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EFFECTIVENESS OF THE CORROSION INHIBITORS FOR THE PETROLEUM INDUSTRY UNDER VARIOUS FLOW CONDITIONS

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ABSTRACT

Several types of corrosion inhibitors were evaluated. Active ingredients of those inhibitors included long chain amines, fatty amides, imidazolines, fatty acids and their salts. Inhibitors were tested at the concentration range of 50 - 200 ppm in the electrolyte and electrolyte/hydrocarbon mixture in the presence of CO_2 and H_2S in static and dynamic conditions. Several evaluations were performed when corrosion inhibitors were added into electrolyte containing flow modifiers. The results, which include the corrosion and electrochemical testing data, show that generally tested corrosion inhibitors are effective in studied range of flow rates and compatible with flow modifiers.

Key words: Corrosion inhibitors, electrolyte, rotation cylinder electrode, concentration, chemical nature.

INTRODUCTION

In today's industrial world there is a focus on cost savings and there is a continuous search for new innovative technologies and solutions to extend the working life of existing assets and infrastructure while lowering environmental impact. The world of pipelines is no different in its search for smarter and greener solutions. As a large number of liquid transport pipelines continue to mature and maintenance and operating costs continue to rise there has been an increased focus on finding environmentally friendly, innovative solutions to achieve these goals.

Utilization of corrosion inhibitors is currently the most common method of protecting against corrosion in all petrochemical facilities in the world. Based on the latest information $3.7 billion is spent per year to mitigate corrosion in the oil and gas industry. The optimal combination of drag reducers (flow enhancers) and corrosion inhibitors will provide end users with an effective way of increasing oil production and significantly prolonging the life of pipelines. Drag

reduction is a physical phenomenon in which friction decreases in turbulent flow through pipelines. It results in increased fluid flow and/or reduced pressure loss. Chemicals that can affect drag reduction-drag-reducing agents (DRAs) - have oilfield application mainly in crude oil transportation and water re-injection lines [1-3].

The new anti-corrosion additives were formulated utilizing volatile corrosion inhibitors (VpCIs). These products provide a very high level of protection for steel subjected to a broad range of corrosive attack and flow restriction from moisture, condensation, oxygen, carbon dioxide, hydrogen sulfide, and other corrosive contaminants. Unlike conventional methods, such as filming amine-based corrosion inhibitors, an injection of VpCI based material into any part of the system will set the VpCI to work immediately with a self-replenishing mono-molecular protective layer [4, 5].

VpCI technology is an environmentally safe and cost-effective option for corrosion protection. VpCIs form a physical bond on the metal surface and create a barrier layer to protect against aggressive ions. The barrier re-heals and self-replenishes, and can be combined with other functional properties for added protective capabilities. It can be used in pipelines, oil and gas wells, refinery units, and fuels. In addition these VpCI-based anti-corrosion additives have been designed to work well in multiphase flow systems in conjunction with different drag reducers.

These different combinations of corrosion inhibitors and drag reducers provide systems with improved water flow and corrosion protection of pipelines carrying water or the mixture of hydrocarbon and water. All of these will lead to energy saving in oil production and increased overall recoverable reserves. The reduction of operating pressure will in turn give a lower back pressure in the well head and lead to additional oil production, enabling a substantial annual revenue increase.

The formulations of corrosion inhibitors and drag reducers were specifically designed to be effective in pipelines carrying either fresh water, sea water, produced water or multiphase systems with a continuous water phase. In many aging oil fields the basic sediment and water increased over time to the point where a water soluble drag reducer/corrosion inhibitor is needed instead of an oil soluble product.

The investigated systems are an effective way to cope with pressure and/or capacity limitations due to increased water production in existing fields. It can increase throughout while reducing internal corrosion rate. This research examines two models of combinations of VpCI-based corrosion inhibitors with different kinds of drag reducers. This work is a continuation of a study of using vapor phase corrosion inhibitors in the Petrochemical Industry[4,5].

The paper is presenting two VpCI products used in conjunction with two different drag reducers.

VpCI-A - Corrosion inhibitor, containing drag reducing ingredient (DR1) in its formulation

VpCI-B – Corrosion inhibitor, used in conjunction with a drag reducer (DR2) as a two part system. This system can be applied using 2 pumps in the same line for continuous treatment.

EXPERIMENTAL MATERIALS

Several classes of substances were found to have drag reducing properties; among them polymers and quaternary ammonium salts[1-3].

It is found that corrosion inhibitors might also have a drag reducing effect and this effect depends on the chain length and increases with the molecular weight [1]. Inhibitors suggested for this purpose are fatty acids, oxylated fatty acid amines, and/or amides with carbon numbers 18 -54. They all have nitrogen containing functional groups which provide strong binding to the substrate.

Considering above findings, the presented corrosion inhibitors were formulated. The chemical nature of VpCI-A and VpCI-B is very similar: they are both based on fatty acid imidazoline chemistry. This group of imidazolines has a very low solubility in water phase, commonly increased by using in conjunction with acetic acid. However acetic acid adds solubility only and doesn't provide additional corrosion protection[4]. That's why the long chain organic acid was used in the formulations of VpCI-A and VpCI-B.

The choice of materials

Fatty Acid Imidazoline:The fatty acid imidazoline consists of the following: an imidazoline, a long hydrocarbon tail group and a short pendent group (Figure 1) According to Ramachandan[4] the best corrosion protection is provided by imidazolines containing ethylamino group as a pendent group and fatty acid radical (hydrocarbon tail) containing not lower the C_{15}. This kind of imidazoline was used in our work and will be further named as a fatty acid imidazoline (FAI).

Organic Acids:The long chain organic acids were chosen for a new formulation based on our knowledge of their film-forming properties: Dimer acid (DA) combined with a small amount of Acetic acid (AA) was used in the formulation.

Vapor Phase Inhibitors: Aminocarboxylates (AC) were used in the formulation to provide protection in the vapor phase.

In addition:

VpCI-A contains Drag Reducing compound (DR1). This compound is based on quaternary amines, from the class of the salt of aromatic heterocyclic compounds. The choice of this material was dictated by the latest publication about drag reducers based on quaternary amines[5].

VpCI-B additionally contains a cosolvent which provides good compatibilies of VpCI-B and DR2. This is important based on the requirement of single dosing systems. DR2 is the emulsion of anionic water soluble polymer in oil. This product is very effective in low concentrations.

TESTING PROTOCOL

The rest of the testing protocol was based on the recommendations of ASTM G 170-01 [6] and NACE International Publication 1D 196 [7].

Corrosion protection properties were tested in the electrolyte: 9.62% sodium chloride, 0.305% calcium chloride, 0.186% magnesium chloride hexahydrate, and 89.89% de-ionized water[7].

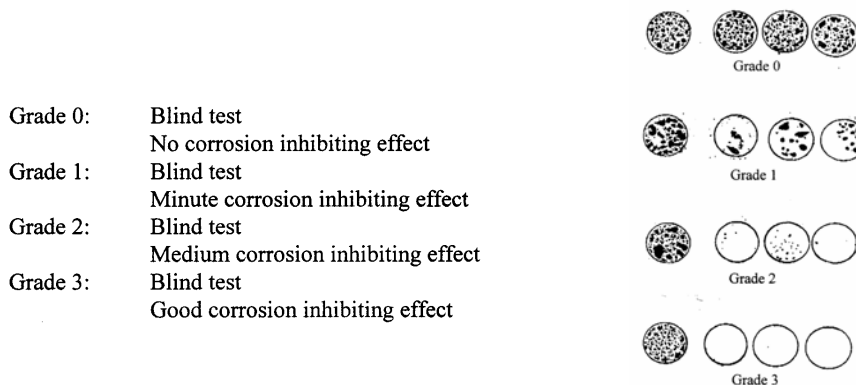Static tests: were carried out in sour and sweet/sour conditions in an oven set at 70°C for 48 hours:
- Electrolyte was purged with carbon dioxide (CO_2) or nitrogen (N_2) for 1 hour. In the case if carbon dioxide was used the resulting pH level was 4.5
- H_2S at concentration level of 500mg/L was generated in the sealed system by adding 1700 mg/L of acetic acid and 3530mg/L sodium sulfide ($Na_2S \times 9\ H_2O$)
- kerosene K-1 was used to simulate hydrocarbon phase
- tests were performed on panels or electrodes made from carbon steel SAE 1018.

The weight loss of the panels was determined and corrosion rate/percent protection calculated.

Dynamic test: was performed using the same electrolyte and hydrocarbon mixture as above, with continuous purging of CO_2 at a temperature of 70°C. Potentiostate 'Versastate' manufactured by EG&G Prinstone Applied Research Company and Rotating Cylinder Electrode manufactured by Pine Instruments were used for the electrochemical testing. The effect of the flow on corrosion inhibition was studied at the rotating rate of 500 - 3000 r/min. Corrosion rate was determined by analyzing the polarization curves obtained in Linear Polarization technique. Corrosion rate of the unprotected electrode was measured after 1 hour of immersion; then the inhibitor or inhibitor and drag reducing additive was added. Corrosion rate was measured after 6 hours of testing.

Vapor corrosion inhibiting ability was evaluated by testing according to the 'VIA' and 'H_2S' following procedures.

'VIA' was performed as follows. One gram of the inhibitor was introduced into the quart jar. The jar was sealed with the lid with the attached carbon steel sample in it. After the conditioning at the room temperature for 2 hours 3% solution of glycerin in de-ionized water was added in to the jar; jar was sealed again and placed into the oven set for 40° C for 2 hours. After the test jars were opened, the condition of the carbon steel samples were examined and provided protection pated according to the follow guidelines (6).

Grade 0:   Blind test
            No corrosion inhibiting effect
Grade 1:   Blind test
            Minute corrosion inhibiting effect
Grade 2:   Blind test
            Medium corrosion inhibiting effect
Grade 3:   Blind test
            Good corrosion inhibiting effect

'H2S' test was performed as follow. One gram sample of inhibitor in the small dish and panel made from the steel SAE 1010   were placed into 1 gallon jar. Jar was sealed and conditioned for 20 hours. After that the hydrogen sulfide was generated in this jar by combining in small beaker 0.02 g of Iron Sulfide (FeS) and 0.5ml of 1N hydrochloric acid (HCl).   The jar was placed in to the oven set for cycling temperature 8 hours – ambient and 16 hours $50^{o}C$. The panels were inspected for the presence of corrosion after one cycle in the oven.

Compatibility: of the system of VpCI-B and DR2 was evaluated. For this purpose VpCI-B and drag reducer DR2 were mixed in the ratio 1:1. Vortex test was performed using the mixture after 10 minutes, 2 hours, 24 hours and 1 week after mixing.

Vortex test: was used for evaluation of the drag reducing ability of DR2 and its combination with of VpCI-B. Vortex test was performed according to the follow procedure: 500 ml of water was poured into 1 liter beaker and stirred with ~ 500rpm. 4 g of the DR2 or 8 g of 1:1 mixture of VpCI-B and DR2 was added into the vortex using a syringe. The time to close for vortex was determined.

RESULTS

The results of the static corrosion tests are presented in Tables 1 and 2. All three types of treatment: VpCI-A, VpCI-B and the combination of VpCI-B and DR1, show effective corrosion protection at sour (Table 1) and sweet/sour (Table 2) electrolyte in the presence of hydrocarbons. Corrosion rates were almost equal in case of the VpCI-B and its combination with DR2. It shows that DR2 does not affect its inhibiting ability in static condition. Considering that the mechanism of the corrosion protection of VpCI-A and VpCI-B mainly depends on their film forming ability[4], one can conclude that DR2 does not prevent the adsorption of the inhibitor on metal surfaces.

Results of the testing in dynamic conditions are presented in Table 3 and Table 4.
Table 3 shows that corrosion rate is low in all three cases when the rotation rate is 500 rpm. Increasing of the rotation rate causes the increase in corrosion rate. At the same time the combination of VpCI-B and DR2 provides better corrosion protection than VpCI-A and VpCI-B separately under elevated rotation rate conditions.
Further increasing of the rotation rate caused the corrosion rate increase. Never the less it can be suppressed by increasing of the concentration of the corrosion inhibitor. (Table 3)

The results of the vapor corrosion inhibition ability of VpCI A and B are presented at the tables 5 and 6 and Fig 2. The data show that studied inhibitors emit the molecules into the surrounding atmosphere providing corrosion protection against the oxygen, moisture and hydrogen sulfide in the gaseous form.

Compatibility data of VpCI-B and DR2 is presented in Table 7. Data show that drag reducer DR2 does not lose it effectiveness when combined with VpCI-B.

The mixture of VpCI-B and DR2 did not visibly change after 1 week of mixing. This fact confirms that the transporting pipelines can be treated with the two part system VpCI-B and DR2 through the jointed feeding system.

CONCLUSION

1. VpCI-A and VpCI-B are effective corrosion inhibitors in sweet/sour electrolyte containing hydrocarbons.
2. The effectiveness of VpCI-A and VpCI-B depends on the flow rate and increased concentration is necessary to suppress corrosion when it is high.
3. According to the test results VpCI A and B provide vapor corrosion inhibition.
4. DR2 is compatible with VpCI-B and enhances protection ability of VpCI-B under high flow rate.

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Table 1
Results of static corrosion test in sour conditions

Sample ID	start weight	end weight	difference	Z,% of Corrosion protection
control	22.0295g	21.9362g	-93.3mg	-
50ppm VpCI-A	22.0289g	22.0157g	-13.2mg	85.8
100ppm VpCI-A	21.6107g	21.6040g	-6.7mg	92.8
50ppm VpCI- B	22.1844g	22.1779g	-6.5mg	93.0
100ppm VpCI B	21.3372g	21.3344g	-2.8mg	96.8

Table 2
Results of static corrosion test in sweet/sour conditions

Material	start weight	end weight	difference	Z, % of Corrosion Protection**
VpCI-A, 50 ppm	21.0804g	21.0782g	-2.2mg	97.9
VpCI-B, 50 ppm	21.3788g	21.3771g	-1.7mg	98.4
VpCI-B, 50 ppm + DR2, 50 ppm	21.7324g	21.7308g	-1.6mg	98.5
Control*	20.5388g	20.4343g	-104.5mg	-

Table 3
Results of the electrochemical dynamic corrosion test in electrolyte purged with CO_2

Material	Corrosion rate, mpy*** x 10^{-3}		Z, % of Corrosion Protection**	
	500 rpm	2000 rpm	500 rpm	2000 rpm
VpCI-A, 50 ppm	15.24	45.81	92.6	87.3
VpCI-B, 50 ppm	17.62	47.33	91.1	86.9
VpCI-B, 50 ppm + DR2, 50 ppm	13.60	31.38	93.4	91.3
Control * (no drag reducer)	206.0	360.7	-	-

Table 4
Results of the dynamic corrosion test in electrolyte purged with CO_2

Material	Corrosion rate, mpy**x 10^{-3}*		Z, % of Corrosion Protection**	
	2500 rpm	3000 rpm	2500 rpm	3000 rpm
VpCI-B, 50 ppm + DR2, 50 ppm	89.71	150.6	84.2	78.3
VpCI-B, 75 ppm + DR2, 50 ppm	23.28	51.36	95.9	92.6
Control * (no drag reducer)	567.8	694.1	-	-

*No inhibitor
**Z=100% (Cc – Ci): Cc; Cc – corrosion rate without inhibitor; Ci- corrosion rate with inhibitor;
*** Surface area of the coupon is 62.5 cm^2

Table 5
VIA Test results

Sample ID	Plug #1	Plug #2	Plug #3
VpCI-A	Grade 3	Grade 3	Grade 3
VpCI B	Grade 3	Grade 3	Grade 2
Control	Grade 0	N.A.	N.A.

Table 6
Test results in the Hydrogen Sulfide containing vapors.

Sample ID	Results
VpCI- A	No corrosion
VpCI B	No corrosion
Control	Corrosion

Table 7
Results of the 'Vortex' test*

Material	Time to close the vortex in seconds			
	Initial data	10 minutes after mixing	2 hours after mixing	24 hours after mixing
DR2	28	-	-	-
VpCI-B + DR2 (1:1)	-	32	32	32

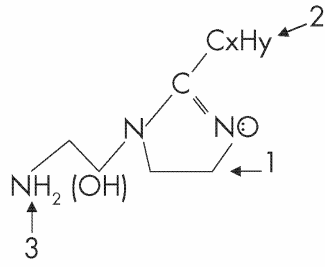* The mixture of DR2 and VpCI-B did not harden 1 week after the 2 products were mixed.

Figure 1
Typical fatty acid imidazoline
1. Head group
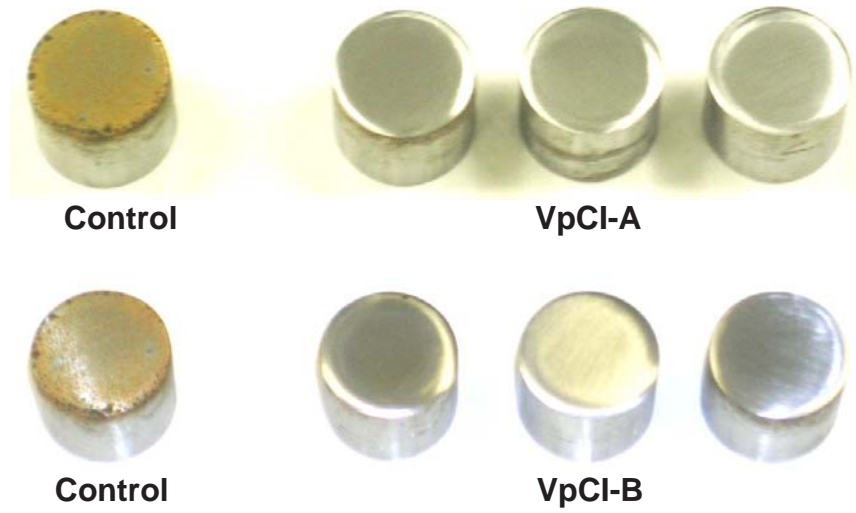2. Hydrocarbon tail group (fatty acid radical)
3. Pendent group

Control   **VpCI-A**

Control   **VpCI-B**

Figure 2
Results of the VIA Test