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Synthesis and Research Progress of Mannich Base Corrosion Inhibitor

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Abstract: The development process and reaction mechanism of Mannich reaction are introduced, the three main structural types of Mannich base corrosion inhibitors are summarized and their characteristics are compared, and the principle and influence of Mannich base corrosion inhibitors are emphasized. The factors are elaborated and analyzed in detail, and finally the research status and application prospects of Mannich bases are discussed.

1. Introduction

At present, acidification is an effective oilfield stimulation method. It improves the recovery rate of the oilfield to a certain extent by injecting acid liquid downhole; but at the same time, this method also affects oilfield pipes and downhole metal equipment. Produce different degrees of corrosion, that is, cause huge economic losses and even safety hazards. Adding corrosion inhibitors to acid is the main way to solve this problem at present; among them, Mannich base corrosion inhibitors, as a typical adsorption type corrosion inhibitor, have significant corrosion inhibition effects. It has good solubility, simple synthesis, stable structure and other characteristics, so it is widely used in various oilfield acidification environments. Based on the Mannich reaction, this article briefly introduces its development process and reaction mechanism; subsequently, the Mannich bases with three different structures, single Mannich base, double Mannich base, and Mannich base quaternary ammonium salt, are slowed down. Corrosion agents are analyzed, and the comprehensive property differences caused by their different structures are explained. The corrosion inhibition principles and influencing factors of Mannich base corrosion inhibitors are also analyzed and discussed. Finally, Mannich The current status of the research on the rare base has a certain discussion on its application prospects.

2. Mannich Reaction

2.1 Development History of Mannich Reaction

The Mannich reaction, also known as the amine methylation reaction, was first discovered in 1917 by the German chemist Carl Ulvich Franz Mannich and conducted a series of in-depth studies.

In the middle of the twentieth century, the research phase of Mannich reaction was advanced by leaps and bounds.

More representatively, in the 1970s, Kinact et al. found that the intermediate obtained by dimethylamine is N,N-dimethyl-methylene ammonium chloride, which has strong reactivity, which can make many difficult under normal conditions. The reaction proceeded smoothly, and this discovery promoted the further development of Mannich reaction to a certain extent.

At the same time, people are also in more in-depth research and understand the broad application prospects of Mannich reaction. As more diversified synthetic routes are developed, more and more organic synthetic production industries such as chemical production, pharmaceutical research and development, etc. All began to try to introduce Mannich reaction to simplify the process or improve the product performance, and most of the attempts eventually affected the initial production process to varying degrees.

Chinese researchers have also made efforts for the research and development of the Mannich reaction. In 1988, Chen Guangxu and others found that aromatic amines can directly carry out the Mannich reaction, so many research and production with aromatic amines as the main body have obtained a diversified reaction. route.

2.2 Mannich Reaction Mechanism

Mannich reaction, that is, the condensation reaction of α-hydrogen substances (usually aldehydes, ketones, etc.) with aldehydes and amines produces β-amino (carbonyl) compounds.The reaction mechanism is shown in Fig. 1.

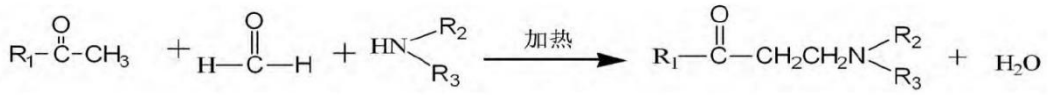

Fig .1Mannich reaction general formula (R1, R2, R3 are alkyl or aryl)

In the further reaction process, the amine and the carbonyl group in the aldehyde undergo nucleophilic addition, through the transfer of electrons on the nitrogen atom, and then through dehydration condensation, first an imine ion intermediate with strong electrophilicity is obtained; at the same time Under the catalysis of acid, the polarity of the carbonyl group in the aldehyde is strengthened, which makes it easier to convert it into an enol structure containing active hydrogen; finally the imine ion intermediate acts as an electrophile to attack the enol structure aldehyde, losing its proton and then Condensation is the product of Mannich base. Since the rate-controlling step is a nucleophilic reaction, the Mannich reaction is realized through a nucleophilic addition-elimination reaction.The microscopic mechanism is shown in Chart 2.

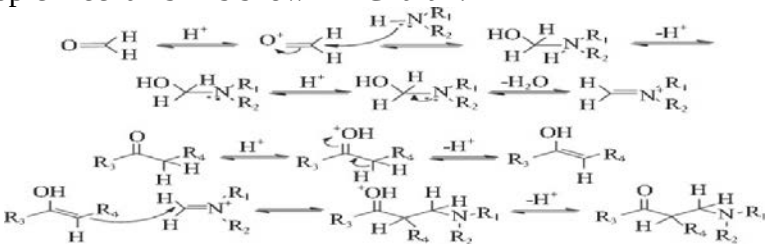

Fig. 2 Mannich reaction mechanism (R1, R2, R3, R4 are alkyl or aryl)

3. Mannich Base Corrosion Inhibitor

3.1 Mono Mannich Base

It is directly obtained from active hydrogen-containing substances, aldehydes and amines through Mannich reaction, and its synthesis is simple, and it is generally achieved by the “one-pot method” in one step; the corrosion inhibition effect is excellent, and the corrosion inhibition efficiency of Mannich corrosion inhibitors is at a high level The plasticity is extremely strong, and the structure and properties of the corrosion inhibitor can be changed by adjusting the reaction materials and reaction conditions, so it is also an excellent reaction substrate, which is one of the reasons why Mannich base has many derivatives.

Chen Lin, Chen Junbin and others use acetophenone, formaldehyde, and a p-phenylenediammonium as raw materials, and formaldehyde: acetophenone: p-phenylenediamine is 2:3:1, at a reaction temperature of 80°C and a pH value of 2~3 The total reaction time is 5 hours to synthesize a Mannich base corrosion inhibitor, which exhibits good corrosion inhibition performance in earth acid and hydrochloric acid.

Yu Hongjiang, Wang Jingguang, etc. used acetophenone, formaldehyde, and benzylamine as raw materials, and the molar ratio of amine, ketone, and aldehyde was 1:1:2.5. The reaction temperature was 80°C and the pH value was 2~3 for 14 hours. A Mannich base hydrochloric acid acidification corrosion inhibitor with good temperature resistance and corrosion inhibition performance.

3.2 Double Mannich Base

Taking the synthesized single Mannich base as an intermediate, and then performing a secondary reaction with active hydrogen-containing substances and aldehydes, the bis Mannich base can be obtained, which has a larger molecular volume than the single Mannich base. The molecule contains more functional groups that can affect the corrosion inhibition effect, which is why the corrosion inhibitors of bis-Mannich bases are usually better than those of single Mannich bases.

In a more detailed series of measurements, the reason why the corrosion inhibition performance of the double Mannich base corrosion inhibitor is higher than that of the single Mannich base corrosion inhibitor is that the molecular structure of the former increases compared with the latter. In the adsorption performance of Mannich molecules, the carbonyl group plays a role in promoting and strengthening the adsorption; at the same time, because the bi-Mannich molecular structure contains more alkyl substituents, it increases the molecular weight. The charge density of higher negative atoms can also promote the adsorption strength of Mannich molecules. Therefore, the adsorption of double Mannich base corrosion inhibitors is better than that of single Mannich base corrosion inhibitors; such as Wu Lanlan, Jiang Hongjuan Et al. used thiourea, benzaldehyde, and acetophenone as raw materials to synthesize a new type of bis-Mannich base by a two-step reaction; the optimal process for the second step of synthesis was determined by the intermediate: aldehyde: ketone 1:1 The ratio of :1, the reaction temperature is 110℃, and the reaction time is 4h, the new bis-Mannich base is obtained.

And some bis-Mannich bases have more oxygen atoms, nitrogen atoms and other atoms with lone pairs of electrons in their molecular structure, and there are several non-coordinating atoms separated from each other, so the lone pair of electrons of the coordination atoms can interact with the metal. The iron atoms with the outer empty orbital on the surface combine to form a more stable cyclic chelate, which can form a more complete hydrophobic protective film on the metal, thereby preventing the anodic reaction of the corrosion process of iron ions diffusion into the solution, and Through its covering effect, the cathodic reaction of the corrosion process is inhibited to a certain extent, so the corrosion rate of the metal is slowed down, and the purpose of improving the corrosion inhibition performance is achieved; for example, Li Jianbo, Lu Jie and others used salicylaldehyde, diethylenetriamine, Acetone and formaldehyde are used as raw materials. First, Schiff reaction is used to synthesize Schiff base intermediates, and then Mannich reaction is used to

synthesize a tetra-Schiff base-bis-Mannich base, which is a mixed type retarder that mainly suppresses the cathode. Corrosion agent has better corrosion inhibition performance.

3.3 Mannich Base Quaternary Ammonium Salt

Take mono Mannich base as a reaction intermediate, and then quaternize it with benzyl chloride to obtain Mannich base quaternary ammonium salt.The reaction mechanism is shown in Chart 3.

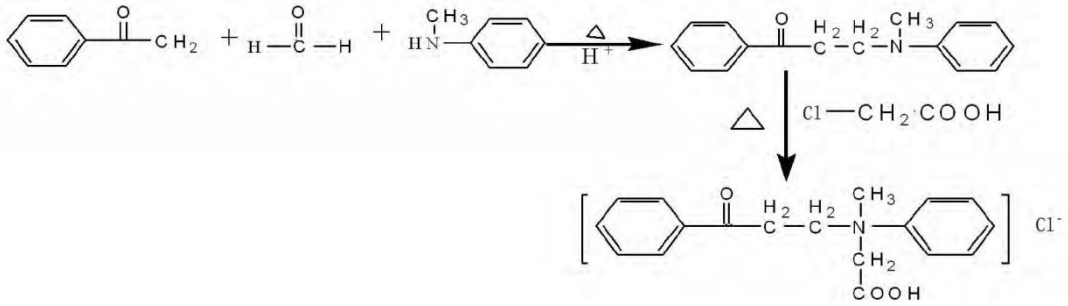

Fig. 3 A kind of quaternization reaction formula of Mannich base quaternary ammonium salt

After the Mannich base is quaternized, nitrogen atoms are introduced into the Mannich molecule, and the molecular structure is larger, and the change in the corrosion inhibition mechanism caused by the structural difference is similar to the above-mentioned bi-Mannich base mechanism; For example, Lu Cong, Yuan Xuefang and others used paraformaldehyde, cyclohexylamine, and acetophenone as raw materials, and first performed Mannich reaction to synthesize intermediates, and then quaternized them with benzyl chloride to obtain a Mannich base quaternary ammonium salt corrosion inhibitor, it is determined that it has a good corrosion inhibition effect on N80 steel sheet in 20% hydrochloric acid at 90 ℃, and it can be compounded with KI to further improve its retardation through synergistic effect. Eclipse performance.

Moreover, due to the formation of quaternary ammonium salt, a hydrophilic group is introduced into the Mannich molecule, which greatly improves the acid solubility of the Mannich base quaternary ammonium salt, and it also increases the Mannich base quaternary ammonium salt. The degree of dissociation of salt into negatively charged halogen ions and positively charged ammonium ions in an acidic environment further improves the degree of adsorption of corrosion inhibitors on metal surfaces; for example, Li Kehua, Xi Wei and others used formaldehyde, acetophenone, Aniline and benzyl chloride were used as raw materials to synthesize Mannich base quaternary ammonium salt corrosion inhibitors, and the optimal conditions for quaternization were determined as follows: reaction temperature 80℃, reaction time 6h, and the ratio of aniline to benzyl chloride was 0 9. The corrosion rate of N 80 steel sheet in 15% hydrochloric acid medium at 40 ℃ is 0.154 1 g (m2·h), which proves its good corrosion inhibition performance.

4. Mannich Base Corrosion Inhibition Mechanism

4.1 The Corrosion Inhibition Principle of Mannich Base

At present, the reaction principle of corrosion inhibitors is still the research direction of many related researchers.

The principles of corrosion inhibitors currently considered mainly include: phase film theory, adsorption film theory, electrochemical theory, quantum chemistry theory and soft, hard acid and

alkali theory. The Mannich base is based on the principle of adsorption membrane, as described in the previous article on the principle of bis-Mannich base and Mannich base quaternary ammonium salt:

The Mannich base molecule contains many coordination atoms containing lone pairs of electrons, such as oxygen atoms, nitrogen atoms, etc., while the Mannich base exerts a corrosion inhibition effect through the lone pair of electrons of the coordination atoms in the active center of the molecule. The outer dsp emptyorbital of the iron atom diffused into the metal surface, and it establishes a coordination bond and simultaneously complexes, that is, a cyclic chelate is formed on the metal surface, thereby adsorbing the metal, and forming a hydrophobic on the metal surface The protective film, and the existence of this protective film, blocks the diffusion of positively charged iron ions (Fe2+) in the corrosion system, and the anode process of the corrosion reaction is effectively suppressed, and the protective film covers the metal surface well. The ground prevents the cathodic corrosion process, that is, the corrosion of the metal is greatly alleviated.

In the Mannich base molecule, while the coordinating atom is bound to the surface iron atom, part of the non-polar group in the molecule will be close to the metal surface and under certain action, will be aligned, which will change the metal to a certain extent. The movement of the electric double layer leads to different degrees of increase in the activation energy required for metal ionization, and also inhibits the occurrence of metal corrosion.

At the same time, in the continuous discussion on the principle of corrosion inhibitors, scientists have found that the corrosion inhibition effect of Mannich base corrosion inhibitor has a certain relationship with the structure of the reaction raw materials and the ratio of ingredients.

4.2 The Relationship between Mannich Base Structure and Corrosion Inhibition Effect

Because Mannich base corrosion inhibitor mainly relies on adsorption to form a film, a protective film is formed between the metal and the corrosive medium to achieve the purpose of alleviating corrosion.

The adsorption of Mannich base on the metal surface and the density of the film depend to a large extent on its structure, that is, the relationship between the structure of Mannich base corrosion inhibitor and its corrosion inhibition effect is also the development direction of many related researchers recently.

Fan Jinfu, Zhang Xiaochen and others synthesized four Mannich bases with different structures (DOP, BPO, TPO, PPO), and through a series of tests and derivations, the following conclusions can be drawn:

(1) When the amino group is directly connected to the benzene ring in the molecule, the lone pair of electrons on the N atom can form a stable electron-rich conjugate system with the π electrons on the benzene ring, which can significantly improve the molecular on the metal surface. The adsorptivity.

(2) When the amino group is directly connected to the benzene ring, but other alkyl groups are connected to the benzene ring, due to the influence of steric hindrance and other factors, its adsorptivity is less than the first case.

(3) When there are other groups separating the amino group and the benzene ring, the stability of the electron-rich conjugated system is obviously weakened. In this case, the adsorption of Mannich base is less than the second case.

(4) When there is an amino group but no benzene ring in the molecule, only relying on the combination of a lone pair of electrons on the nitrogen atom and the metal empty orbital, its adsorption is significantly lower than the third type.

5. Conclusion

With the rapid growth of energy demand in today's era and the global popularity of sustainable development strategies; the development of green and efficient new corrosion inhibitors has gradually become the research topic of more researchers; and Mannich base corrosion inhibitors are just right It has the characteristics of simple synthesis, easy introduction of functional groups, and good corrosion inhibition effects. It is in line with the theme of the current era. Therefore, the development of a new type of corrosion inhibitor with Mannich base as the main body is likely to become a major research direction in the future .

Part of the current research focus on corrosion inhibitors:

Develop a new type of corrosion inhibitor that can play a good corrosion inhibition effect in an acidic oil and gas environment at 210°C and above.

Try to explore the corrosion inhibition mechanism from more angles, especially the adsorption process, in order to improve the corrosion inhibition effect of the corrosion inhibitor in more diverse ways.

Study the mechanism of action of Mannich base and other corrosion inhibitors, and try to establish its regular system.

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