

Research Article

The Nitrogenous Corrosion Inhibitors Used in Petroleum Production

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ABSTRACT

The corrosion inhibitors are commonly used in variety of industrial fields such as storage and transportation facilities, oil and natural gas production, oil refineries, heat exchangers, condensers, desalination plants as well as cooling water installations, etc. Many of the commercial corrosion inhibitors are unique mixtures that may contain surfactants, film enhancers, demulsifiers, or an oxygen scavenger in addition to the inhibitor moiety. The majority of corrosion inhibitors used in petroleum production are nitrogenous in nature. There are other, non nitrogenous inhibitors that contain phosphorous, sulphur, or oxygen atoms but they are used less frequently. The purpose of this paper is to provide a few illustrative examples of formulation considerations. This paper does not attempt to describe all the commercially available formulations, but rather the broad chemistries within which they fall. This paper also presents the chemistry of nitrogen containing macrocyclic compounds which constitute a potential class of corrosion inhibitors. The inhibiting action was evaluated on corrosion of mild steel in HCl and H₂SO₄ by weight loss method.

INTRODUCTION

A corrosion inhibitor may be defined as a substance which, when added in small amounts to a normally corrosive medium, reduces the corrosion rate of the metal by action at or near the metal surface¹. In order to identify a given substance as a corrosion inhibitor it is important to specify both the metal and the environment. It follows that a given inhibitor may be ineffective, or even aggressive, if the metal and/or the environment is changed². The application of corrosion inhibitors is common in variety of industrial fields such as storage and transportation facilities, oil and natural gas production, oil refineries, heat exchangers, condensers, desalination plants as well as cooling water installations, etc^{3,4}.

Corrosion inhibitors are routinely used in oil production at varying rates. Many of the commercial corrosion inhibitors are unique mixtures that may contain surfactants, film enhancers, demulsifiers, or an oxygen scavenger in addition to the inhibitor moiety. The majority of corrosion inhibitors used in petroleum production are having nitrogen containing inhibitor moieties and can be classified into the following categories

1. Amides/ imidazolines
2. Salts of nitrogenous molecules with carboxylic acids
3. Nitrogen quaternaries
4. Polyoxyalkylated amines, amides and imidazolines
5. Nitrogen heterocyclics

There are other, non-nitrogenous inhibitors that contain phosphorous, sulphur, or oxygen atoms but they are used less frequently.

Amides / Imidazolines

Many of the common oil and water soluble corrosion inhibitors contain amides and/or imidazolines. They are produced by the reaction of carboxylic acid with a primary amine. The carboxylic group is often derived from low cost natural sources such as crude or refined tall oil⁵. The typical fatty acid derived from tall oil is composed primarily of C₁₃ linear saturated and unsaturated chains with minor amounts of C₁₆ linear chains and some rosin acids⁶. Naphthenic acid mixtures derived from petroleum are also used⁷. The amine frequently used in the reaction is a polyamine having the structure H₂N(-R-NH)_xH where R is an alkylene group containing 2 to 6 carbon atoms and x is a small whole number greater than 1. A frequently used polyamine is diethylene triamine (R = CH₂CH₂ and x = 2). Mixtures of higher homologs (x = 4 etc.) can also be used³. A water soluble and water dispersible inhibitor

blend is often made from such imidazolines by adding a low molecular weight organic acid and a mixture of solvents and perhaps a surfactant^{8,9}. The composition of some corrosion inhibitors are shown below

Ingredient	Weight %
Imidazoline	19.0
Phosphoric acid	5.5
Water	5.5
Isopropyl alcohol	5.0
Heavy aromatic naphtha	65.0

A mixture of imidazolines was prepared from ethylene diamine and tall oil fatty acids, as described in U.S. Patent 2,468,163. The composition shown above provided 97.5% inhibition of calcium sulphate scale deposition when used in a concentration sufficient to give about 4.6 ppm of the phosphoric acid. A standard, static bottle test to determine the hydrogen sulphide inhibiting ability of the above composition indicates that the concentration of 83 ppm gave 76.4% inhibition, while 167 ppm provided 93.8% inhibition.

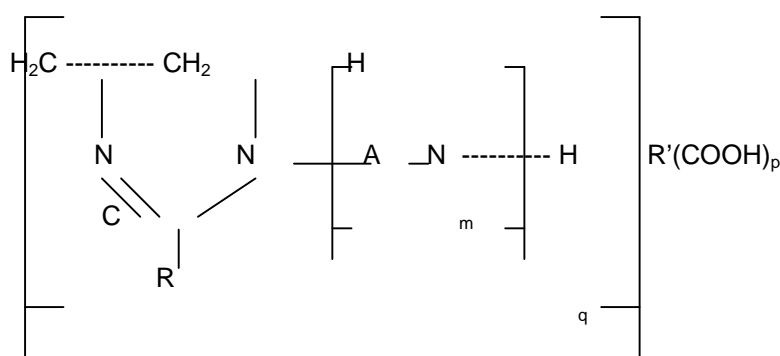
Ingredient	Weight %
Imidazoline	19.0
Phosphoric acid	4.0
Water	4.0
Dimer-trimer acid	5.0
Isopropyl alcohol	5.0
Heavy aromatic naphtha	63.0

This composition provided 95.3 % inhibition of hydrogen sulphide corrosion in the standard, static bottle test when the concentration was 83 ppm. A concentration of 167 ppm provided 95.9% inhibition.

Salts of Nitrogenous Molecules with Carboxylic Acids

There are numerous references that discuss salts formed by the neutralization of the basic nitrogen by tall oil fatty acids, polymerized fatty acids, naphthenic acids, or simple organic acids¹⁰⁻¹³. The use of polymerized fatty acids in inhibitor formulations is established to be the millions of pounds per year¹⁴.

According to Maddox¹², water soluble dispersant-free corrosion inhibitors are produced by reacting water-soluble saturated aliphatic mono- and dicarboxylic acids and a substituted imidazoline to produce members of a class of imidazoline-aliphatic acid salts having the formula which is given below:



In this formula R is the residual radical of a fatty acid selected from the group consisting of a tall oil fatty acid, and a polymerized carboxylic acid containing 15 to 70 carbon atoms; A is an ethylene or propylene group and m is an integer from 1 to 6, p indicates the value of R and is the integer 1 for monocarboxylic acids and 2 for dicarboxylic acids, R is a saturated aliphatic residual radical containing 0 to 2 carbons; q is 1 when p is 1 and 1 or 2 when p is 2.

Quaternary Nitrogen

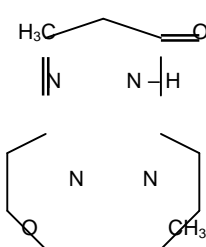
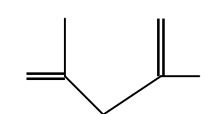
The term quaternary nitrogen applies to compounds in which all the hydrogens of the ammonium ion have been replaced by linkages to carbon. These are often referred to as cationics. The quaternary nitrogen compounds are excellent cationic surfactants and may possess biocidal, demulsifying, or corrosion inhibiting properties^{15,16}. In the fatty amine quaternaries, at least one of the alkyl groups consists of a long alkyl chain and may have more than one cationic nitrogen atoms^{17,18}. Other nitrogen containing compounds that are quaternized include imidazolines¹⁹, Polymerized amines^{16,20} and pyridines¹⁰.

Polyalkylated Amines, Amides and Imidazolines

Any reactive site can be oxyalkylated to modify solubility or dispersability of the inhibitor intermediates. Examples include an ethoxylated resin amine, polyamines with epichlorohydrin²⁰, beta amine ethoxylates²¹ and ethoxylated imidazolines and amines²².

Nitrogen Heterocyclics

Corrosion scientists and engineers have shown a great deal of interest in the study of macrocyclic compounds as corrosion inhibitors in recent years owing to their significant corrosion inhibiting properties for industrial metals and alloys^{23,24}. In present study the following compounds are used

Structure Formula	Designation and Abbreviation
	7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraazacyclotetradeca-1,7-diene (MOAT)
	2,3:9,10-dibenzo-7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraazacyclotetradeca-1,7-diene (BMOAT)
	2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (OAH)
	7,8,15,16-dibenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (BOAH)

These macrocyclic compounds can be synthesized by condensing o-ethylenediamine and o-phenylenediamine with ethylacetoacetate and succinic acid. Their inhibiting action was evaluated on corrosion of mild steel in HCl and H₂SO₄ by weight loss method.

Experimental

Mild steel strips having size 2 cm x 2 cm x 0.025 cm (C = 0.14 % ; Mn = 0.35% ; Si = 0.017% ; S = 0.25% ; P = 0.03% and the rest being iron) were used for weight loss measurements. Weight loss experiments were carried out in 1N HCl and 1N H₂SO₄ at different concentrations, temperatures and immersion time. The results are presented in Table 1. The results show that IE increases with the increase in inhibitor concentration for all of the compounds. The better performance of the BMOAT and BOAH as corrosion inhibitor than that of MOAT and OAH may be attributed to the presence of aromatic rings containing π electrons, which facilitate greater adsorption of BMOAT and BOAH on the metal surface. Desai et al.²⁴ have also reported that the condensation products derived from aromatic amines and carbonyl compounds give better inhibition efficiency than those derived from ethylene diamine and carbonyls.

The better inhibition efficiency observed in 1N HCl than that of 1N H₂SO₄ may be explained by the fact that chloride ions being less hydrated than sulphate ions are preferentially adsorbed on the metal surface, thereby creating an excess negative charge towards the solution phase which favours synergistic adsorption of protonated inhibitors on the metal surface.^{26,27}

Table 1: Corrosion inhibition and corrosion rates obtained from weight loss studies in 1N HCl and 1N H₂SO₄ containing different concentration of macrocyclic compounds at 40 °C for three hours

Inhibitor Concentration (ppm)	1 N HCl		1 N H ₂ SO ₄	
	I.E. (Percent)	C.R. (mppy)	I.E. (Percent)	C.R. (mppy)
BMOAT				
0	-	12.39	-	19.13
100	64.4	4.41	30.5	13.48
200	77.5	2.78	37.1	11.23
300	82.7	2.13	40.2	11.82
400	85.0	1.85	50.0	9.40
500	90.2	1.20	51.4	9.13
1000	98.5	0.18	65.2	6.52
MOAT				
0	-	12.39	-	19.13
100	48.1	7.19	20.3	15.23
200	62.9	4.59	28.3	13.69
300	64.7	4.36	31.1	13.14
400	68.1	3.94	40.5	11.37
500	71.9	3.48	42.4	11.0
1000	84.6	1.90	54.1	8.77
BOAH				
0	-	12.39	-	12.39
100	56.1	5.43	23.0	14.72
200	66.2	4.17	32.7	12.64
300	70.7	3.62	35.9	12.25
400	74.1	3.20	41.2	11.23
500	74.9	3.05	46.3	10.26
1000	88.0	1.46	59.7	7.70
OAH				
0	-	12.39	-	19.13
100	47.5	6.50	10.9	17.04
200	53.1	5.80	18.6	15.55
300	63.3	4.55	21.1	15.09
400	68.5	3.90	25.2	14.30
500	68.9	3.85	27.1	13.93
1000	83.5	2.04	31.3	13.14

Reference: M. Ajmal, J. Rawat and M.A. Quraishi (1998). Corrosion inhibiting properties of some polyaza macrocyclic compounds on mild steel in acid environments. *Anti-corrosion methods and Materials*, Vol. 45, No. 6, 00. 419-425.

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