

Testing Investigation of Protective Coatings for Downhole Oil Tube

Liping Zhang[†], Qibin Zhang, Yanjun Zhang, Beibei Xie, and Yingying Zhang

CNPC Research Institute of Engineering Technology, Tanggu Tianjin, 300451 China

Aiming at the corrosion circumstances and corrosion prevention needs of downhole oil tubes, series protective coatings for downhole oil tubes have been developed in the authors' laboratory, including a baked type coating YG-01 and an air curing type coating YG-03, etc. The performance investigation of the coatings has been done for testing their corrosion resistance, mainly including salt fog test, immersion test in oil-field waste water and various acid solutions, high temperature and high pressure test in alkali solution or H₂S/CO₂ environment, as well as some other performances. The investigation results show that oil tube anti-corrosion coatings developed here can endure over 4000 hrs salt fog test, over 1000 hrs immersion in various acid solutions at room temperature and in boiling oil-field waste water. In addition, the coatings can keep intact after experiencing test in alkali solution under 70 MPa pressure at 150°C for 24 hrs, and in simulative sour gas environment under the total pressure of 32 MPa (P_{H₂S}=3.2 MPa, P_{CO₂}=3.2 MPa) at 90°C for 168 hrs, which show that the coatings can be used for corrosion prevention in downhole environments with specific high temperature and high pressure, such as sour gas wells. The other testing results show the oil tube protective coatings have excellent comprehensive performance.

Keywords : oil tube, protective coating, anti-corrosion, performance.

1. Introduction

The anti-corrosion measures for downhole oil tubes mostly contain replacing common steel tube termly, using alloy tubes, injecting inhibitors, applying anti-corrosion internal coating etc. Thereinto, applying anti-corrosion internal coating is an effective method worldwide used to prevent oil tubes from corrosion.¹⁾ Aiming at the corrosion circumstances and corrosion prevention needs of downhole oil tubes in China, a series of protective coatings for downhole oil tubes has been developed in the authors' Laboratory, containing a baked type oil tube anti-corrosion coating YG-01 and an air curing type oil tube anti-corrosion coating YG-03, etc. The performance investigation of developed oil tube protective coatings is mainly introduced in this paper based on the interrelated industrial standard and application environment characteristics.

2. Preparation of testing specimens

2.1 Specimen's dimensions

The mild steel's specimens of different type and dimensions are coated and used according to the characteristics of the performance test. Thereinto, the panels with the dimension of 70 mm×150 mm×1 mm are used for

salt fog spraying test. The plates with the dimension of 20 mm×30 mm×3 mm are used for alkaline medium corrosion resistance test under high pressure and at high temperature, and all surfaces are coated in order to ensure the medium not to enter the interface between the coat and steel. The test sticks with the dimension of $\phi 10$ mm×120 mm, of which one end is spherical and the other is flat with a small hole 5 mm from the top for hanging, are used for tests of acid resistance and boiling oil field waste water resistance as well as H₂S/CO₂ corrosion resistance at high temperature and high pressure.

2.2 Coating system of specimens

The specimens are coated by brushing process. The coating system consists of one pass of primer and two passes of top coat, totally dry film thickness of 250 μ m minimum.

2.3 Curing schedule of the coatings

The curing schedule of YG-01 oil tube anti-corrosion coating is as follows. The specimens are first placed in air for one hour after applying each pass primer or first top coat, and then put into the oven, the temperature in which is increased to 60°C±2°C at the rate of 1°C/min and keep for 30 min at 60°C±2°C; and increased to 85°C±2°C and keep for 30 min; and then to 120°C±2°C. After 30 min at 120°C±2°C, the specimens are taken out from

[†] Corresponding author: zhanglp10@yahoo.com.cn

the oven and cooled to normal temperature before coated with next coating. The very top coat should be cured following above curing schedule and finally cured at $185^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 60 min.

YG-03 air cured oil tube anti-corrosion coating is a two components coating, is made of epoxy resin modified with phenol resin, curing agent, acid resistance anti-corrosion pigments and fillers, additive agents, mixed solvent. It can be coated with airless spraying process and cured at room temperature.

3. Performance evaluation of the coatings

3.1 Anti-corrosion performance

There are two requirements for the anti-corrosion performance of oil tube anti-corrosion internal coating in present Chinese Petroleum Industry Standard SY/T 5951-2004, "The Technical Specification for Oil Tubes Coated with Epoxy Epoxy-Phenolic Resin Coating".²⁾ The coating should be intact after immersed in mud acid solution (HCl : HF =7:3) for 180 hrs at room temperature and boiled in oil field waste water for 10 hrs. Besides above-mentioned two test evaluation, the salt fog test and many kinds of acid solution immersion tests have been done for the performance investigation of developed oil tube protective coatings.

3.1.1 Test for salt fog resistance

Test method: According to the testing method in Chinese National Standard GB/T 1771 (equivalent to ASTM B117), the coating specimens are put in Type SASS/450 Salt Fog Cabinet. The concentration of salt water is 50 ± 1 g NaCl per liter with pH 6.5-7.2. The test temperature is $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$, and the salt water is sprayed continuously.

Test result: Both YG-01 coating and YG-03 coating remain intact and glossy. No underfilm corrosion, blister or cracks in coating is observed after over 4000 hours in the salt spray cabinet.

3.1.2 Test of acid resistance

After the coating cured, the specimens were immersed in various acid solutions, including 20% H_2SO_4 , 20% HNO_3 , 26% HCl +12% HF (mud acid), 12% HCl +3% HF +3% HCHO +3% HAc and 28% HCl +0.01% HCHO +0.02% HAc at normal temperature. The test results show that both YG-01 baked cured oil tube internal coating and YG-03 air cured oil tube anti-corrosion internal coating remain intact without blister, cracks and other defects after over 1000 hrs.

3.1.3 Test of boiling oil field waste water resistance

After the coating cured, the specimens are put in

three-necked flask with oil field waste water. A condenser is attached and the three-necked flask is placed into an electric heating set with thermal insulation to keep the oil field waste water boiling. The specimens were inspected after over 1000 hrs. The result shows that both the coating YG-01 and the coating YG-03 keep intact without under-film corrosion, blister and cracks.

3.2 Performances in the condition of high temperature and high pressure

According to the provision in the Chinese Petroleum Industrial Standard SY/T 0544-2004, "The Technical Specification for Solvent Internal Coatings of Oil Drilling Pipes",³⁾ the internal coating of oil drilling pipes should be in accordance with: abrasion resistance or wearability (falling sand test) of 0.2 L/ μm minimum; no blister and no obvious change of coating's adhesion in the condition of high temperature and high pressure: pH12.5, 148°C , 70 MPa for 16 hrs. The tests of $\text{H}_2\text{S}/\text{CO}_2$ corrosion resistance and alkaline medium resistance at high temperature and high pressure are separately done for the two oil tube anti-corrosion coatings.

3.2.1 Test of $\text{H}_2\text{S}/\text{CO}_2$ corrosion resistance at high temperature and high pressure

Test method: According to the testing method specified in NACE standard TM0185, the coating specimens were put in GSH-2T Type Autoclave. The test environment is the static condition simulated that of No.8 gas well in LuoJiaZhai Gas Field: total pressure of 32 MPa, H_2S partial pressure of 3.2 MPa, CO_2 partial pressure of 3.2 MPa, and temperature of 90°C . After test duration of 168 hrs in above condition, the coating's appearance and adhesion were inspected.

Test result: YG-01 oil tube anti-corrosion coating remains intact and good glossy, but a little changed color compared with the specimens not tested. And YG-03 oil tube anti-corrosion coating keeps intact, good glossy and original color after tested for 168 hrs. Both coating's adhesion is almost no change and the metal surface under the coating displays white metal brightness by chiseling V Type line through the coating to inspect.

The test results show that the two oil tube anti-corrosion coatings developed are of very good performance of $\text{H}_2\text{S}/\text{CO}_2$ corrosion resistance at certain high temperature and high pressure. YG-03 oil tube anti-corrosion coating is better than YG-01 oil tube anti-corrosion coating in performance of $\text{H}_2\text{S}/\text{CO}_2$ corrosion resistance at certain high temperature and high pressure.

3.2.2 Test of alkaline corrosion resistance at high temperature and high pressure

Test method: Two specimens insulated each other were

fixed on the special sample frame and put in a static autoclave. The autoclave was filled with corrosion medium of NaOH solution at pH12.5 and closed tightly.

Oxygen in the autoclave was removed by aerating N₂ before testing, and then the autoclave was pressurized to raise temperature and pressure. The testing temperature was set at 150°C and the pressure in autoclave was maintained at 70 MPa by aerating N₂ for 24 hrs. After testing, the pressure in the autoclave was decreased slowly with the autoclave's temperature was naturally cooled down to 93°C. Then the pressure in the autoclave decreased to normal pressure at even rate during 15-30 min. The specimens were taken out and rinsed with clean water, and then the coatings' appearance was inspected at once. The coating's adhesion was tested according to the method specified in appendix C of standard SY/T 0544-2004, when the specimens' temperature cooled down to room temperature.

Test result: Both YG-01 and YG-03 oil tube anti corrosion coatings have no softening and no bulging, but color thinned down a little. The coating's adhesion keeps class A.

3.3 Heat resistance of the coatings

The heat decomposition temperatures of the primer and top coat of both YG-01 and YG-03 oil tube anti-corrosion coatings are determined by using the Differential Scanning Calorimeter (DSC). The results show that the heat decomposition temperature of the primer and top coat of YG-01 is 292°C, and that of YG-03 is 268°C.

The specimens of YG-01 and YG-03 coating are tested in 210°C and 150°C constant temperature ovens respectively. Both coatings keep intact and no blister, cracking, pulverization and other defects appear after 200 hrs' heating test.

3.4 Comprehensive performance of the coatings

In addition to the above performance investigation, com-

prehensive physical and chemical performances of YG-01 and YG-03 oil tube anti-corrosion coatings have been tested according to relevant test standards. The results are shown in Table 1.

4. Conclusions

(1) YG series oil tube anti-corrosion coatings are of excellent salt fog spraying resistance, various acids resistance and boiling oil field waste water resistance. In addition, YG series oil tube anti-corrosion coatings are of good H₂S/CO₂ corrosion resistance and alkaline medium resistance at certain high temperature and high pressure. They have very good comprehensive performance and can meet the spraying needs of internal coating for downhole oil tubes for different corrosion environments.

(2) The application performance of YG-01 baked type oil tube anti-corrosion coating can meet the technical characteristics of existing internal spraying line for oil tubes and drilling pipes in several factories. YG-03 two-component oil tube anti-corrosion coating is of excellent cold setting characteristics and it can be applied by using standard high pressure airless spraying process, easy application.

References

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Table 1. Comprehensive Performance of YG Series Oil Tube Anti Corrosion Coatings

Test item	YG-01	YG-03	Test standards
Adhesion [class]	0	0	GB9286
Impact resistance [cm]	50	50	GB/T1732
Abrasion resistance (1000g, 1000r) [mg]	15.8	16.3	GB/T1768
Abrasion resistance (sand falling test) [L/μm]	2.3	2.0	SY/T0315
Pencil hardness	6H	4H	GB/T6739
Shearing strength [Mpa]	7.2	9.6	SY/T0047
Volume resistivity [Ω·cm]	2.2×10 ¹⁴	3.2×10 ¹⁴	GB/T1410
Dielectric strength [MV/m]	28.7	27.6	GB/T1408.1
H2S saturated solution immersion (R.T.,1000h)	Intact	Intact	GB/T1763
Alkali resistance (20%NaOH, 70°C, 1000h)	Intact	Intact	GB/T1763
Gasoline resistance (R.T.,2000h)	Intact	Intact	GB/T1734
Kerosene resistance (R.T., 2000h)	Intact	Intact	GB/T1734