Paper No.
4247

CORROSION 2014
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March 9-13, 2014 • Henry B. Gonzalez Convention Center • San Antonio, Texas, U.S.A.

Categorization of Crude Oils Based on Their Ability to Inhibit Corrosion and Alter the Steel Wettability

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ABSTRACT

Field experience in oil and gas transportation shows that, in certain cases, the presence of crude oils can be beneficial in minimizing corrosion despite relatively high water cuts. In other cases, corrosion may occur at low water cuts. Limited research has been conducted to study what in the crude oil chemistry can explain this phenomenon. In the present work, fifteen different crude oils were tested for corrosion inhibition and wettability alteration (change from water wet to oil wet surface). The corrosion inhibition was measured in 4 steps: *precorrosion*, *partitioning*, *direct inhibition*, and *persistency*. The wettability of the surface was assessed by measuring the water-in-oil contact angle on a crude oil pre-wet steel surface. The results showed that some crude oils were capable of inhibiting corrosion, while others were not, and some were able to change the steel surface wettability from water wet to oil wet, while others could not. Interestingly, not all crude oils that could inhibit corrosion would alter the wettability and vice versa. Four different categories of crude oils were identified with respect to their ability to inhibit corrosion and alter steel wettability and mechanisms were suggested to explain this behavior.

Key words: corrosion inhibition, crude oils, wettability,

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INTRODUCTION

Crude oils can have corrosion inhibitive properties when it comes to internal corrosion of pipelines made from mild steel[1]. It is therefore of great interest to find what it is in the crude oil chemistry that can be inhibitive. This knowledge can help reduce the risk of internal pipeline corrosion and to optimize corrosion inhibitor usage. However, the crude oil chemistry is very complicated, comprising thousands of chemical compounds, that cannot all be analyzed individually, let alone in a synergy with each other.

In the early 2000's a series of papers on corrosion inhibition behavior of Venezuelan crude oils was published. The authors found that corrosion rate could be decreased by exposure to either the crude oil itself or the aqueous phase after it had been separated from the crude oil[2]. It was determined that the corrosion inhibition was due to adsorption of organic compounds on the steel surface[3] These organic compounds could come from any of the components indicated by a SARA analysis. To complicate the matter further, a statistical analysis[4] showed that the most influential corrosion inhibitive components of crude oils were not the same for paraffinic crude oils compared to asphaltenic crude oils.

The next step was to identify and isolate the chemical compounds from the crude oil that are responsible for the corrosion inhibition. It was found that nitrogen containing compounds that were able to partition into the water phase were the most protective[5], along with oxygen containing compounds, typically the carboxylic acids. A later study by a different group confirmed these findings[6]. This latter study concluded that the largest factor in inhibition was related to so-called "partitioning" of oil based components into the water phase, *i.e.*, the more compounds partitioned into the water phase, the more inhibitive it became.

In the late 2000's, work was done at Ohio University, where the different components of crude oils were studied in isolation. It was found that asphaltenes[7] could be very beneficial for corrosion inhibition, especially when they reached their solubility limit. Likewise, paraffins[8] were found to provide some protection against corrosion, however one that was easily altered. In another study, model compounds mimicking naturally occurring surface active crude oil compounds where systematically studied[9]. The compounds were grouped by the chemical composition of their head groups (the part that adsorbs to the surface) into three categories: oxygen containing compounds (carboxylic acids, including naphthenic acids), sulfur containing compounds (mercaptans (thiols), sulfides and thiophenes), and nitrogen containing compounds (both pyridinic and pyrrolic). It was found that the chemical structure of the surface active group was a deciding factor in corrosion inhibition, more so than the composition of the head group.

Due to all these reasons, individual crude oils have very different corrosion inhibition characteristics, which make a systematic study of the individual compounds responsible for the inhibition very lengthy and complicated and the mechanisms of inhibition hard to decipher. The work presented in this paper aims at proposing a simplified and more practical type of analysis of crude oils by presenting a method for characterizing crude oils based on their interaction with the steel surface, whether it is corrosion inhibition or their effect on the surface wettability.

EXPERIMENTAL PROCEDURE

Materials

The electrolyte used in all experiments was 1wt% NaCl DI water, purged with CO_2 and adjusted to pH5 with sodium bicarbonate.

A list of the properties for the crude oils presented in this paper is provided in Table 1. The crude oils have been given a nomenclature of Crude 1 through Crude 15 in order to mask their origin. The model oil used is LVT200™(3), a clear, low odor paraffinic solvent. It comes from the refining process as a hydrotreated light distillate. It has no direct effect on aqueous corrosion, *i.e.*, neither reduces or increases the corrosion rate, and is neutral towards wettability (doesn't change the wettability of the steel surface from hydrophilic to hydrophobic)[8].**Table 1**

Properties of the oils presented in this work

Oil Type	*Density (kg/m3)*	*API (°)*	*Viscosity (cP)*	*Interfacial Tension (mN/m)*
Model Oil	825	40.0*	2.0	47.0
Crude 1	778	39.9	1.6	25.2
Crude 2	830	36.0	4.7	26.2
Crude 3	853	32.0	9.1	28.1
Crude 4	879	29.2	22	23.2
Crude 5	891	30.6	36	26.5
Crude 6	849	36.2	8.4	28.0
Crude 7	838	37.1	5.1	31.0
Crude 8	843	36.9	7.4	22.3
Crude 9	926	20.3	560	25.6
Crude 10	841	37.4	6.9	28.2
Crude 11	926	12.6	13,000	29.3
Crude 12	872	30.8*	27	26.5
Crude 13	842	36.0*	58	29.6
Crude 14	910	24.0*	140	25.2
Crude 15	858	33.4*	6.8	25.5

* Calculated value

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(3) Trade name

Corrosion Inhibition

The corrosion inhibition tests were carried out using a standard three electrode glass cell set-up with a Rotating Cylinder Electrode (RCE) working electrode made out of API(4) 5L X65 carbon steel, platinum counter electrode and Ag/AgCl reference electrode. At the beginning of each experiment 1.8 liters of 1wt% NaCl solution in DI water was poured in the glass cell together with 0.23g of solid $NaHCO_3$ (for pH adjustment) and the solution was purged for 1-1.5 hours with CO_2. After purging, the solution pH was adjusted to 5.0 with CO_2 saturated 1M $NaHCO_3$ solution. After pH adjustment, a working electrode with a surface area of 5.3 cm^2, was mounted and placed inside the glass cell. The working electrode had been polished with 600 grit silicon carbide and cleaned in an ultrasonic bath with isopropanol prior to testing.

The rotational speed of the working electrode was set to 1000 RPM and the open circuit potential was measured for at least 30 min until it reached the stable value around -690 mV (vs. Ag/AgCl). The corrosion measurements (Linear Polarization Resistance, LPR) started after the solution resistance, R_s, had been measured using Electrochemical Impedance Spectroscopy (EIS), and consisted of four consecutive steps:

1. *Precorrosion step*
2. *Partitioning step*
3. *Direct inhibition step*
4. *Persistency step*

Precorrosion step

During this step, the working electrode was immersed in the aqueous solution and corrosion rates were recorded by using LPR every 20 min for 4 – 7 hours. Purpose of this step was to determine the corrosion rate “baseline” in each experiment, and to obtain a more realistic steel surface morphology, before adding the crude oil.

Partitioning step

After finishing the precorrosion step, 0.2 liters of crude oil (purged with CO_2 for 20 to 30 min) were poured into the glass cell, forming a layer on top of the water solution. The working electrode rotation was 1000 RPM and LPR corrosion measurements were taken every 20 minutes for 12 hours. The purpose of this step was to detect the presence of surface active compounds in the crude oil which can partition from the oil phase into the water phase and adsorb on the working electrode surface to reduce the corrosion rate.

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Direct inhibition step

In this step, which came immediately after partitioning step, the working electrode was lifted up from the water phase into the crude oil layer above it and left there rotating for 12 hours. Rotation speed was kept constant at 1000 RPM. No measurements were taken during this step, since the working electrode was immersed in crude oil which is a nonconductive liquid. Purpose of this step was to allow adsorption of crude oil compounds onto the steel surface directly from the oil phase. For some crude oils, the working electrode was periodically inserted into the water phase during this step in order to monitor the reduction of corrosion rate with time.

Persistency step

After the direct inhibition step, where the working electrode was immersed in the crude oil for 12 hours, it was lowered back in the water phase and rotated at 1000 RPM for at least 20 hours more. Corrosion rate was measured every 20 minutes by LPR. Purpose of this step was to determine whether corrosion inhibition was obtained during the direct inhibition step and if so whether the corrosion inhibition was persistent.

Contact angle

It is possible to measure the contact angle either on a water droplet surrounded by oil or on an oil droplet surrounded by water. In this work, the contact angle was measured on a water droplet, which is also referred to as *water-in-oil* contact angle. The measurements were performed using a goniometer set-up that included a video camera recording the evolution of the water droplet spreading on the steel surface and a backlight. There was a removable sample holder inside the cell, which fits a flat, API(5) 5L X65 carbon steel sample.

The steel sample was polished with a 600 grit silicon carbide sand paper and cleaned in ultrasonic bath with isopropanol. Then it was prewetted by immersing it in crude oil for 24h. After immersion, the sample was rinsed with toluene to remove any deposited or physiosorbed oil from the surface. What is left on the surface is what has been chemisorbed from the oil. After the rinsing, the sample was placed inside the goniometer, which was previously filled with a clear model oil (Table 1) purged with CO_2. Since the crude oil is opaque, the water droplet could not be detected visually unless a transparent oil is used.

Water droplet from a 1wt% NaCl DI water solution purged with CO_2 and pH adjusted to 5 was injected from above and dropped onto the steel surface. The droplet was recorded with a camera and the contact angle was measured using image processing software.

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RESULTS

A total of 15 crude oils were tested according to the experimental plan outlined in the section above. There were four different types of corrosion inhibitive behavior observed for the 15 crude oils. In two cases, persistent corrosion inhibition was observed, and in two cases, no persistent corrosion inhibition was observed. In the case shown in Figure 1, the corrosion rate steadily decreases in the *partitioning* step, where chemical compounds from the crude oil phase partition into the water phase and inhibited corrosion. After the *direct inhibition* step the corrosion rate reduces slightly more, and stays low during the *partitioning* step.

In the case shown in Figure 2, the corrosion rate stays consistent around 0.8 mm/y during both the *precorrosion* step and the *partitioning* step. However, after the *direct inhibition* step, the corrosion rate decreased to around 0.4 mm/y. Together, the two cases shown in Figures 1 and 2 represent crude oils which were inhibitive to corrosion.

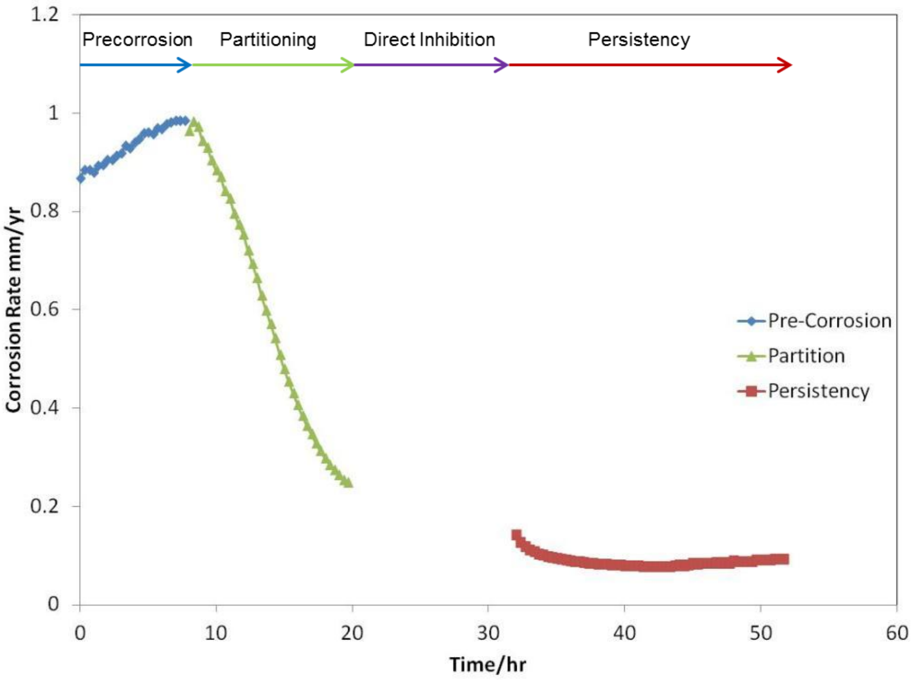


Figure 1: Corrosion testing of Crude 3 showing corrosion inhibition occurring in the *partitioning* step.

Figures 3 and 4 represent cases where an exposure to a crude oil did not result in corrosion inhibition. In Figure 3, there was quite significant reduction in the corrosion rate during the direct inhibition step, but this reduction in the corrosion rate was not persistent and the corrosion rate steadily increased and reached the precorrosion values within 24 hours of exposure.

The final sample of corrosion behavior of a crude oil is given in Figure 4, where no corrosion inhibition was detected. In fact, the corrosion rate steadily increased. The increase in the corrosion rate is *not* attributed to the crude oil itself, *i.e.*, the crude oil is not considered corrosive, but rather to the formation of iron carbide. Iron carbide forms on a carbon steel as the ferrite phase is corroded, leaving behind the cementite structure. This has been shown to accelerate corrosion due to the iron carbide acting as an additional cathodic site[10].

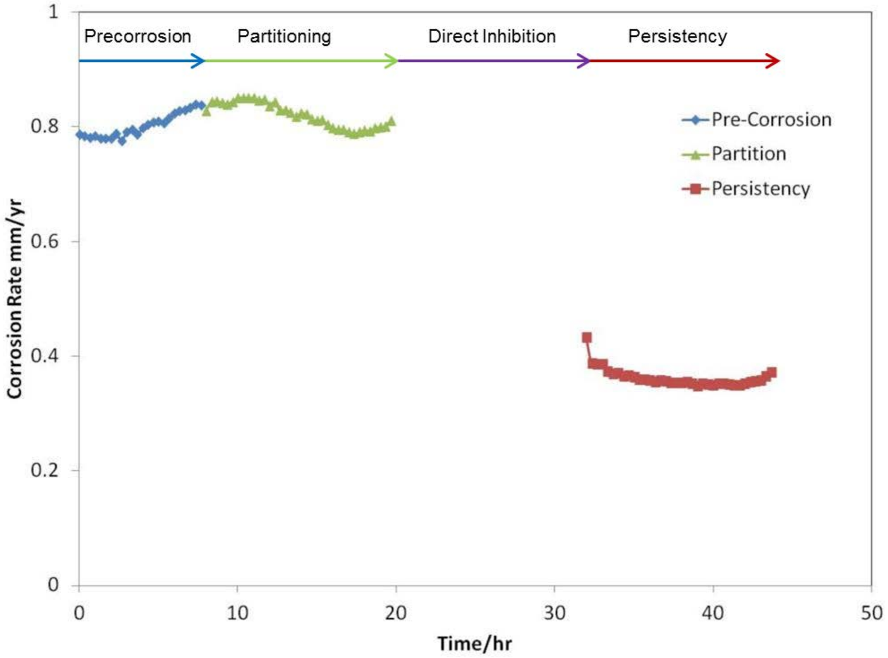


Figure 2: Corrosion testing of Crude 4 showing corrosion inhibition occurring in the *direct inhibition* step.

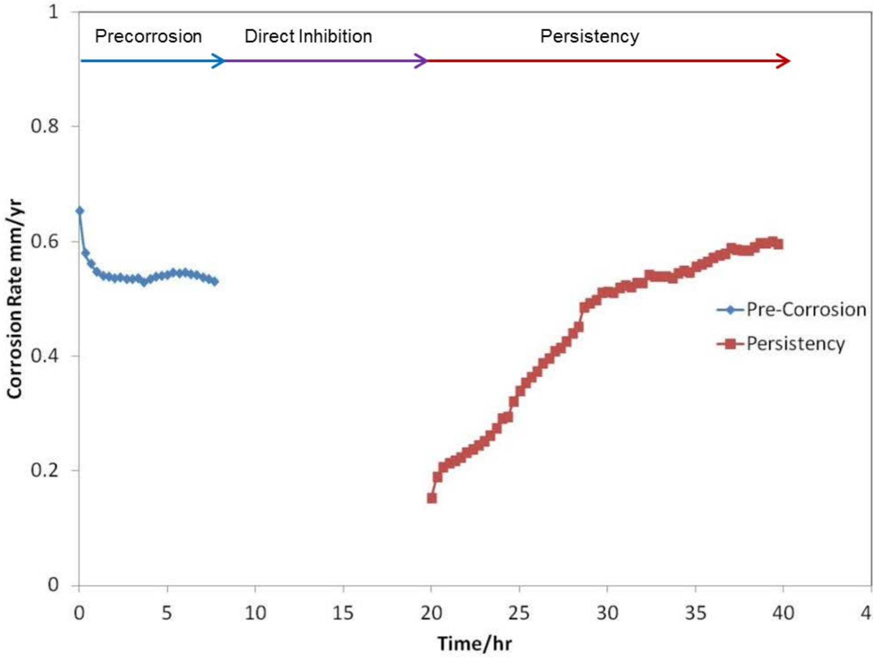


Figure 3: Corrosion testing of Crude 1 showing corrosion inhibition occurring in the *direct inhibition* step, but it is not persistent. For Crude 1, the partitioning step was not included.

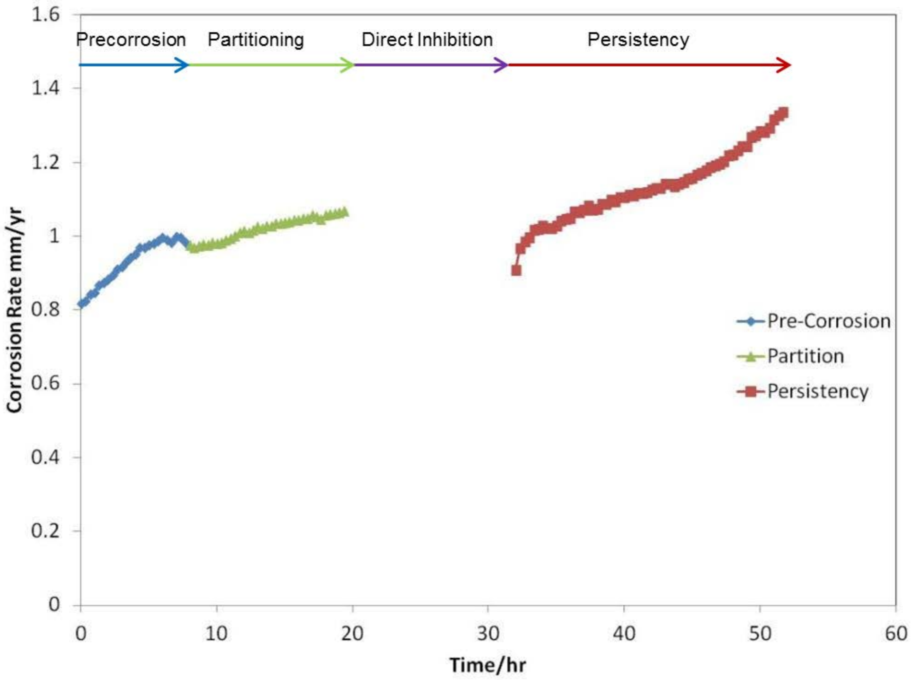


Figure 4: Corrosion testing of Crude 7 showing no corrosion inhibition.

When looking at the wettability of a steel surface, which was prewetted by crude oil, two scenarios were recorded. In one scenario, the water droplet never wettted the steel surface. In fact, it never came in direct contact with the steel surface and literally rolled off (Figure 5a). In this case the steel surface was considered to be completely <u>hydrophobic</u>, with a contact angle of 180°. A contact angle ranging from 90° to 180° is generally considered hydrophobic, with 90° being closer to a neutral surface (having no preferential affinity for neither water nor oil) and a higher contact angle indicating a more hydrophobic the surface.

In the case where the water did wet the crude oil prewetted steel (Figure 5b), the measured contact angles were close to a neutral surface as shown in Table 2, ranging from 81° (slightly hydrophilic) to 109° (slightly hydrophobic).

a) b)

Figure 5: Water droplet on a crude oil prewetted steel surface. a) Hydrophobic surface, the water does not wet the steel, b) hydrophilic surface, the water partially wets the steel.

The results for the corrosion inhibition of each crude oil is summarized in Table 2. The corrosion inhibition was calculated based on the percentage difference between the precorrosion rate and the final corrosion rate at the end of the *persistency* step. In the case where the final corrosion rate was close to (or higher than) the precorrosion rate, the inhibition is determined to be 0%. Only 6 out of the 15 crude oils showed corrosion inhibition and out of those six, half showed good corrosion inhibition (≥90%) and half showed moderate corrosion inhibition (56-75%),.

Despite the fact that many of the crude oils didn't produce significant corrosion inhibition, most of them were able to change the wettability of the steel surface from hydrophilic (<90°) to hydrophobic (>90°). In the absence of surface active species found in the crude oil or, the contact angle is measured[8] at 40°. However after immersion in a crude oil for 24 hours, the contact angle typically increased toward more hydrophobic values. For 11 out of the 15 crude oils, a completely hydrophobic surface was obtained, where the water droplet never wetted the surface. In the case of the 4 crude oils where this did not happen, the contact angle was close to 90°, which represents a neutral surface where neither oil nor water show more affinity for wetting the surface.

In order to see if there is a simple relationship between corrosion inhibition and the physical properties of the crude oil, the corrosion inhibition data (from Table 2) are plotted as a function of API (Figure 6a), dynamic viscosity (Figure 6b), interfacial tension (Figure 6c), and the water-in-oil contact angle (Figure 6d). Clearly there is no recognizable trend obtained in these laboratory experiments. However, it should be recognized that in a pipeline flow there would be a difference between the behavior of the light and heavier crude oils as the denser and more viscous crude oils entrain the water more easily and keep it away the pipe surface, thereby reducing corrosion.

As can be seen from these results (Figure 6d), not all crudes that are inhibitive can alter the wettability of the steel surface and not all crude oils that alter the wettability can inhibit corrosion. Clearly, the corrosion inhibitive mechanism is more complicated than simply that of compound(s) from the crude oil adsorbing on the steel surface to form a hydrophobic film blocking iron from dissolving. When the data in Table 2 are looked at more closely, the behavior obtained by different crude oils can be grouped into two categories with respect to persistent corrosion inhibition: *inhibitive* or *not inhibitive*. With respect to wettability the two groups are: crudes producing a completely hydrophobic surface (180°)) or those which do not. It is then possible to see four different behaviors (categories):

1. The crude oils that both inhibit corrosion and alter the wettability of the steel (Category 1).
2. The crude oils that inhibit corrosion but do not alter the wettability of the steel (Category 2).
3. The crude oils that do not inhibit corrosion but alter the wettability of the steel (Category 3).
4. The crude oils that neither inhibit corrosion, nor alter the wettability of the steel (Category 4).

These categories are summarized in Table 3 in the way they are used in Table 2 (Yes/No denomination). After these categories were established, the next step was to try and understand what the underlying reason for the different behavior was and whether it is possible to derive any further, more in-depth information from these results. Following is an attempt to explain the different behaviors found for various crude oils.

Crude oils that alter wettability *and* inhibit corrosion fall into **Category 1**, which is depicted in Figure 7a. A possible explanation is that surfactant compounds found in these crudes form a persistent hydrophobic layer at the surface which water cannot penetrate or spread on. Molecules that form the layer cannot be displaced with water, not even under flow conditions (rotating cylinder test). This behavior compares to that of corrosion inhibitors as seen in Figure 8a of *oil-in-water* contact angles. The increased addition of an inhibitor (fatty amino type) changes the surface from hydrophilic (the oil droplet does not spread) to hydrophobic (the oil droplet spreads on the surface).

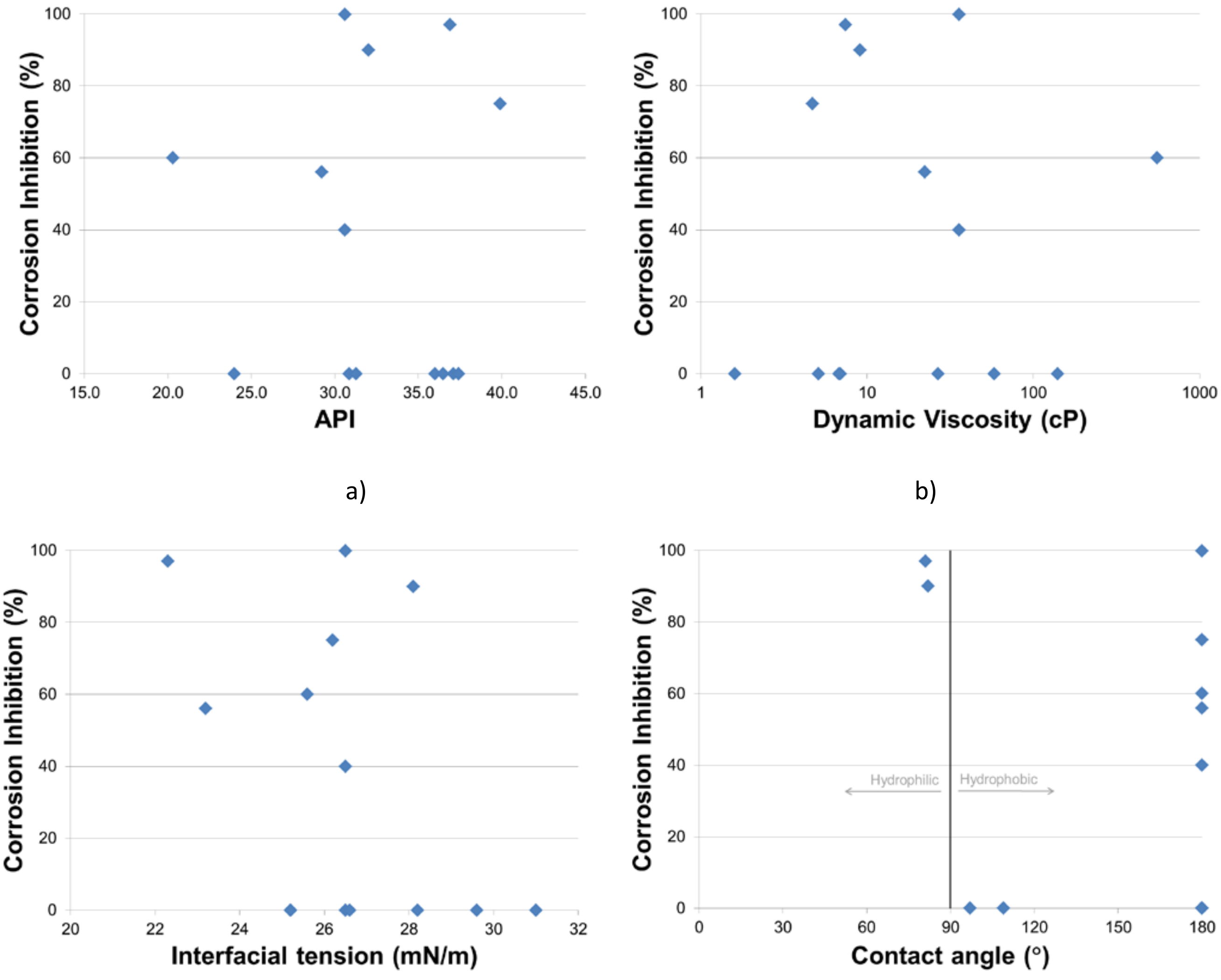
Crudes that inhibit corrosion, but do not change the wettability are classified as **Category 2** and shown in Figure 7b. Those crude oils are believed to form a *hydrophilic* protective barrier. The molecules are bonded to the surface, but they are not surfactants (do not consist of a hydrophilic head group and a hydrophobic tail) and do not form a hydrophobic barrier. A similar behavior is seen for example in experiments with sodium thiosulfate, which is a common non-surfactant component of corrosion inhibitor packages. Sodium thiosulfate can chemically react with the steel surface and inhibit corrosion[11], however, it has no effect on the contact angle (Figure 8b). Even with an addition of 200 ppm of sodium thiosulfate (which is a very high dose), the oil-in-water contact angle stays the same (20°). This shows that sodium thiosulfate inhibits corrosion without changing the wettability of the surface and it is therefore possible that there are compounds in the crude oils that fall into this category and display the same behavior.

Table 2
Summary of the persistent corrosion inhibition and the water-in-oil contact angle for crude oil prewetted surface along with a classification whether the crude oil was inhibitive and changed the wettability.

Crude Oil	*Corrosion Inhibition (%)*	*Is Inhibitive? (Yes/No)*	*Contact Angle (°)*	*Alters Wettability (Yes/No)*	*Category (Table 3)*
Crude 1	0	No	180	Yes	3
Crude 2	75	Yes	180	Yes	1
Crude 3	90	Yes	82	No	2
Crude 4	56	Yes	180	Yes	1
Crude 5	99	Yes	180	Yes	1
Crude 6	0	No	180	Yes	3
Crude 7	0	No	97	No	4
Crude 8	97	Yes	81	No	2
Crude 9	60	Yes	180	Yes	1
Crude 10	0	No	180	Yes	3
Crude 11	0	No	180	Yes	3
Crude 12	0	No	109	No	4
Crude 13	0	No	180	Yes	3
Crude 14	0	No	180	Yes	3
Crude 15	0	No	180	Yes	3

Table 3
Summary of the categorization of crude oils used in Table 2 depending on whether the oils inhibit corrosion and/or alter the steel wettability

	Persistent Corrosion Protection	Wettability Alteration
Category 1	Yes	Yes
Category 2	Yes	No
Category 3	No	Yes
Category 4	No	No



a)

b)

c)

d)

Figure 6: Corrosion inhibition compared to the properties of the crudes. a) API gravity, b) dynamic viscosity, c) Interfacial tension, and d) contact angle.

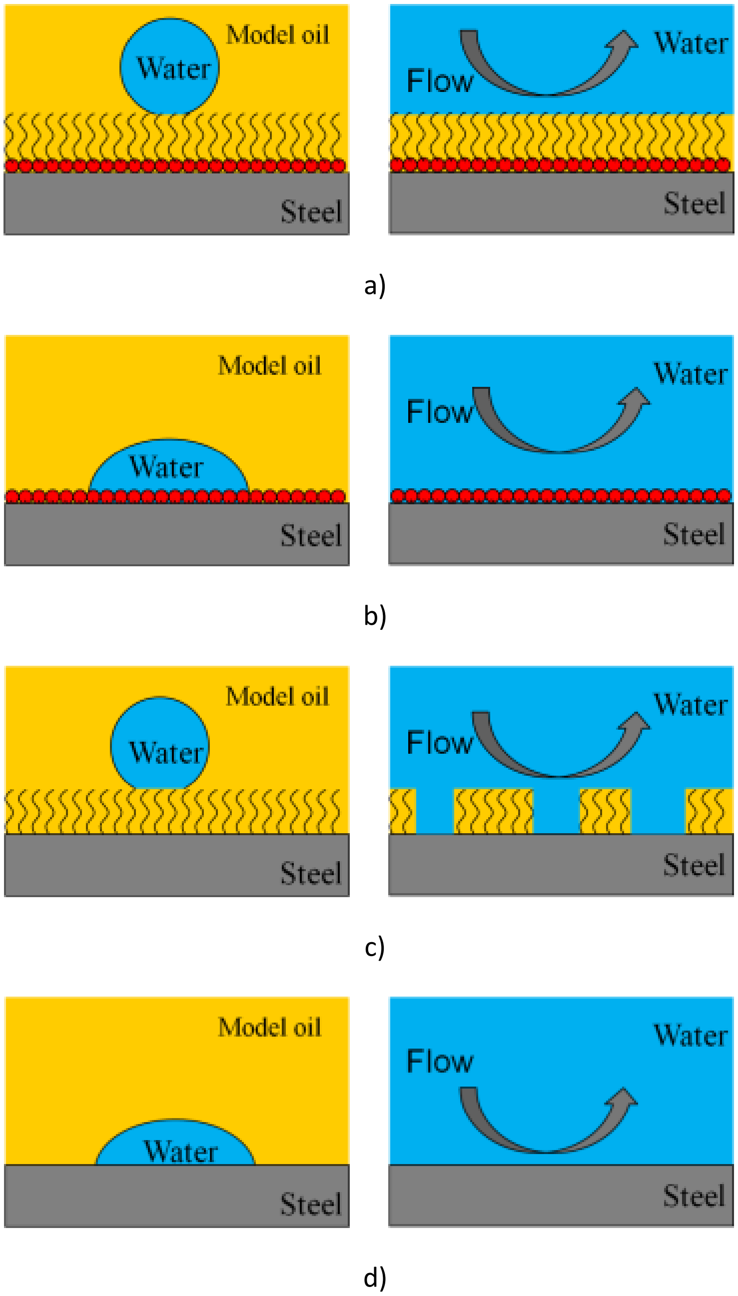


Figure 7: Proposed mechanism of the effect of crude oils on wettability alteration (schematics on the left) and wettability alteration (schematics on the right). a) Category 1, b) Category 2, c) Category 3, and d) Category 4.

Total of seven (7) out of the fifteen (15) crude oils fall into **Category 3**, which includes crude oils that alter the wettability but do not inhibit corrosion. Crude oils from this category can have chemical compounds that form a weakly bonded surface layer, which eventually gets displaced by the water (Figure 7c). Since the contact angle measurements were taken at stationary conditions, with a limiting amount of water (just one droplet in a vessel full of oil), while the corrosion inhibition measurement was done with a rotating cylinder surrounded by vast amount of water, the surface layer was not challenged as much during the contact angle measurement as during the corrosion inhibition measurement. This suggests that the crude oils falling into this category can be protective against corrosion providing that the water phase is entrained in the oil phase (such as under dispersed flow) and even if the water droplets periodically come into contact with the pipe wall, they are not able to wet it and sustain the electrochemical corrosion process.

Finally, crudes that are grouped in **Category 4** do not have components that can adsorb on the steel surface and inhibit corrosion or change the wettability (Figure 3d). For pipelines carrying crude oils falling under his category, it is important to pay special attention to the mitigation of corrosion by use of corrosion inhibitors and by ensuring that the water phase does not settle on the pipe walls to cause corrosion.

It should be noted that a complete production history of the crude oils presented in this paper is not available. Some of the crude oils may have been treated with additives, such as inhibitors (corrosion, scale, wax, etc.), that can change the behavior of the crude oils towards the steel surface (corrosion inhibition and/or wettability). This does not invalidate the methodology presented in this paper, but it is important to remember that the present results are pertinent for the sample as received (and not for the native crude oil) and can change, for instance if the amount of additives is changed.

a) b)

Figure 8: Oil-in-water contact angle images when the inhibitors are added to the water phase. a) Fatty amino film forming inhibitor – surfactant[12], and b) Sodium thiosulfate - inorganic salt

CONCLUSIONS

Despite the complexity of the crude oil chemistry, it is possible to gain some insight into their corrosion inhibitive behavior by using a simple testing methodology that looks at the corrosion inhibition under different scenarios (partitioning, direct inhibition and persistency) and to look at the effect of the crude oils on other surface phenomena, such as the surface wettability. By grouping the crude oils into categories based on their effect on the surface activity, more insight can be gained into the mechanism of crude oils and corrosion inhibition. Possible mechanisms for this behavior are discussed and depend on whether or not an inhibitive adsorption layer is formed and whether this layer is hydrophobic or hydrophilic.

ACKNOWLEDGEMENTS

The work presented in this paper was done as a part of the Water Wetting Joint Industry Project at Ohio University and the authors would like to acknowledge the sponsors of the project for their financial support, and for providing samples of crude oils to test. The companies are: BP, ConocoPhillips, ENI, ExxonMobil, Petrobras, Saudi Aramco, Shell and Total.

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