Study on High-efficiency Thermal Conductive Anticorrosion Coating Technology for Temperature and H₂S Corrosion Resistance

Qingshan Liu¹, Wenwen Xiao¹, Qian Zhang¹, Lei Wang²,*, Xiaojun Guo², Shaoming Duan², Pengli Ge¹ and Yanyan Xu¹

¹Petroleum Engineering Technology Research Institute, SINOPEC Northwest Oil Field Branch, Luntai, China
²Anticorrosion insulation Technology Company, CNPC Engineering Technology Research Company Limited, Tianjin, China

*Corresponding author: wanglei98@cnpc.com.cn

Abstract. In order to deal with the anticorrosion problem of heat exchangers containing H₂S, CO₂ and other acidic media, the heat-conducting anticorrosion coating which can be used in acidic media at 200°C was prepared by adopting the combination system of the high-temperature curing epoxy phenolic resin film forming system and acid-resistant filler and filled heat-conducting filler. The results show that the coating has excellent acid and alkaline resistance, salt spray resistance, heat resistance and good thermal conductivity. It meets the technical requirements of heat exchanger corrosion protection under the acidic corrosion environment of H₂S and CO₂.

Keywords: Acid resistance, heat exchanger, heat-resistant coating, sulfuretted hydrogen, internal anticorrosion.

1. Introduction

Tahe Oilfield is located in the central part of Tarim Basin. The oil and gas contain high concentration of H₂S and CO₂. The formation water of Tahe oilfield is characterized by high Cl⁻ concentration and low pH, which form a strong corrosive environment, leading to serious corrosion of oil and gas field devices in this area [1, 2]. As the dissolved gas of crude oil and formation water, H₂S, CO₂ and other gases make metals exposed to acidic aqueous solution environment, which have a serious impact on the corrosion of oil and gas drilling, production and refining equipments [3]. With the reinforcement of temperature and pressure, the reaction rate of hydrolyzed H₂S, CO₂ and other acidic gases to the substrate metal increases rapidly [4], leading to the increase of the corrosion rate, which seriously affects the intrinsic safety of equipment.

Equipments, such as heat exchangers, air coolers and pressure vessels commonly used in oil and gas fields, are exposed to corrosive environments with H₂S and other acidic gases for a long time. Because some of the equipment works in high temperature and pressure environment, oil and gas field equipment is in a harsh internal corrosive environment. At present, the carbon steel heat exchanger tube bundle without anticorrosion treatment can be corroded and perforated within 40–60 days. Therefore, solution for the problem of acid gas corrosion prevention under high temperature of heat...
exchanger and pressure vessel equipment has become the key to restrict the intrinsic safety of oil fields.

In this paper, a thermal conductive anticorrosion coating which can be used in 200℃ at the condition of H₂S and other acidic media was prepared by adopting the high temperature curing epoxy phenolic resin film forming system, combining with acid-resistant fillers and filled thermal conductive fillers. The results show that the coating has excellent acid and alkali resistance, salt spray resistance, heat resistance and good thermal conductivity. It meet the anticorrosion need for the technical requirements of heat exchanger under H₂S and CO₂ acid corrosive environment.

2. Development of heat resistant and H₂S resistant thermal conductivity coating

2.1. Film-forming system

Phenolic resin has the characteristics of high hardness, high compactness and excellent acid and alkali corrosion resistance, but the anticorrosion coatings prepared by phenolic resin alone also have the disadvantages of high rigidity and poor adhesion. The bisphenol A epoxy resin has the characteristics of excellent corrosion resistance, strong adhesion, strong temperature variation ability and pressure resistance, which can effectively improve the deficiency of phenolic resin.

When phenolic resin combines with bisphenol A epoxy resin [7], the epoxy group of the epoxy resin is cross-linked with phenolic hydroxyl group and hydroxymethyl group of phenolic resin under high temperature baking to form a mesh three-dimensional structure coating. It can be prepared into a stable storage of single-component coating at room temperature. As the function of the film forming resin is increased, the heat resistance, solvent resistance and chemical medium resistance of the coating are also enhanced with the cross-linking density improved.

The cross-linking reaction between epoxy resin and phenolic resin under the action of high temperature are mainly as follow:

(1) Reaction of the hydroxyl group of phenolic resins with the epoxy group of epoxy resins

\[ \text{HO} + \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \]

(2) Reaction of the hydroxymethyl group of phenolic resins with the hydroxyl group of epoxy resins

\[ \text{CH}_2\text{OH} + \text{HO} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \]

(3) Reaction of the phenol group of phenolic resins with the epoxy group of epoxy resins

\[ \text{OH} + \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{O} \]

In this paper, modified alcohol-soluble phenolic resin and E42 epoxy resin were used as the main film forming materials to carry out experimental research. The varnish film properties were tested under different proportions of epoxy resin and phenolic resin, and the results were shown in Table 1.

| No. | Ratio of resin (epoxy: phenolic) | Flexibility/grade | Strength of impact/cm | Adhesion/level | Shear strength /MPa |
|-----|---------------------------------|-------------------|-----------------------|---------------|---------------------|
| 1-1 | 5:5                             | 1                 | 50                    | 1             | 5.96                |
| 1-2 | 6:4                             | 1                 | 50                    | 1             | 9.06                |
| 1-3 | 7:3                             | 1                 | 50                    | 1             | 9.88                |
| 1-4 | 8:2                             | 1                 | 50                    | 1             | 9.45                |
| 1-5 | 9:1                             | 1                 | 50                    | 1             | 8.21                |
The results showed that the epoxy resin and phenolic resin had good flexibility, strength of impact and adhesion at different ratios. The varnish film had higher shear strength when the ratio of resin was between 6:4 and 8:2. Therefore, we chose the ratio of epoxy resin and phenolic resin to be 7:3.

2.2. Pigments and fillers system

As the important component of coating, pigments and fillers system can be used to adjust the coating pigment volume concentration (PVC), improve the coating construction suitability, increase the thickness of the coating film, improve coating adhesion, heat resistance, density, surface hardness and wear resistance, lower coating contraction, and improve the water resistance and permeability of the coating. It can reduce the cost of coating at the same time, and have great influence on the performance of the coating film and the production process. This paper mainly focuses on acid resistance and thermal conductivity to carry out research on coating performance, so that there is no requirement for coating’s pigments, and the selecting and adjustment of pigments can be ignored.

On the basis of film-forming materials, carbon black, silicon carbide, iron oxide red, chromium oxide green, talcum powder, AlN, precipitated barium sulfate, alumina, mica powder, barite powder and so on were selected as fillers for tests. The test coatings were prepared according to the ratio of 1:1 resin to fillers. The coatings were soaked in a mixture of hydrochloric acid and hydrofluoric acid 7:3 at 50°C for 120 hours, and taken out to observe the foaming condition of the coating. The results show that silicon carbide, chromium oxide green, mica powder and precipitated barium sulfate have good acid resistance and can be used as acid resistant fillers for coating.

It is an economical and efficient way to optimize the thermal conductivity of the film-forming material by using fillers with high thermal conductivity in order to improve the thermal conductivity of the heat exchanger coating [8]. According to the mixed particle system polymer composite material model established by Agari [9] et al., the mathematical expression of the model is as follow:

\[
\lg \lambda = V(1) C_1 \lambda_1 + V(2) C_2 \lambda_2 + V(3) C_3 \lambda_3 + \ldots \ldots + (1-V) C_4 \lambda_4 
\]

In formula (1), \(\lambda_1\) represents the thermal conductivity of the resin polymer; \(\lambda_2, \lambda_3, \ldots\) represent the thermal conductivity of different particles; \(\lambda\) denotes the thermal conductivity of the polymer material; \(V\) represents the volume fraction of a variety of fillers in the system; \(X_2, X_3, \ldots\) represent the statistical fraction of each particle in different fillers in the total mixed particle respectively, and the sum of statistical fraction of all particles is 1; \(C_1\) represents the size factor affecting the cleanliness and crystallization of the polymer; \(C_2, C_3, \ldots\) is the free factor of forming the thermal conductivity chain of the thermal conductivity packing particles, and represents the degree of difficulty of forming the thermal conductivity chain. The easier the particles are to form the thermal conductivity chain, the greater the influence on the thermal conductivity of the polymer material is, and the value is closer to 1.

It can be seen from the expression that, in order to improve the thermal conductivity of polymer materials under the condition of constant thermal conductivity of resin, the thermal conductivity of different particles should be increased for one necessary way. On the other hand, the statistical fraction of thermal conductivity filler should be increased to improve the free factor of particles forming thermal chain in the coating.

It is generally believed that ordered lattice filling materials (such as silicon nitride, silicon carbide, etc) have higher thermal conductivity compared with disordered lattice structure materials (such as epoxy resin, glass, etc) [10], and their thermal conductivity is obviously better than that of disordered lattice materials. In this paper, silicon carbide, \(\beta\)-Si\(_3\)N\(_4\) and AlN with excellent thermal conductivity were selected as thermal conductivity fillers to carry out matching tests with other conventional coating fillers. The thermal conductivity and adhesion of coating PVC were changed, and the results were shown in Table 2.
Table 2. Test sheet for thermal conductivity matching between thermal conductive filler and conventional filler.

| No. | Ratio of fillers | PVC/% | 50℃ mixture of hydrochloric acid and hydrofluoric acid, 120h | Adhesion/level | Thermal conductivity, 80℃/(W/(m·K)) |
|-----|-----------------|-------|------------------------------------------------------------|---------------|-----------------------------------|
| 2-1 | 4:1             | 60    | Good                                                      | 0             | 6.74                              |
| 2-2 | 4:1             | 70    | Blister                                                   | 1             | 15.49                             |
| 2-3 | 4:1             | 80    | Blister                                                   | 2             | 23.19                             |
| 2-4 | 3:1             | 60    | Good                                                      | 0             | 5.24                              |
| 2-5 | 3:1             | 70    | Good                                                      | 1             | 13.94                             |
| 2-6 | 3:1             | 80    | Blister                                                   | 1             | 19.89                             |
| 2-7 | 2:1             | 60    | Good                                                      | 0             | 3.12                              |
| 2-8 | 2:1             | 70    | Good                                                      | 1             | 8.25                              |
| 2-9 | 2:1             | 80    | Blister                                                   | 2             | 14.02                             |
| 2-10| 1:1             | 60    | Good                                                      | 0             | 2.63                              |
| 2-11| 1:1             | 70    | Good                                                      | 1             | 7.02                              |
| 2-12| 1:1             | 80    | Good                                                      | 1             | 11.21                             |

The results show that the increase of thermal conductivity filler has a great influence on the acid resistance of the coating, and the coating is prone to blister. common fillers affect the thermal conductivity of the system. Therefore, the ratio of thermal conductivity filler and ordinary filler is decided with 3:1, and PVC is 70%, which not only ensures the thermal conductivity of the system, but also does not have a great impact on the acid resistance of the coating.

2.3. Solvent system

Solvent selection should fully consider its dissolution capacity and volatilization rate. Since the film is made of phenolic resin and epoxy resin, the addition of solvent needs to improve the solubility of the film. At the same time, because the coating is constructed by high temperature curing process, it needs to maintain the appropriate volatilization rate at higher temperature. In order to avoid pinholes, bubbles and improve the coating property, the volatile speed by using high boiling point solvents, isophorone and mixed dibasic acid dimethyl esters (DBE) and mixed soluble strong low boiling point solvent (xylene) and ethanol as solvent coating system to improve the coating construction suitability, control the volatilizing speed and dissolving performance of thermal coating. It ensures that no defects occur during the heating curing process of the coating.

2.4. Auxiliaries system

Although the amount of auxiliaries is small, they can effectively improve the coating leveling, wetting, defoaming, sagging, anti-sinking and other properties, is an important component in the coating. Silicone oil, as a common and good compatibility of silicone resin defoamer, can meet the technical requirements of the coating production process and the high temperature curing process for construction at room temperature. In order to improve the leveling performance, this paper has conducted experiments and comparisons and found that the leveling performance of the polyacrylate-based leveling agent on the thermally conductive coating is good. The coupling agent can be used to reduce the pores and defects between the coating film forming material and the thermal conductivity filler, common filler, reduce the phonon scattering at the interface, effectively improve the thermal conductivity of the system, and enhance the interface bonding strength between the film forming material and the filler test, improve the adhesion of the coating.
The experiment results show that the amount of coating auxiliaries is determined as follows: 0.1% silicone oil defoaming agent, 1% polyacrylate leveling agent, 0.5% silane coupling agent and 1.5% modified polyurethane dispersant.

3. Study on properties of thermal conductivity coatings with heat and H₂S resistance

The basic formulation system of the coating was formed by the above experimental study on the preparation of thermal conductivity coating. In this paper, the addition of solvent and auxiliaries is optimized to improve its rheological property and settlement property according to the state of the coating, so as to obtain the formula of heat-resistant, acid-resistant and heat-conducting coating, as shown in Table 3.

3.1. Study on chemical resistance

Firstly, we prepared the coating samples. The four layer coatings were applied on the Φ10mm×120mm carbon steel test specimens. The dry film thickness of single layer was 40~50μm. High temperature curing process was adopted, which was programmed to rise to 180℃. The total dry film thickness of the coatings was ≥160μm. After curing the coating for 7 days, the coating test specimens were soaked into the chemical as shown in Table 4, and were observed during the next 1000h.

| No. | Reagents                  | Temperature/℃ | Time/h | Results |
|-----|--------------------------|---------------|--------|---------|
| 3-1 | 30%H₂SO₄                 | 80            | 1000   | Good    |
| 3-2 | 10%HNO₃                  | 80            | 1000   | Good    |
| 3-3 | 20%H₃PO₄                 | 80            | 1000   | Good    |
| 3-4 | 12%HCl+3%HF              | 80            | 1000   | Good    |
| 3-5 | 12%HCl+3%HF+3%HCHO+3%HAc | 80            | 1000   | Good    |
| 3-6 | 20%NaOH                  | 80            | 1000   | Good    |
| 3-7 | Saturated H₂S solution   | RT            | 1000   | Good    |

As can be seen from the test results in the table, the acid-resistant thermal conductive coating is in good condition after soaking for 1000h, with good acid and alkali resistance, and can meet the requirements of the use of acidic medium environment.
3.2. Study on resistance to neutral salt spray

According to GB/T 1771, three samples coated with four layer coatings were put into the sample shelf in the neutral salt spray chamber. NaCl solution with pH value of 6.5 ~ 7.2 was prepared, and the concentration was 50±10g/L. The temperature of the salt spray chamber was set at 35℃±2℃, and the continuous salt spray test was conducted for 2000h to observe the apparent and foaming state of the coating in the process of salt spray.

The results show that the acid-resistant thermal conductive coating has good salt spray resistance after the neutral salt spray for 2000h, except that the color of the coating becomes slightly lighter. The coating has no foaming and no rust, and has good apparent state.

3.3. Study on H₂S corrosion resistance

Suspend the carbon steel test specimens coated with 4 heat-resistant and heat-conducting coatings into the high-temperature autoclave as shown in Fig. 1.

According to NACE TM 0187, the temperature and pressure of the autoclave were set at 90℃ and 9.0MPa (H₂S partial pressure, 1.5MPa; CO₂ partial pressure, 1.5MPa) simulating water heat transfer corrosion environment in oil and gas field. The Cl⁻ concentration was 20429mg/L.

After 168 hours of high temperature and high pressure static corrosion test, the coating appearance and adhesion state were examined. The results of test showed that the coating of acid-resistant thermal conductivity coating specimen was well, without peeling off and foaming. The coating still had good adhesion to the metal matrix. It was shown that the acid-resistant thermal conductive coating still had good corrosion resistance in the environment of high temperature and high pressure acid gas.

3.4. Study on the heat resistance

The heat resistance test of the thermal conductive coating was carried out by differential scanning calorimeter (DSC). The test result is shown in Fig. 2. It can be seen from the DSC curve that the thermal decomposition rate of the coating is 293℃, and the coating can be used stably at 200℃ for a long time.
Figure 2. The DSC curve of acid-resistant thermal conductive coating.

4. Comprehensive properties of thermal conductivity coatings with heat and H$_2$S resistance

Based on the tests of coating above, the comprehensive physical and mechanical properties of heat and H$_2$S resistant thermal conductivity coatings were tested in this paper. The test results are listed in Table 5.

| No. | Test item                              | Results     | Methods          |
|-----|----------------------------------------|-------------|------------------|
| 1   | Non-volatile content, %                | ≥60         | GB/T1725         |
| 2   | Adhesion, Grade                        | 0           | GB9286           |
| 3   | Flexibility, mm                        | 1           | GB/T1731         |
| 4   | Impact resistance, cm                  | 50          | GB/T1732         |
| 5   | Shear bond strength, MPa               | 11.4        | SY/T0041         |
| 6   | Hardness (pendulum bar damping test)    | 6H          | GB/T6739         |
| 7   | Air pressure bubbling test (9.0MPa, 24h) | Good       | SY/T6530         |
| 8   | Volume resistivity, Ω·m                | 3.6×10$^{14}$ | GB/T1410        |
| 9   | Electric strength, MV/m                | 37.6        | GB/T1408.1       |
| 10  | Abrasion resistance (1000g/1000r), mg   | 12.1        | GB/T1768         |
| 11  | Thermal conductivity, W/(m·K)          | 12.16       | GB/T10297        |
| 12  | Salt fog resistance test, h            | 2000, Good  | GB/T1771         |
| 13  | Resistance to mud acid (HCl: HF=7:3, RT, 800h) | Good | GB/T1763         |
| 14  | Saturated H$_2$S solution (RT, 1000h)  | Good        | GB/T1763         |
| 15  | Acid resistance (80°C, 1000h)          | 30%H$_2$SO$_4$ | Good  | GB/T1763         |
| 16  |                                        | 10%HNO$_3$  | Good             | GB/T1763         |
| 17  |                                        | 20%H$_3$PO$_4$ | Good    | GB/T1763         |
| 18  |                                        | 12%HCl+3%HF+3%HCHO+3%HAc | Good | GB/T1763         |
| 19  | Resistance to oilfield sewage boiling (100°C, 1000h) | Good | GB/T1763         |
| 20  | Alkali resistance (20%NaOH, 80°C, 1000h) | Good | GB/T1763         |
| 21  | Resistance to kerosene (RT, 500h)      | Good        | GB/T1763         |
| 22  | High temperature and pressure (70MPa, 180°C, pH=12.5, 24h) | No bubbles, no shedding, adhesion grade≤1 | SY/T0544 |
| 23  | 1.5 MPa for H$_2$S, 1.5 MPa for CO$_2$ 90°C, pressure 9.0MPa, 168h | No bubbles, no shedding, adhesion grade≤2 | NACE TM 0185 SY/T0544 |
5. Conclusions
In this paper, we prepared a kind of high-efficiency heat-conducting anticorrosion coating for temperature and H₂S resistance, which adopted epoxy resin and phenolic resin for heating curing and filling thermal conductivity process for heart conducting. The heat-resistant thermal conductivity coating can be used at 200°C. In view of the characteristics of acid medium such as H₂S and CO₂ contained in the produced fluid of oil and gas fields, acid resistant fillers were selected to improve the performance of acid and alkali resistance, salt spray resistance and adhesion of the coating.

In this paper, the comprehensive properties of the coating was evaluated by chemical resistance research, neutral salt spray resistance test, H₂S corrosion resistance test, heat resistance test and other performance tests. The results show that the thermal conductive coating has excellent acid resistance, salt fog resistance and heat resistance performance. The coating thermal conductivity coefficient can reach 12.16W/(m K), and heat conduction performance is good. The coating has good adhesion, flexibility and other basic physical and mechanical properties. It can be used at 200°C for a long time. It effectively solves the problem of temperature resistance and heat conduction in the environment of acid corrosive media in oil and gas fields, and meeting the requirements of the petroleum and petrochemical industry for heat conduction coatings in acid corrosive environment.

Acknowledgments
First Author: Qingshan Liu, 1978, graduated from Southwest Petroleum Institute with a master’s degree in oil-gas field development in 2004, Senior Engineer, engaged in oil and gas field anticorrosion engineering. E-mail: 276404102@qq.com.

* Corresponding author: Lei Wang, 1988, graduated from China University of Petroleum (East China) with a master's degree in material science and engineering in 2014, Intermediate Engineer, engaged in anticorrosion and heat preservation technology research work. E-mail: wanglei98@cnpc.com.cn.

References
[1] ZHAO Zhen, HUANG Xuefeng, LIU Qiang. Cause analysis of corrosion perforation of Tahe oilfield ground gathering processing system [J]. Corrosion & Protection, 2013, 34 (5): 442-445.
[2] WANG Dan, JIA Xingliang, ZHAO Ruiming, et al. Hydrogen sulfide corrosion products and damage in Tahe oilfield [J]. Xinjiang Geology, 2013 (Supplement): 127-130.
[3] CHEN M J, LUO X. Anticorrosion measures of drilling equipment in the natural gas well containing thickness hydrogen sulfide and carbon dioxide [J]. Surface Technology, 2006, 35 (1): 80-82.
[4] YA Yameng, ZHANG Shengli, LI Wei, et al. High temperature, H₂S environment equipment inner wall ceramic metal coating corrosion protection technology [J]. Natural Gas and Oil. 2016, 34 (2): 72-77.
[5] YU Hui, HE Yi. The influence of CO₂/H₂S on the corrosion resistance of epoxy coating[J]. Corrosion Prevention, 2011, 14 (12): 55-57.
[6] TANG Cheng, ZHU Zhilu, FENG Jun. Preparation and performance study of phenol aldehyde-epoxy anticorrosive coatings [J]. Marine & Heavy-duty anticorrosion coatings and application. 2010, 25 (7): 32-34.
[7] XIA Tao, WANG Zhuang, HUANG Ying, et al. Preparation and property of EP modified PF nanocomposite [J]. New Chemical Materials, 2019, 47 (12): 66-70.
[8] LI Junming, YU Xinhai, LUO Daoming. Application of Thermally Conductive Filler in Insulating Polymer Materials [J]. Insulating Materials, 2013, 46 (2): 25-28.
[9] Agair Y, Tanka M, Nagai S, et al. Thermal conductivity of a polymer composite filled with mixtures of particles [J]. J. Appl. Polym. Sci. 1987: 34 (1): 429-434.
[10] ZHOU Wenying. High Thermal Conductivity and Electrical Insulation Polymeric Composites [D]. XI’AN: Northwestern Polytechnical University, 2007: 18-25.
[11] FANG Kun, MA Yuran, LI Yixuan, et al. Influences of pigments and fillers on performance of phenol aldehyde epoxy resin coating [J]. Plating and Finishing, 2013, 35 (6): 26-29.

[12] ZHONG Zhaokui, LIU Liangliang, NI Peichao. Development of heat and humidity-resistant, acid-resistant coating for silica gel industry [J]. Paint & Coatings Industry, 2010, 40 (2): 40-44.

[13] ZHOU Wenying, QI Shuhua, WANG Caifeng, et al. High temperature and insulating heat conductive coating [J]. Acta Materiae Compositae Sinica, 2007, 24 (2): 52-56.

[14] LI Jing, LIANG Ju, LIU Yeming. High-Thermal Conductive Coating Used on Metal Heat Exchanger [J]. Materials and Product Engineering, 2014, 22 (5): 596-601.

[15] FENG Haimeng, WANG Li. Research of heat-resistant anti-corrosion coatings for heat exchangers [J]. Corrosion & Protection in Petrochemical Industry, 2009, 26 (3): 1-4.

[16] YU Qingjie. Progress in multi-functional coatings applied for surface of heat exchangers [J]. Paint & Coatings Industry, 2011, 41 (11): 66-69.

[17] WANG Jing, YUE Wenhua. Research on the acid resistant epoxy coatings [J]. Shanghai coatings, 2015, 53 (5): 11-13.