Study on Atmospheric Corrosion Mechanism and Coating Technology of Steel Oil Storage Tank

Xin Chang

China National Aviation Fuel limited, Northwest Company, xi an, shaanxi, 710082, China.

Abstract

With the rapid development of our country's industry, our country's dependence on petroleum and refined oil is becoming higher and higher, and the use of metal storage tanks is also increasing, but the storage tanks may have certain corrosion during use. The corrosion rate is related to the contact medium conditions, environmental conditions and the structure of the storage tank, Taking certain anti-corrosion measures on the storage tank can effectively extend the design service life of the storage tank and effectively reduce the probability of sudden failure accidents. This article discusses the influencing factors of metal. atmospheric corrosion and the electrochemical mechanism of metal atmospheric corrosion. Modern steel metal storage tanks generally adopt surface spraying anti-corrosion paint for anti-corrosion. Their performance and use are different, and their construction methods are also various. According to its anti-corrosion mechanism to the base metal, it can be divided into three categories: isolation coating, corrosion inhibitor coating and sacrificial coating. Among them, zinc-rich paint is the most typical sacrificial paint, which is widely used in steel oil storage tanks.

Keywords

Steel Oil Storage Tank; Atmospheric Corrosion of Metals; Corrosion Mechanism; Zinc-rich Paint.

1. Introduction

With the development of China's petrochemical industry, the use of metal storage tanks in petroleum and petrochemical products is increasing, and more and more people pay attention to the corrosion prevention problem of oil storage tanks. At present, there are 10 000 m3, 20 000 m3, 50 000 m3 and 100 000 m3 of oil tank volume specifications used in the petrochemical industry in our country. According to the structure, there are vault tank and floating roof tank and other types. According to the steel material, there are 20, 20R, 16Mn, Q235 series. Generally, the designed service life of the oil storage tank is 20 years. If the oil storage tank is not treated with effective anti-corrosion treatment during this period, leakage or corrosion perforation will occur and damage will be caused, which is bound to cause huge economic losses[1].

It is a simple, economical and reasonable method to protect metal oil tank with coating. At present, it is widely used at home and abroad to brush anticorrosive coating on the inner surface of oil tank. Early tank coatings were red lead flaxseed oil, asphalt, phenolic, and vinyl. But red lead flaxseed oil coating service life is short, already eliminated. Bituminous paint when used smell is big, is not conducive to the construction of workers, and in the construction below zero, the paint will become brittle, now rarely used alone, phenolic paint has good water resistance, acid resistance, but the mechanical strength is low, poor adhesion to metal, vinyl resin paint is the drawback of poor adhesion, low solid content. With the development of coating industry, researchers have developed many new high-performance and long-life anticorrosive coatings for oil tanks. Typical anticorrosive conductive coatings include epoxy resin coatings, polyurethane coatings and inorganic zinc-rich coatings.

2. What is corrosion and its harm

We refer to the phenomenon of material damage or deterioration caused by the reaction between materials and environment as corrosion, which can also be considered as a variety of damage of other materials excluding mechanical damage [2]. With time and the progress of science and technology, people for concept also gradually a new understanding of corrosion, corrosion of metal and nonmetal is two part of material corrosion, due to the role of medium such as air, water, metal physics chemical reaction happens, into a new material, and then destruction, this is what people often say that the metal corrosion. From the perspective of thermodynamics, metal corrosion is actually a spontaneous nature, which is a phenomenon that metal materials are affected by the action of the medium and thus change their state, transform into a new phase, and thus suffer damage. And in daily life is also easy to see, therefore, in the corrosion science of metal corrosion research is the top priority.

According to statistics, the steel consumed by corrosion accounts for about 10% of the world's steel production. The direct economic losses caused by metal corrosion are about $700 billion worldwide every year, and the losses caused by metal corrosion in China account for 4% of the gross national product (GNP). Various measures have been used to combat metal corrosion to ensure the reuse of metal resources. Therefore, metal corrosion protection has become a hot research issue in the field of materials.

3. Influencing factors of metal atmospheric corrosion

Atmospheric corrosion of metals is a relatively complex process, which is affected by many factors. It is not only related to the metal itself, but also directly affected by external factors, including meteorological and environmental factors, etc. In general, the corrosion of metals is affected by both meteorological and environmental factors.[3,5]

4. Electrochemical mechanism of atmospheric corrosion of metals

Atmospheric corrosion of metal refers to the phenomenon of electrochemical damage caused by water, oxygen and corrosive media. The corrosion rate of the metal is determined by the thickness of the electrolyte layer on the metal surface, the atmospheric temperature and the speed of oxygen diffusion into the interface between the liquid film and the metal.

4.1 Cathode process

When atmospheric corrosion occurs to metals, depolarization of oxygen is generally the cathodic reaction of corrosion in neutral or alkaline solution, while depolarization of hydrogen is the main reaction in acidic solution. The reaction equation of the cathodic process is:

The reaction equation of the cathodic process in neutral or alkaline medium is:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

The reaction equation of cathodic process in acid medium is:

$$O_2 + 4H^+ + 4e^+ = 2H_2O \tag{2}$$

Under the condition of atmospheric corrosion, oxygen reaches the metal surface rapidly through the liquid film and is continuously replenished. The thinner the liquid film is, the faster the diffusion rate is, and the more effective the depolarization process of oxygen on the cathode is.

4.2 Anode process

The anodic reaction of metal corrosion, The reaction equation is:

$$M + XH_2O \rightarrow M^{n+} \bullet XH_2O + ne^- \tag{3}$$

formula:M is for metal; M^{n+} is N valence metal ions; $M^{n+} \bullet XH_2O$ is Metallic ions combined with hydrates.When the atmosphere corrodes, the electrolyte layer on the metal surface is very thin, and oxygen is easy to reach the metal surface. With the thinning of the electrolyte layer, the role of anode depolarization is also reduced. When the relative humidity is less than 100% and the water absorption of corrosion products is very small, the water supply is not enough to maintain the need of the anodic process, and the anodic process retardation behavior is particularly obvious.

4.3 Rust mechanism

The atmospheric corrosion of metal is very complex. The existing academic conclusion is that the atmospheric corrosion of carbon steel consists of two rust layers inside and outside

Forming, the structure of the inner rust layer is relatively close, and the adhesion between the carbon steel is better, mainly composed of dense amorphous FeOOH and grain Fe3O4; The outer rust layer is mainly composed of loose crystals α-FeOOH and γ-FeOOH. In the case of high atmospheric relative humidity, the rust layer mainly plays the role of a strong oxidant, and the anodic reaction occurs on the metal Fe3O4 interface:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{4}$$

Cathodic reaction occurs at the Fe3O4 /FeOOH interface:

$$6Fe\mathrm{OOH} + 2\mathrm{e}^{-} \rightarrow 2Fe_3O_4 + 2H_2O + 2OH^{-} \tag{5}$$

Therefore, the rust layer on the surface of carbon steel directly participates in the cathodic reaction. When the rust layer is dry, under the action of oxygen, the rust layer forms new oxides. Therefore, in the alternately wet and dry environment, the existence of the rust layer can accelerate the corrosion of carbon steel.

5. Corrosion prevention methods of commonly used metals

Many protective measures have been taken to reduce the damage caused by metal corrosion. At present, in many anti-corrosion methods, the use of coating for anti-corrosion method because of its manufacturing convenience, low price, strong economic applicability, excellent performance and some other methods of incomparable advantages and exclusive first. It not only plays a protective role on the substrate, but also has the function of decoration and beautification, so it often becomes the object of priority for anticorrosion measures.

The commonly used coating is organic coating, metal coating, inorganic coating, etc. Among them coating is widely used in the application of coating. China's coating products are divided into 17 categories, nearly 900 varieties and models, their performance and use are different, the construction method is also a variety of, according to the corrosion mechanism of the base metal can be divided into isolation coating, corrosion inhibition coating and sacrificial coating three categories [6]. The zinc-rich coating widely used today is a typical sacrificial coating.

5.1 Classification and film forming mechanism of inorganic zinc-rich coatings

According to the film forming materials, inorganic zinc-rich coatings can be divided into two categories: water-based inorganic zinc-rich coatings based on silicate and solvent based on ethyl orthosilicate. At present, solvent-based inorganic zinc-rich coatings are widely used at home and abroad.

Zinc - rich coating zinc powder has granular (spherical, amorphous) and flake two. In the world, the performance of flake zinc powder is better than that of granular zinc powder and is widely used. But the production process of flake zinc powder is complex and expensive, so it is less used in our country.

The commonly used inorganic zinc rich coatings are composed of a group (solid) and a group (liquid) composed of two components.The mixture of group A and group B interacts with the substrate and finally forms a stable film with excellent properties. At present, the base material of inorganic zinc rich coating is mainly composed of silicate aqueous solution, in which Si-O bond (liquid) and zinc powder (solid), iron on the surface of steel to generate silicate polymer. At the same time, the absorption of water and carbon dioxide in the air, to generate an insoluble film and mesh zinc silicate complex, the complex is insoluble, due to the special structure of the complex, thus polymerized into a huge network, play a role in protecting steel, the reaction is irreversible.

5.2 Anti-corrosion mechanism of inorganic zinc-rich coatings

The protection mechanism of zinc-rich coating includes electrochemical protection, shielding effect, self-repair and passivation of coating film.

In the early stage of corrosion, zinc powder, the main material of zinc rich coating, is relatively active compared with the main material of steel oil storage tank. The potential of zinc powder is lower than that of iron, so the zinc in the coating film is corroded first as the anode, and Fe is corroded as the cathode. Its reaction formula is:

$$\text{Anode area: } Zn \rightarrow Zn^{2+} + 2e^{-} \tag{6}$$

$$\text{Cathode area: } Fe^{2+} + 2e^{-} \rightarrow Fe \tag{7}$$

In the later stage of corrosion, zinc powder in the zinc rich coating produces oxides in the form of sacrificial anode to play a shielding role on the coating, so that the system is still separated from the outside world. Air and moisture are not easy to enter the system to avoid contacting steel, so the coating can be strengthened to protect the bottom material of the oil storage tank. At the same time, the corrosion product of zinc blocks the shielding and the corrosion of the corrosion medium, reacts with the H20 and CO2 in the air to generate "white rust" (Zn CO3·3 Zn(OH)2), and through the sacrifice of anode to generate Zn(OH)2 to achieve corrosion resistance, so that zinc powder has a certain self-repair effect. The reaction equation is as follows:

$$Zn + 2\mathrm{H}_2O \rightarrow Zn(0\mathrm{H})_2 + H_2 \tag{8}$$

$$\mathrm{Zn} + \mathrm{H2O{+}CO_2} \rightarrow \mathrm{Zn\ CO3{+}\ H_2} \tag{9}$$

$$\mathrm{Zn(OH)2} \rightarrow \mathrm{ZnO{+}\ H2O} \tag{10}$$

$$\mathrm{5\ ZnO{+}\ 3H2O{+}2CO2} \rightarrow \mathrm{2ZnCO_3} \bullet \mathrm{3Zn(OH)2} \tag{11}$$

During production, once the damaged part on the coating film is coated, the anti-corrosion current will flow to the damaged part on the steel, and the corrosion products of zinc will be deposited on the damaged part to form a new protective film, which can protect the container through the automatic repair method of the coating film [7,8]. The pH value of the solution is related to the water content in the solution. When the water evaporates, the concentration of the solution in the coating gradually increases, and the pH value of the coating changes accordingly, which leads to the change of the electrode potential of the substrate. Due to the obvious passivation effect of coating on steel, corrosion phenomenon will not occur in the process of coating drying and film forming [9,10].

5.3 Development status and application of zinc-rich coatings on storage tanks

Zinc rich coating is a kind of coating which contains a lot of active catalpa powder, and the content of zinc powder in dry film is between 85% and 95%. Generally used as a primer, it has excellent rust and corrosion resistance in extremely harsh atmosphere, oil and water candle decay environment [11,13]. Zinc rich coating can be divided into inorganic catalpa rich coating and organic catalpa rich coating. Inorganic zinc-rich coatings use inorganic curling agent, whose zinc powder reacts with the base paint and forms an inorganic chemical structure with the coated metal. Inorganic zinc-rich coatings are used for corrosion prevention of various storage tank equipment in production and life . Inorganic zinc-rich coating can achieve good antistatic purpose in the current complex storage tank area, because of its small surface resistance, the national antistatic coating standard surface resistance is 5×105-5×107Ω, its resistance is only 5×103-5×104, less than the national standard. Organic rich zinc coating, generally use ring gas resin, get together atmosphere vinegar resin for the base paint, and inorganic rich catalpa coating compared, its characteristic is paint film adhesion is strong, mechanical property is good, but its heat resistance, electrical conductivity, solvent resistance as inorganic rich catalpa coating. The commonly used organic zinc - rich coatings are H06-4 epoxy catalpa - rich primer. But in recent years along with the development of science and technology, and the regulation of environmental protection law to VOC (organic volatile matter) limit, each country in the world also gradually attaches importance to environmental protection rise, the research and development of coating also gradually to environmental protection coating close. Inorganic coatings also gradually, from the initial most basic solvent-based ethyl orthosilicate to the general research of water-based silicate direction.

6. Summary

The wide use of large steel oil tanks, to modern anti-corrosion technology research has a good promoting effect, due to limited space, this paper briefly from the influence factors of metal atmospheric corrosion and electrochemical corrosion mechanism aspects elaborates the research, reveals the root cause of the metal atmospheric corrosion, enable us to follow-up in terms of metal steel oil tank corrosion have good understanding. At the same time, the classification, film forming mechanism and corrosion prevention mechanism of inorganic zinc-rich coatings are explained according to the research on corrosion prevention methods of commonly used metal coatings in recent years. It is described that inorganic zinc-rich coatings have good rust prevention and corrosion prevention effects in extremely harsh atmosphere, oil and water decay candle environment, so that they are widely used in steel oil storage tanks.

References

[1] JIANG Zhenhai. Corrosion and Protection of Crude Oil Storage Tank [J]. Corrosion and Protection, 2006, 027(003):161-162.

[2] Wang Xingqing. Corrosion and protection of thermal equipment. Beijing: Water Conservancy and Electric Power Press, 1998:1.

[3] Arroyave C, Lopez FA,Morcillo M.The early atmospheric corrosion stages of carbon steel in acidic fogs[J]. Corrosion Science, 1995,37(11):1751-1761.

[4] Yamashita M, Miyuki H, Matsuda Y, et al. The long term growth of the protective rust layer formed on weathering steel by atmospheric corrosion during a quarter of a century[J]. Corrosion Science, 1994, 36(2):283-299.

[5] Qu Q. Soluble salt deposition and the role of SO2 in the early atmospheric corrosion of metals [D]. Institute of Metal Research, Chinese Academy of Sciences, 2002.

[6] Yu Xiaohui, Zhu Xiaoyun, Guo Zhongcheng, Long Jinming. Preparation of scaly zinc based epoxy zinc-rich anticorrosive coatings. Surface Technology, 2005,34 (1) : 53-55.

[7] Cai S. Research progress of waterborne inorganic zinc rich coatings [J]. Shanghai Paint & Coatings, 2009, 47(002): 23-27.

[8] Xie Beibei, Zhang Yingying, Han Wenli. Research and application of alcohol-soluble inorganic zinc rich coating [J]. Modern Paint and Coating, 2011(07):10-13.

[9] REN Hongxing. Research on Spraying Process of Inorganic Zinc-rich Primer [D]. 2015.

[10] Brevoort Gordon H. Inorganiczinc-rich coating sand galvanizinga comparison. J. Protective Coatings &Linings, 1996, 13(9):66-74.

[11] Li Jingui. Inorganic zinc-rich coating on the surface of pot iron components. China Surface Engineering, 2003, (5):1~4.

[12] Zhang Zuwen, Wang Jun. Salt resistance and stability of epoxy zinc rich coatings [J]. China Coatings,2003 Supplement: 29~32.

[13] ZHOU Wentao, LI Xiaoqin. Properties and application of inorganic zinc-rich coatings. Hubei Chemical Industry, 2002 (5); 26 ~ 27.