

Structure and Related Effectiveness of Naphthenic Acid Corrosion Inhibitors

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ABSTRACT

Petroleum refineries often encounter naphthenic acid corrosion when processing opportunity crudes with a high total acid number (TAN). The formation of oil soluble iron carboxylates in refinery units operating at high temperature regimes (200 °C to 400 °C) with corresponding high fluid velocities, can lead to high rates of corrosion where susceptible metallurgies are used in the affected zones.

To mitigate naphthenic acid corrosion, the application of chemical additives (i.e., corrosion inhibitors) can be implemented. The type of inhibitor traditionally used to mitigate this type of corrosion are largely composed of phosphorus-based compounds. However, P-based inhibitors have come under scrutiny due to their potential impact on refinery process units. Consequently, a variety of new inhibitors, where the amount of phosphorus has been reduced or eliminated have been developed to mitigate naphthenic acid corrosion.

In the present study, a variety of corrosion inhibitors, phosphate esters (mono, di, or triesters), thiophosphate esters, and organo-polysulfides were used to inhibit naphthenic acid corrosion in hydrotreated base oils with a TAN of 10 mg KOH/g or higher. The results presented herein not only describe the mechanism by which such molecules inhibit naphthenic acid corrosion, but also provides insight into the relationship between the chemical functionalities of these inhibitors and their ability to successfully mitigate naphthenic acid corrosion. These findings serve as a blueprint for determining the effectiveness of a naphthenic acid corrosion inhibitor with respect to the structural features of the inhibitor.

Keywords: Naphthenic acid corrosion, phosphate esters, thiophosphates, and organo-polysulfide

INTRODUCTION

Opportunity crudes are generally defined as petroleum crudes bearing a high level of sulfur, metals, or total acid number (TAN). These crudes are typically offered at a discounted value. Thus, refining such crudes carries with it a lucrative incentive. However, due to the above-mentioned characteristics, processing such crudes presents numerous operational challenges as well, such as naphthenic acid corrosion, which is commonly associated with the high TAN content in these crudes. In refinery units such as the crude distillation tower, these carboxylic acids react with the iron atoms of the metal surfaces to produce oil soluble iron carboxylates.^{1,2} The continued formation of such complexes would then erode the metal surface. Equipment failure due to such corrosion results in shutting down a large segment or the entire refinery. Therefore, establishing a means for mitigating this type of corrosion is paramount for processing crude oils with an elevated TAN due to naphthenic acids.

Over the past few decades, refiners have pursued a variety of options to minimize the risks of naphthenic acid corrosion failure. Permanent Ultrasound sensors have been developed to non-invasively monitor changes in wall thickness in susceptible areas of the refinery.¹ Blending high TAN crudes with lower TAN ones can bring the naphthenic acid level to an acceptable level. Blending can also be used to increase the sulfur content of the crude, which is known to moderately inhibit naphthenic acid corrosion.^{1,3} Metallurgical upgrades can also be used to slow down the corrosion rate. By incorporating a high molybdenum content alloy, such as stainless steel 316H or 317L, the corrosion resistance of the surface towards naphthenic acid corrosion increases.⁴ However, these options are either very costly (metallurgical upgrade) or would not fully prevent the actual occurrence of corrosion. Alternatively, the use of corrosion inhibitors at the right dose is a more economical and effective option. These chemical species are typically inert to the hydrocarbon environment, thermally stable at the point of introduction, and chemically tailored to react with the metal surface. The resulting protective layer prevents the metal surface from reacting with naphthenic acid moieties.⁵

The study presented herein evaluates a variety of corrosion inhibitors that are typically used to inhibit high temperature corrosion. These inhibitors include phosphate esters (mono, di, or triesters), thiophosphate esters, as well as some sulfur-based inhibitors. The corrosion data aims to describe the mechanism by which such molecules inhibit naphthenic acid corrosion, the relationship between the thermal stability and chemical makeup across the different chemistries, and their ability to successfully mitigate naphthenic acid corrosion. These findings serve as a blueprint for determining the effectiveness of a naphthenic acid corrosion inhibitor with respect to the structural features of the inhibitor

EXPERIMENTAL PROCEDURE

The chemical inhibitors described in this study were evaluated via high temperature autoclave testing following ASTM G1111. The class of inhibitors includes phosphorous based inhibitors, i.e., phosphate esters and thiophosphate esters, as well as sulfur-based inhibitors, such as alkylated polysulfides. Table 1 summarizes the experimental conditions used in the autoclave testing for high temperature naphthenic acid corrosion of C1018 carbon steel metallurgy.

The corrosion inhibition of the products evaluated herein was calculated using corrosion rate assessment derived from weight loss analysis of C1018 carbon steel coupons using Equation 1:

$$\text{Corrosion rate} = \frac{3.45 \times 10^6 \times (\Delta W)}{A \times T \times D} \quad (1)$$

where, ΔW is weight loss in grams, A is the coupon area in cm^2 , T is experimental time in hours, and D is the density of the metal coupon in g/cm^3 .

Table 1. Experimental Parameters used in High Temperature Corrosion Testing

Experimental Variable	Parameter
Temperature	320 °C
Shear Rate	440 rpm after the temperature reaches 320 °C
N ₂ Pressure	100 PSI @ r.t. and ~220 PSI @ 320 °C
Reaction Time	4 -12 Hr.
Testing Medium	Naphthenic* acid in Paraffin oil*
Metallurgy	Carbon Steel (C1018) Disc (ø1.25", 0.125" thick)
TAN	11.5
Pre-Passivation Dose	1000 ppm
Inhibitor Dose	500, 350, 250, and 175 ppm

Coupon Pre-Passivation Procedure

1. Metal coupons were weighed on an analytical balance (four-decimal).
2. 500 mL of paraffin oil solution was placed in a 1L glass reactor.
3. Metal coupons were immersed in the oil under continuous N₂ purging.
4. The solution was heated to 250 °C at which a 1000 ppm dose of the corrosion inhibitor was injected, and the resulting solution was stirred at 250 °C for the desired time duration.
5. After passivation, heating was stopped, the oil was allowed to cool down, and the coupons were lifted above the oil phase.
6. Once the temperature was sufficiently low, the coupons were removed, washed with toluene as well as isopropanol, and dried using a stream of N₂ gas.

Autoclave Corrosion Testing

1. In a 1L autoclave reactor, a solution of 500 mL of paraffin oil with a specific TAN was added.
2. Pre-passivated coupons (various metallurgy can be used) were weighed on an analytical balance (four-decimal) and attached to the rotating shaft of the reactor via a set of ceramic spacers that are held together by a screw.
3. Subsequently, the reactor was assembled and tightened using a set of bolts/screws.
4. Prior to placing the vessel in the heating element, the system was purged with N₂ using three rounds of 100 psi N₂ fills / releases. The vessel was then pressurized with N₂ to 100 psi and inserted inside a heating mantle.
5. The system was set to rotate at 50 rpm while the vessel heated up to 320 °C.
6. Once the target temperature was reached, the rotation rate was increased to 440 rpm and the experiment was run for 4-12 hours.