ISSN 2959-6157

Green Film Forming Technology Based on Polydopamine Galvanized

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Abstract:

At present, the mainstream passivation agent is chromate passivation agent, but it has the disadvantages of high toxicity and high price, so this project seeks to find a safer, cheap and green chromium-free passivation agent. Because dopamine and chitosan derivatives have certain corrosion inhibition properties on metals in acidic media, these polymer corrosion inhibitors can achieve high corrosion inhibition rates at high concentrations. Therefore, in this experiment, dopamine was added on the basis of sodium silicate, and the sample was passivated to explore the potential enhancement effect of dopamine on the passivated film performance. After the sample was treated, the impedance value could be fitted by electrochemical impedance spectroscopy and Zsimpwin software, and then the Tafel polarization curve was drawn. It was found that the addition of dopamine significantly improved the corrosion resistance of the passivated film. By promoting the positive shift of self-corrosion potential and greatly reducing the self-corrosion current density, the protective barrier effect of passivation film on metal matrix is effectively enhanced. Finally, the experiment successfully proved that the corrosion resistance of the passivation film after adding dopamine was better.

Keywords: Inorganic passivation; polydopamine; corrosion resistance; passivation film.

1. Introduction

Passivation is widely used in the field of metal corrosion prevention and is one of the important means to improve the corrosion resistance of metal materials. Since the metal body is prone to rust in the air, in order to improve the corrosion resistance of the metal, passivation treatment is usually carried out. Passivation can not only form a protective film on the metal surface to improve the corrosion resistance of the metal, but also play a decorative role in the appearance of different colors on the metal surface. At present, chromate passivation is the most widely used at home and abroad, which can effectively improve corrosion resistance, the process is mature, the cost is low, and the generated film layer has self-healing ability, but the hexavalent chromium contained in chromate has great toxicity, high carcinogenicity, and great harm to the environment. In order to reduce the harm to the environment and the human body, low chromium passivation appears, but there is still hexavalent chromium. It has not fundamentally eliminated its harm. The study found that the toxicity of trivalent chromium is 1% of the toxicity of hexavalent chromium, in addition, the heat resistance of the trivalent chromium passivation film is also better than that of hexavalent chromium passivation film, and the service life of the passivation solution is also longer than that of hexavalent chromium, because of its excellent characteristics, trivalent chromium passivation solution has been gradually put into production, but because trivalent chromium is easy to oxidize into hexavalent chromium in the air, especially in the oxidizing environment. It is still harmful to the environment and human body. It is urgent to research and develop a new chromium-free passivation process [1].

The existing chromium-free passivation is mainly divided into inorganic passivation and organic passivation two categories. Inorganic passivation mainly includes molybdate passivation, tungstate passivation, silicate passivation and rare earth metal salt passivation, and organic passivation mainly includes phytic acid passivation, organosilane passivation, resin passivation and tannic acid passivation. However, the effects of these passivators are not particularly ideal.

In recent years, affected by the epidemic, the current international economic situation is not too optimistic, and most of the passivation fluids currently put into production are high cost, which is extremely pressure for many companies, the current market requirements for passivation films of galvanized layer not only have good corrosion resistance and self-healing ability, but also certain heat resistance and electrical conductivity and other properties. Therefore, it is necessary to explore a high environmental protection and low cost chromium-free passivation process [2].

natural resources are becoming more and more valuable, and the call for green environmental protection is getting higher and higher. At present, the mainstream chromate (chromate is commonly found in the passivation of traditional galvanized layer, but has the disadvantages of high toxicity and high price, so this project seeks a safer and cheaper chromium-free passivation agent) although it can protect the metal well enough, it has polluted the environment while protecting the metal, and even has high harm to the human body, which does not meet the current national green and sustainable development policy. In order to be able to protect the metal without damaging the environment, it is necessary to develop a product whose performance is close to that of chromate passivator, but which is green, non-toxic and relatively inexpensive. Most of the chromate passivation technology is used in industrial production, which can form a self-healing passivation film on the surface of the metal, so that the comprehensive anti-corrosion performance of the metal is improved. However, hexavalent chromium has great harm to human body and the environment, so the research and development of new passivation solution has become a hot spot in recent years, but the existing passivation solution, including trivalent chromium and chromium-free passivation solution under development, can not achieve the passivation effect of hexavalent chromium [3, 4]. In view of the current international economic situation, this study will compare the performance of various passivation fluids through experiments and finite element analysis, and try to find a new passivation solution with lower cost and higher environmental protection.

2. Experimental

2.1 Materials

Q235B steel (Shandong Jiujia Metal Material Ltd), 180 mesh, 400 mesh, 800 mesh, 1000 mesh and 1500 mesh sandpaper (MYTEC), anhydrous sodium silicate and sodium hydroxide standard titration solution were both bought from Xilong Scientific Ltd., silica powder (Aladdin), sodium hydroxide standard titration solution was bought from Silong Science and was formulated in the laboratory according to the standard, dopamine (Sigma-Aldrich), phytic acid and dilute nitric acid, anhydrous ethanol were both bought from Sinopharm Group Chemical reagent Ltd.

2.2 Preparation of Polydopamine Galvanized Steel

In order to prepare suitable samples, the first step is metallographic grinding: the Q235B steel is polished, and the sandpaper scales are 200#, 400#, 1000#, 2000#. Pay attention to keep the scratch vertical, try to make the surface uniform force; After grinding the water system is dry, try not to contact with the skin such as hands to prevent the adhesion of impurities such as sweat. Then the samples were pretreated before electroplating. The metal matrix was deoiled by ultrasonic ethanol for 180s, then washed, then chemically deoiled for 30min, washed again, then activated for 5-10min (the surface can turn gray), washed again, and air dried. Then, the Q235B steel is polished with sandpaper until the surface is bright, and the ultrasonic cleaning is carried out. After ultrasonic cleaning, the sample is rinsed with pure water and blown dry, and then soaked in oil remover for about 30 minutes to remove the surface oil. After the oil removal is completed, the sample is rinsed with pure water and blown dry, and then the sample is soaked in the activator for about 5 minutes to improve the activity of the sample surface. In the process of oil removal and activation, take a small zinc sheet, sand its surface to remove the oxide film on the surface of the zinc sheet, and clean it with deionized water; The zinc sheet is polished, cleaned with dilute sulfuric acid, and cleaned with deionized water; The plating solution is poured into the plating bath, and the power supply is connected through the anode to connect the zinc sheet, the cathode to connect the steel, and put into the plating bath; Turn on the power supply, the current density is controlled at 2A/dm2, and the plating time is 10min. During electroplating, it is necessary to place the surface of the sample and the zinc sheet relative to each other. After electroplating, turn off the power and remove the electroplated steel for cleaning with deionized water. After the completion of galvanizing, the sample is taken out, rinsed with pure water and dried, and then soaked in the passivation agent for about 1 minute (the composition, concentration and passivation temperature of the passivation agent are shown in the table below, among which the PH of sodium silicate solution and sodium silicate + dopamine solution should be adjusted to 3~4 before passivation). The glass stirring solution is used during immersion until the passivation is finished.

2.3 Precautions for Preparation

The problems and solutions that may be encountered in this sample preparation step are, first of all, the problem of zinc impurities in the galvanized passivation solution: if no subsequent post-treatment is carried out after galvanizing, black spots appear in the oxidation of galvanizing quickly, and white corrosion products appear one after another. In order to reduce the chemical activity of zinc, zinc plating needs to be treated with passivation liquid in order to cover the zinc with a layer of chemical conversion film, so that the active metal is in a blunt state. The dissolution of zinc on the surface of galvanized parts is a necessary condition for the formation of passivation film, but the dissolved zinc ions may not be fully involved in the film formation process, and more exist in the galvanized passivation tank. A small amount of zinc ions in the galvanized passivation tank can promote the formation of passivation film and thus improve the corrosion resistance of the passivation film layer. However, when the zinc content reaches a certain level, the higher the zinc content, the worse the corrosion resistance, thus reducing the performance of the galvanized passivation tank. The components of the passivation tank often change during the production and application process of galvanized parts passivation. It is necessary to regularly monitor whether the content of each component of the passivation tank is within the appropriate range, so as not to affect the passivation effect of the passivation tank. In order to solve the zinc impurity problem and avoid affecting the passivation effect, the team decided to adopt the following solution: With potassium fluoride masking iron ions, thiourea masking copper ions, and xylenol orange as the indicator, the content of zinc impurities in cyanide-free alkaline galvanized passivation solution is titrated with EDTA standard solution. The operation is simple, and the interference of impurity ions such as Fe3+ and Cu2+ to titration can be avoided, and the defects of the sealing effect of the indicator can be overcome [2, 5]. The color change of the end point is obvious, and its precision and recovery rate are high. It can be used to monitor zinc impurities in cyanide-free alkaline galvanized passivation solution. Secondly, it is also necessary to pay attention to the effect of electrogalvanizing time on the corrosion resistance of the coating: different electroplating time determines the thickness of the galvanizing layer. With the increase of plating time, the thickness of galvanizing layer also increases, so it is necessary to determine the appropriate galvanizing layer thickness. To ensure that other process conditions remain unchanged, the corrosion resistance of the coating obtained after the treatment of zinc coating with different thickness is studied by using AC impedance and polarization curve method, and the corresponding impedance value can be obtained, and the impedance value can be fitted by Zsimpwin software, so as to judge [5].

2.4 Characterisation

2.4.1 Electrochemical impedance spectroscopy

AC impedance corrosion measurement is a test method that superimposes AC signals on the electrode to obtain a variety of electrochemical information. The superimposed signal is a series of sinusoidal signals of small amplitude (e.g., <20mV) with a wide frequency range (e.g., from 1mHz to 100kHz). The resulting response signal is often described by complex planar graph and Bode diagram, which is characterized by the superposition of the AC signal under any external direct current potential and little influence on the surface blood state of the electrode. After the samples are treated with passivating agents of different compositions, the steady-state corrosion rate of metal samples can be measured by electrochemical impedance spectroscopy, so as to judge and compare the anti-corrosion effects of different passivating agents on the samples.

2.4.2 The Tafel polarization curve tests

The steady-state polarization curve, which is to determine the relationship between the overpotential and the current density when the electrode process reaches a steady state. The dynamic parameters of the control steps in the electrode process can be determined by using the steady-state polarization curve, and then the dynamic laws and influencing factors of the electrode process can be studied. Corrosion potential and corrosion current density are usually used to characterize the corrosion resistance of zinc coating, that is, the higher the corrosion potential, the lower the corrosion current density, and the better the corrosion resistance of the film. Tests were performed using an electrochemical workstation. In this experiment, a three-electrode system was used. The starting potential of Tafel polarization curve was as follows: open circuit potential +250mV; Stopping potential: open circuit potential -250mV; The scanning rate is 1mV/s. By comparing the difference of current and potential of samples with different passivating agents in Tafel polarization curve test, the difference of corrosion resistance of samples with different passivating agents can be judged and compared.

3. Result and discussion

Table.1 Composition and ratio of passivating agent

Numble	Passivator	Concentration	Passivation temperaturet
1	Sodium silicate	Sodium silicate 0.1mol/L	60℃
2	Sodium silicate +dopamine	Sodium silicate 0.1mol/L, dopamine 4g/L	60℃
3	Phytic acid	Phytic acid 10mL/L	Room temperature

4	Phytic acid + dopamine	Phytic acid 10mL/L, dopamine 4g/L	Room temperature

Various passivating agents used in this experiment are shown in Figure 9. In order to enhance the corrosion resistance of metal materials or change their surface properties, a variety of passivation treatment schemes were explored in this experiment. Among them, the first scheme uses a solution of sodium silicate with a concentration of 0.1mol/L and is passivated at a temperature of 60 ° C in order to form a protective film on the surface of the metal. Further, the second regimen added 4g/L of dopamine on the basis of sodium silicate, also performed at 60 ° C, to explore the potential enhancement of dopamine on the performance of the passivated film. In addition, there are two schemes that make use of phytic acid, a natural organic acid. The third solution uses a 10mL/L phytic acid solution to passivate the metal at room temperature. The special number passivation agent that phytic acid can work effectively under mild conditions is fully utilized. Concentration Passivation temperature 1 sodium silicate 0.1mol/L60℃ Sodium silicate 2 sodium silicate + dopamine sodium silicate 0.1mol/L, dopamine 4g/L60℃3 phytic acid phytic acid 10mL/L room temperature 4 phytic acid + dopamine phytic acid 10mL/L, dopamine 4g/L room temperature point. The fourth option is to add 4g/L of dopamine to the phytic acid solution, also at room temperature, to investigate whether dopamine can further improve the adhesion, corrosion resistance or other key properties of the passivation film to meet the higher requirements of metal surface treatment for specific applications.

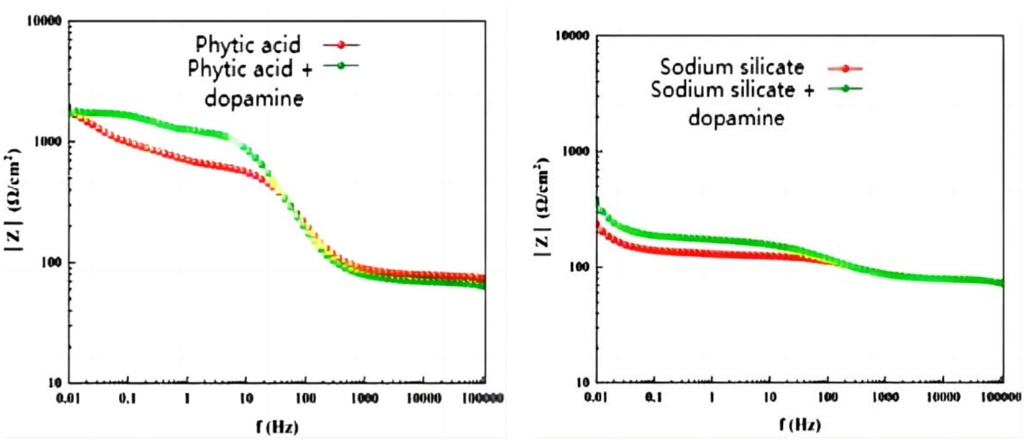

Fig. 1 Bode spectrum of AC impedance: a) phytic acid : b) sodium silicat

The passivating agent of dopamine can significantly improve the corrosion resistance of galvanized layer and affect the subtle changes of AC impedance Bode spectra. Bode spectra, as a form of electrochemical impedance spectroscopy, intuitively show the impedance behavior of the system at different frequencies through the frequency response function, which provides valuable information for understanding the electrochemical performance of passivated films.

Specifically, when dopamine was added to the passivating agent, the passivating film showed a higher impedance value on the Bode spectrum, which directly reflected the improvement of the protective ability of the passivating film. Behind this elevation is a complex chemical and physical interaction between dopamine molecules and zinc groups. The functional groups in dopamine can bind closely to the surface of zinc to form a more dense and uniform passivation layer, which not only effectively blocks the direct contact of corrosive media such as water, oxygen and ions, but also significantly reduces the dissolution rate of zinc. More importantly, the addition of dopamine also significantly inhibits the diffusion and transfer process of electrons and Zn^{2+} ions between the matrix interface and the corrosive medium. In the corrosion process, the flow of electrons and the migration of ions are the key factors leading to metal corrosion. The dopamine passivation film, through its unique chemical structure and dense physical barrier, blocks the transport path of these charge carriers, thereby reducing the rate of corrosion reaction. This inhibition not only reduces the active site on the surface of the galvanized layer, but also weakens the formation and development of corrosion microbatteries, and further improves the corrosion resistance of the galvanized layer [7, 8].

In summary, it can be seen from the AC impedance Bode spectrum that the impedance values of passivation films formed with dopamine-added passivation agents are all higher than those without dopamine-added passivation films, because the passivation films with dopamine-added reduce the dissolution of zinc, and inhibit the diffusion and transfer of electrons and Zn2+ between the matrix interface and the corrosive medium, thus reducing the corrosion rate of galvanized layer. The corrosion resistance is improved. The analysis results of AC impedance Bode spectra strongly support the active role of dopamine as a passivating additive in improving the corrosion resistance of galvanized layer. By reducing the dissolution of zinc and inhibiting the diffusion and transfer of electrons and ions, dopamine significantly enhances the protective efficiency of passivation film, which provides a reliable guarantee for the long-term stable application of galvanized materials. This discovery not only enriched the theoretical knowledge in the field of metal corrosion and protection, but also provided a new idea and method for the design and development of anti-corrosion materials in actual industrial production.

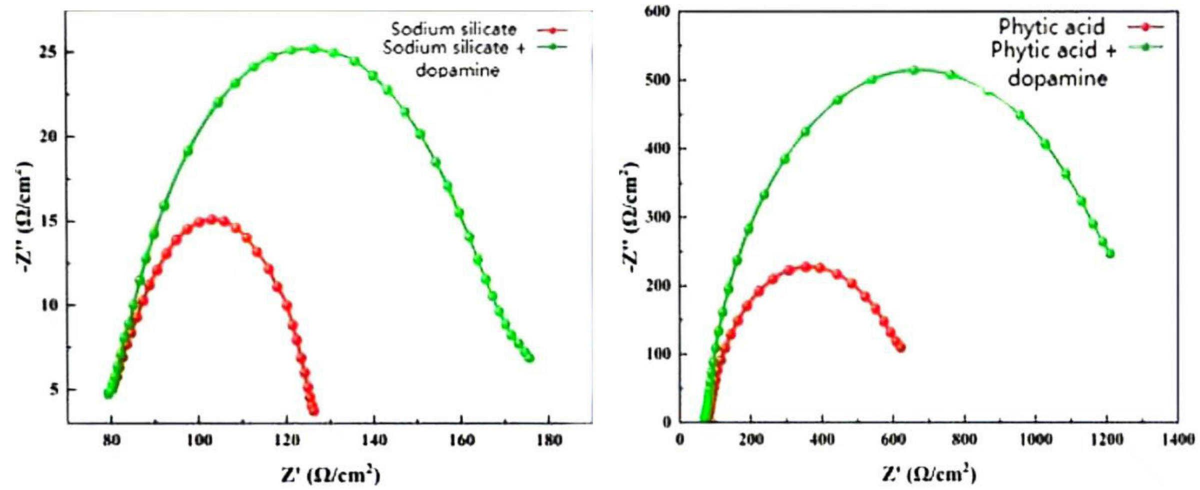

Fig. 2 Nyquist of passivated membrane: a) sodium silicate: b) phytic acid

In the study of electrochemical corrosion, Nyquist diagram, as a powerful analytical tool, can intuitively show the electrochemical behavior of passivated films on the surface of materials, especially its impedance performance. By depicting the relationship between the real and imaginary parts of the impedance, this chart reveals the response of electrochemical elements such as resistance and capacitance of the material in a corrosive environment, so as to evaluate the corrosion resistance of the material. The arc resistance is a key feature in Nyquist diagram, and its radius is directly related to the protective efficiency of passivated film. Specifically, the radius of the capacitive arc resistance represents in the Nyquist diagram the ability of the passivation film to impede the charge transfer process, that is, the resistance that charges need to overcome to pass through the film layer. The larger the radius, the more difficult the charge transfer process, reflecting that the passivation film has higher density and lower defect density, so it can more effectively cut off the contact between the corrosive medium and the base material, thereby improving the corrosion resistance of the material.

When discussing the effect of dopamine as an additive on the performance of the passivation film, the experimental results showed that the passivation film formed after adding dopamine to the passivation agent exhibited a larger arc radius of capacitive reactance in the Nyquist diagram. This finding not only verified that dopamine played a positive role in the passivation process, but also further demonstrated that the addition of dopamine can significantly improve the structure and performance of the passivation film. The reason why the passivation film containing dopamine shows better corrosion resistance is probably because the functional groups of dopamine molecules can strongly interact with the metal surface to form a more dense and uniform passivation layer. At the same time, its unique chemical structure may also promote the repair of the internal defects of the passivation film and reduce the infiltration channel of corrosive media.

In summary, the analysis results of Nyquist diagram clearly point out the effectiveness of dopamine additives in improving the corrosion resistance of passivation film. It can be seen from the Nyquist diagram that the larger the arc radius of the passivation film layer, the better the corrosion resistance of the passivation film. The arc radius of bulk reactance of passivation film formed by dopamine-added passivation agent is greater than that of the passivation film without dopamine-added, indicating that the passivation film containing dopamine has better corrosion resistance. Dopamine is also widely used in the field of antisepsis because of its special structure and good properties. Zhou et al. coated a dopamine-gelatin composite with 5β-TCP/ Mg-3Zn, and the corrosion current density of the metal was greatly reduced after coating [9].

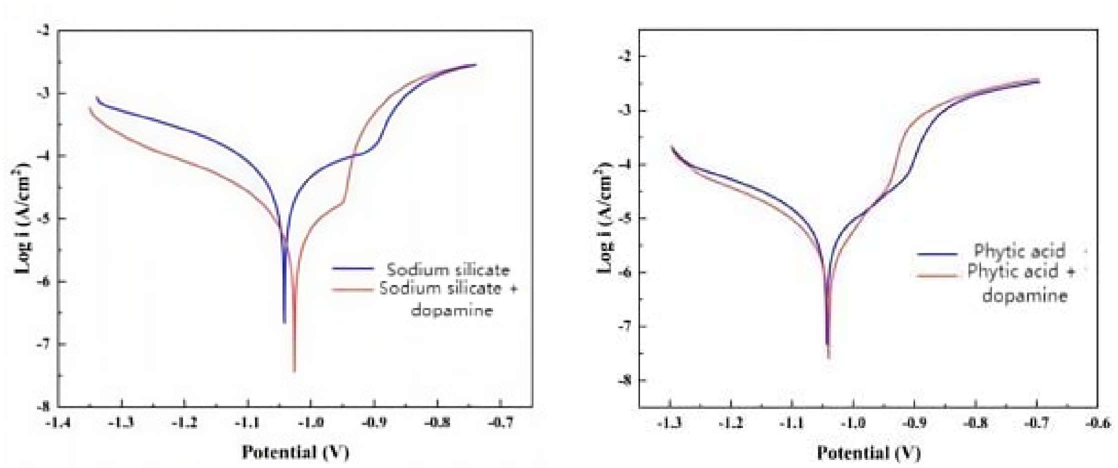

Fig. 3 Tafel polarization curve: a) sodium silicate: b) phytic acid

Table 2. Electric potentia and Electric current statistics table

Numble	Passivator	Electric potential	Electric current
1	Sodium silicate	- 1.0424	1.2119x10-5
2	Sodium silicate +dopamine	- 1.0263	4.5271x10-6
3	Phytic acid	- 1.0435	6.1217x10-6
4	Phytic acid + dopamine	- 1.0402	2.3664x10-6

From the Tafel polarization curve, it can be clearly observed that when dopamine is introduced into the passivation agent formulation, the passivation film prepared shows a significant change in electrochemical behavior. In particular, the self-corrosion potential showed an obvious positive trend compared with the control group without dopamine addition, which is one of the key indicators to evaluate the improvement of the corrosion resistance of the metal surface protective layer. The positive shift of the self-corrosion potential means that the corrosion reaction can only begin on the metal surface at a corrected potential, that is, a stronger driving force is needed to trigger the corrosion process, which implies that the passivation film has a stronger protection ability for the base metal. At the same time, through careful comparison with the data table in the polarization curve, the self-corrosion current density corresponding to the passivation film after adding dopamine is significantly reduced, by about 3 times. Self-corrosion current density is an important parameter to measure the corrosion rate of metal. The lower its value, the slower the corrosion reaction rate occurs on the metal surface under the same conditions, that is, the better the corrosion resistance. Therefore, the significant change of this data not only directly reflects the significantly improved effect of dopamine on the corrosion resistance of the passivation film, but also further confirms the excellent performance of the passivation film in protecting the metal matrix from corrosion after adding dopamine. Mobin et al. [6] found that high concentration of polymer corrosion inhibitors can improve the corrosion inhibition rate. In addition, starch and chitosan derivatives also have certain corrosion inhibition properties for metals in acidic media. But in general, these polymer corrosion inhibitors need to reach high concentrations to achieve high corrosion inhibition rates.

In summary, the information revealed by the Tafel polarization curve and its data table fully indicates that the addition of dopamine significantly improves the corrosion resistance of the passivation film. By promoting the positive shift of self-corrosion potential and greatly reducing the self-corrosion current density, dopamine effectively enhances the protective barrier effect of passivation film on metal matrix, which provides a strong support for extending the service life of metal materials and improving their stability in harsh environments.

4. Conclusion

This experiment successfully proved that the corrosion resistance of the passivation film after adding dopamine was better. Zinc surface was treated with modified polydopamine combined with existing chromium-free passivation solution instead of traditional chromate. By changing the composition and proportion of the formula, the team tried to study a modified polydopamine with good performance and combined with the existing chromium-free passivation solution to replace the chromate passivation solution and achieve green environmental protection.

The researches on chromium-free passivation of galvanized products at home and abroad mainly include inorganic passivation and organic passivation. Inorganic passivation includes molybdate passivation, silicate passivation, rare earth metal salt passivation, etc. Organic passivation includes phytic acid passivation, tannic acid passivation, resin passivation, organosilane passivation, etc. Although the above passivation treatment has been studied, the passivation effect is not ideal. Dopamine can self-polymerize to form polydopamine, polydopamine contains a large number of phenolic hydroxyl and amino groups, with strong adhesion properties, it can adhere to any material surface, even to the surface of polytetrafluoroethylene such as difficult to adhere to the material. Polydopamine itself has certain anti-corrosion properties, which can modify the metal surface and protect the metal from corrosion. Compared with the unmodified polydopamine coating, the modified polydopamine coating has better corrosion resistance. At the same time, there are a large number of active sites on the surface of organic or inorganic materials modified by polydopamine, and the functionalization of the substrate can be realized again by covalent or non-covalent forces, Therefore, we used the modified polydopamine and the existing chromium-free passivating agent to treat the surface of zinc plating, and the feasibility of the improved passivating agent was proved by the experimental results.

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