Corrosion-inhibiting oil for potential application as float coat for temporary protection of mild steel

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Abstract: Oil tanks are often made from mild steel, and as such, they are subject to corrosion damage that can cause leaks which pose a danger to public health and safety and to the environment. Critical parts of the above ground storage tank such as the bottom plate, the lower part of the shell and the roof are often protected with protective coatings, while the other surfaces in contact with oil are not permanently protected. Special attention should be addressed to such bare surfaces when mild steel is in direct contact with water such as during hydrostatic testing. One possible solution is application of a corrosion inhibiting oil which floats on the surface of the water and, in contact with tank walls, forms a protective layer.

Electrochemical testing of mild steel samples protected by corrosion-inhibiting oil in natural sea water at elevated temperature (30±2) °C was performed. The three test mixtures were pure sea water, sea water inhibited by oxygen scavenger, and sea water inhibited by oxygen scavenger and treated with biocide. The study included determination of corrosion potential, metal resistance and corrosion rate. The tested corrosion-inhibiting oil showed significant prevention of general corrosion of the mild steel samples.

Key words: corrosion-inhibiting oil, float coat, temporary protection, mild steel, sea water

Introduction

The cost of corrosion influences many industries and brings the need for development of corrosion resistant materials and improvement of corrosion protection measures in focus. It is estimated that the annual cost of corrosion reaches 3-4% of GDP in developed countries [1]. In the oil, gas and chemical industry alone, corrosion is one of the most challenging tasks and is estimated to cost 170 billion USD annually [2,3]. In addition to high costs of corrosion, it also concerns the health and environmental issues connected with the possible failure of oil and gas equipment, production line and storage tanks. Therefore, effective corrosion prevention has a high economic and ecological impact [4].

Storage tanks are an integral part of all industries. They serve to store various liquids including crude oil, oil derivatives, wastewater, chemicals, food products and many others. Tanks are most often made of non-alloyed carbon steel, and as such are subject to corrosion damage that can cause leaking and thereby endanger public health, the environment and safety.

There are basically eight types of tanks used to store liquids: tanks with a fixed roof, external floating roof tanks, internal floating roof tanks, external floating roof tanks with a dome, horizontal containers, pressure tanks, tanks with variable steam space, LNG (liquefied natural gas) tanks [5].

The above ground storage tank (AST) is placed on the ground, so it can have a larger volume to meet the needs of oil storage, while the construction technology is simpler and more practical, which can reduce the construction cost. In addition, increasingly strict environmental protection requirements require more attention to be paid to the safety of oil storage, and an above-ground oil storage tank makes it possible to avoid the stored oil leaking into the ground. Aboveground storage tanks in the petroleum industry come in a wide variety of sizes, ranging from sizes of 200 m^3 up to storage volumes more than 100,000 m^3 [6].

Corrosion is the primary reason of the deterioration of steel storage tanks and therefore, control and prevention of tank corrosion is of prime importance for efficient plant economics and safety [7]. If not repaired in a timely manner, corrosion damage will gradually reduce wall thickness, which can weaken or destroy tank components resulting in pits, reduced structural capacity, and tank failure.

The corrosion intensity is greatly influenced by several factors including environmental conditions, tank material and construction (joints, insulation, etc.), length of exposure of unprotected steel to moisture, chemical properties of the liquid, and undesirable temperature ranges.

Figure 1 shows damage to the ground plate of the product storage tank after 6 years in operation, due to microbiologically induced corrosion by sulphate-reducing bacteria (SRBs). The insulation in the tank pad below the tank was found to be contaminated with sulphate. In combination with the high groundwater level, this led to the growth of sulphate-reducing bacteria. The resultant sulphide attacked the steel. Remedy is to raise the pad so that the tank no longer stands in the groundwater and use sulphate-free insulation [8].

Figure 1. Microbiologically induced corrosion of product storage tank bottom plate after 6 years (CASE HISTORY 01.11.17.01) [8]

Figure 2 shows the damage to the tank floor in the zone of the welded joint which was exposed to contaminated water that settles out with solids on the bottom of the tank. The heat-affected zone dissolved electrolytically because this zone was less noble in relation to the rest of the plate. Attack by aggressive water in bottom sediment can be prevented by application of a coating to the bottom. In this case, no measures have been taken because the lowest bottom plate was still intact, so there was no danger of leakage [8].

Figure 2. Bottom plate weld corrosion of crude oil storage tank after 5 years (CASE HISTORY 01.11.02.05) [8]

The corrosion of the tanks could be external and internal. The occurrence of internal corrosion of a storage tank depends on the aggressiveness of the stored product and the material of which the tank is constructed. In some cases, it is necessary to use linings (coatings) that are more resistant to the corrosive properties of the stored fluid than are the tank construction materials. In some particularly corrosive services, it may be necessary to construct the tanks of a corrosion resistant material [9]. This paper deals with internal corrosion and corrosion prevention of crude oil tanks.

The internal corrosion could occur in permanent use due to accumulation of water at the bottom of storage tanks but also during hydrostatic testing with fresh water and in some cases with sea water. That is the reason why corrosion inhibitors are often used for corrosion mitigation of bare carbon steel tank surfaces. These treatment systems have proven to be effective for short-term exposure. However, for such applications, possible solution is corrosion-inhibiting oil as float coat which requires much less material vs treating a very large tank body with water, and possible use of seawater, which itself can be huge saving at places where there is no fresh water.

The float coat, being a hydrocarbon-based product, floats on the surface of the water, allowing for a unique application using a much smaller volume of product than typical chemical/inhibiting additives. The vessel floor and initial meter of wall height is sprayed with a layer of the float coat before any water is added to the system. Water is slowly added, until a point just below the initial spray treatment. The remainder of the float coat is applied to the top of the water layer. Hydrotesting is then carried out as normal with care to fill the system at such a rate that the float coat layer on the water's surface is not disturbed. As the hydrotest proceeds, the walls of the vessel are coated with the float coat and further recoated as the vessel is drained [10].

Experimental study

In this paper, corrosion-inhibiting oil M645 for potential application as float coat for temporary protection of mild steel during hydrotesting with seawater was studied. In this study three types of corrosion protection of carbon steel in natural seawater at 30 °C were tested, that is:

1. Carbon steel protected with M-645.
2. Carbon steel protected with M-645 and addition of 100 ppm oxygen scavenger S7 in natural seawater.
3. Carbon steel protected with M-645 and addition of 100 ppm oxygen scavenger S7 and 1% biocide Izosan G (chlorine solution) in natural seawater.

The carbon steel samples DIN C10 (0.08 %C, 0.2 %Si, 0.41 %Mn, P < 0.045 %, S < 0.045 %) were prepared by sandpaper granulation 220-600, washed with water and degreased in ethanol. M-645 was applied on prepared samples by immersion, hold for two hours, drained, and then immersed in testing solution. S7 and biocide were dosed into testing solution before immersion of testing sample.

To evaluate corrosion inhibiting performance, electrochemical polarisation study of mild steel samples protected by corrosion-inhibiting oil in natural sea water at elevated temperature (30±2) °C was performed.

The study included determination of corrosion potential, metal resistance and corrosion rate. The testing was conducted in a standard three electrode test cell in relation to the reference saturated calomel electrode (SCE), using a Potentiostat/Galvanostat device, Model VersaSTAT 3 (Princeton applied research AMETEK). Polarization curves were registered after 1000 seconds of exposure to the testing solution to allow corrosion potential (E_{corr}) stabilization. Polarization resistance (R_{p}) was determined in a ± 20 mV potential range around the corrosion potential. During the potentiodynamic measurements, the working electrode was polarized to the potential of ± 250 mV relative to the corrosion potential and the current (I_{corr}) response was measured.

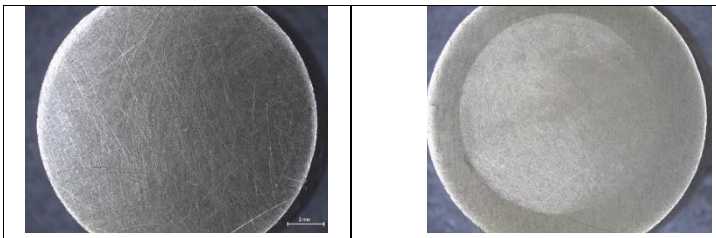
For interpretation of the obtained data, the ZSimpWin Version 3.2 software was used. Besides electrochemistry, gravimetric method for determination of weight loss was performed, whereas assessment of surface after corrosion testing was conducted using microscope.

Results

Testing electrochemical polarization results of blank sample – carbon steel in seawater are shown in Table 1 and Figures 3 and 4.

Table 1. Polarization test results of unprotected carbon steel after 24 hours in natural seawater

Electrolyte	Natural seawater
Temperature	(30±2) °C
Testing material	Carbon steel, DIN C10, **blank sample**
Corrosion potential, E_{corr} **vs. SCE**	-726.281 mV
Metal resistance, R_{p}	0.351 kΩ/cm^{2}
Corrosion current, I_{corr}	16.044 µA
Corrosion rate, v_{corr}	0.18678 mmpy
Tafel slope, $ß_{a}$	58.357 mV
Tafel slope, $ß_{c}$	224.697 mV



Before testing

After 24 h immersion in seawater

Figure 3. Carbon steel sample view before and after polarization testing in seawater

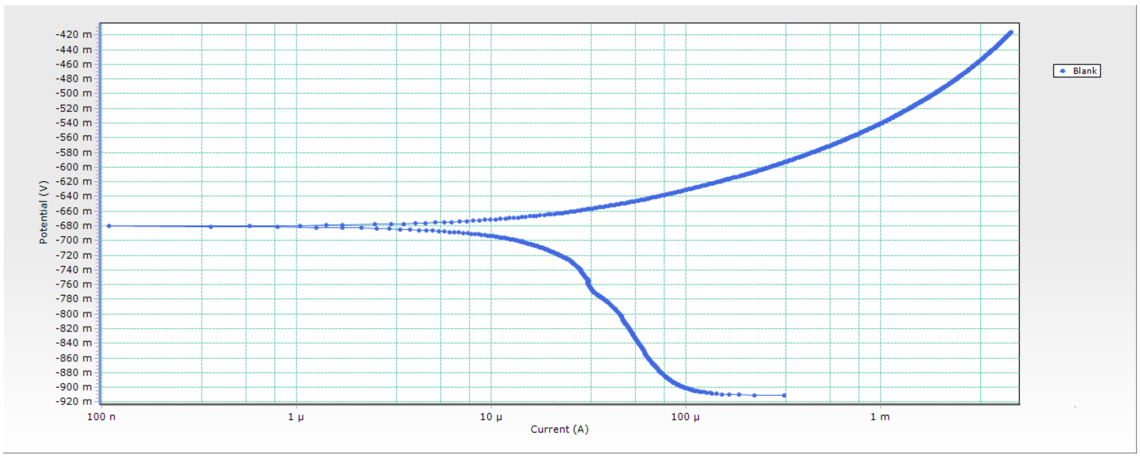


Figure 4. Tafel plot of blank sample after 24 h testing in seawater

Polarization test results and gravimetric test results of protected carbon steel tested in natural seawater after 1- and 3-days immersion are presented in Table 2.

Table 2. Polarization test results of carbon steel in natural seawater

Immersion time (days)		Δm [g]	Corrosion potential, E_{corr} vs. SCE (mV)	Corrosion current, I_{corr} (µA)	Corrosion rate, v_{corr} (mmpy)	$ß_A$ (mV)	$ß_K$ (mV)
M-645	1	0.0013	-328.789	0.45158	0.0052571	20.701	74.836
	3	0.0010	-501.465	0.578	0.0067255	28.302	94.172
M-645 + S7	1	0.0005	-368.661	0.138341	0.0016105	31.401	98.996
	3	0.0015	-218.988	0.567963	0.006612	58.516	228.675
M-645 + S7 + B	1	0.0019	-223.909	0.975162	0.011352	110.194	110.194
	3	0.0011	-142.312	0.35307	0.0041103	95.209	56.785

Overlapped Tafel diagrams after 1 and 3 days immersions in natural seawater are shown in Figures 5 and 6.

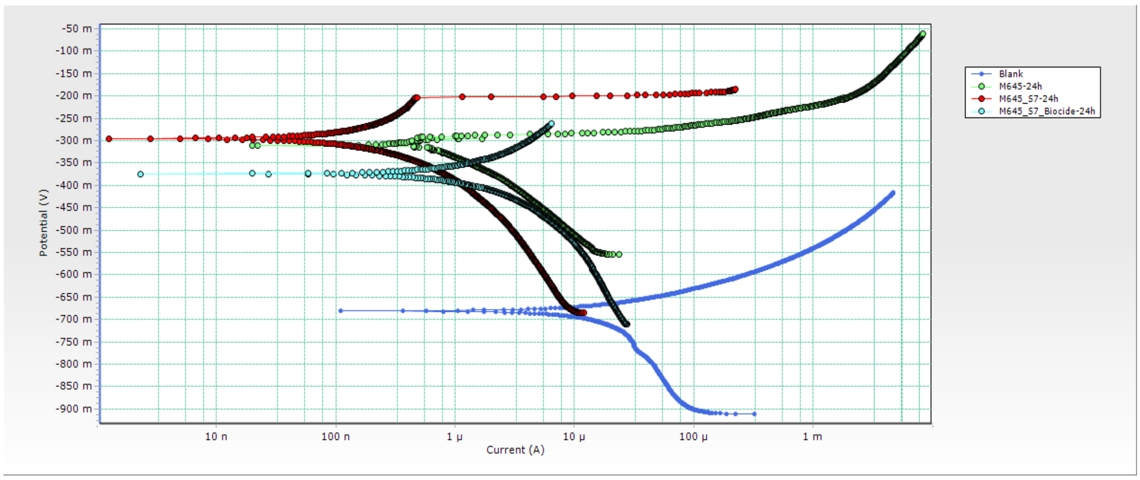


Figure 5. Tafel plots for all types of corrosion protection after 24 h in seawater

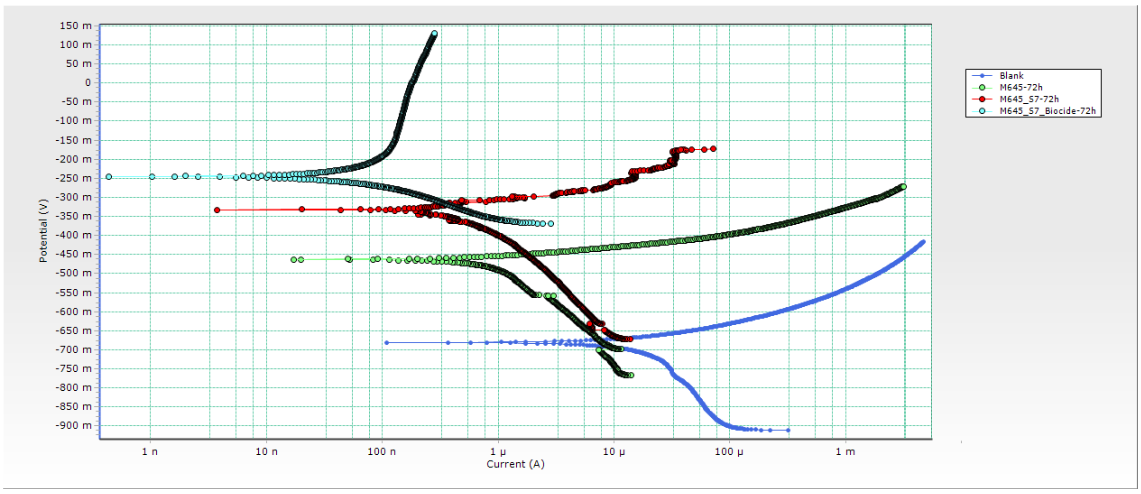


Figure 6. Tafel plots for all types of corrosion protection after 72 h in seawater

From the obtained research results the lowest corrosion rate of carbon steel after 72 hours in the natural seawater was achieved by third method of corrosion protection by application of M-645 on test coupons and adding the 100 ppm of S7 and 1% of chlorine-based biocide in solution (Figure 7).

It should be considered that this result refers to uniform or general corrosion, which represents a uniform loss of metal over the entire surface. Visual examination of samples showed localized pitting initiation on testing samples after polarization testing, possible due to local cracking of protective film in chlorine environment.

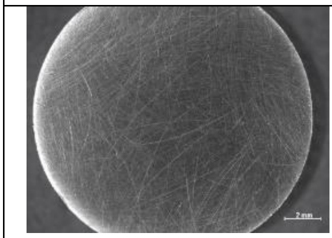
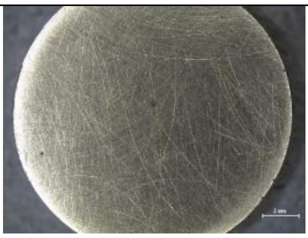
Before testing	After 72 hours of immersion in seawater
	
Grinding traces on the surface	Spot damage visible at intersection of the grinding traces

Figure 7. Sample view before and after 72 hours of immersion in sea water and Tafel extrapolation testing, sample protection by M-645 + S7 + BIOCIDE

Conclusion

Based on the conducted electrochemical testing at elevated temperature after 1 and 3 days in natural seawater on carbon steel samples protected by M-645 float coating, with and without addition of S7 and biocide, the following may be concluded:

1. All tested corrosion protection solutions showed lower general corrosion rate compared to unprotected carbon steel in natural seawater at elevated temperature.
2. All tested corrosion protection solutions shift corrosion potential to more positive values, meaning that they exhibit anodic inhibitor behaviour.
3. Additive S7 slows down the cathodic reaction of the redox process and directly affects the reduction of the corrosion rate. The corrosion rate values of mild steel treated with M645+S7 are slightly lower than the sample treated only with M645.
4. The lowest general corrosion rate after 3 days of testing in natural seawater was achieved by application of M645+S7+biocide.
5. Weight loss measurement showed the approximately same results provided by electrochemical polarisation testing.
6. The general corrosion is effectively suppressed but pitting prevention should be additionally addressed in a future study.

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