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Research Progress of Mannich Base Corrosion Inhibitor

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Abstract: The latest development of mannich base corrosion inhibitors in recent ten years was reviewed, including high efficiency Mannich base inhibitor, low toxicity Mannich base inhibitor and new Mannich base inhibitor. The inhibition rate and mechanism of different Mannich base inhibitors were compared, and the advantages and disadvantages of different inhibitors were summarized.The development process of various corrosion inhibitors is mainly discussed.In order to meet the needs of acidizing construction in petroleum industry, the synergistic effect of corrosion inhibitors and the modified new Mannich base corrosion inhibitors are deeply considered. It is one of the future development directions of mannich base corrosion inhibitors that have the advantages of high efficiency, environmental protection and low cost.

1. Introduction

Acidizing of oil and gas wells is a common measure to increase production and stabilize production[1], but the acid added will cause serious corrosion to metal equipment.According to statistics, the economic loss caused by metal corrosion accounts for about 1.5% ~ 4.2% of the GDP of the national economy. With the increasing proportion of population, the available resources are decreasing day by day. With the problem of environmental deterioration, the corrosion loss of metals is still increasing[2].However, the injection of acid will cause corrosion, hydrogen embrittlement cracking and even brittle fracture[3-4]of oil and gas well pipelines and downhole equipment.In order to reduce the harm of corrosion, it is usually necessary to add corrosion inhibitors into the acid solution. These inhibitors can form a protective film on the metal surface and slow down the corrosion rate.At present, the corrosion inhibitor is widely used in the fields of steel industry, chemical industry, chemical industry and so on.In this context, the corrosion inhibitor is required to have low toxicity, good effect, low cost, annual high temperature and high acid, and environment-friendly. Mannich base is currently commonly used corrosion inhibitor, which has good solubility, high temperature resistance and good corrosion inhibition performance, and has a broad development prospect[5-6].Based on different types of mannich bases, this paper reviews the research on different types of corrosion inhibitors.

2. Inhibition Mechanism of Mannich Base

Mannich base is the condensation product of aldehydes, ketones and amines. When ketones contain benzene ring, the effect is better.At present, it is generally believed that the inhibition

mechanism of mannich base is adsorption mechanism.Mannich base can be compounded with other corrosion inhibitors, and its molecular structure contains non-polar groups, which has strong hydrophobicity. It interweaves with Mannich base to form a chain or network structure, forming a complete and dense adsorption film on the metal surface, which makes the corrosion difficult.There are a lot of atoms in Mannich base.The polar groups on the surface of the molecules will form polar bonds on the surface of the molecules.In this process, the organic corrosion inhibitor molecules will be aligned and adsorbed on the metal surface to form a hydrophobic film, which hinders the corrosion of the metal.

3. Mannich Base Corrosion Inhibitor

Mannich base inhibitor is usually used in metal corrosion protection.At present, it is widely used in oil and gas fields.First of all, Mannich base inhibitor compound has small molecular weight and contains many N and o with lone electron pairs.Secondly, Mannich base is a kind of chelating ligand, which is easy to form coordination bond with metal.Then Mannich base has the advantages of stable structure, simple preparation, low toxicity, good acid solubility and high temperature resistance.

3.1 High Efficiency Mannich Corrosion Inhibitor

In the 20th century, the development of mannich base is mainly aimed at the corrosion of steel pipe materials, which is limited to the condensation of small molecules of aldehydes, ketones and amines.In recent years, macromolecular Mannich base compounds have been introduced to further improve the corrosion inhibition effect. S. vishwanatham and n. haldar introduced furfuryl alcohol as the raw materials for Mannich base synthesis. The effects of nitrogen, sulfur, oxygen atoms and various chemical bonds on Mannich base were studied, and the relationship between molecular structure and inhibition performance of mannich base[7]was explored.Later, ishtiaque ahamad et al. Synthesized four Mannich Base Derivatives from indigo red. Their adsorption and corrosion inhibition properties for mild steel in 1molll hydrochloric acid were tested by EIS, weight loss method and quantum chemistry. The activation energy (EA) and various thermodynamic parameters were calculated and discussed. The adsorption process was in accordance with Langmuir adsorption isotherm[8].Cao Huaishan, Zhang Jinghua and others developed the compound of mannich base and aldehyde amine condensation compound, and tested the corrosion performance in 15% hydrochloric acid, 12% hydrochloric acid and 3% hydrofluoric acid. The inhibition efficiency of mannich base was increased to 88%[9].

The performance of corrosion inhibitor is greatly affected by molecular structure.In general, when the polar group is a common electron group, the higher the electron cloud density on the central atom, the better the corrosion inhibition effect, while the polar group is the electron withdrawing group, the corrosion inhibition effect is poor.The larger the number of intercalation sites, the worse the inhibition effect. Tomnesani and Erignani et al[11] Studied the effect of BTA hydrocarbon derivatives on the corrosion resistance of steel alloy. The experimental results show that the inhibition effect of BTA increases with the increase of carbon chain and carbon atom number. When the number of side chain carbon atoms is 6, the effect is the best, and if the side chain is too long, the corrosion inhibition effect will decrease.

Benzotriazole (BTA) is a metal rust inhibitor and a corrosion inhibitor for copper and copper alloys.Benzotriazole can be used with a variety of corrosion inhibitors to improve the corrosion inhibition effect.For benzotriazole inhibitors, at present, more people tend to film theory.After the surface of carbon steel is treated with benzotriazole, a layer of Fe BTA complex will be formed on the surface of carbon steel. The reason is that benzotriazole contains benzene ring and three

nitrogen atoms, while the compound containsnd lone electron pair are easy to form coordination bond with metal atom[10].Yinglu[12]responding mannich bases were synthesized by the reaction of Benzotriazole and formaldehyde (40%) with diethylamine,dimethylamine,morpholine and piperazine,respectively.The inhibition rates of these inhibitors are shown in Table 1.

Table 1 Corrosion Inhibition Rate of Benzotriazole and Formaldehyde Reacting with Different Introduced Substances

Serial number	raw material	Introduction of substances	Corrosion inhibition rate of 10% HCl	50000mggl sodium chloride solution
1	Benzotriazole and formaldehyde	Diethylamine	92%	91%
2	Benzotriazole and formaldehyde	Dimethylamine	90%	93%
3	Benzotriazole and formaldehyde	Morpholine	88%	90%
4	Benzotriazole and formaldehyde	piperazine	93%	91%

It can be seen from table 1 that the corrosion inhibitor synthesized by the reaction of Benzotriazole and formaldehyde with piperazine is more effective for metal corrosion under acidic conditions, and the inhibitor synthesized by intermediate product of Benzotriazole and formaldehyde and dimethylamine is more effective for metal corrosion protection in salt solution.However, this kind of corrosion inhibitor also solves the problem of environmental pollution.

3.2 Low Toxicity Mannich Base Corrosion Inhibitor

Acid corrosion inhibitors developed in the 1990s are mainly composed of alkynols, quaternary ammonium salts and metal salts. However, alkynols or aldehydes have high toxicity and high cost, which have a serious impact on the development of corrosion inhibitors. They are mainly used in some special environments.Therefore, it is urgent to develop environmental friendly green corrosion inhibitors.With the maturity of the preparation technology of mannich base corrosion inhibitor, there are requirements of low toxicity, low cost and high efficiency.A series of new Mannich base inhibitors have been developed.O. M. ohabib, H. M. Hassan et al. Synthesized imidazoline from azolone and p-aminophenol in glacial acetic acid. Mannich base was prepared from pyridine and paraformaldehyde. Several new antioxidants and antiseptic additiveswere synthesized [13]. P. Thiraviyam, K. Kannan et al. Synthesized aminocyclohexane-n-methylurea Mannich base (acmu) and determined its corrosion inhibition effect on carbon steel at 303k-333k. The inhibition rate increased with the increase of concentration and decreased with the increase of temperature. chanism of corrosion inhibition is discussed from the point of view of thermodynamics[14].Li Kehua et al.[15]synthesized HJ Mannich base corrosion inhibitor by furfural, acetophenone and hydrazine hydrate.Compared with formaldehyde, furfural in raw materials is a low toxic aldehyde compound. In addition, there are two nitrogen atoms in hydrazine hydrate which can provide lone electron pairs to form coordination bond with metal. The compound can be stably adsorbed on the metal surface and form a relatively complete adsorption film.After measurement, the corrosion rate of N80 steel sheet in 15% hydrochloric acid solution is 0.6235g · m^{-2}· H^{-1}.

Zhou Shusheng et al.[16]synthesized Mannich base corrosion inhibitor with 2-aminothiazole, acetophenone and acetaldehyde.Thiazoles are heterocyclic orbitals containing N and S atoms, so they have strong adsorption and form stable complexes or chelates, and hydrogen bonds are easy to form within or between molecules to enhance the adsorption.The corrosion inhibitor synthesized

with the raw material has the advantages of low toxicity and high efficiency.After measurement, the corrosion rate of N80 steel sheet in 15% hydrochloric acid is 0.4129 g · m^{-2}· H^{-1}.This kind of corrosion inhibitor is widely used at present, and has little impact on the environment. However, with the expansion of oilfield production industry, the modification of existing corrosion inhibitors is the next step.

3.3 New Mannich Base Corrosion Inhibitor

In recent years, the modification of mannich base corrosion inhibitors has been carried out to meet the more stringent acidification process environment and improve oil recovery.Li Weijia and Liang Ping synthesized Mannich base from aldehydes and ketoamides with benzyl chloride, then compounded with Urotropine and thiourea, and tested its corrosion inhibition performancein mud acid and hydrochloric acid[17].Sodium tungstate is a well-known high-efficiency corrosion inhibitor. The combination of sodium tungstate and Mannich base has become an important subject. The research shows that the inhibition rate of mannich base is 95.48%, that of sodium tungstate is 68.41%, and that of sodium tungstate is as high as 99.65%.The inhibition rate of the composite inhibitor is obviously higher than that of any single inhibitor[18].At present, most of the Mannich base corrosion inhibitors are single Mannich base, so the modification of single Mannich base is particularly important.Based on the synthesis of monomannich base, bismannich base was prepared by adding a certain amount of formaldehyde and acetone.Two steps of synthesis of conoconazole were carried out.The results of static weight loss method, electrochemical polarization curve method, electron microscope scanning method and electron energy spectrum method show that the inhibitor has the advantages of high efficiency, temperature resistance, acid resistance and long action time. It can form a complete and dense protective film on the surface of N80 steel. It belongs to the mixed adsorption corrosion inhibitor, which greatly improves the performance of mannich base[19].Chen Yuefeng et al.[20]tested the inhibition rate of double Mannich base inhibitor under different temperature, corrosion time and inhibitor concentration. The results showed that the inhibition rate of the inhibitor was 99.82% at 90 ℃, 99.82% at 4 h, and 99.89% at 0.2% concentration.Xiao Peng, Li Kehua, etc. used thiourea as raw material, added benzaldehyde, acetophenone and bismannich base, and compared with monomannich base under the same corrosion conditions. The results are shown in Table 2[21].

Table 2 Comparison of Properties of Monomannich Base and Double Mannich Base

Mannich base	Corrosion rate (g · m^{-2}· H^{-1})	
	40℃	60℃
Monomannich base	1.774	3.195
Double Mannich base	0.653	1.121

It can be seen from table 1 that the corrosion inhibition performance of double Mannich base is higher than that of single Mannich base. The reason is that there are more oxygen atoms and nitrogen atoms with lone pair electrons in the molecule of double Mannich base, which forms stable complex with steel sheet and covers the metal surface. The film is hydrophobic and prevents the steel sheet from being corroded.Based on the Mannich base synthesized by thiourea, Jin Minghuang and Li Kehua were added with benzyl chloride for quaternization. The corrosion inhibition performance[22]was tested in 15% hydrochloric acid.The corrosion inhibition rate of corrosion inhibitor to metal is not only affected by itself, but also affected by corrosion temperature, concentration of corrosion inhibitor, corrosion time and hydrochloric acid concentration.The effect of temperature can be calculated by Arrhenius equation. The relationship between the natural logarithm of corrosion rate and 11T is as follows:

$\ln v=\frac{-E_a}{RT}+\ln A$

Where: V is corrosion rate [GG (m^2· h)]; $E_a$is activation energy (kjjmol); t is temperature (k); a is pre exponential factor.

Yang Xiufang et al. Synthesized a new Mannich base corrosion inhibitor and explored its corrosion inhibition performance for N80 steel sheet in hydrochloric acid. The corrosion temperature, inhibitor concentration, corrosion time and hydrochloric acid concentration were also tested. The experimental results show that the corrosion inhibition rate is above 99% when the temperature is 40 ℃ ~ 60 ℃, and decreases obviously when the temperature is higher than 60 ℃; when the concentration of the inhibitor is 4ggl, the corrosion inhibition rate is higher than 99%,The corrosion inhibition rate is 99.49%, and the inhibition rate is basically unchanged with the increase of inhibitor concentration; when the corrosion time is 7h, the maximum corrosion inhibition rate is 99.5%, and the corrosion inhibition rate decreases with the increase of corrosion inhibition time; when the mass fraction of hydrochloric acid is 5% ~ 15%, the corrosion inhibition rate increases gradually, and when the concentration of hydrochloric acid is more than 15%, the inhibition rate decreases[23].

This kind of corrosion inhibitor can solve the existing problems because of its high inhibition rate. Therefore, it is the direction of the future development of corrosion inhibitors to develop a kind of corrosion inhibitor with good solubility, high efficiency, environmental protection and low cost.

4. Conclusion

Mannich base corrosion inhibitor has a good development trend in anti-corrosion, and excellent effect can be obtained by modifying Mannich base.As a new type of corrosion inhibitor, bis (Mannich base) and other compounds have the advantages of high efficiency, environmental protection and low cost.In order to make the Mannich base corrosion inhibitor can be widely used in industry, some problems need to be solved: (1) using cleaner raw materials to replace traditional raw materials, so as to reduce the environmental pollution.(2) It should be noted that the raw material is cheap and easy to use in different acid environment and high temperature. (3) Mannich base can be modified from the perspective of solubility, which can increase the corrosion inhibition rate and stability, and make it have excellent corrosion inhibition performance.

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References

[1] Zhao Fulin.Oilfield chemistry[M].Dongying:Petroleum University Press,2010.
[2] Yang Dejun,SHEN Zhuoshen.Metal corrosion(Second edition)[M].Beijing:Metallurgical Industry Press.
[3] Hong Pyokim,Dong-Jin Kim.Corrosion of materials in sulfuric acid[J].Journal of Engineering for Gas Turbines and Power,2009,131(4):19.
[4] A.S.Derbyshev,A.N.Suriew.Corrosion of material in hydrochloric acid solutions[J].Chemical and petroleum Engineering,2002,47(9-10):632-634.
[5] Liu Zhihui,WANG Xia,WU Yichen,Research progress of Mannich base acidification inhibitor[J].Applied Chemical Industry,2014(1):148-150.
[6] Feng Xiahui,LI Jian,WANG Yi,et al.Compound and properties of Mannich base hydrochlorization inhibitor[J].Applied Chemical Industry.
[7] S.Vishwanatham,N.Haldar.Furfuryl alcohol as corrosion inhibitor for N80 steel in hydrochloric acid[J].Corrosion Science,2008,50(1):2999-3004.
[8] Ishtiaque Ahamad.Adsorption and inhibitive properties of some new mannich bases of isatin derivatives on corrosion of mild steel in acidic media[J].Corrosion Science,2010,52(4):1472-1481.

[9] Cao Huaishan,ZhANG Jinghua.BH961 Acidizing corrosion inhibitor[J]. Oilfield Chemistry,2002,19(4):25-327
[10] Fang Daozheng.Mannich reacation and mannich chemistry[M].Beijing Science Press,1986:78-84.
[11] Luo Yi,LIE Wei.Study on anti-salt spray corrosion and anti-rust oil[M].Meterial Protection,2002,5(5):38-39.
[12] Yin Lu.Study on synthesis and inhibition performance of Mannich base inhibitor[D].Xi'an:Xi'an Petroleum University,2015:40.
[13] O.M.OHabib,H.M.Hassan.Synthesis of some novel antioxidant and anticorrosiveadditives for Egyptian lubricating oils[J].Petroleum Science and Technology,30(23):2435-2439.
[14] P.Thiraviyam,K.Kannan.A study of synthesized Mannich base inhibtion on mild steel corrosion in asid medium[J].Iranian Chemical Society,2012,9:911-921.
[15] Li Kehua,LAN Zhiwei,YANG Bingbing,SHI Dongpo.Compound and properties of HJ Mannich base inhibitor[J].Corrosion and Protection,2016(6):467-470.
[16] Zhou Shusheng.Preparation and properties of ZS Mannich base inhibitor[J].Science and Technology Protection,2017(8):23-27.
[17] Li Weijia,LIANG Ping.Study on the compound performance of Quaternary Aminated Mannich base[J].Advances in Fine Petrochemicals,2011,12(4):49-52.
[18] Hu Jun,WANG Zhen,WANG Tiantian,HE Shijun,FAN An. A new mechanism of compound inhibitor of Mannich base and sodium tungstate[J].Chemical Machinery,2018,45,(1):109-113.
[19] Kang Hongyuna. Synthesis and performance evaluation of new double Mannich base inhibitor[J]. Advances in Fine Petrochemicals,2012,29(6):25-29.
[20] Chen Yuefeng. Synthesis and performance evaluation of double Mannich base inhibitor[D].Chengdu: Southwest Petroleum University,2016:27-30.
[21] Xiao Peng.Synthesis and Performance evaluation of new double Mannich base inhibitor[J]. Advances in Fine Petrochemicals,2012,29(6):25-29.
[22] Jin Minghuang,LI Kehua. Synthesis and evaluation of Mannich base Quaternary Ammonium salt inhibitor[J]. Advances in Fine Petrochemicals,2012,13(9):22-25.
[23] Yang Xiufang,TANG Minmin,MA Yangmin.Mannich Base as Corrosion Inhibitor for N80 Steel in HCl Solution[J].Surface Thchnology,2017,46(1):175-181.