剂的水解电导率

从图 1 可以看出,氨基硅烷促进剂在很短的时间(2 min)内就达到很高的电导率,稍微下降趋于平缓达到水解平衡,表明氨基硅烷偶联剂水解能力强。平衡时溶液为醇、水、硅烷偶联剂铵根离子及硅烷的混合溶液,由于大量水分的存在,硅羟基浓度小,自缩合速度慢,溶液中硅烷铵根离子和硅羟基共同形成导电物质,因此,电导率在一定时间内保持在较高的水平。图 2

表明,氨基硅烷偶联剂在少量水的情况下也能快速水解,产生大量的硅羟基;图中电导率急剧下降表明产生的硅羟基自缩合导致硅羟基大量地减少,而没有足够的水分产生硅羟基补充,仅由硅烷铵根离子产生电导。因此,电导率下降迅速,这也说明在氨基硅烷偶联剂溶液中,硅羟基是产生电导的主体。图中氨基硅烷偶联剂水解的电导率都很高,表明硅烷偶联剂水解形成的硅羟基浓度很高,也说明氨基硅烷偶联剂极易水解。也就是说,氨基硅烷偶联剂在极少量水的情况下也能水解产生硅羟基。因此,在无溶剂环氧涂料中直接加入氨基硅烷偶联剂来改善涂层与底材的附着力是可行的。

### 2.2 氨基硅烷偶联剂对附着力的影响

将氨基硅烷偶联剂按涂料试验配方直接添加到环氧涂料中,混匀后涂刷试片,待完全固化后用拉拔法测试涂层与底材的附着力。图 3 是氨基硅烷偶联剂对附着力的影响。

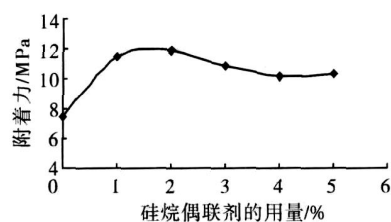


图 3 不同硅烷促进剂对附着力的影响

图 3 中零点附着力表示没有加氨基硅烷偶联剂时的附着力,大小为 7.0 MPa 左右。从图中可以看出:开始时,随着氨基硅烷偶联剂量的增加附着力逐渐增大;当用量增到总量的 2% 时,附着力达到最大 12.9 MPa,之后有下降的趋势,但附着力仍在 10.0 MPa 以上。氨基硅烷偶联剂的加入显著地提高了涂层与底材的附着力,这一方面是硅羟基与底材以化学键作用的结果,另一方面是氨基与环氧涂料中的环氧基反应形成互穿网络结构的作用。

### 2.3 红外分析

试验发现,氨基硅烷偶联剂直接加入到环氧涂料中能够显著地增加涂层与底材的附着力,为了进一步研究其作用机理,采用红外及反射红外进行了分析。

图 4 是氨基硅烷偶联剂的红外光谱,图 5 是涂层与底材界面层的反射红外光谱。

图 4 中,  $3266\text{ cm}^{-1}$  处的强吸收峰以及  $1067\text{ cm}^{-1}$  处出现的较强峰,表明氨基硅烷偶联剂中存在  $\text{Si-OH}$ ,也就是说,所用的氨基硅烷偶联剂由于强的水解

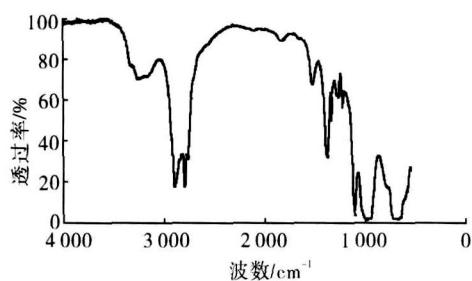


图4 纯氨基硅烷偶联剂的红外光谱曲线

性吸收空气中的水分而水解产生了硅羟基; 2 839 ~ 2 936  $\text{cm}^{-1}$  出现强的烷氧基吸收峰, 表明溶液中存在较多的烷氧基没有被水解; 在 773  $\text{cm}^{-1}$  处强的硅氧烷基吸收峰以及 1 306 ~ 1 411  $\text{cm}^{-1}$  的烷基吸收峰进一步表明体系中有较多的烷氧基未被水解。

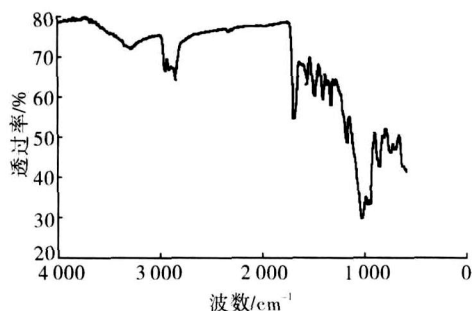


图5 涂层与底材界面层的反射红外光谱

图5中在 799  $\text{cm}^{-1}$  处的硅烷氧烷基峰以及 909  $\text{cm}^{-1}$  处较强的 Si—OH 吸收峰, 表明在涂层与界面上有硅烷偶联剂的存在, 表明氨基硅烷偶联剂向底材发生了迁移; 与图4相比, 图5中羟基峰明显减弱, 说明硅羟基与涂层或底材发生了作用从而被消耗了, 同时羟基峰从图4中 3 266  $\text{cm}^{-1}$  位移到 3 296  $\text{cm}^{-1}$ , 表明硅羟基与底材或涂层形成了新的化学键; 图4中 2 839 ~ 2 936  $\text{cm}^{-1}$  的烷氧基峰在图5中相应位置的强度变弱, 表明有更多的烷氧基水解, 而硅羟基的量却减少了, 又由于硅烷偶联剂分散在涂料中, 硅羟基缩合形成 Si—O—Si 的几率小 (图5中 1 225  $\text{cm}^{-1}$  处的 Si—O—Si 的弱吸收峰就说明了这一点), 这也进一步说明大量的硅羟基与涂层及底材发生了作用。

### 3 结论

(1) 氨基硅烷偶联剂水解作用很强, 在极少量水分的条件下也能够水解形成硅羟基。

(2) 氨基硅烷偶联剂直接加入到环氧涂料中能够显著提高涂层与底材的附着力, 与纯环氧涂层相比, 可以提高 5 ~ 6 MPa。

(3) 通过红外和反射红外分析, 添加氨基硅烷偶联剂的涂层与钢铁底材有化学键的作用。

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## 佛山产业转移园严禁引入电镀等重污染项目

2008年初, 从佛山市经贸局获悉, 佛山 (清远) 产业转移工业园刚被省政府认定为广东省产业转移工业园, 至此佛山与兄弟城市共建的产业转移工业园已有 6 个获省认定。

佛山 (清远) 产业转移工业园位于清远经济开发区百嘉工业园内, 开发面积为 437.32 公顷, 首期环评批准引进的主要产业是无污染或轻污染、低水耗、低能耗、低物耗的电子信息、移动通信等高新技术产业, 同时严禁引入生物制药、电镀、制革、印染、化工、造纸等重污染以及废水大量排放或排放含有第一类污染物的项目入园。

广东省经贸委的相关公告要求, 两地政府严格执行省政府《关于我省山区及东西两翼与珠江三角洲联手推进产业转移的意见 (试行)》、《广东省产业转移工业园认定办法》以及相关的政策规定, 依法依规做好产业转移工业园的环保、规划、投资、开发、建设和招商引资等工作, 加快完善产业转移工业园基础设施等配套条件, 确保产业转移工业园健康、快速、可持续发展。

(据珠江商报)

above  $12 \text{ A/dm}^2$ , the hardness of the coating decreased as well. Moreover, the coating with a grain size of about 20 nm had the highest hardness and strength, and it was able to increase the service life of the diamond tools by about 20.2% as compared with conventional Ni-Co coating.

Key words: electroplating; nanomaterials; nickel; diamond; tools

#### The Microstructure and Phase Composition of Micro-Arc Oxidation Coating on Magnesium Alloy

ZHANG Zhi-you, ZHAO Qing, CHEN Ning (College of Materials Science & Engineering Nanchang Institute of Aeronautical Technology, Nanchang 330063, China). *Cailiao Baohu* 2008, 41(03), 19~21 (Ch). The corrosion resistance of micro-arc oxidation coating on Mg alloy was investigated based on the analysis of the cross-sectional microstructures and elemental distributions. Thus the morphology, structure, phase composition and elemental distribution of the micro-arc oxidation coating were analyzed by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive spectrometry (EDS). The results showed that there existed a large amount of relatively uniform discharge micro-pores on the surface of the ceramic coating, and the compact layer was about 60% as thick as the whole coating. Moreover, the ceramic coating was mainly composed of  $\text{MgSiO}_4$  and MgO phases, and the transition layer and compact layer had a phase composition of  $\text{MgO}:\text{MgSiO}_4 = 5:1$  and  $\text{MgO}:\text{MgSiO}_4 = 1:1$ , respectively. Besides, the content of Mg gradually decreased, the contents of O and Si increased initially and then decreased, while the content of P kept almost unchanged from the inner to the outside of the coating.

Key words: magnesium alloy; micro-arc oxidation; phase composition; elemental distribution

#### Effect of Amido-Silane Coupling Agent on Adhesion of Epoxy Resin Coatings

XIE Guo-xian, QIU Da-jian, LI Chao-yang, XIAO Xiang-ding (Wuhan Research Institute of Materials Protection, Wuhan 430030, China). *Cailiao Baohu* 2008, 41(03), 22~24 (Ch). Amido-silane coupling agent was used to increase the adhesion of the epoxy resin coating on iron and steel substrates. Thus the hydrolysis behavior of the amido-silane coupling agent and its effect on the adhesion of the epoxy coating on iron-steel substrate were investigated, while the action mechanisms of the coupling agent was examined by means of reflective infrared spectrometry. It was found that the amido-silane coupling agent had very strong hydrolysis ability and was able to greatly increase the adhesion of the epoxy resin coating by forming chemical bond between the coating and the substrate. Namely, the adhesion of the coating with the coupling agent was 5~6 MPa higher than that of the epoxy resin coating without the coupling agent.

Key words: amido-silane coupling agent; iron and steel substrate; hydrolysis; adhesion

#### Effect of Pretreatment on the Adhesion of Electroless Ni-P Coating on Stainless Steel

HAO Long<sup>1a</sup>, FENG Quan-fen<sup>1b</sup>, SHEN Wei<sup>2</sup>, LIN An<sup>1a</sup>, GAN Fu-xing<sup>1a,3</sup> (1a. School of Resource and Environmental Science; 1b. Department of Municipal Engineering, School of Civil and Architecture Engineering, Wuhan University, Wuhan 430079, China; 2. Wuhan Research Institute of Materials Protection, Wuhan 430030, China; 3. State Key Laboratory for Corrosion and Protection, Institute of Metals, Chinese Academy of Sciences, Shenyang 110016, China). *Cailiao Baohu* 2008, 41(03), 25~27 (Ch). In order to get qualified electroless Ni-P coating on stainless steel, the influences of three different pretreatment techniques, chemical activation, chemical activation plus strike nickel plating, and anodic activation plus strike nickel plating on the adhesion of electroless Ni-P plating on stainless steel were studied. The adhesion force between the Ni-P coating and stainless steel substrate was examined making use of thermal shock test and scratch test. It was found that the samples pretreated by chemical activation plus strike nickel plating and anodic activation plus strike nickel plating had qualified adhesion. However, the sample pretreated by chemical activation had no qualified adhesion, which could be attributed to the formation of corrosion product on the stainless steel surface after chemical activation at elevated temperature. Moreover, after being immersed in NaCl solution for 168 h, the stainless steel had a weight loss of 1.2 mg, while the electroless Ni-P coating had no weight loss, indicating that the electroless Ni-P coating had better corrosion resistance than the stainless steel.

Key words: pretreatment; electroless plating; Ni-P coating; activation; stainless steel; adhesion

#### Effect of Activation on Coloring of Stainless Steel

CHENG Zuo-hui<sup>1,2</sup>, XUE Yong-qiang<sup>1</sup>, DUAN Yan-fang<sup>1</sup>, ZHANG Chun-ting<sup>1</sup>, DU Hui-ling<sup>2</sup>, ZHANG Jin-tong<sup>2</sup> (1. Department of Applied Chemistry, Taiyuan University of Technology, Taiyuan 030024, China; 2. The Arts and Science College, Shanxi Agricultural University, Taigu 030801, China). *Cailiao Baohu* 2008, 41(03), 28~30 (Ch). The effects of various activations including HCl activation at room temperature,  $\text{H}_2\text{SO}_4$  activation at room temperature, anodic  $\text{H}_2\text{SO}_4$  activation, cathodic  $\text{H}_2\text{SO}_4$  activation,  $\text{H}_2\text{SO}_4$  activation at elevated temperature of 65 °C, and  $\text{H}_2\text{SO}_4\text{-CrO}_3$  activation on the uniformity and wear resistance of coloring films of stainless steel were investigated. The potential-time curves of the coloring films on the stainless steel were determined. The relationship between the potential-time curve parameters  $t_b$  and  $t_c$  and their influence on the quality of the coloring films on the stainless steel were also explored. It was found that the activation was able to speed the coloring process and helped the formation of bright, uniform, and wear-resistant coloring films. At the same time, the coloring rate of the stainless steel increased with increasing temperature, and anode electrolysis activation was superior to cathode electrolysis activation. Moreover, HCl and  $\text{H}_2\text{SO}_4$  with the same concentration had the same activation effect, and the optimal activation was realized by anode electrolysis in 10%  $\text{H}_2\text{SO}_4$ . In addition, the potential-time curve parameters  $t_b$  and  $t_c$  could be used to express the activation effect and the readiness of coloring.

Key words: stainless steel; activation; coloring

#### Preparation and Characterization of Fe Doped Ti-Based $\text{SnO}_2/\text{Sb}$ Electro-Catalytic Electrode

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Key words:  $\text{SnO}_2/\text{Sb}$  electrode; Fe; electro-catalysis; phenol

#### Corrosion Resistance of Phosphating/Silane Composite Film on Hot-Dip Galvanized Steel Sheet

YOU Wei, LU Jin-tang, LIN Bi-lan (School of Material Science and Engineering, South China University of Technology, Guangzhou 510640, China). *Cailiao Baohu* 2008, 41(03), 34~36 (Ch). A composite film was prepared on the surface of hot-dip galvanized steel sheet by phosphating and treatment with bis-[triethoxysilylpropyl] tetrasulfide (BTESPT) silane. The composition and microstructure of the composite film were analyzed by means of scanning electron microscopy and energy dispersive spectrometry, while its corrosion resistance was evaluated using electrochemical polarization measurement and neutral salt-spray test. It was found that the micro-pores in the phosphating coating of the hot-dip galvanized steel were sealed by silane film after being post-treated with BTESPT solution, and a continuous, compact and complete composite coating was subsequently formed. After being phosphated for 300 s and post-treated with BTESPT solution, the resulting composite coating had greatly increased polarization resistance  $R_p$ , significantly decreased corrosion current density, and was free of white rust after 5 cycle neutral salt-spray test.

Key words: hot-dip galvanized steel; phosphating; silane; seal-