

Review Paper on The Research and Development of Corrosion Inhibitors

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ABSTRACT

Corrosion problems are widely found in various industries, and corrosion inhibitors also play an important role in various corrosion environments, especially in oil exploration. However, as China's oilfield exploitation enters a high water injection period, the mining environment is becoming more and more harsh, and the requirements for oilfield corrosion inhibitors are getting higher and higher. At the same time, various scaling phenomena have emerged one after another in the process of oilfield exploitation. The corrosion and scale inhibitor with good scale inhibition reflects its advantages, and the integration of corrosion and scale inhibition has become a major tendency in the development of corrosion inhibitors. This review introduces different corrosion inhibitors, and focuses on the research on corrosion inhibitors at home and abroad. At the end of the review, it puts forward views on the future development direction of corrosion inhibitors.

KEYWORDS

Corrosion inhibitor; mechanism of action; development prospects of corrosion inhibitor.

1. RESEARCH BACKGROUND

As the exploitation of most oil fields in China enters the middle and late stage, in order to improve the mining efficiency, the water injection of the oilfield has increased, resulting in a gradual increase in the moisture content of crude oil and the mineralization of the extracted liquid. For low-permeability oil layers, the production rate can be effectively improved by injecting CO₂ into the oil layer, which is one of the important means to improve the recovery rate of crude oil.

While enjoying the higher benefits brought by CO₂, the corrosion problem caused by CO₂ cannot be ignored. In fact, in a specific pH environment, the acid corrosion formed by CO₂ may be more serious than that of sulfuric acid and hydrochloric acid [1]. In the collection and transmission system, the dissolution of CO₂ in the extract will form a corrosive medium with a certain acidity, which is easy to cause serious problems such as pipeline corrosion and perforation leakage, shortening the service life of the equipment, causing huge economic losses and damage to the environment.

The method of slowing down the corrosion of pipeline equipment in the process of oil and gas collection is not single, but the injection of corrosion inhibitors is more economical and convenient than other methods. The special environment brings new adsorption stability, performance persistence and synergy effect of corrosion inhibitors. Challenge. [2]

2. RESEARCH ON CORROSION INHIBITORS AT HOME AND ABROAD

As early as the 1860s, Britain published the first corrosion inhibitor patent. Foreign scholars continue to deepen their research on corrosion inhibitors on the basis of their predecessors. In 1973, L.A. Mc Dougall et al. found that the compounding of alkyne alcohols, quaternary ammonium salts, carboxylic acid derivatives and surfactants had a good effect on corrosion inhibition in high concentrations of hydrochloric acid [3]. At the same time, various types of corrosion inhibitors are also constantly developing and improving, and play a dominant role in modern environmentally friendly corrosion inhibitors.

The research on corrosion inhibitors in China started later than that in foreign countries, but after continuous exploration by Chinese scholars, the relevant research has been continuously improved. In the 1990s, antimony compounds were introduced as high-temperature corrosion inhibitors for the first time in China. More and more research results have appeared in domestic corrosion inhibitors. Li Qianding [4] and others added acetone to the Mannich reaction. By controlling the reaction conditions, different hydrogen atoms in the molecule had a Mannich reaction separately, and obtained a main agent of an oil and gas well acidification corrosion inhibitor. Zhang Jun [5] and others used quantum chemical simulation to study eight kinds of imidazoline corrosion inhibitors, and found that the reactive activity areas of imidazoline molecules were distributed on the imidazole ring and its polar functional groups. Until now, corrosion inhibitors tend to be multi-functional, corrosion inhibitory and scale-inhibition integration, and are becoming more and more friendly to the environment.

3. MECHANISM OF ACTION OF CORROSION INHIBITORS

3.1. Adsorption theory

Adsorption theory usually refers to chemical adsorption and physical adsorption, which are mainly chemical adsorption types. In acidic media, corrosion inhibitors form a directional arrangement by adsorbing on the metal surface, thus isolating metals and corrosive substances and play a role in slowing down corrosion. In addition to chemical adsorption and physical adsorption, there are other adsorption theories. Double bonds, three bonds or benzene ring organic molecules containing π electrons can also effectively adsorb on the metal surface to inhibit corrosion.

3.1.1. Factors affecting physical adsorption

In addition to being affected by temperature and corrosion inhibitor concentration, electrostatic gravity or van der Waals force is the main factor affecting the physical adsorption effect, especially electrostatic gravity. Under the action of electrostatic gravity, the indium ion is adsorbed on the metal surface, which greatly improves the activation energy required by the hydrogen ion to obtain the electron, thus slowing down the corrosion of the metal surface. [6]

3.1.2. Factors affecting chemical adsorption

The empty orbit of the atom in the center of the corrosion inhibitor can form a coordination bond with the lone electron pair on the metal surface, so as to have the effect of corrosion inhibition. Therefore, this adsorption is greatly affected by the molecular structure, and the corrosion inhibition effect is affected by the density of the central atomic electron cloud.

3.2. Electrochemical Theory

The corrosion inhibitor participates in the electrochemical reaction in the electrolyte and slows down the corrosion of the metal by affecting the cathode or anode. Corrosion inhibitors can be divided into

anode corrosion inhibitors, cathode corrosion inhibitors and mixed corrosion inhibitors according to the electrochemical mechanism.

3.3. Phase-membrane theory

In film formation theory, the corrosion inhibitor forms a dense film on the metal surface through chelation with metal ions to inhibit the corrosion of the metal in the corrosion environment; or the corrosion inhibitor reacts with the ions in the corrosion solution on the metal surface to form a deposition film, covering the metal surface to play a protective role. [7] Because it is relatively difficult to form a protective film in acidic media, it is often used in neutral media.

4. CLASSIFICATION OF CORROSION INHIBITORS

Corrosion inhibitors are widely used in various corrosion environments due to the advantages of low cost, high efficiency and simple operation, and the addition of corrosion inhibitors does not affect the corrosion environment. [8] You only need to add a small amount of corrosion inhibitors to slow down the corrosion and protect the metal material, and while slowing down the corrosion, it can also keep the original physical and mechanical properties of the metal material unchanged. In particular, it has played an important role in oil and natural gas exploration and drilling projects, effectively reducing the corrosive effect of acidic substances contained in oil and natural gas on drilling equipment and oil and gas pipelines, and prolonging the service life of equipment. [9] Different corrosion inhibitors vary due to their different structures and groups.

4.1. Classification according to chemical composition

4.1.1. Organic corrosion inhibitor

Organic corrosion inhibitors are often used in acidic environments. Organic corrosion inhibitors containing nitrogen have a good corrosion inhibitory effect in oilfield sewage. For example, Manich base corrosion inhibitors, quaternary ammonium salt corrosion inhibitors, imidazoline corrosion inhibitors and other corrosion inhibitors are the main research objects of acidic corrosion inhibitors. [10]

(1) Manich base corrosion inhibitor

Manich alkali corrosion inhibitors are mixed corrosion inhibitors, which can be adsorbed on the anode and the cathode at the same time to form a protective film, inhibiting the cathode and anode reaction process, thus playing a role in corrosion inhibition.

(2) quaternary ammonium salt corrosion inhibitor

Quaternary ammonium salt is the salt of quaternary ammonium cations formed when four hydrogen ions in ammonium ions are replaced by hydrocarbon groups. As an ionic salt, it has excellent high temperature resistance [11]. At the same time, quaternary ammonium salt corrosion inhibitors have the advantages of no special irritating odor and low toxicity, and are widely used in industry.

(3) Imidazoline corrosion inhibitor

Imidazole corrosion inhibitor is a mixed corrosion inhibitor, which is an organic compound formed by connecting alkyl hydrophobic branch chains of different carbon chain lengths on the basis of imidazoline structure [12].

(4) Compound corrosion inhibitor

At present, in the oil and gas mining corrosive media rich in CO₂, corrosion inhibitors are not only facing the problem of acidic corrosion, but also the problem of metal scaling. In order to develop

corrosion inhibitors with better performance, two different corrosion inhibitors are often compounded to improve corrosion inhibitory performance while enhancing scale inhibitory performance.[13]

4.1.2. Inorganic corrosion inhibitor

Inorganic corrosion inhibitors also represent a large class of corrosion inhibitors. Because of their different chemical structures, they have different corrosion inhibitory mechanisms. It is mainly divided into two types: metal cationic corrosion inhibitor and extreme passivation corrosion inhibitor.

4.2. Classification according to the type of protective film

According to the different types of protective films generated, corrosion inhibitors can be divided into: oxide film corrosion inhibitors, precipitation film corrosion inhibitors, and adsorption film corrosion inhibitors.

4.2.1. Oxidizing film-type corrosion inhibitor

The oxide film corrosion inhibitor can form a passivated film on the metal surface. The passivated film can effectively isolate the metal and the corrosive medium, which has a good corrosion inhibition effect. Common oxide film corrosion inhibitors are: aluminate, nitrite, chromate, borate, etc. However, the corrosion inhibitor effect of this type depends on the concentration of the corrosion inhibitor. When the amount of corrosion inhibitor is insufficient, the corrosion inhibitor effect becomes worse.

4.2.2. Precipitation film-type corrosion inhibitor

The precipitation corrosion inhibitor forms a precipitation film on the metal surface through chemical reaction. Common precipitation film corrosion inhibitors are: sodium polyphosphate, sodium hexametaphosphate, etc. However, this corrosion inhibitor has obvious drawbacks:

1. The precipitation film has poor adsorption on the metal surface;
2. As the chemical reaction continues, it is easy to scale.

4.2.3. Adsorption film corrosion inhibitor

Most adsorption film corrosion inhibitors are organic corrosion inhibitors, and their polar groups can be directionally adsorbed on the metal surface to form a layer of adsorption film. The adsorption corrosion inhibitor has excellent corrosion inhibition performance, but when the metal surface is scaled, it will affect the formation of the adsorption film, and it should be used at the same time. Common adsorbent corrosion inhibitors include some amines and azole corrosion inhibitors. However, the high temperature will promote the shedding of the adsorption film to a certain extent. [14]

5. CONCLUSION

In the face of high corrosion, high temperature and various severe corrosion environments caused by H_2S and CO_2 , corrosion inhibitors will develop in the direction of high temperature resistance, H_2S and CO_2 corrosion resistance. At the same time, the complex medium environment requires that corrosion inhibitors continue to develop towards a multi-functional type, and the demand for composite corrosion and scale inhibitors has increased. In the process of development, improving the performance of corrosion inhibitors is only one aspect, and it is becoming more and more important to find more environmentally friendly and less toxic corrosion inhibitors.

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REFERENCES

- [1] He San, Rossi, Zhao Haotong, etc. Research progress on corrosion of carbon steel under inorganic scale in CO₂ environment [J]. Surface technology, 2023,52(02):148-157. DOI:10.16490/j.cnki.issn.1001-3660.2023.02.013.
- [2] He Shasha, Han Xinfu, Lai Xixiang, etc. Research progress on corrosion inhibitor strategy and corrosion inhibition behavior of CO₂ corrosion of carbon steel [J]. Surface technology, 2023,52(07):117-129.
- [3] Dusen. Synthesis of heterocyclic corrosion inhibitors and evaluation of corrosion inhibition performance [D]. Xi'an Petroleum University, 2019.
- [4] Li Qianding, Wang Jingguang, Yu Hongjiang, etc. Development of a new type of high-efficiency oil and gas well acidification corrosion inhibitor [J]. Natural gas industry, 2008(02): 96-98+171-172.
- [5] Zhang Jun. Theoretical study on the corrosion inhibition mechanism of imidazoline corrosion inhibitors [D] Qingdao: School of Mechanical and Electrical Engineering, China University of Petroleum, 2008.
- [6] Li Congni. Research progress of acidifying corrosion inhibitors in oilfields [J]. Surface technology, 2016, 45(08):80-86. DOI:10.16490/j.cnki.issn.1001-3660.2016.08.014.
- [7] Li Qing. Synthesis and properties of Manich base quaternary ammonium salt corrosion inhibitor [D]. China University of Petroleum (East China), 2021. DOI:10.27644/d.cnki.gsydu.2021.000842.
- [8] Li Jing, Li Ke, Zhao Shilin. Synthesis and application of polyphosphate pickling corrosion inhibitor [J]. Natural Gas Industry, 2004(11):79-81+20.
- [9] Sui Yanze. Performance evaluation and theoretical research of dithiazole corrosion inhibitors [D]. Harbin Institute of Technology, 2022. DOI:10.27061/d.cnki.ghgdu.2020.006495.
- [10] Dong Qiuchen. Study on the synthesis, corrosion inhibition performance and mechanism of aromatic cyclic quaternary ammonium salt organic corrosion inhibitors [D]. Shaanxi University of Science and Technology, 2021. DOI:10.27290/d.cnki.gxbqc.2020.000192.
- [11] License, Liu Boxiang, Liu Chen, etc. Research progress of high-temperature fracturing fluid and high-temperature corrosion inhibitor [J]. Chemical Engineer, 2023,37(09):72-77. DOI:10.16247/j.cnki.23-1171/tq.20230972.
- [12] Pang Honglei. Synthesis and compounding of imidazoline oleate corrosion inhibitors [D]. North China University of Technology, 2020. DOI:10.27108
- [13] Yang Qingzheng, Zhang Tailiang, Liu Congsheng, Bai Yi, Cheng Xin, Zheng Cunchuan. Preparation and corrosion inhibition mechanism of Gemini imidazole quaternary ammonium salt corrosion inhibitor [J]. Chemical progress: 1-13.
- [14] Huang Jiahe, Yuan Xi, Chen Wen, etc. Study on the influence of temperature on the corrosion behavior of N80 and TP125V steel in the environment of CO₂ saturated shale pressure cracking liquid [J]. China Journal of Corrosion and Protection, 2023,43(02):251-260.