Preparation and properties study of graphene-enhanced acid-resistant anticorrosion coating for subsea oil and gas

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Abstract. In order to solve the corrosion problem of the existence of acidic material such as H₂S, CO₂ in the subsea pipelines, this article studied the coating film forming matter, which is combined with phenolic epoxy resin and phenolic aldehyde amine, acid-resistant filler system, etc. With the addition of the graphene dispersion, it significantly improves the abrasive resistance, salt fog resistance, adhesion and chemical character. This article took out the coating with good acid resistance. The results showed that the acid-resistant anticorrosion coating enhanced by graphene has excellent comprehensive physical and chemical properties, such as salt fog resistance, chemical resistance, hydrogen sulfide corrosion resistance, and alkali resistance, which meet the corrosion protection requirements of H₂S and CO₂ in acidic oil and gas fields subsea pipelines.

1. Introduction

As an important way to transport offshore oil and gas resources, subsea pipelines can effectively improve the transport efficiency, and play a significant role in the development of offshore oil and gas fields. With the continuous development and application of offshore oil and gas resources in China recently, the problem of subsea pipeline corrosion has become increasingly prominent, especially when H₂S, CO₂ and other corrosive media exist in offshore oil and gas. Due to the limitations of offshore working conditions and the influence of the environment, H₂S, CO₂, water and other corrosive media cannot be separated before oil-gas gathering and transportation. Therefore, it is urgent to adopt reasonable and effective anticorrosion scheme to solve the corrosion problem under the conditions of H₂S and CO₂ acidic oil and gas fields.

As an efficient, reliable and convenient barrier material, anticorrosive coatings have been widely used in oil and gas fields and refining and chemical equipment. Epoxy coatings are characterized by strong adhesion and salt fog resistance, and the corrosion resistance to alkali, acid, salt and other media. Epoxy coatings, which are widely used in petroleum and petrochemical industries, are better than that of thermosetting resins such as unsaturated polyester resin and phenolic resin[1]-[3]. However, if the working medium contains strong acidic substances, the epoxy anticorrosive coating will result in serious anticorrosion failure. Ordinary epoxy coating is sensitive to the temperature and pressure range of internal corrosion protection. When H₂S and CO₂ coexist, the failure rate of coating...
is proportional to the temperature, and it is more likely to aggravate the failure of coating once bubbles occur[4]. Acid-resistant anticorrosion coating not only has strong acid and corrosion resistance, but also equips with better physical and chemical properties than epoxy corrosion resistant coatings[5]-[10]. Graphene[11], as a new single layered carbon nanomaterial, has excellent chemical stability, high electrical conductivity, extraordinary mechanical properties and corrosion resistance[12], [13], and is increasingly used in anticorrosion coatings.

In this paper, based on the special corrosion environment and high production transportation conditions of subsea pipelines in acidic oil and gas fields, the acid-resistant anticorrosion coating was prepared with high physical and chemical properties and acid oil and gas corrosion resistance. At the same time, graphene was added to improve the wear resistance, salt fog resistance and other anticorrosive properties. By testing the basic physical and chemical properties and the anticorrosive properties of coatings under different acidic environments, the coating solution was proposed to improve the internal corrosion status of subsea pipelines in H₂S, CO₂, strong acid and other harsh acid corrosion environments.

2. Development of acid-resistant anticorrosion coating

2.1. Determination of film-forming resin

Phenolic epoxy resin is a multi-functional linear structural polymer synthesized by heat-stable phenol phenolic resin with epichlorohydrin, and the molecular diagram is shown in Fig. 1. Compared with ordinary epoxy resin, phenolic epoxy resin has more epoxy groups.

The resin can be cured with aliphatic amine or amine adduct at room temperature. Because the cured product can form an interpenetrating network structure with high crosslinking density, as shown in Fig. 2, its heat resistance and chemical resistance are higher than ordinary epoxy resin. The main chain of the cured product contains a large number of rigid benzene ring structure, and the benzene rings are connected by methylene. This structure is regular and compact, so the corrosion medium such as acid is difficult to penetrate through the coating.

![Fig. 1 Molecular schematic diagram of phenol phenolic epoxy resin.](image)

![Fig. 2 Network structure diagram of solidified resin.](image)
Curing agent determines the curing speed of coating system and the properties of cured film. Polyamides, fatty amines and phenolic amines are commonly used for epoxy curing agents. Polyamide has excellent comprehensive performance, easy construction and thick coating, but has poor low-temperature curing performance. Fatty amine has low viscosity and high reactivity, and can be rapidly cured at room temperature (RT). The curing performance of phenolic amines is outstanding at low temperature, and it has better high temperature resistance. In order to improve the temperature resistance of coating, phenolic amine was chosen as curing agent of phenolic epoxy resin. Three commonly used phenolic amine curing agents A, B and C on the market were selected for comparison with phenolic epoxy resin to screen the film forming system with good mechanical properties. The test results are shown in Tab. 1.

| No. | Curing agent | TFT min (25℃) | Adhesion, grade | Suppleness, mm | Impact resistance, cm |
|-----|--------------|----------------|-----------------|----------------|----------------------|
| 1-1 | A            | 90             | 0               | 2              | 50.0                 |
| 1-2 | B            | 24             | 2               | 4              | 50.0                 |
| 1-3 | C            | 156            | 0               | 1              | 50.0                 |

By comparison, the three curing agents have a great difference in the properties of coating film former. The curing agent C has the best adhesion and flexibility with the phenolic epoxy resin system, therefore C is selected as the supporting curing agent of phenolic epoxy resin.

2.2. Study on the pigments and fillers

Based on the study of coating film former system, the pigment and filler system with strong acid resistance was studied. There is no special requirements of color for internal anticorrosive coatings, while the acid resistance of coating is the point of study that should be taken into account. We chose the better filler combinations from carbon black, iron oxide yellow, precipitated barium sulfate, chrome oxide green, aluminum triplyphosphate, barite powder, silicon carbide, micaceous iron oxide, PTFE powder, graphite powder and other fillers[3], [5], [6], [14]. The fillers were used to make coating film with phenolic epoxy resin system. The coatings were soaked in hydrochloric acid and hydrofluoric acid mixture at 50 ℃ for 72 hours. The ratio of hydrochloric acid and hydrofluoric acid was 7:3. The coating bubbling and staining were compared to screen out the suitable fillers. The results showed that iron oxide yellow, chromium oxide green, aluminum triplyphosphate and precipitated barium sulfate have good acid resistance.

For this purpose, we conducted test gradations of four determined fillers, iron oxide yellow, chromium oxide green, aluminum triplyphosphate, and precipitated barium sulfate. Testes such as condition in container for 30 days at room temperature, coating appearance, adhesion, flexibility and immersion test in hydrochloric acid and hydrofluoric acid mixture were conducted. The results are shown in Tab. 2. It can be seen that coating of No. 2-2 has good physical and chemical properties. This proportion of fillers was selected for the next test.
Tab. 2 Test gradations table for pigments and fillers.

| No. | Mass ratio (iron oxide yellow: chromium oxide green: aluminum triopolyphosphate: precipitated barium sulfate) | Binder ratio | Condition in container | Coating appearance | Adhesion, grade | flexibility, mm | Immersion test in strong acid |
|-----|-------------------------------------------------------------------------------------------------|--------------|------------------------|--------------------|----------------|-----------------|------------------------------|
| 2-1 | 10: (20~30): (30~40): (5~10)                                                                 | 1.4:1        | Precipitated           | Good               | 1              | 1               | Good                        |
| 2-2 | 10: (15~20): (30~40): (10~15)                                                                 | 1.2:1        | Without precipitation  | Good               | 0              | 1               | Good                        |
| 2-3 | 10: (20~30): (40~50): (10~15)                                                                 | 1.9:1        | Without precipitation  | Good               | 0              | 2               | Good                        |
| 2-4 | 10: (15~20): (20~30): (5~10)                                                                 | 1.0:1        | Precipitated           | Particulate        | 1~2            | 1               | Good                        |

Graphene has high specific surface area, outstanding mechanical properties, excellent thermal conductivity and chemical stability, etc. When applied to the field of heavy anticorrosion coating, the graphene plays an important role and effectively improves the salt fog resistance, impact resistance, abrasion resistance and adhesion[15], [16]. Due to the shielding effect, graphene can effectively prevent water molecules and corrosion ion diffusion in coating. It can obviously improve the coating medium resistance. Based on the determination of the basic color filler system, 0.5~2% of graphene dispersion was added into coating to conduct the salt fog resistance, impact resistance, pulling adhesion, 50 ℃ hydrochloric acid and hydrofluoric acid mixture solution immersion test. The test results were compared with the basic color filler system coating, as shown in Tab. 3.

Tab. 3 Effect of graphene dispersion on properties of coating.

| Performance tests                      | Coating added graphene dispersion with basic color filler | Coating with basic color filler |
|----------------------------------------|----------------------------------------------------------|---------------------------------|
| Coating appearance                     | Good                                                     | Good                            |
| Salt fog resistance                    | 2000h, Good                                              | 1478h, Blister                  |
| Impact resistance, cm                  | 50                                                       | 50                              |
| Adhesion, MPa                          | 14.8                                                     | 11.4                            |
| 50 ℃ hydrochloric acid and hydrofluoric acid mixture (7:3) solution immersion | 600h, Good                                              | 600h, Blister                   |

As can be seen from the above table, the salt fog resistance and adhesion of the coating were significantly improved after adding graphene dispersion. The 600h hydrochloric acid and hydrofluoric acid immersion test results showed that the shielding ability of the coating to corrosion ions is enhanced after adding graphene, and the acid resistance of the coating is improved.

2.3. Study on solvent and auxiliary system
Solvent selection should fully consider its solubility and volatilization rate. Volatilization too fast will affect the film leveling pinhole, and result in the film density reducing. In order to avoid needle holes and bubbles, improve leveling, and solvent volatilize slowly in the paint drying early stage, we chose high boiling point solvent mix dibasic ester (DBE) and xylene, ethanol, n-butanol composition as the solvent system.
Different kinds of additives can effectively improve the coating's appearance, construction applicability and physical mechanical properties as an important part. Although the additive amount is precious little, it has significant effect for coatings. It showed that the addition of defoaming agents and levelling agents have obvious effects on eliminating bubbles, improve leveling and compactness in coating production and coating process. The additives in the coating were determined by experiments: 0.1~0.3% silane defoamer, 1~3% polyacrylate defoamer, 2~4% modified polyurethane dispersant.

3. Study on properties of acid-resistant anticorrosion coating

The basic formula system of coating was formed by the preparation experiments above. In order to giving consideration to wettability and appearance of the primer, the anticorrosion requirements of finish, we adjusted the ratio of resin, curing agent and solvent to enhance its rheological properties, retrogradation. The final acid-resistant anticorrosion coating formulas are showed in Tab. 4 and Tab.5.

| Tab. 4 Reference formula of acid-resistant anticorrosion priming coating. |
|-----------------------------------------------|
| Materials | Mass ratio /% | Materials | Mass ratio /% |
| Part A | | Levelling agent | 1~3 |
| Phenolic epoxy resin | 20~35 | Dispersant | 2~4 |
| Iron oxide yellow | 2~5 | Xylene | 15~25 |
| Chromium oxide green | 4~8 | Ethyl alcohol | 3~8 |
| Aluminum tripolyphosphate | 8~15 | Normal butanol | 3~6 |
| Precipitated barium sulfate | 3~6 | DBE | 3~8 |
| Thixotropic agent | 0.8~1.5 | Part B |
| Graphene dispersion | 0.5~2 | Phenolic amine curing agent | 8~16 |
| Other fillers | 10~15 | Xylene | 4~8 |
| Defoamer | 0.1~0.3 | Normal butanol | 1~2 |

| Tab. 5 Reference formula of acid-resistant anticorrosion finishing coating. |
|-----------------------------------------------|
| Materials | Mass ratio /% | Materials | Mass ratio /% |
| Part A | | Levelling agent | 1~3 |
| Phenolic epoxy resin | 30~50 | Dispersant | 2~4 |
| Iron oxide yellow | 2~5 | Xylene | 10~15 |
| Chromium oxide green | 4~8 | Ethyl alcohol | 2~6 |
| Aluminum tripolyphosphate | 8~15 | Normal butanol | 1~2 |
| Precipitated barium sulfate | 3~6 | DBE | 3~8 |
| Thixotropic agent | 1~2 | Part B |
| Graphene dispersion | 0.5~2 | Phenolic amine curing agent | 13~20 |
| Other fillers | 10~15 | Xylene | 2~4 |
| Defoamer | 0.1~0.3 | Normal butanol | 0.5~1 |

Performance researches were tested from chemical resistance test, salt fog resistance test, resistance to H2S corrosion test, alkali resistance test, coating resistance to chloride ion permeability test and other aspects to test the performance of acid-resistant anticorrosion coating.

3.1. Chemical resistance test

Chemical resistance is the most effective parameter to evaluate the corrosion resistance of coating directly. Paint the acid-resistant anticorrosion coating with two primers and two finishes on ordinary
mild steel test bars with diameter of 10mm and length of 120mm. The total dry film thickness was more than 300 microns. The test bars were soaked in the following chemicals after the coating curing. The results showed that the acid-resistant anticorrosion coating enhanced by graphene was intact after being soaked for 1000h.

### Tab. 6 Results of chemical resistance test.

| Reagent                     | Time (h) | Temperature (℃) | Coating status |
|-----------------------------|----------|-----------------|----------------|
| 30%H₂SO₄                    | 1000     | 70              | Good           |
| 10%HNO₃                    | 1000     | 70              | Good           |
| 20%H₃PO₄                   | 1000     | 70              | Good           |
| 12%HCl+3%HF                | 1000     | 70              | Good           |
| 12%HCl+3%HF+3%HCHO+3%HAc  | 1000     | 70              | Good           |
| 28%HCl+0.01%HCHO+0.02%HAc | 1000     | 70              | Good           |
| 20%NaOH                    | 1000     | 70              | Good           |
| Saturated H₂S solution     | 1000     | RT              | Good           |
| 5%NaCl+0.5%CH₃COOH         | 1000     | RT              | Good           |

3.2. Salt fog resistance test

The improvement of the salt fog resistance of graphene-enhanced acid-resistant anticorrosion coating was studied. We painted two primers and two finishes of coating to 70mm×150mm×1mm ordinary mild steel specimens, and the total dry film thickness of 3 parallel specimens was more than 300mm. According to GB/T 1771, the test specimens were put into the neutral PH salt fog test chamber with temperature of (35±2) ℃ and salt water concentration of (50±10) g/L to conduct the salt fog resistance test.

In order to fully test the salt fog resistance of acid-resistant coating, the specimens were firstly taken out of the 2000h salt fog resistance test to observe the coating status, and tested for long-term salt fog resistance to obtain the coating failure time. After 2000h salt fog test, the specimens were found to be in good condition with good gloss in salt fog test chamber. Subsequently, the test specimens were placed back to continue the experiment. Finally, the first test specimen bubbled at 8464 hour. The second specimen bubbled at 9231 hour, and the third specimen still showed no bubbling at 10000 hour. Therefore, it can be seen that the graphene-enhanced acid-resistant oil and gas anticorrosion coating has good salt spray resistance.

3.3. Resistance to H₂S corrosion test of coating

Two primers and two finishes were painted onto steel test bars with diameter of 10mm and length of 120mm. The dry film thickness of coating was more than 300mm. Then the bars were putted into the high-temperature and high-pressure autoclave as shown in Fig. 3 according to NACE TM 0187. The simulated medium corrosion environment of oil and gas wells with a temperature of 90℃ and a pressure of 32.0MPa (including 3.2 MPa for H₂S and 3.2 MPa for CO₂) and a concentration of 20429mg/L for Cl⁻ was studied. The static high temperature and high pressure test was carried out continuously for 168 hours. After the test, the high temperature autoclave was opened to check the appearance and adhesion of the acid-resistant anticorrosion coating.
Result showed that the coating specimen was in good appearance after the acid-resistant corrosion test, and the coating had no obvious color change. V-groove method is adopted to test the adhesion of the coating, and the adhesion between the coating and the substrate changes to "slight loss of adhesion". Under the coating, the metal surface of the substrate reveals silver-white metallic luster. It is shown that the acid-resistant coating has good corrosion resistance to \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) under high temperature and pressure.

3.4. *Alkali resistance test*

In order to simulate the corrosion state in strong alkaline substances of oil and gas field working medium, the acid-resistant coating was soaked into alkaline medium under high temperature and pressure. The acid-resistant anticorrosion coating was applied on the 20mm×30mm×3mm ordinary low carbon steel specimen and coated with two primers and two finishes. The total film thickness was no less than 300mm. The specimens were fixed on the special specimen plane and placed into the high temperature autoclave, and NaOH solution with PH value of 12.5 was poured into autoclave. The temperature of the high temperature autoclave was raised to 150\( ^\circ\)C after deoxygenation with nitrogen. The pressure was set at 70MPa.

The results are shown in Fig. 4. It is shown that the acid-resistant anticorrosion coating has a good appearance and slightly lighter color after the high-temperature and high-pressure corrosion resistance test against alkaline medium. The adhesion test of the coating, which is conducted by the method of SY/T 0544-2004 appendix C, shows that the coating has good alkali resistance and temperature resistance of 150\( ^\circ\)C.
3.5. Coating resistance to chloride ion permeability test

For further understanding of the ion shield mechanism, acid-resistant anticorrosion coating was painted on 200 mm×200 mm of glass surface, two primers and two finishes with the total dry film thickness of coating between 250microns and 300 microns. After curing, the coatings were peeled from glass and cut into a circle with diameter of 60 mm. According to the requirements of JTJ 275-2000 appendix C specimens circle were put into the resistance to chloride ion permeability test device as shown in Fig. 5. The coating faced one side toward 3% salt water and the other toward distilled water.

Fig. 5 Test device of coating resistance to chloride ion permeability.

The device was placed at room temperature for 30 days to determine the content of chloride ions in distilled water and calculate the permeability of chloride ions through the coating sheet. The result showed that the penetration rate of chloride ions through the coating is 2.4×10⁻³mg/cm²·d, which is lower than the standard of chloride ions in ordinary coatings. It is indicated that the acid-resistant anticorrosion coating with graphene enhanced has a better ability to block the diffusion of corrosion ions.

4. Comprehensive physicochemical properties of acid-resistant coating

In addition to the above experimental research, we also tested other physical and chemical properties of acid-resistant anticorrosion coating. The comprehensive test results are listed in Tab. 7.
**Tab. 7 Comprehensive test results of acid-resistant anticorrosion coating.**

| No. | Test item                                                                 | Primer | Finish | Test methods  |
|-----|----------------------------------------------------------------------------|--------|--------|---------------|
| 1   | Non-volatile content, %                                                   | ≥75    | ≥70    | GB/T1725      |
| 2   | Adhesion, Grade                                                           | 1      | 1      | GB9286        |
| 3   | Flexibility, mm                                                           | 1      | 1      | GB/T1731      |
| 4   | Impact resistance, cm                                                     | 50     | 50     | GB/T1732      |
| 5   | Shear bond strength, MPa                                                  | 10.8   |        | SY/T0041      |
| 6   | Hardness (pendulum bar damping test)                                      |        | 0.62   | GB/T1730      |
| 7   | Air pressure bubbling test (8.3MPa, 24h)                                  | Free of bubbles |        | SY/T6530      |
| 8   | Water pressure bubbling test (20MPa, 150℃, 24h)                           | No blisters |        | SY/T6530      |
| 9   | Volume resistivity, Ω·m                                                   | 5.7×10^{16} |        | GB/T1410      |
| 10  | Electric strength, MV/m                                                   | 32.8   |        | GB/T1408.1    |
| 11  | Abrasion resistance (1000g/1000r), mg                                     | 16.5   |        | GB/T1768      |
| 12  | Abrasion resistance (falling abrasive), l/μm                              | 2.01   |        | ASTMD968      |
| 13  | Salt fog resistance test, h                                               | 8464   |        | GB/T1771      |
| 14  | Resistance to mud acid (HCl: HF=7: 3, RT, 800h)                           | Good   |        | GB/T1763      |
| 15  | Acid resistance (70℃, 1100h)                                             | 30%H₂SO₄ | Good   | GB/T1763      |
| 16  |                                                                           | 10% HNO₃ | Good   | GB/T1763      |
| 17  |                                                                           | 20%H₃PO₄ | Good   | GB/T1763      |
| 18  |                                                                           | 12%HCl+3%HF+3%HCHO+3%HAc | Good   | GB/T1763      |
| 19  |                                                                           | 28%HCl+0.01%HCHO+0.02%HAc | Good   | GB/T1763      |
| 20  | Resistance to oilfield sewage boiling (100℃, 4200h)                       |        |        | GB/T1763      |
| 21  | Alkali resistance (20%NaOH, 70℃, 1100h)                                 |        |        | GB/T1763      |
| 22  | Alkali resistance (5%NaOH, 100℃, 1000h)                                 |        |        | GB/T1763      |
| 23  | Petrol-resistance (RT, 500h)                                             |        |        | GB/T1763      |
| 24  | Resistance to kerosene (RT, 500h)                                        |        |        | GB/T1763      |
| 25  | High temperature and pressure (70MPa, 150℃, pH=12.5, 24h)                | Adhesion grade A |        | SY/T0544      |
| 26  | 3.2 MPa for H₂S, 3.2 MPa for CO₂ 90℃, pressure 32MPa, 168h               | No bubbles, no shedding, adhesion grade≤2 |        | NACE TM 0185  |

**5. Conclusion**

For subsea oil and gas pipelines containing H₂S, CO₂ or other acid corrosion ions of harsh environment, we chose a phenolic epoxy resin and phenolic aldehyde amine curing agent system with a good temperature resistance and high crosslinking density, acid fillers in the coating preparation research. The graphene dispersion was added into the coating to improve the performance of salt fog resistance, adhesion and resistance to acid, alkali and salt medium.

A series of test, which included salt fog resistance test, the H₂S corrosion resistance test, the alkaline medium resistance and resistance to chloride ion permeability test and other performance test, had been conducted to evaluate the physical and chemical properties of acid-resistant anticorrosion coating. The results showed that the coating has excellent acid and salt fog resistance performance. It can be used under 100℃ for long-term use. The coating can effectively slow down the corrosion of H₂S, CO₂, mud acid, hydrochloric acid, sulfuric acid and other strong acidic substances. It meets the needs of acid-resistant corrosion in petroleum and petrochemical industry.
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