Preparation and Comparison Anticorrosive Properties of Graphene Anticorrosive Coatings

Qiang Chen1,2*, Yue-Ju Zhao1,2, Ji-Lin Teng1,2, Yi-Qin Xia1,2, Bao-Qin Yu1,2 and Yongli Zheng1,2

1 Beijing Guo Dian Futong Science and Technology Development Building 14, zone 6, No. 188, West Nansihuan Road, Fengtai District, Beijing China
2 Nanrui Group Co., Ltd. (State Grid Electric Power Research Institute Co., Ltd.), Nanjing, China
Email: 1092963843@qq.com

Abstract. Since graphene was successfully stripped from graphite in 2004, its excellent properties and unique two-dimensional layered structure have attracted great interest in the field of coatings. Graphene can be used as a filler in anticorrosive coatings. Its good electrical conductivity and sheet-like barrier properties which can isolate oxygen and corrosive media. So, graphene powders can improve the corrosion resistance of the coating. With the development of the industrialization of graphene, which made the production cost of graphene is gradually reduced, it made graphene can be used in coatings be possible. This article introduces a method for preparing graphene heavy-duty anticorrosive coating, the anticorrosive principle of graphene heavy anticorrosive coating was described. The salt spray resistance of graphene heavy anticorrosive coatings and international brand heavy anticorrosive coatings were compared.

1. Introduction
With the development of economy and the improvement of scientific and technological level, And the rich geographical characteristics of China’s Marine resources. The anti-corrosion coatings and anti-corrosion measures have attracted much attention. To improve the anti-corrosion performance of equipment and extend the service life of equipment is the pursuit of researchers [1-4]. At the same time, due to the development of graphene industrial production, the preparation of graphene anticorrosive coatings has also been rapidly developed [3]. For example, preparation of graphene oxide epoxy primer, application of graphene in epoxy zinc rich, application of graphene in waterborne anticorrosive coatings. The preparation technology of graphene anticorrosive coating is becoming mature, and the mechanism of graphene anticorrosive coating is becoming clear [5-8].

2. Experiment Section

2.1. Materials
Epoxy f-51: industrial, Nantong Xingchen Co., Ltd. Mica powder: industrial grade, Chuzhou Gerui Mining Co., Ltd. Iron oxide red: industrial grade, Shanghai Yipin Pigment Co., Ltd. Zinc powder 500 mesh: industrial grade, Qingdao Xutai Chemical; Bentonite 325 mesh: industrial grade, Hunan Xinweiling Metal New Material Technology Co., Ltd. Dispersant byk104s: industrial grade, BYK Chemistry; Defoaming agent 066N industrial grade, BYK Chemistry; Leveling agent 466: industrial grade, Qingdao Xutai Chemical; Graphene: industrial grade, Qingdao Haihua Institute; Test sample:
carbon steel 70 × 150 × 2 mm.

2.2. Preparation of Graphene Coating

2.2.1. Preparation of Component A. Preparation of graphene dispersion by adding graphene powder 3wt% to solvent (xylene + n-butanol). Then, it was stirred for 2 hours by a high-speed mixer, and after being dispersed uniformly. After that, the mixture was placed in the ultrasonic dispersion instrument and the mixture was dispersed for 4 hours. Finally, a uniform black suspension was obtained. Preheat of epoxy resin: heat epoxy resin f-51 in the oven at 60 °C for 30 minutes, and then the viscosity of the resin come down, which is conducive to the addition of filler. After preheating the resin, several additives in the formula were added, in the order of defoamer 066N, dispersant and leveling agent. After stirring for 5 minutes, diluent (xylene + n-butanol) was added and stirred for 5 minutes. After that, graphene dispersion is added and dispersed at high speed for 20 minutes. Add the foundation fillers in turn, the fillers: bentonite, iron oxide red, zinc powder, mica powder. The order of filling is mainly based on its dispersibility. After adding the filler, stir for 40 minutes at high speed.

2.2.2. Preparation of Component B. The modified polyamide agent was heated to 90 °C in the oven, after 10 minutes it can achieve serviceable fluidity. The compound diluent was configured, and the adhesion enhancer was added in accordance with the corresponding proportion. After evenly stirring, we got the component B.

2.3. Sample Preparation

The surface of carbon steel is sandblasted, swabbed with alcohol and then dried for later use. Components A and B of the coating were mixed evenly at A ratio of 10:1 and waited for 20 min. Air spraying is adopted, with 2.0 spray gun for primer and intermediate paint and 1.5 spray gun for top paint. The coating viscosity is controlled at 30-40 s (coated with -4 cups). Primers each coat of paint is approximately 30-40 microns thick, with an interval of 6-12 hours. Intermediate paint: each coat is 60 to 80 microns thick, and each coat is 12 hours apart. The thickness of each coat is 30-40 microns and the interval of each coat is 6-8 hours. Then, suitable thickness comparison samples are selected according to experimental requirements. The curing temperature is room temperature curing, the low and middle surface after spraying is put in place for 5-7 days until dry to test the salt spray resistance.

3. Result and Discussion

3.1. Analysis on the Anticorrosive Principle of Coatings

Anticorrosive coating is generally composed of three parts: primer, intermediate paint and finish paint. The primer contains a large amount of zinc powder, and the electrode potential of zinc is lower than that of iron, so it is coated on the surface of steel and formed a galvanic cell. When corrosion occurs, the zinc in the coating reacts preferentially (that is, the anode protection act) to prevent corrosion of the steel surface. At the same time, the oxidized zinc powder can further prevent the infiltration of water vapor and oxygen ions, and also prevent the corrosion of the material surface. Zinc powder plays a crucial role in the primer. The zinc content in the zinc-rich primer is more than 60%, and the low zinc content is not conducive to the bond between the zinc powder and the formation of effective electrochemical protection. The use of flake zinc powder is 20% lower than that of spherical zinc powder, which still achieves the same anti-corrosion effect. This is also because flake zinc powder is easier to bond with to form effective electrochemical protection than ordinary zinc powder.

As figure 1a shows the SEM images of graphene. It can be seen that the graphene sheet layer is thinner and of better quality, figure 1b shows graphene dispersion solution. After dispersion, graphene is relatively stable and uniform. It is well known that graphene has good conductivity. Adding a small amount of graphene to the zinc-rich primer can effectively promote the formation of an electrochemical pathway between zinc powders, so that zinc powders can participate in the
electrochemical protection reaction more effectively. Graphene is used as the bridge of electron movement in the electrochemical reaction of zinc powder (figure 1d), which can effectively reduce the consumption of zinc powder under the same anti-corrosion grade. As the content of zinc powder decreases, the content of resin increases, the adhesion of the coating on the surface of the substrate will improve, the overall performance of the coating will be due to the rich zinc primer. Another reason is the two-dimensional flake structure of graphene powder, which can effectively block the permeation path of water, so as to improve the anti-corrosion performance of the coating. It can be seen from figure 1c that graphene is good at lapping zinc powder particles together, forming a good conductive pathway, and spreading in the coating at the same time, extending the permeation path of water and oxygen.

3.2. Comparison of Graphene Primer and Brand Heavy-Duty Anticorrosive Primer

The Salt spray resistance properties of the graphene primers were compared with zinc-rich primers from three brands. The paint film thickness of the four primers is 70-80 microns. It can be seen from figure 2, After the neutral salt spray experiment 360 hours, the graphene primer only had slight rusting at the scratch, and the surface of the sample was intact. There was a large bulge at the scratch of product A, which was caused by the decreased adhesion force of product A after water penetration. After 360 hours of neutral salt spray test, a small amount of bubbles appeared on the surface of product B. It can be seen that the salt spray resistance of graphene primer is higher than that of product A and B. There was no obvious change on the surface of the sample, which indicated that the salt spray resistance of product C was same like graphene primer at 360 hours. After 800 hours of salt spray, Bubbles appeared near the scratch of the graphene primer, but did not spread on the surface. The corrosion product C was not very serious on the scratch surface. But a large number of bubbles appeared on the back of sample C, which indicating that the anticorrosive performance had been lost. In conclusion, the salt fog resistance of graphene primer is better than zinc rich primers.

Figure 1. (a) SEM of graphene, (b) dispersion of graphene, (c) SEM of graphene primer and (d) Schematic cross section of anticorrosion coating.
3.3. Comparison of Graphene Heavy-Duty Anticorrosive Coating and Brand Heavy-Duty Anticorrosive Coating

Because heavy anticorrosive coatings often need primers, intermediate coat, Salt spray resistance of a primer does not indicate the corrosion resistance of the paint. Therefore, we matched the graphene primer, micaceous iron oxide anchor coat and aliphatic polyurethane top coat, and then tested the salt spray resistance. The thickness of the graphene primer was 60-70 microns, micaceous iron oxide anchor coat was 160-170 microns, aliphatic polyurethane top coat was 60-70 microns, and the total thickness of the coat was 280-300 microns. The coats of the other three brands are micaceous iron oxide anchor coat and aliphatic polyurethane top coat, which are matched with the coating of this brand. The thickness of the coating is the same as that of the graphene coat sample.

After 800 hours of neutral salt spray test (figure 3), there was a small amount of rust in the scratch of the sample graphene coating. The rust phenomenon of other 3 kinds of coating is more serious and A small number of bubbles appear on the surface of product B. Although products A and C have flow rust, but they still have good protective performance. After 1300 hours, the rust in the scratch of graphene coating increased, and the rust in the scratch on the surface of the product A/B/C were more serious. Bubbling appeared on the surfaces of the three products, and the bubbling of product B was the most serious, and the corrosion protection performance had been lost. This indicates that the salt spray resistance of graphene coating is much better than zinc-rich heavy-duty anticorrosive coating.

4. Conclusion

This paper briefly describes the preparation method and principle of graphene anticorrosive primer. Graphene in the primer helps to form a closed galvanic circuit between zinc particles, thus enhancing the electrochemical anticorrosive performance of the primer. Graphene is a good barrier to water and oxygen, which can also improve the anticorrosion performance of the coating. The anticorrosion performance of graphene primer is better than that of zinc-rich primer. The salt spray resistance time of graphene primers was 800 hours, higher than that of zinc rich primers. After the graphene primer was matched with micaceous iron oxide anchor coat and aliphatic polyurethane top coat, the salt fog resistance of the graphene primer was more than 1300 hours, while the salt fog resistance of the other three brand heavy anticorrosive coatings was less than 1300 hours. Which means that the anticorrosion performance of graphene coating is much higher than that of zinc-rich coating.
Figure 3. Comparison of salt spray resistance of graphene anticorrosive coating and heavy-duty anticorrosive coating from different company.

Acknowledgments
The authors thank the Nanrui Group Co., Ltd. and Beijing Guo Dian Futong Science and Technology Development Beijing for their financial support.

Reference
[1] Berry V 2013 Carbon 62 1-10
[2] Li J, Zhou H, Zhao H, Chen J 2017 European Polymer Journal 89 150-161
[3] Zhao Y, Zhang Z, Yu L, Tang Q 2016 Synthetic Metals 212 84-90
[4] Zheng Q, Geng Y, Wang S, Li Z, Kim J-K 2010 Carbon 48 (15) 4315-4322
[5] Kausar A 2018 Polymer International 67 (11) 1470-1477
[6] Mišković-Stanković V, Jevremović I, Jung I, Rhee K 2014 Carbon 75 335-344
[7] Nine,M J, Cole M A, Tran D N H, Losic D 2015 Journal of Materials Chemistry A 3 (24) 12580-12602
[8] Singh Raman R K, Tiwari 2014 Jom 66 (4) 637-642