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Innovative Technologies For Reduction Of Galvanic Current Caused Pitting In The Tanks

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***Abstract*- The paper deals with electrochemical pitting in coated storage and transportation tanks with massive stainless steel structures – pipes, coils, pumps and ladders. Technical measures are proposed to prevent and reduce pitting caused by galvanic current flows which result from electrochemical potential differences of stainless steel and carbon steel structure elements. A galvanic current flow model and an electrical equivalent diagram are created. An innovative method for reducing galvanic current pitting effect is proposed.**

Keywords: galvanic pitting, storage tanks, corrosion protection, galvanic currents, conductive coatings

I. INTRODUCTION

Safe and durable tank coating is essential for storage and transportation tanks, especially for marine chemical tankers. Polymer materials are used to coat such tanks. Due to smooth surface with low surface energy and partial non-wetting, polymer coatings of cargo and slop tanks are easy to clean, thus keeping man-hours to a minimum, as well as ensuring the purity of cargoes.

II. GALVANIC PITTING PROBLEM IN TANKS

Various polymer materials are available for Chemical tanker tank coatings – Phenolics, Vinyl esters, Phenolic Epoxy and various Epoxies and Epoxy Resins [1,12]. The strongest and well tested coating solution for chemical tankers is Cross- linked polymer lining providing better chemical fitness than Stainless steel.

This article analyses the cause of one of the most common problem of coated tanks – local coating damages and proposes technological solutions.

Local paint defects such as pine holes and microcracks that originate during flaws on application or may be caused by steel surface defects or mechanical damages during pump repair and maintenance processes, as well as while cleaning or inspection the tanks. Coating defects usually develop from pine holes or other tiny defects which eventually progress and become evident by galvanic current flow effect (Fig.1).

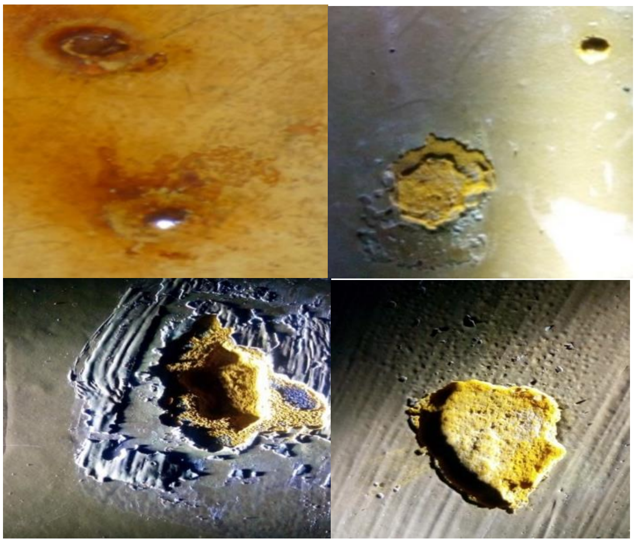

Fig.1 *Typical tank coating pitting erosion caused by Galvanic impact.*

The reasons for pinholes in the polymer coating leading to steel pitting could be defects in the steel surface which have not been corrected during surface preparation, flaws in coating application or defects of the coating material itself.
Even using HV (High Voltage) detection brushing it is not possible to detect all pinholes, especially in more

than one coat system. So, any pinhole or even a tiny microcrack as well as mechanical damage of the coat is a starting point for further development of steel substance cavities and erosions.

Onboard ships the most affected are Slop tanks characteristic with high concentration of Stainless-steel elements like heating coils and piping and frequently containing mixt cargoes and sea water. One of the principal causes is the galvanic current flow caused by dissimilarity of the metals in the storage or transportation tanks.

A great number of construction elements in the coated tanks such as piping, heating coils (Fig.2), access ladders, submerged cargo pump bodies, level and other sensors and supports, etc. are made of stainless steel, mostly ANSI 314 or ANSI 304.

Fig. 2. *SS heating coils and ladder in Chemical tanker tank (visible points of pitting repairs)*

A difference in electrochemical potentials (depending of the metal grades 0.2 to 0.6 V) between the stainless steel of the construction elements and the mild carbon steel wall of the tank results in the galvanic current affecting the paint damage points of the coating. The most common chemically resistant coatings are based on polymer materials. These coatings are not electrically conductive, thus, if the coating of the tank's wall is damaged, the galvanic current flows from the stainless steel construction elements to the damage point(-s) of the coating. As a result, the galvanic corrosion arises and the carbon steel of coating damage points works as sacrificial anodes and steel substance there is loosing substance.

Thus, stainless steel electrically coupled to a surface of carbon steel through the electrically conductive liquid (electrolyte) will result galvanic corrosion of the carbon steel. At the same time, the parts made of stainless steel will be protected from corrosion because the carbon steel acts as an anode.

The difference between the electrochemical potentials is about 0.2 - 0.6 V, depending on the composition of the stainless steel and its surface state, i.e. passive or active state.

In case the polymer coating of the tank is flawless, which is practically difficult to achieve, i.e. without any pinholes or other defects or cracks, the galvanic current will not flow. However, even insignificant damages may result in the occurrence of a galvanic current flow which causes a voltage drop equal to the difference between the electrochemical potentials of the metals.

Fig.3. show two Polymer paint MarineLine 784 coated test panels immerged in Atlantic sea water tank for 14 days with equal small damages done in the coating. Panel on left was electrically coupled with immerged SS 316L element. Panel on right was insulated from it thus preventing the flow of the Galvanic current.

Difference in the eroded surface and volume is considerable and proving the destructive action of the Galvanic current inducted by electrochemical potential differences of the Carbon and Stainless steel.

Fig. 3. *Test panels after 14 days in North Sea water tank coupled (left) and insulted (right) from immerged SS 316 L details*.

A. Factors influencing the galvanic current

Galvanic corrosion is an electrochemical process, which involves the flow of electric current. It occurs due to the galvanic effect caused by the contact of two dissimilar metals in an electrically conductive liquid. The following are the three major conditions for galvanic corrosion [2,9,10] to happen:

- Surfaces of the metal shall be bridged by an electrolyte.
- Two dissimilar metals must be in electrical contact with each other.
- Two metals should be distant from each other on the galvanic series.

1) Galvanic series of metals:

Stainless steel electrically connected via electro-conducting liquid (electrolyte) to the bare surface of carbon steel will cause galvanic corrosion of the carbon steel. By the same effect the stainless steel parts are protected against corrosion as carbon steel acts as a sacrificial anode for the stainless steel [2.4.10.]

Where the coating is perfect – without any damage or cracks – no galvanic current is generated. The potential between the surfaces immersed in the electrolytic liquid in the tank – SS parts and the hull steel (Voltage on the coating) is the difference of electrochemical potentials of the paired metals- SS and carbon steel (abt 0.2 -0.4 V as per data below). With the smallest damage the galvanic current will start to flow creating a voltage drop (also dependent on the resistance of all the current loop + surface polarization effects) equal to the potential difference as above. Another important adverse factor is the low resistance contact of the stainless steel items to the hull by supports which results in low resistance loop for the galvanic current and high value of the current accordingly.

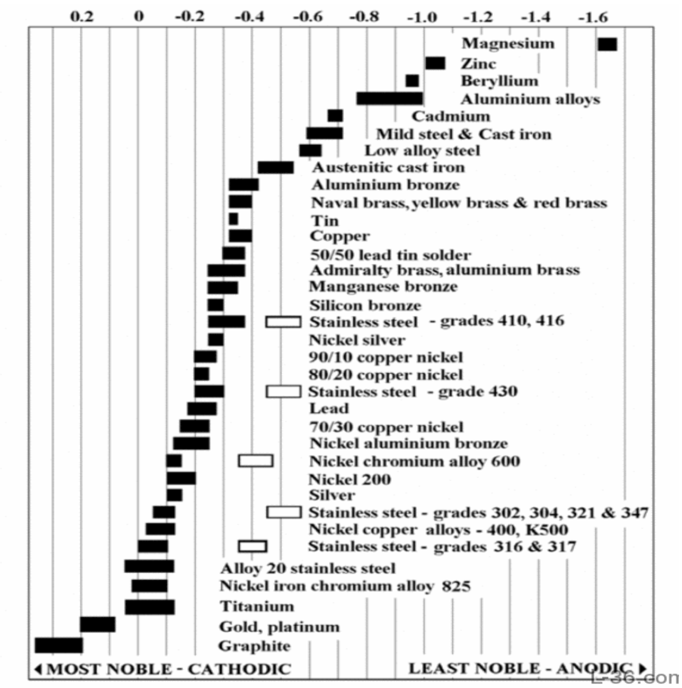

Fig.4. *Nobility table (Galvanic Series) of metals in flowing Sea water [4,9,10]. SS :Active -blank, Passive - shaded*

Fig.4 shows corrosion potentials or Galvanic Series of metals in flowing sea water at normal ambient temperature. The liquid in tanks of the ship is mostly in flow conditions due to the movements of the vessel and pitching and rolling, which is why the results could be considered for cargo and slop tanks of the tanker.

The unshaded symbols show ranges exhibited by stainless steel in a corrosive water such as may exist in the crevices or in stagnant or low velocity, poorly aerated water where stainless steel becomes active, while the shaded areas show the potentials of stainless steel, when in the passive mode [2.9].

The difference between the electrochemical potentials depend on the grade of the stainless steel and its surface state, i.e. passive or active state [A Guide to the Selection of Marine Materials. International Nickel Ltd., London. 1967]. The corrosion potential exists at the surface of the coating even though the coating and insulation properties thereof are flawless, however, in such a case the galvanic current is not flowing since the galvanic current loop is not closed.

2) Galvanic circuit factors:

The galvanic current flow depends on a number of factors [2.5,9]:

- Differences in electro-chemical potential of the metals involved
- Geometric configuration of the galvanic couple
- Overall circuit resistance between the coupled metals
- Conductivity of the electrolyte and the current path length
- Areas of the exposed metal surfaces wetted by the electrolyte
- Availability of oxygen and certain ionic species, particularly chlorides
- Temperature

Most of the chemical substances as well as sea water during tank cleaning operations and ballasting are conductive but their conductivity is within a rather wide range. So the galvanic current will depend on this parameter as well on the level of the liquid in the tank.

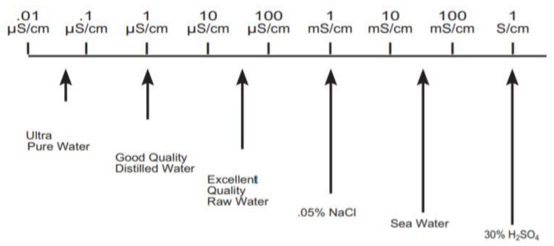

Fig .5. *Electrical conductance of the liquids.* Source:https://www.emerson.com/documents/automation/application-data-sheet-theory-application-of-conductivity-rosemount-en-68442.

3) Effect of the passive layer of stainless steel:

The corrosion resistance of stainless steels is achieved by alloying the base iron with Chromium. As per BS EN 10088-1 the steel must have a minimum of 10.5% (by weight) of Chromium and a maximum of 1.2% Carbon to be classified as 'Stainless'. Other alloying elements including Nickel, Molybdenum, Titanium (or Niobium) are added to form the various grades of stainless steel. The corrosion resistance of stainless steel arises from a 'passive', Chromium-rich, oxide film that forms naturally on the surface of the steel [3]. This film is extremely thin at 1-5 nanometers only. The protective film is chemically stable (passive) under conditions which provide sufficient oxygen to the surface. If the film is damaged, the surface is said to be in the Active state. If there is sufficient oxygen available, it

will self-repair [3]. So, passivation influences the electrochemical potential of stainless steel and also increases the surface resistance whereby reducing anodic current levels.
The majority of situations in practice involving galvanic corrosion in waters arise under conditions where the Cathodic reaction is the reduction of dissolved oxygen and it is controlled by the rate at which oxygen can diffuse to the surface from the bulk of electrolyte. The flow rate of the electrolyte has an influence as well.

Stainless steels become nobler with increasing flow rate, their passivity increases and corrosive effect is less .In neutral electrolytes complete de-aeration can suppress galvanic corrosion [2,10].

Aggressive chemicals - acids and alkalis in the tank are influencing galvanic processes. There are few data published on galvanic corrosion in alkalis but, because of the risk of caustic cracking under coupled conditions with many metals, it is advisable to carry out testing or seek previous experiences with such couples. In most acids, particularly the mineral acids, corrosion rates can be high and the tendency is to select corrosion resistant high alloy materials.
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Low conducting Hydrocarbon products as part of the galvanic loop could limit galvanic current value.
In case of carriage of electrolytic liquids such as acids and caustics or sea water in the tank, substance resistance in the galvanic current loop is minor but galvanic current is the highest.

Galvanic potential differences between different alloys can produce a variety of effects which are not seen in other electrolytes. A galvanic series has been produced for some acids [2,5] but because of variety of conditions – chemical properties, temperatures, aeration, concentrations it is difficult to give certain practical recommendations.

4) Surface area effect:

Galvanic corrosion effect is also based on the areas of dissimilar metals. The corrosive effect may be negligible if the area of less noble material is larger than that of a more noble material. By contrast, the contact via liquid of a large area noble metal with a small area of non-noble metal will increase the rate of galvanic corrosion [2.9,10].

The effective ratio of cathodic to anodic surface area is a critical aspect of galvanic corrosion [5] and the surface exposed to the electrolytic reaction is considerably influencing the rate of the loss of the substance.

To avoid corrosion, it is recommended to avoid a small anodic area relative to the Cathodic area [2,9]
Recommendations from Nickel Development Institute [2]:
- Use large Anode area.
- The larger the relative Anode area, the lower the galvanic current density on the anode, the lesser the attack.
- The amount of galvanic corrosion may be considered as proportional to the Cathode/Anode area ratio.
- Design for a small Cathodic/Anodic Ratio (CAR).

Field corrosion tests in seawater (the North Sea) [6] show that when changing Stainless steel /Unalloyed steel Metal area ratio from 1:1 to 10:1 there is an increase in loss of metal substance from 0.31 to 2,1 mm/year.

This confirms that increasing the cathode surface area causes significant increase in the corrosion rate. In this test we used stainless steel 1.4439 containing 4.0-5.0% molybdenum and for this reason is a strong cathode. [2].
Galvanic corrosion will occur if the anodic metal has a small surface area in relation to the cathode as is the case for screws, bolts, rivets, washers, brazing and welding metals. Therefore fasteners, brazing alloys and weld metals must be cathodic to the parts they join. In seawater, which is a highly conducting electrolyte, the effective surface areas will be greater and the galvanic corrosion will be more severe.
Cracks or damages in corrosion resisting coatings are almost impossible to prevent and they are very vulnerable to accelerated galvanic corrosion [2,4,11].
The effective ratio of cathodic to anodic surface area is a critical aspect of galvanic corrosion [4].
So galvanic corrosion factor in cargo and slop tanks is intensified in the proximity of relatively large (in comparison to open damaged coating areas) stainless steel surfaces – heating coils, deep well pumps and ladders. In slop tanks more heating coils are usually installed (Fig.4), which makes slop tanks more vulnerable than cargo tanks to galvanic corrosion - these are well observed facts.

III. MODEL FOR ESTIMATION AND ANALYSES OF THE GALVANIC CURRENT FLOW

Galvanic current flow in the tank is 3-dimentional and conductance of the all circuit elements is variable on rather a large scale. For analyses of the Galvanic current loop a simplified 2-dimensional model could be used as per Fig. 6.

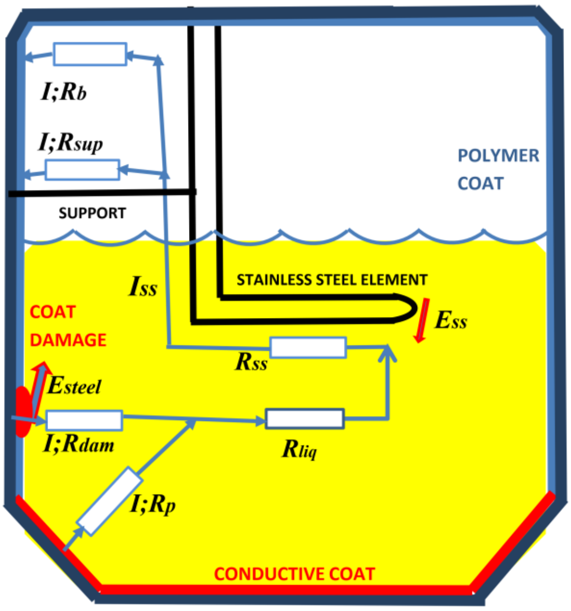


Fig.6. *Simplified 2- dimensional Galvanic current flow loop in the tank*

On base of the model as per Fig 6 for estimation and analyses purposes is possible to use Equivalent circuit as per Fig .7.

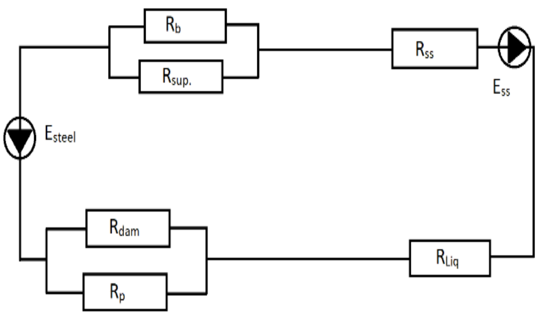


Fig .7 *Equivalent electrical circuit*

Value of the current via damaged area could be estimated by (1) based on the circuit diagram Fig 7.

$$I_{dam} = \frac{\Delta E \cdot R_p}{(R_{dam}+R_p)\cdot(R_{Liq}+R_{ss}+\frac{R_{sup}\cdot R_b}{R_{sup}+R_b})+R_{dam}\cdot R_p}$$

(1)

Where:

Idam: current (-s) flowing via paint damage point

Ess: Electro-chemical (Galvanic) potential of Stainless Steel

Esteel: Electro-chemical (Galvanic) potential of tank construction steel

Rp: Resistance of the coating paint,

Rliq: Resistance of the stored liquid,

Rsup: Resistance of conductive supports of SS elements,

Rb: Resistance of SS element bondage to hull,

Rss: Resistance of SS constructive element including SS surface .

Projecting that *Rss* also includes connected in parallel circuits of *Rsup* and *Rb* as per diagram Fig. 7 for estimation and analysis of the value of *Idam* = f (*Rdam*) a simplified formula (2) could be used.

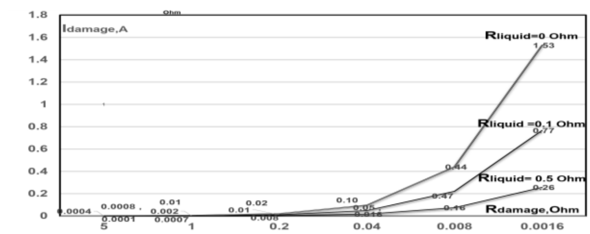
$$I_{dam} = \frac{(E_{ss}-E_{steel})\cdot R_p}{(R_{dam}+R_p)\cdot(R_{Liq}+R_{ss})+R_{dam}\cdot R_p}$$

(2)

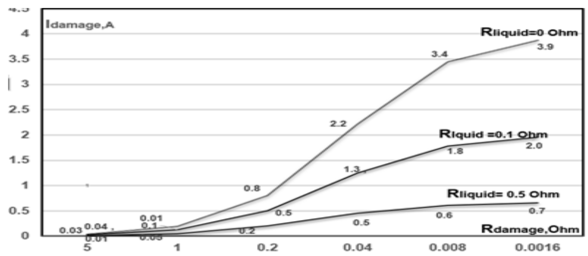
On calculating of Idam=f(Rdam) for various liquid Resistance following values used:

ΔE= Esteel – Ess = 0.4V and *Rss* = 0.1 Ohm.

Because of the three-dimentional flow of the current and dependence of the geography of SS construction elements in the individual tank the values for *Rliq* from zero to 0.5 Ohms are used for analyses. As the electromotive force is only fractions of the Volt, even a small increase in resistance of support and bonding elements (*Rsup* , *Rb*), resistance elements (or just not provision of the perfect contacts) as per Fig. 6,7 and formulas (1,2) can considerably reduce the galvanic current. It may be also noted that electrical conductivity of SS is up to five time lower than that for mild steel.



Rp = 0.01 Ohm



Rp = 0.1 Ohm

Fig. 8. *Calculated value of the current via coating damage point Id*

As per Fig 8 coating of the tank bottom part with anti-static coating only (*Rp* = 0.1 Ohm) provides much less reduction of the current via coating damage point in comparison with the case of using electro-conductive coating (*Rp* =0.01 Ohm).

Typical surface area of the bottom surface for Handy size Chemical tanker cargo tank could be estimated about 200 sqm. The surface of SS heating coils and other SS elements in the tank amounts to 20-35 sq.m.

From graphs it could be concluded that on provision of the paint surface with a coat resistance of 2.5 Ohm per sq.m even 200 sq.m of conductive paint surface, i.e. the bottom could only provide a reduction in the galvanic current of coating damage below 0.1 A on damage point(-s) if R_{dam} is above 0.2 Ohm. If, for example, only 20 sq.m. (R_p=0.1 Ohm) were coated for the same equal parameters, a considerable current reduction via paint defect point could be achieved only if R_{dam} is above 2 Ohms. Graphs as per Fig.8 demonstrate the difference in protection capability of these coating options. It could be suggested that paint coating resistance below 0.01 Ohm could provide a radical decrease in the Galvanic current via coating damage point to the tank steel thus preventing intensive Galvanic pitting.

IV. 4. TECHNOLOGIES FOR REDUCTION OF GALVANIC CURRENT CAUSED PITTING

It is possible to use several technical means to reduce galvanic impact and prevent development of pitting crevices and larger local coating damages.

A. Anodic protection

Furthermore, anti-corrosion protection of cargo tanks by anodic protection technique, i.e. by mounting zinc or Aluminum electrodes with more negative electrochemical potentials than that of stainless steel, is not suitable for protection of chemical tankers or cargo tanks as it substantially limits the transportation of acid-containing cargoes.

D. Reduction of active Cathode surface by coating

Galvanic corrosion can also be prevented by painting or applying electrically nonconductive coating to the more noble metal in our case stainless steel thus excluding it from galvanic process. [5,9] also, coating expert David Leyland (Painting Solutions, Dec, 2015). It is not a perfect solution since the inner surfaces of cargo pipes and pumps are involved,too. Coating of these surfaces has always been technologically problematic. Also the coating of heating coils is limited by max thermal fitness of the coatings. Thermal efficiency of the coils will be lower as well due to some thermal insulation effect by the coating applied.

The inner surfaces of cargo pipes and pumps are also involved as galvanic current sources. So complete coating of SS surfaces is not technically viable.

Electrically-insulating coating applied to the lager surface elements made of stainless steel minimizes the ratio between exposed stainless-steel surfaces and defective mild steel coating areas and could be used to achieve some reduction of the flow of the galvanic current to the coating damage areas, thus reducing the damage to the tank walls by galvanic current impact.

B. Insulation of the heating coils from the hull

It is recommended to provide galvanic insulation of the active metals from each other. [2,5,9.]. The largest SS surfaces in the tank usually are heating coils, cargo pipes and access ladders. Complete insulation of them from the hull will be technically complicated and is not recommended from the point of view of protection from static electricity.

On the other hand, this may reduce galvanic current, especially in case of carrying acids in the tank when liquid resistance element in the galvanic current flow loop is extremely low.

Coils could be insulated from supports by low conductivity pad or surface of the support to coil.

Similarly, the ladder end to tank top could be bolted via low conductivity inserts. This technology could keep static electricity risk low at the same time decreasing galvanic current flow.

Production of the pipe supports from low electrical conductivity composite materials may be considered. Similarly, deepwell pumps, ladders and other SS elements to be set on the static dissipative material surface.

C. Installation of Sacrificial anodes

Installation of Al or Zn alloy sacrificial anodes in chemical cargo storage and transportation tanks for diverting galvanic current flow from damaged coating spots to these anodes is problematic because of eventual chemical reaction with the cargoes, especially those containing acid.

The installation of naked carbon steel or cast steel sacrificial anodes could be considered in the proximity of the SS items to divert galvanic current flow from damaged coating spots to these anodes. Such a solution for the same substances could work but is not acceptable for chemically aggressive chemical cargoes. This is a simple and economical solution however for each project it shall be investigated separately in relation to chemical reaction with the cargoes to carry.

Prospects of this method are better for use in slop tanks where cargo chemical purity is of no importance [11].

Prospects of this method are better for use in Slop tanks where are no problem of Cargo chemical purity [11].

D. Arrangement of ICCP (Impressed Cathodic Current Protection) for each of the tanks

Theoretically, it **is** possible to install such a corrosion protective element (device). If there is no coating damage, “0” value of impressed current is needed, only nearly static potential difference (up to 0,85 V) needs to be kept. In such a case only a small element may be required. In case coating damage has occurred, ICCP shall provide power to secure current densities required to protect steel [8]. To create protection voltage 850 mV [8] current densities are necessary – for Acidic solutions 350 – 500 A/ m-2; Saline solutions 0.3 – 10 A/ m-2; Sea water 0.05 – 0.15/ A m-2. As we shall create potential difference between SS and mild steel at 0.3 - 0.4 V (max) only the current densities accordingly could be up to 40% of the figures above. For example, a 1000 cb.m. tank with 600 sq.m of surface. In case of heavy coating damages, the damaged area could amount to 0.1%. Damaged and exposed to galvanic effect the surface is 0.6 sq.m. (in one tank). As per figures above, estimated ICCP current required for Acidic solutions is 85 – 120 A; for Saline solutions 0.07 – 2.4 A; for Sea water 0.012 - 0.036 A.

From figures above we can suggest that in the case of sea water such a protection is very realistic, for saline solutions achievable but for acid solutions (which may be in the tank) looks unsuitable and impracticable – too heavy installation and this may be unsafe because of possible electrolytic influence on cargo.

This measure will also require sensitive Class approvals and relevant changes in Class Rules and other Statutory norms therefore does not seem practical.

E. Innovative technology: provision of electro-conductive properties for coated area

As effective and promising method for reduction of galvanic pitting in coated mild steel tanks containing stainless steel elements is the coating of the bottom area or entire tank inner surface of the tank by conductive polymer coating. In this way a by-pass loop of galvanic current flowing to a local paint damage point is created. [6,7]

For this purpose it is recommended to use electrically well conductive paint (with a conductivity at least 1.0 E-04 S/cm) [6,7].

To provide for the paint electro-static dissipation properties to 1.0 E+0 5 to 1.0 E +0 9 Ohms /square as per ASTM D257 or similar standards various technologies are known. For example, by incorporation into the polymer coating material the metal or metal oxide particles or conductive fiber or Carbon black or Polyaniline and Carbon nanotubes (Chinese patent documents CN105623490A, CN109384919A, CN20190226, CN201710961404.0 , ,CN103031035A CN201810128179.7 and not only).

However, for cargo tanks technologies of polymer coating materials should provide the chemical endurance for substances to be stored or carried, including sea water.

Polymer materials reinforced with nanotubes (for example https://ocsial.com/en/material-solutions/tuball/) are preferable as they provide electrical conductivity and as per laboratory studies [12] do not have a significant negative impact on chemical resistance of the high endurance polymer base coating material . However farther tests on Chemical resistance of 1 % w/t or more individual Carbon dopped polymer materials to various chemicals recommended.

To produce chemically resistant and well electro-conductive polymer paint doping with carbon nanoparticles is necessary by Single (SWCNT) or multiple wall (MWCNT) nanotubes or amorphous carbon of 1 % or more from polymer weight. With a coating thickness (DFT) of 250 mic this could provide resistance of 1sq m of the coat about 2.5 Ohm. SWNT and MWNT are rather expensive. The cost of these additives mostly depends on their purity grade, the ratio of SWNT/MWCNT and amorphous carbon contents as well as on different suppliers.

To produce such a chemically resistant and conductive polymer paint necessary doping with carbon nanoparticles in form of Single (SWCNT) or multiple wall (MWCNT) nanotubes or amorphous carbon of 1 % or more from polymer weight. On coating thickness (DFT) 250 mic this could provide resistance of 1sq m of the coat about 2.5 Ohm. SWNT and MWNT are rather expensive. The cost of these additives mostly depends from purity grade and ratio of SWNT/MWCNT and amorphous Carbon contents as well as from the supplier.

The cost of carbon nanotubes has been dropped considerably in the recent years. From various web sources: the MWCNTs cost could be estimated between 0.5-100 US$/g. The cost of SWCNTs also varies a lot, depending of purity and supplier could be estimated between 20-2000 US$/g.

So, this doping for getting electroconductive properties is increasing the cost of the polymer coating material.

However prior application tests on Chemical resistance of 1 % w/t or more individual Carbon dopped polymer materials to various chemicals needed.

Observed pitting areas in the tanks mostly are located in bottom as tank area closest to stainless steel elements – heating coils, cargo pumps and pipes etc. alias the area is also the most exposed to eventual mechanical damages due to works and tank cleaning and inspection and maintenance operations.

That is why it is economically reasonable to apply conductive polymer paint primary to the area mostly covered with the cargo – the bottom part of the tank.

CONCLUSIONS

1. Stainless Steel equipment constructive parts in steel cargo tanks are source of galvanic corrosion and are decreasing coating quality and longevity.
2. As simplest method to reduce progressive coating damages caused by galvanic current could be recommended coating of SS surfaces in the tank.
3. As radical method of reduction of the Galvanic current caused pitting in the tank is proposed

coating of entire or only bottom part of the tank by electro-conductive paint.

4. The proposed conductive paint technology principally could be used also for protection of the other industrial piping where corrosive and conductive liquid like seawater is stored or transported and gaping coated construction metals with dissimilar electrochemical potentials.

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