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Research Progress on Types and Mechanism of Common Organic Corrosion Inhibitors

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Abstract: In this paper, several kinds of common organic corrosion inhibitors, such as heterocyclic, aldehydes and ketones, organic phosphonic acid, are introduced. The development prospects and application limitations of some corrosion inhibitors are discussed and pointed out. There are also studies have shown that usually two or more corrosion inhibitors are combined or better than a single corrosion inhibitor. Taking the effect as the introduction point, the mechanism of action of organic corrosion inhibitors is generally recognized. Finally, the future research direction of organic corrosion inhibitors is prospected.

Keywords: Organic Corrosion Inhibitor; Compound; Corrosion Inhibition Mechanism.

1. Foreword

In the process of oil and gas field development, metal materials are widely used, and most metals are generally subjected to irreversible corrosion damage, causes huge economic losses. It may also cause huge security threats due to factors such as corrosion perforation. According to statistics, the economic losses caused by corrosion account for about 3.4% of world GDP [1].

In order to solve the economic and property losses caused by pipeline corrosion, adding corrosion inhibitors to pipelines is one of the commonly used pipeline corrosion protection technologies. Organic corrosion inhibitors are usually composed of polar groups centered on atoms such as N/O/S with large electronegativity and non-polar groups composed of atoms such as C/H, which can be combined with metal surfaces in the form of certain bonds to inhibit corrosion [2]. This paper focuses on different organic corrosion inhibitors and their mechanism.

2. Common Organic Corrosion Inhibitors

2.1. Heterocyclic Compounds and Their Mechanism of Action

Organic heterocyclic corrosion inhibitors have excellent corrosion inhibition effect, no special odor, low toxicity and good thermal stability. Heterocyclic organic corrosion inhibitor compounds include imidazoles and their salts, quinolines and their salts, pyridines and their salts, benzotriazole and their derivatives. They can interact with the metal surface to form a dense insoluble protective film to achieve the isolation of metal and corrosive medium to achieve corrosion inhibition.

2.1.1. Imidazoles and Their Derivatives

Although heterocyclic corrosion inhibitors have a long history, only imidazoline corrosion inhibitors have been continuously developed and gradually become the mainstream of heterocyclic corrosion inhibitors [2].

Imidazoline corrosion inhibitors are five-membered heterocyclic compounds containing (inter) nitrogen atoms. The heterocyclic ring is composed of a hydrophilic group R1 (amide group, hydroxyl group, amino group, etc.) with different activities bonded to nitrogen and an alkyl hydrophobic branch R2 with different carbon chains [3]. The polar groups on the nitrogen-containing five-membered ring can increase its solubility in corrosive solutions, and the atoms containing the lone pair electrons of the P orbital in the polar group will form a coordination bond with the iron atoms of the empty d orbital on the metal surface, increasing the activation energy of the metal surface makes the adsorption a permanent behavior [3]. The non-polar groups on the ring will be far away from the metal surface, forming a directional hydrophobic film in the corrosion solution, effectively preventing the ion exchange between the metal surface and the corrosion medium, and playing a role in slowing down the corrosion [4].

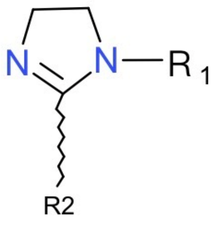

Figure 1. Molecular structure of imidazoline

Ordinary imidazoline is difficult to cope with different corrosion environments. Through modification, structures or groups that enhance molecular adsorption are introduced into imidazoline, so that the film forming and adsorption of imidazoline molecules are stronger, and the purpose of increasing corrosion inhibition effect is achieved. For example, Guo et al. [5] synthesized a corrosion inhibitor with lauric acid and hydroxyethyl ethylenediamine as raw materials, and the corrosion inhibition rate of A3 steel reached 93.1% at 50°C in 10% HCL solution. Wang Tengfei and Zhang Guanghua [6] synthesized thiourea imidazoline quaternary ammonium salt. When the mass concentration of corrosion inhibitor was 50mg / L, the corrosion inhibition rate was 98.3% in 1.0mol/L HCl solution at 80°C. The oleic acid imidazoline benzyl chloride quaternary ammonium salt synthesized by Liu Libo [4] et al.by solvent method has a corrosion inhibition rate of 99.05% for A3 steel sheet at 20°C when the corrosion inhibitor concentration is 1400 mg/L. The SEM analysis of A3 steel sheet after static corrosion shows that its pitting resistance is better than that of imidazoline sulfate quaternary ammonium salt.

2.1.2. Quinoline and its Derivatives

Quinoline is a nitrogen-containing bicyclic heterocyclic organic compound with a molecular formula of C9H7N, in which the pyridine part is fused with the benzene ring. The structural formulas of quinoline and 8-hydroxyquinoline are shown in the figure. Quinoline is a hygroscopic liquid with strong odor. It has high solubility in hot water and most organic solvents [8]. Because it contains nitrogen-containing heterocycles, it has low toxicity.

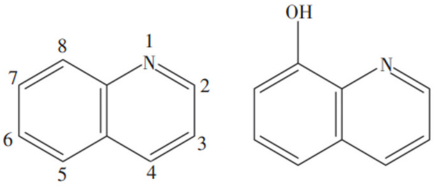

Figure 2. Quinoline and 8-hydroxyquinoline structural formula

Due to its high electron density, quinoline can interact strongly with the metal surface. Quinoline derivatives have better corrosion resistance than quinoline itself. Chen et al. [9] tested the corrosion inhibition efficiency of 5-phenyl-8-propyl quinoline on Q235 steel in 0.5mol/L sulfuric acid. When the concentration is 8mol/L, it can provide 97.5% protection efficiency. Verma et al. [10] studied the anticorrosion effect of 2-amino-4-(2,4-dihydroxyphenyl) quinoline-3-carbonitrile on SAE1006 steel in 1mol/L hydrochloric acid solution. Wang et al. [11] showed that 8-aminoquinoline and 8-nitroquinoline (8-NQ) could provide 89.5% and 87.0% protection efficiency. Ergodan et al [12] found that the higher the electron-donating tendency of the substituent, that is, (-NMe2) > (-OMe) > (-Me) > (-H), the better the protective effect of quinoline derivatives.

2.1.3. Benzotriazole Corrosion Inhibitors

Benzotriazole has been widely known as an efficient copper corrosion inhibitor, which can prevent some adverse surface reactions. The chemical structure of benzotriazole (BTA) is C6H5N3, which is the most important azole derivative and is generally considered to be a very effective corrosion inhibitor.

The corrosion inhibition performance of benzotriazole is better than that of triazole, and it mainly inhibits the cathodic corrosion process. Therefore, benzotriazole is used as raw material for modification. Zuo et al. [13] prepared two bisbenzotriazole compounds by reacting benzotriazole and anhydrous ethanol with methylamine and aniline, respectively. Li Weiguang et al. [14] first reacted with oleic acid and β-hydroxyethyl ethylenediamine to form an imidazoline intermediate, and then reacted with benzotriazole to form a new benzotriazole imidazoline corrosion inhibitor. Diethylaminomethyl benzotriazole (DMBM), a Mannich base corrosion inhibitor, was synthesized from formaldehyde, benzotriazole and diethylamine by Wang Jingang [15].

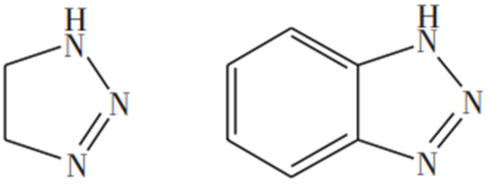

Figure 3. Triazole and benzotriazole

2.2. Aldehydes and Ketones and Their Mechanism of Action

The main feature of these compounds is that the molecule contains a double bond or ketene structure, which can adsorb metals. Because of its good stability, it is generally used in harsh environments such as high temperature acidification, and shows good corrosion inhibition effect in strong acid medium.

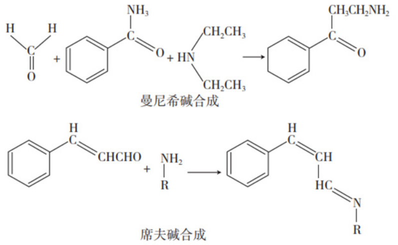

Figure 4. Aldehyde ketone corrosion inhibitors

The Mannich base molecule is a chelating ligand, which contains multiple oxygen atoms and nitrogen atoms with lone pair electrons, and these atoms are separated by 2-3 non-coordinated atoms. The lone pair electrons of its coordination atoms enter the dsp empty orbit of the iron atom to form a coordination bond, and complexation occurs to form a more complete hydrophobic protective film [16]. The adsorption film increased the reduction oxidation potential of H^+, weakened the discharge effect, and mainly inhibited the cathodic reaction. Schiff base compounds contain heteroatoms such as N and O and C=N bonds. Heteroatoms containing lone pair of electrons are easy to form coordination covalent bonds with metals to produce chemical adsorption. Organic compounds containing π bonds are easy to interact with metals. Therefore, Schiff base compounds are easy to adsorb on the surface of metals to form a dense molecular film, which can effectively block the erosion of metals by corrosive media [17].

2.3. Organic Phosphonic Acid and its Action Mechanism

The organic phosphonic acid molecule contains a phosphate group directly connected to the carbon atom. it has good stability. The monodentate, bidentate or tridentate structure contained in their molecules can easily adsorb on the metal surface to form a protective layer and reduce the area of the active metal exposed to the corrosive environment [18]. It is suitable for cooling water system with high hardness, high humidity, high pH value and high temperature.

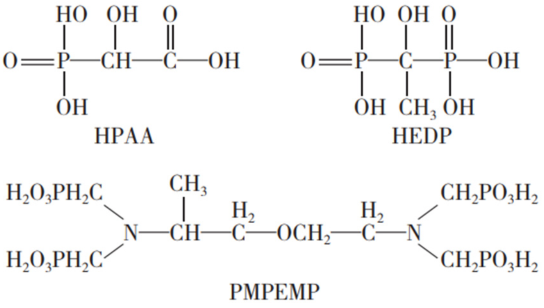

Figure 5. Organic phosphonic acid anticorrosion agent

Ether-containing organic phosphonic acids represented by polyaminopolyether methylidene phosphonic acid (PAPEMP) have developed rapidly and showed good corrosion inhibition effect. AMAR et al [19] studied the corrosion inhibition of piperidine-1-phosphonic acid (PPA) and (4-phosphono-piperazin-1-yl) phosphonic acid (PPPA) on iron in 3.5% NaCl solution. The results showed that the adsorption of the two inhibitors was consistent with the Langmuir adsorption isotherm. When the concentration of the inhibitor was 5×10^3 mol/L, the inhibition efficiencies of PPA and PPPA were 77.1% and 93.2%, respectively. The results of PRABAKARAN et al. [20] showed that the synergistic corrosion inhibition system composed of PPA with mass concentration of 75mg/L and Zn^{2+} with mass concentration of 100mg/L had the best effect, and the corrosion inhibition efficiency could reach 90%.

The phosphonate group of organic phosphonate compounds is a polar group. In a specific molecular structure, if the 2p orbital of the phosphorus atom in the molecule enriches electrons, these unpaired electron clouds will form a coordination bond with the empty orbital of the metal surface under the action of the polar group 'pushing electrons' to inhibit corrosion in the form of an adsorption film. If the organic phosphonate compound molecule has two (or more) 'push electron sites', the compound may act on the metal surface in a planar adsorption manner and become an excellent organic corrosion inhibitor [21].

2.4. Green Environmental Protection

Green, environmentally friendly and efficient corrosion inhibitors have become the focus of attention. Natural, pollution-free and non-toxic products have become one of the main research objects.

People have extracted some effective components from animals and plants for research, and found that some of them showed a certain corrosion inhibition effect. For example, the extracts of pepper, tea, peel, etc., such as piperine, caffeine, amino acids, etc., are compounded with water-soluble imidazoline derivatives. In 5%-10% hydrochloric acid, the corrosion inhibition rate of carbon steel at 40°C can reach 95%. When the tea saponin was compounded with amines and nitrogen-containing compounds, the corrosion inhibition rate of carbon steel could reach 93% at 40°C in 10% hydrochloric acid. Ma Wei [22] proposed to polymerize the natural polymer kelp extract with related substances. The obtained corrosion inhibitor has good protection for carbon steel and copper in acidic and neutral media. StephemJJ extracts rosin amine biology, imidazoline and its derivatives from rosin, as a highly stable low-toxic corrosion inhibitor for steel, the application effect is good. These substances can play a role in corrosion inhibition, mainly because these substances contain the required functional groups (N, S, O, P and other heteroatoms and unsaturated bonds, etc.), can play a role in corrosion inhibition [22-23].

3. The Compounding of Corrosion Inhibitors

The synergistic mechanism of corrosion inhibitors generally has the following several kinds : 1) When there is an active anion, the bridging effect of the negative end of the active ion-metal dipole towards the solution is beneficial to organic adsorption;2) The corrosion inhibitor forms an adsorption layer on the metal surface, and the adsorption promotes the stability of the adsorption layer;3) The same adsorption mechanism between substances produces a synergistic effect by adding cooperation[24]. Using the synergistic effect, less corrosion inhibitors can be used to obtain better results and solve the problem that a single agent is difficult to overcome.

Using the synergistic effect, less corrosion inhibitors can be used to obtain better results and solve the problem that a single agent is difficult to overcome. Xu Guomei et al [25] combined BTA with inorganic substances such as sodium silicate and sodium nitrate, and applied it to 10% NaCl solution, the corrosion inhibition rate was greatly improved. In the seawater purification system, BTA is compounded with sodium molybdate and sodium polyphosphate, and the corrosion inhibition rate can reach more than 95%.

4. Mechanism of Organic Corrosion Inhibitor

4.1. Film Forming Principle

Film inhibition is divided into two ways: one way is to add oxidants such as chromate and nitrite to the corrosive medium, and form an oxide film or passivation film on the metal surface to inhibit the corrosion process; another way is that the groups on the organic corrosion inhibitor molecules interact with the corroded metal ions to form an insoluble film to play a corrosion inhibition role. For example, benzotriazole reacts with copper to form an insoluble polymer film to inhibit copper corrosion, and mercaptan, quinoline and iron in acidic media. The formation of a precipitation film inhibits corrosion.

4.2. Adsorption Principle

The non-polar groups composed of C and H atoms form a hydrophobic protective layer on the metal surface, which hinders the transfer of charges or substances related to the corrosion reaction and reduces the corrosion rate. According to the nature and strength of the adsorption force of the corrosion inhibitor on the metal surface, it can be divided into two categories: physical adsorption and chemical attachment.

4.3. Principle of Electrode Process Inhibition

If the generated protective film is in the cathode region, it will hinder the supply of electron acceptor, resulting in polarization of the cathode. Therefore, it can be seen that because of the addition of corrosion inhibitors and the formation of a protective film, whether it is on the anode or cathode of the corrosion system, or both have a polarization, it will reduce the corrosion current, resulting in a slower rate of metal corrosion.

5. Summary and Prospect

The low toxicity and high efficiency of organic heterocyclic corrosion inhibitors are one of the priority choices for corrosion inhibition. There are many kinds of organic heterocyclic corrosion inhibitors. They are combined with metals through heteroatoms N/O/S, etc., covering a layer of protective film and forming coordination bonds with metals. In the future, considering the corrosion inhibition effect in combination with all the above types, organic corrosion inhibitors with larger systems and more compounding schemes will be developed through modification. The corrosion inhibition mechanism of corrosion inhibitor system was studied by atomic calculation. The necessary toxicology experiments should also be carried out, and the green development route should be taken to evaluate the possibility of toxicology and secondary chemical reaction pollution of organic corrosion inhibitors.

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