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Influence of Different Acid on the Interfacial Compatibility between Rusted Steel and Water-Based Coating

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Abstract: We aimed to improve the corrosion resistance of transmission network cabinet equipment in high temperature and humidity environment. In this paper, using acid modified acrylic acid as the main component, the composite conversion agent was obtained by adding phosphoric acid phytic acid and other components. Through the surface morphology, electrochemical test and adhesion force test of rust conversion coating, the versatility and corrosion resistance of rust conversion coating on the substrates were analyzed. Combined with zinc phosphate primer, the effect of rust conversion agent on the adhesion and salt spray corrosion resistance of the commercial primers was studied. The composite conversion agent has good effect on atmospheric corrosion rust layer. The corrosion resistance and adhesion force of the atmospheric corrosion rust layer treated with rust conversion agent were significantly increased. The adhesion of zinc phosphate primer on atmospheric corrosion rust coating with rust conversion was three times higher than that of atmospheric corrosion rust coating without rust conversion, respectively. Composite rust conversion agent has broad versatility, which can be used for rust conversion of atmospheric corrosion rust layer. At the same time, it has a good corrosion resistance, that can obviously improve the corrosion potential of the corroded surface and reduce the corrosion current density. In addition, the composite rust conversion agent can significantly improve the adhesion and corrosion resistance of the primer coating.

Keywords: rust conversion; corrosion resistance; adhesion

1. Introduction

Infrastructure networks, especially power grids, are the lifeblood of industrial production and daily life. They are a necessary premise for guaranteeing economic activities to ensure the safe and reliable operation of power grids. In the operation of the power grid in a high humid and hot industrial pollution environment, it is important to control some components, such as metal cabinet equipment, and to limit corrosion-accelerated damage caused by long-term condensation from the humid atmosphere. For the protection of metal corrosion, organic anticorrosive coating is the most effective and feasible method at present by its shielding effect [1], chemical protection effect [2,3] and electrochemical protection [4]. However, previous studies show that the function of anticorrosive coating can only be realized by ensuring good coating/metal interface bonding [5–7].

Commonly, substrate pretreatments include mechanical and chemical cleaning [8–11]. They all can ensure the good bonding between coating and metal. However, in the field, due to the limitations of equipment, site and environmental protection, effective substrate treatment cannot be carried out. Therefore, low surface treatment coatings have become a research point. Low surface treatment coating, which is also called low surface tolerant coating, can transform the active rust layer to be stable passivation directly, to achieve the dual purpose of cleaning and protection of the metal surface. Now, low surface treatment...
coating, which is widely studied, includes three types: permeable [12,13], stable [3,14,15] and transformed [16–19]. Some solvent-based epoxy resin products have been developed with excellent performance [20,21]. However, due to environmental protection restrictions, it is not conducive to promotion and use.

Water-based coating is one of the important directions in the future development of coating industry. Phosphate acid [22], phytic acid [23] and phosphate functional component [24] are the most commonly used functions in the low surface treatment coating composition. If the amount of functional component added is small, the reaction with rust will not be complete. If the amount is too much, it will more dangerous. As these functional compositions were mostly acidic, they may damage the stability of the water-based film-forming system and accelerate metal corrosion, which limits the development of high-performance low-surface treatment coating. Understanding the effect of multiple acids on the rust layer, and analyzing the combined effect with other functional components in antirust coatings, will provide a basis for developing high performance rust conversion components.

Based on this, this paper, by using new type of modified acrylic resin as film forming system, combined with the function of phosphate acid, phytic acid and other phosphate composites, an environmentally friendly water-based low surface treatment coatings was produced. The synergistic effect of each functional component, and the compatibility with the resin system were studied. At the same time, compatibility with commercially available zinc phosphate anticorrosive primer were tested systematically. This provides a basis for the development of new water-based low-surface treatment coatings.

2. Experiment
2.1. Sample Preparation

Q235 carbon steel (C ≤ 0.22 wt%, Mn ≤ 1.4 wt%, Si ≤ 0.35 wt%, S ≤ 0.05 wt%, P ≤ 0.05 wt%) was used as a metal substrate, and was first polished by a 240-grit abrasive paper to remove the surface oxide layer. After polishing, the metal surface was carefully washed in ethanol and acetone, and then dried prior to corrosion. The substrate was treated in two ways to form rust layer as the coating substrate: 1 damp and heat test (according to GJB150), 2 natural exposure (according to GB/T 14165).

This work used waterborne acrylic resin made in a chemical plant in Guangzhou. Phosphoric acid, phytic acid and tannic acid used in this paper were analytically pure from Aladdin. A commercially available zinc phosphate anticorrosive primer was got for a comparison test. All coating samples were prepared by brush. There were two runs.

2.2. Test Methods

The micromorphology of the coated section sampled was performed using SEM (Phenom ProX). The micromorphology of the coating defects was obtained using a digital camera.

XRD (Ultima IV X, Cu target, working voltage 40 kV, working current 40 mA, step length 0.02°) was used to qualitatively analyze the composition of samples. The scanning speed was 5°/min, and the scanning range of the diffraction angle was 10–110°.

The electrochemical studies on the coating specimens were conducted using an electrochemical workstation (CHE E604). A three-electrode cell system was used in this experiment. The system was assembled with the coating sample as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and platinum as the auxiliary electrode. Open circuit potential has been tested for one hour first. The EIS measurements were taken in a 3.14 cm² area for the coating samples in 3.5 wt% NaCl solution in the frequency range of 100 kHz–0.01 Hz and a disturbance alternating potential voltage of 20 mV. Polarization curve was measured after EIS. All tests were conducted at 22 °C. Tafel extrapolation method was used for monitoring corrosion. ZSimpWin, CHI and Origin were used for results plotting, graphing, data fitting and calculating.
According to ISO4624 standard, PosiTest drawing was used to determine the adhesion strength of the organic coating. The 20-mm diameter dollies were degreased using acetone and then glued to the surface of the coated plates using a two-component epoxy-based cyano-acrylate adhesive. After adhesive curing, a testing apparatus was attached to the loading fixture and was strained at 5 mm/min until the coating material had detached from the substrate.

According to GB T 1771-2007 standard, the corrosion performance of samples was tested by neutral salt spray.

Three parallel samples were used for each measurement and the results were reproducible.

3. Results and Discussion

3.1. Effects of Different Acids on Damp-Heat Rust

In some industrial environments, because of its special structure, even if there is no salt spray, there can still be corrosion under the condition of high temperature and humidity. For this, a damp-heat test in the laboratory was used to accelerate the corrosion of Q235 steel for the study of rust layer. The experiment reference from GJB150, the temperature control of humid environment simulation is shown in Figure 1. Figure 2 shows the macroscopic morphology before and after damp heat environment. As can be seen from the figure, the rust layer generated in the damp heat environment is uneven and spot-like. XRD was used to conduct phase analysis on corroded Q235 steel plate (Figure 3), and the results show that the corrosion product of steel plate was mainly magnetite Fe₃O₄.

![Figure 1. Schematic diagram of temperature control in damp and heat.](image-url)
In order to explore the influence of the main components of the rust converter on the rust layer, single component phosphate, phytic and tannic acid were respectively coated on the rusty surface after damp heat test for rust transformation. The macroscopic morphology and XRD results of the transformed surface are shown in Figure 4. By comparison with Figure 2, it can be seen that the surface has obvious appearance changes after the treatment by the all three kinds of rust transforming functional acids. The rust layers were transformed into conversion layers with different colors, phosphoric acid and phytic acid formed a gray transformation layer, and tannic acid formed a black transformation layer. Compared with the phase composition before the rust transformation (the surface is a single magnetite), the phase composition of the rust transformation surface had obviously changed, and there is an obvious peak of elemental Fe on the surface, indicating that the rust layer was transformed into elemental Fe after various acid treatments. However, the peak relative to the strength of Fe is slightly different after the three acid treatments. Among them, the peak relative to the strength of Fe is stronger after phosphoric acid and tannic acid treatments, indicating that phosphoric acid and tannic acid had a higher degree of transformation on the rust layer than phytic acid.
Figure 4. Macroscopic morphology and X-ray diffraction patterns of damp-heat corroded Q235 samples after treated by different acid, (a) phosphoric acid, (b) phytic acid and (c) tannic acid.

In order to explore the corrosion resistance of corroded surfaces before and after single acid treatment, electrochemical impedance and electrochemical polarization methods were used to analyze the samples of damp heat corrosion samples before and after single acid treatment. The results are shown in Figures 5 and 6, respectively. Single acid treatment did not change the electrochemical properties of the samples. The equivalent circuit in Figure 5a was used for fitting EIS data of the samples of damp heat corrosion samples before and after single acid treatment. Figure 6a was used for both alloys at the initial period of immersion. Rs is the solution resistance; Qf and Rf represents the constant phase element of corrosion/converted product and their resistance, respectively; Qdl is double layer capacitance and Rp is the charge transfer resistance between the corrosion/converted product and metal substrate. The curves obtained by fitting are in good agreement with those measured by experiment. Samples treated by phosphoric acid and tannic acid had little change in EIS, while the low frequency modulus of electrochemical impedance of the sample treated by phytic acid was significantly increased compared with that of the...
damp-heat corroded sample, and the value is about twice as much as that of the damp-heat corroded sample, as shown in Table 1. This result indicates that phytic acid improves the corrosion resistance of the corroded substrate to a certain extent.

![EIS spectra](image1.png)

**Figure 5.** EIS spectra of damp-heat corroded Q235 sample before and after treated by different acid, (a) Nyqusit plots, (b) Bode plots.

![OCP and Tafel curves](image2.png)

**Figure 6.** OCP(a) and Tafel (b) curves of damp-heat corroded Q235 sample before and after treated by different acid.

**Table 1.** Results from electrochemical measurement of damp-heat corroded Q235 sample before and after treated by different acid.

<table>
<thead>
<tr>
<th>Acid Type</th>
<th>Module Value in Low Frequency (ohms)</th>
<th>Corrosion Potential (mV)</th>
<th>Corrosion Current Density (10⁻⁵ A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damp heat</td>
<td>114.00 ± 21.31</td>
<td>−782.00 ± 56.21</td>
<td>2.48 ± 0.62</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>103.20 ± 16.42</td>
<td>−767.50 ± 32.36</td>
<td>1.64 ± 0.46</td>
</tr>
<tr>
<td>Phytic acid</td>
<td>205.90 ± 32.26</td>
<td>−759.30 ± 43.23</td>
<td>0.76 ± 0.21</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>112.60 ± 13.69</td>
<td>−808.10 ± 51.61</td>
<td>2.80 ± 0.56</td>
</tr>
</tbody>
</table>

**Table 1.** Results from electrochemical measurement of damp-heat corroded Q235 sample before and after treated by different acid.

Figure 6 indicates that the cathodic behavior of all samples was controlled by the limit diffusion of dissolved oxygen, and the process can be written as (1). The anodic
electrochemical dissolution process was controlled by charge transfer occurring on the sample surface, as below (2). The corrosion potential of samples after treatment with phosphoric acid and phytic acid was raised, and corrosion current decreased at the same time. It means that the corrosion resistant performance of sample was improved after treatment by the phosphate and phytic acid. However, the corrosion potential of the sample decreased after treated by tannic acid. The electrochemical parameters are shown in Table 1.

\[
\begin{align*}
O_2 + 2H_2O + 4e^- &\rightarrow 4OH^- \\
Fe &\rightarrow Fe^{2+} + 2e^-
\end{align*}
\]

It shows that phytic acid obviously improved the corrosion performance of samples. There are 24 oxygen atoms, 12 hydroxyl groups and 6 phosphate groups in phytic acid molecule. So, it can simultaneously complex with metal ions, which is a relatively rare metal multi-tooth chelating agent, and can improve the corrosion resistance of metal surface. Phosphoric acid can dissolve unstable rust into an ionic state. Tannic acid hydrolysis has strong complexation. The rust conversion function of them is good, but not for corrosion resistance.

In order to investigate the surface morphology changes before and after the rust transforming treatment on the rusty surface, SEM was used to observe the surface microstructure. The results are shown in Figure 7. It can be seen that there are loose granular rust spots on the original rusty surface, which are not uniform and fail to fully cover the substrate surface. After different acid treatments, the corroded surface has obvious changes. All kinds of acid can transform the loose corroded products on the corroded surface. After treatment by phosphoric acid, the corrosion products on the surface of the sample were transformed into fine granular products attached on the surface uniformly. After treatment by phytic acid, a product film was attached to the surface of the sample, but the film was incomplete and there were a lot of cracks. For tannic acid, the surface morphology of it was different from that of phosphoric acid and phytic acid. There were not a lot of transformation products attached to the surface of the sample, but there were scattered granular products.

![Figure 7. Microtopography of damp-heat corroded Q235 sample before (a) and after treated by different acid (b) phosphoric acid, (c) phytic acid and (d) tannic acid.](image-url)
XRD analysis shows that single acid can effectively transform the corrosion products on the surface of samples. However, based on the analysis of electrochemical test and microscopic surface, corrosion products were transmuted by the single acid treatment: there was no complete film with protective performance formed on the surface of corrode sample. Both electrochemical impedance spectrum and polarization curve show that the corrosion electrochemical characteristics of samples had no change before and after treatment by the single acid, although the corrosion restraint of the sample was improved by the single acid. The treated samples remain the electrochemical activity. It means that there was no protective film formed on the surface of samples. The results of SEM showed that the surface of samples after the phytic acid phosphate processing was also full of cracks, and there were tannins on the surface without product coverage. As phosphoric acid is a highly acidic, it caused uncorroded parts of the sample flash rust, as there were obvious yellow parts on the surface of treated sample. Therefore, a design which combined different acid, flash rust inhibitor and coalescing agent was studied.

For further study the transformation effect of compound conversion agent, except for the damp-heat sample, actual natural exposure samples were added.

3.2. The Interfacial Compatibility between Rusted Steel and Water-Based Coating

The macro morphology of actual hot and humid atmosphere corrosion (outdoor exposure one month) before and after being converted by compound conversion agent is shown in Figure 8. The figure shows that there are red-brown corrosion products uneven distribution on the surface of the outdoor exposure samples (Figure 8a). XRD analysis shows that the corrosion product was mainly magnetite, and was consistent with the result of damp heat samples. After rust transformation, uniform and dense film was formed on the surface of the sample (Figure 8c), and the magnetite content was greatly reduced.

![Figure 8](image-url)

**Figure 8.** Macroscopic morphology (a) before, (b) after and X-ray diffraction patterns (c) of outdoor exposure Q235 samples before and after treated by compound conversion agent.

The microstructure of actual hot and humid atmosphere corrosion (outdoor exposure one month) before and after converted by compound conversion agent is shown in Figure 9. As shown in Figure 9a, the surface of the outdoor exposed sample was sprinkled by corrosion product, and scratches of metal processing can also be observed. After rust transformation, a relatively dense membrane layer was formed on the surface of the sample. By EDS analysis, such as Table 2 before rust conversion, the sample surface corrosion products approximation for magnetite After the conversion of rust, oxygen content decreased obviously, and the conversion layer containted C and P.
In order to analyze the combination between the rust transformation layer and the substrate, a cross-cut test was conducted on the rust transformation layer and the bonding force was tested according to ISO 2409. The morphology of the sample after the test under the light microscope is shown in Figure 10. The results show that the scratch was smooth and no damage was observed at the scratch intersection. The grade is 0 according to ISO 2409 standard. The above results indicate that the transformation layer was well bonded with the substrate. The bonding between transformation layer and substrate was very good.

The EIS spectrum of the outdoor exposed rust layer before and after rust transformation is shown in Figure 11. The impedance pattern was changed from diffusion to single capacitive arc, indicating that there is a conversion layer formed on the surface of sample and the corrosion conversion layer had a good protective performance. So, there were different equivalent circuits for samples before and after rust transformation. Outdoor exposure samples were the same as the damp heat samples. For the transformed sample, $R_c$ and $Q_c$ represent the constant phase element and resistance of converted coating. They all fitted well. The low frequency modulus of the sample was significantly improved (the value is shown in Table 3), and The EIS results showed that the composite corrosion conversion agent improved the corrosion resistance of the corroded substrate.

**Table 2.** EDS results of outdoor exposure Q235 samples before and after treated by compound conversion agent (wt.%).

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Fe</th>
<th>Cl</th>
<th>P</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>25.82</td>
<td>73.00</td>
<td>1.17</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>After</td>
<td>12.87</td>
<td>61.25</td>
<td>0</td>
<td>13.54</td>
<td>12.33</td>
</tr>
</tbody>
</table>
Figure 10. Cross-cut test area of outdoor exposure Q235 samples after treated by compound conversion agent.

Figure 11. EIS spectra of outdoor exposure Q235 samples before and after treated by compound conversion agent, (a) Nyqusit plots, (b) Bode plots, (c) Open circuit potential, (d) equivalent circuit.
Table 3. Results from electrochemical measurement of outdoor exposure Q235 samples before and after treated by compound conversion agent.

<table>
<thead>
<tr>
<th>Module Value in Low Frequency (ohms)</th>
<th>before</th>
<th>after</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>168.6 ± 36</td>
<td>424.2 ± 55</td>
</tr>
</tbody>
</table>

In order to verify the practical application performance of the conversion agent, the commercially available zinc phosphate primer was selected as a reference and painted on the surface of the outdoor exposure Q235 samples before and after rust transformation. Pull-off tests were carried out on the samples coated with primer on the surface of atmospheric corroded rust layer without and with rust transformation. The results are shown in Figure 12. It can be seen that adhesive force of zinc phosphate primer coated on the surface of the sample after rust transformation was nearly three times higher than that of the sample without rust transformation.

![Figure 12. Adhesive force of commercially zinc phosphate anticorrosive primer on the surface of outdoor exposure Q235 samples without and with compound conversion agent.](image)

For further validation of corrosion resistance of conversion coating system, the continuous salt spray test was used. Results are shown in Figure 13. The zinc phosphate primer without rust transformation showed obvious rust after 24 h of testing, and a large amount of bubbling appeared on the surface of the sample after 120 h. However, there was still no obvious change on the surface of the coating system with rust transformation after 120 h of testing. Therefore, compared with the coating system without rust transformation, a compound conversion agent can significantly improve the corrosion resistance of the coating system, and the corrosion resistance is increased by more than five times.

![Figure 13. Optical images of zinc phosphate coating after neutral salt spray test for 120 h, without (a–d) and with (e–h) compound conversion agent.](image)
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Figure 13. Optical images of zinc phosphate coating after neutral salt spray test for 120 h, without (a–d) and with (e–h) compound conversion agent.

4. Conclusions

In this paper, the transformation function of a single acid rust transforming functional component on damp-heat corrosion products was studied by means of physical phase analysis combined with electrochemical method. Based on this, a composite rust transforming agent was designed, which achieved good rust transformation effect on the outdoor exposure samples and had good combination with the commercial anti-corrosion coating. XRD showed that all the three acids had rust transformation function, phosphoric acid and tannic acid have a higher degree of transformation of rust layer than phytic acid. All single acid functional component cannot improve the corrosion resistance of the sample. Meanwhile, it caused flash rust on the surface of sample and had a bad effect on the subsequent coating.

Through combining a variety of acidic with anti-rust functional components, a kind of water-based compound conversion agent was prepared. It made the rust of outdoor exposure samples form a rust conversion layer. The EIS showed the rust conversion layer was intact and protective. There was good bonding between the transformation layer and the surface of the sample, and it showed better corrosion resistance. Meanwhile, it improved the adhesion force (more than two times) and corrosion resistance (more than five times) of the commercial anti-corrosion coating on rust sample.

Author Contributions: W.L.: conceptualization, methodology, investigation, writing. Y.J.: writing—review and editing. D.L.: writing—review and editing. J.Z.: data curation, writing. Y.X.: project administration, funding acquisition. L.L.: visualization, supervision. All authors have read and agreed to the published version of the manuscript.
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