APPLICATION OF NANOTECHNOLOGY IN THE CORROSION PROTECTION OF STEEL OIL PIPES

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Abstract

A review of the application of nanotechnology in the corrosion protection of steel oil pipes using appropriate coating has been carried out. Nanotechnology is playing an important role in supporting innovative technological advances to manage the corrosion of steel oil pipes. This paper covers the application related to the management of steel oil pipes corrosion including the use of nanotechnology to produce high-performance coatings with superior abrasion resistance and good corrosion resistance. Anti-corrosion coatings in the form of suspension in which nanoparticles (e.g., 1 Gal of Gloss: NANO10029, Satin: NANO10033 and Stainless Steel: NANO20001 nanoparticles) are coated layer-by-layer. After the use of nanocomposite additives for anti-corrosion coatings the surfaces of steel oil pipes designed for very oxidizing and corrosive coastal environments are greatly enhanced.

Keywords: Nanotechnology, nanoparticles, corrosion protection, anti-corrosion coating, steel oil pipes

1 INTRODUCTION

Steel is a widely-used engineering material for many industrial applications in manufacturing, construction, defense, transportation, medical, etc. The corrosion of steel as a result of chemical or electrochemical reaction with its service environment is a spontaneous process, which can compromise the materials integrity and impact assets, environment and people if no measures are taken to prevent or control it. The corrosion of steel is generally electrochemical in nature and may take many forms such as uniform corrosion, galvanic corrosion, pitting corrosion, crevice corrosion, under-deposit corrosion, dealloying, stress corrosion cracking (SCC), corrosion fatigue, erosion corrosion and microbially influenced corrosion (MIC) [1]. The corrosion of steel [2], as shown in Fig. 1, is an electrochemical process [3] as given in equations (1-5):

$$Fe \rightarrow Fe^{2+} + 2e^{-}(1)$$

 $2H_2O + O_2 + 4e^- \rightarrow 4OH^-(2)$

 $2Fe + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^{-}(3)$

$$4Fe^{2+} + 8OH \rightarrow 4Fe(OH)_2(4)$$

 $4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3.H_2O$ (Rust) (5)

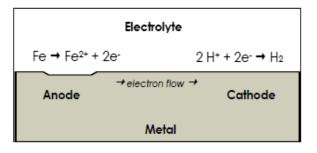


Fig. 1 Corrosion process in steel [2].

Where Fe₂O₃.H₂O is the rust butmost steel pipelines are usually cathodically protected against corrosion and in addition to cathodic protection, there are many traditional technologies available to mitigate the corrosion of steel by either enhancing the inherent corrosion resistance and performance of the steel itself (e.g., use of stainless steel in place of carbon steel for rebar in concrete), or reducing the corrosivity of the service environment (e.g., electrochemical chloride extraction for steel reinforced concrete [4]) or altering the steel/electrolyte interface (e.g., corrosion inhibitors, metallic coatings, non-metallic coatings, and surface treatment of steel) [1]. Most buried pipelines are usually insulated and with time localized corrosion will occur under the insulation. This can be a particularly severe form of corrosion because of the difficulty in detection due to the corrosion occurring beneath insulation. The corrosion is often times more severe due to the insulation not allowing evaporation and the insulation acting as a carrier whereas moisture occurring in one area moves through the insulation to another area causing the corrosion to spread more rapidly [5]. There is therefore a compelling need to introduce a coating that provides corrosion resistance and also has a low thermal conductivity, which allows it to act as an insulator. This paper reviews works carried out in protecting the surface of oil pipelines with nanoscale coatings.

2 USE OF NANOTECHNOLOGY TO CONTROL STEEL CORROSION

Recently, significant advancements have been made to improve the management of steel corrosion through research, development and implementation; and nanotechnology has been playing an increasing important role in supporting innovative technological advances. Nanotechnology is generally understood to involve the manipulation of matter on a near-atomic scale to produce new structures, materials, systems, catalysts and devices that exhibit novel phenomena and properties. Some materials exhibit unique physical, chemical and biological properties at the nanoscale. Nanotechnology offers the possibility of introducing technologies that are more efficient and environmentally sound than those used today [6]. Nanotechnology has been employed to enhance the inherent corrosion resistance and performance of the steel itself, by achieving the desirable finely crystalline microstructure of steel (e.g., nanocrystallization) or by modifying its chemical composition at the nanometer scale (e.g., formation of copper nanoparticles at the steel grain boundaries) [1]. Nanoparticles are smaller than wavelength of visible light (400-700 nm) and hence are transparent to the human eye. They are occupied by 5-10 atoms and molecules, stacked in two or three dimensions [3]. When such nanoparticles are incorporated in a coating, the physical property of the system gets altered without affecting the clarity. Tiny sizes of nanoparticles produce an extra ordinary high surface energy [3]. Advanced materials using nanotechnology may extend service life, reduce failure rates and limit the potential for environmental damage. Nanocoating metallic surfaces can help achieve superhardening, low friction and enhanced corrosion protection. Stronger materials may reduce wear, corrosion and the chances of puncturing associated with third-party damage. Also, because nanomaterials can be stronger per unit volume than conventional materials, the use of pipe materials that contain or are coated with nanomaterials may mean fewer disturbances to the environment during installation, maintenance and dismantling.

Nanostructure coatings have excellent toughness, wear and adhesion properties. Nanostructure powders have grains less than 100 nm in size, which are agglomerated to form particles large enough to be sprayed using conventional thermal spray methods. These coatings may be used to repair component parts instead of replacing them, resulting in reduced maintenance costs and disturbance. Additionally, the nanostructure coatings may extend the service life of the components because of their improved properties over conventional coatings [6]. Additionally, nanotechnology has been employed to reduce the impact of corrosive environments through the alternation of the steel/electrolyte interface (e.g., formation of nanocomposite thin film coatings on steel). Significant improvements in the corrosion protection of steel have been reported through the codeposition of Ni-SiC or Ni-Al2O3nanocomposite coatings on mild steel [7-8] and the application of TiO₂-naoparticle sol-gel coatings or multilayer polyelectrolyte nanofilms on 316L stainless steel [9,10]. The incorporation of nano-sized particles (e.g., polyaniline/ferrite, ZnO, Fe₂O₃, halloysite clay and other nanoparticles) into conventional polymer coatings also significantly enhanced the anti-corrosive performance of such coatings on steel substrates [11-16]. Recent progress in the use of nanomaterials for corrosion control is summarized in a 2007 review article [17], which discussed the incorporation of nanoparticles in ceramic coatings, polymer coatings and hybrid sol-gel systems for improved properties (e.g., resistance to corrosion and high-temperature oxidation, self-cleaning and anti-fouling). Nanotechnology has been utilized in endowing the steel bulk materials with excellent corrosion resistance and other enhanced properties, mainly by refining their crystal grains to the nanometer scale [5].

2.1 Nanotechnology Solution to Pipeline Corrosion under Insulation

Corrosion is the deterioration of essential properties in a metal due to reactions with its environment. In the most common usage of the word, corrosion means the loss of electrons of metal reacting with either water or oxygen. Corrosion under insulation is a localized corrosion occurring at the interface of a metal surface and the insulation on that surface. This can be a particularly severe form of corrosion because of the difficulty in detection due to the corrosion occurring beneath insulation [17]. Inspections for corrosion under insulation are generally not completed regularly enough to eliminate this problem due to the cost of insulation removal and replacement and cost of labour. Moisture combined with oxygen is the largest contributing factor to corrosion. The closed environment of the insulation material over the pipe, tank or equipment creates conditions that encourage build up of moisture and resulting corrosion [18]. The corrosion is often times more severe due to the insulation not allowing evaporation and the insulation acting as a carrier whereas moisture occurring in one area moves through the insulation to another area causing the corrosion to spread more rapidly [3]. Warm temperatures normally result in more rapid evaporation of moisture and reduced corrosion rates; however a surface covered with insulation creates an environment that holds in the moisture instead of allowing evaporation. Traditional thermal insulation materials contain chlorides. If they are exposed to moisture, chlorides may be released into a moisture layer on the pipeline surface and pitting/stress corrosion cracking may result. Acids, acid gases and strong bases like caustics and salts are aggressive corrosive agents and will not only cause but also accelerate existing corrosion under insulation. Corrosion under insulation [19] occurs at the interface of a metal surface as shown in Fig. 2.



Fig. 2 Gas and Liquid Transmission Pipeline Corrosion under Insulation [19].

2.2 Use of Nanotechnology for Intelligent Corrosion Protection Systems

One of the most exciting and very interesting field of application for nanotechnology is its use for intelligent corrosion protection systems. A recent invention [20] discloses a novel approach for the preparation of "smart" corrosion-inhibiting pigment and its use in self-healing anti-corrosion coatings in the form of a powder or a suspension in which nanoparticles (e.g., SiO₂, ZrO₂, TiO₂, CeO₂ nanoparticles) are coated layer-by-layer [21] with one or more layers of polymer or polyelectrolyte shell (e.g., poly (alkylene amine), polyalkylene glycol and biopolymers and polyamino acids) responsive to a specific stimulus or trigger. These particles thus act as nanoscale reservoirs for the effective storage of the corrosion inhibitor (e.g., quinaldic acid and mercaptobenzotriazole). The method of producing the intelligent coatings was reported to be cost-effective

and easy-to-implement as the nanoreservoirs provide prolonged release of the inhibitor. The corrosion inhibitors are released in a regulated fashion, mainly to the damaged coating zones and/or corrosion defects where they are most needed, thereby providing active, long-term corrosion protection of the coated substrate (e.g., steel and aluminium alloys). In one example, the layer by layer deposition technology was utilized to coat ZrO₂ particles (with average size of 150 nm) with multiple poly (allyl amine) /poly(acrylic acid) layers, within which quinolinol was entrapped as the corrosion inhibitor [22-24]. The self-healing effect of a sol-gel coating doped with such nanoreservoirs was demonstrated by the scanning vibrating electrode technique and attributed to the release of quinolinol in the damaged area when initiated by pH changes caused by the corrosion of the steel alloy substrate.

3 GENERAL PROCEDURE OF APPLICATION

Surface preparation for nanotech metal coating involves the following processes: The initial process is general cleaning which includes solvent cleaning (either cold soaking or vapour phase), aqueous cleaning, abrasive cleaning, and other types of cleaning such as ultrasonic cleaning, chemical polishing and electropolishing. Cleaning is usually carried out before the main metal finishing operation and sometimes between operations. The final and processes are chemical electrochemical conversion coatings which include chromating, phosphating, anodising and colouring. "Conversion" refers to the fact that these processes involve changing or converting the surface layer to impart various properties to the surface. These processes are usually applied before painting to improve coating adhesion and provide corrosion protection. A sample of nanotech metal coating [25] is shown in Table 1.

 Table 1 NanoTech Metal Coating Details.

Amount Stock Keeping Unit (SKU)	
1 Qt	Stainless Steel: NANO20033
1 Gal	Gloss: NANO10029, Satin: NANO10033,
Stainless Steel: NANO20001	
5 Gal	Gloss: NANO10030, Satin: NANO10034,
Stainless Steel: NANO20002	
55 Gal	Gloss: NANO10031, Satin: NANO10035,
Stainless Steel: NANO20003	
275 Gal	Gloss: NANO10032, Satin: NANO10036,
Stainless Steel: NANO20004	

A sample of nanotech metal coating [25] container is shown in Fig. 3



Fig. 3 NanoTech Metal Coating Gloss [25].

Nanotechnology has been employed to reduce the impact of corrosive environments through the alternation of the steel/electrolyte interface (e.g., formation of nanocomposite thin film coatings on steel). The coating prevents corrosion by preventing the cathodic reaction, anodic reaction and presenting high resistance for the current circuit of the galvanic pair. The additives and pigments which are used in paints in order to increase their corrosion preventing properties usually prevent both the cathodic and the anodic reactions. The finished product of nanotech metal coating is transparent and used for bridges, pipelines, and other industrial metals, as well as everyday metals in the home. Nanotechnology metal coating also offers scratch resistant surface coatings based on nanocomposites [26].

3.1 Airless Spraying

After proper surface cleaning, airless spray is used for protective coatings. In airless spraying the paint is fed by high pressure, through a pressure resistant hose, to the spray gun, where the paint is forced through a narrow, hard, metal nozzle. The paint is atomized due to the air resistance and arising pressure difference and the shape of the nozzle orifice [27], Fig. 4.

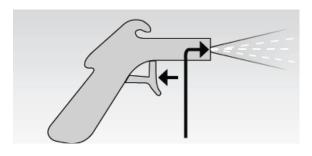


Fig. 4Airless Spray Gun [27].

The paint pressure is achieved by a piston or membrane pump. The power can be pneumatic, electric, internal combustion engine and a hydraulic piston pump. Because no compressed air is used in the atomization of the paint, as with conventional spray, the method is called airless. A pump with the pressure ratio of 40:1 gives a pressure of 200bar (1 bar = 10^5 Pa, 1 Pa = 1 N/m²) at the spray nozzle when the pressure of the compressed air is 5bar (5 x 10⁵ Pa i.e., 5 x 10^5 Nm⁻²) [27]. The final pressure in the nozzle depends also on the length and diameter of the hose, the number and position of the filters, the size of the nozzle, the type of paint and its viscosity and temperature. The spraying is carried out keeping a standard distance between the spray gun and the object. The spraying distance for conventional spraying is about 150-300mm and about 200-400mm for airless spraying [27], Fig. 5.

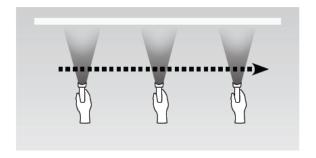


Fig. 5 Spray Gun kept perpendicular to the surface [27].

The distance is kept constant for the whole surface. The spray gun should not be moved in a curve, as this will constantly vary the spraying distance and give poor results. Airless spray causes less waste and overspray then conventional spraying, it is the general application method used for most protective coating work. If the spray gun is turned so that the angle changes, the coat becomes uneven and over-spraying occurs at the edges [27], Fig. 6.



Fig. 6 Uneven Spray Angle [28].

Nanotech coating products deeply penetrate a material, alters the molecular/atomic structure and creates an inseparable bond and impenetrable shield. In conventional steel pipeline systems, Fig. 7, down

times of up to about two months is used to replace pipe systems [28]. The costs connected with this could be substantially cut through the use of nanotechnology.



Fig. 7 Conventional oil pipes [28].

Nanotech metal protective coating contains nanoparticles that protect pipeline system from corrosion, Fig. 8 and the coating is only 50 to 90 micrometers (90,000 nanometers) thick [27].



Fig. 8 Nanotech coating of oil pipes [27].

Nanotechnology is therefore promising as it offers vast potentials in the field of coatings. The future of the nanotech coating market will further expand in different industry such as marine, building, defense, agriculture, infrastructure and human health. Thus, nanotechnology development may conserve natural resources and improve the overall performance of corrosion protection of metal pipeline systems and structures [29, 30], as shown in Fig. 9.



Fig. 9 Nanotech coated associated tank farm and pipelines [30].

Nanotechnology has been utilized in endowing the steel bulk materials with excellent corrosion resistance and other enhanced properties, mainly by refining their crystal grains to the nanometer scale [31]. The steel substrate with a nano-phased grain structure tends to have less defects or inhomogenities where corrosion attack traditionally initiates and propagates. Steel pipes, metals and other materials are subject to degradation brought on by salt, chemicals, UV rays, water, oxygen and normal wear and tear but nanotech product hardens the surface to protect against these destructive forces [30] thereby ensuring the durability of steel pipes, Fig. 10.



Fig. 10 Nanotech coated steel oil pipes [30].

Nanotechnology has brought fundamental changes to the methods of mitigating corrosion risk at the steel/electrolyte interface. Nanotechnology has been utilized in surface treatments to improve the performance and service life of steel and other alloys used in oxidizing and corrosive environments [17, 32]. Also nanotechnology has been employed to enhance the inherent corrosion resistance and performance of the steel itself, by achieving the desirable finely crystalline microstructure of steel [33] (e.g., nanocrystallization) or by modifying its chemical composition at the nanometer scale (e.g., formation of nanoparticles at the steel grain boundaries).

4 CONCLUSION

A review of the application of nanotechnology in the corrosion protection of steel oil pipes using appropriate coating has been carried out. Nanotechnology is playing an important role in supporting innovative technological advances to manage the corrosion of steel oil pipes. Traditional types of insulation create the perfect environment for moisture and resulting corrosion and create a conduit for that corrosion to spread more rapidly. Nanotechnology coatings offer a solution for corrosion resistance and insulation for pipelines, tanks and other plant equipment and maintains its effectiveness over time while enhancing its resistance to damaging oxidation and corrosion under extreme environmental conditions. After the use of nanocomposite additives for anti-corrosion coatings the surfaces of steel oil pipes designed for very oxidizing and corrosive coastal environments are greatly enhanced. It is expected that in the coming years much more attention will be paid to the use of nanotechnology in intelligent corrosion protection systems focusing on environmental best practices.

References

- [1] X. Shi, Recent Patents on Engineering **4**(1), 1-6 (2010).
- [2] L.T. Popoola1, A.S. Grema, G.K. Latinwo, B. Gutti and A.S. Balogun, Int J of Industrial Chemistry 4, 35 (2013).
- [3] Instructions/Use of Metal Coatings, <u>www.nanotechcoatings.com</u> Retrieved 18/03/2014.
- [4] Y. Liu and X. Shi, Corros **21**(1-2), 53-82 (2009).
- [5] Industrial Nanotech Inc, The Global Leader in Nanoscience Solutions, <u>www.industrial</u> <u>anotech.com</u> Retrieved 17 March, 2014.
- [6] K.L. Vasanth and D.M. Taylor, Corrosion 2002, paper No. 02142. Available at <u>http://www.nace</u>.org/nacestore/assets/paperabstr acts/2002/02142.pdf. Retrieved 17/03/2014.
- [7] M. Lekka, N. Kouloumbi, M. Gajo and P.L. Bonora, Electrochimica Acta 50(23), 4551-4556 (2005).
- [8] Q. Feng, T. Li, H. Teng, X. Zhang, Y. Zhang and C. Liu, Surface and Coatings Techno, **202** (17), 4137-4144 (2008).
- [9] G.X. Shen, Y.C. Chen and C.J. Lin, Thin Solid Films 489(1-2), 130-136 (2005).

- [10] M. Khaled, B. Abu-Sharkh, E. Amr, B.S. Yilbas, A. Manda and A. Abulkibash, Corros Engin Sci Technol 42(4), 356-362 (2007).
- [11] J. Alam, U. Riaz, S.M. Ashraf and S. Ahmad, J Coatings Technol Res 5(1), 123-128 (2007).
- [12] S.K. Dhoke, A.S. Khanna and T.J.M. Sinha, Prog Org Coatings 64 (4), 371-382 (2009).
- [13] S.K. Dhoke and A.S. Khanna, Corros Sci 51(1), 6-20 (2009).
- [14] X. Shi, T.A. Nguyen, Z. Suo, Y. Liu and R. Avci, Surface And Coatings Technology, in press (2009).
- [15] M. Sekharand and M. Ramana, Int J of Engineering Science and Technology 4(07), 3118-3123 (2012).
- [16] B.M. Praveen and T.V. Venkatesha, Int J Electrochem Sci **4**, 258 – 266 (2009).
- [17] V.S. Saji and J. Thomas, Current Science 92(1), 51-55 (2007).
- [18] H. Muralidhara and Y. Naik, Bull Mater Sci 31(4), 585–591 (2008).
- [19] N.G. Thompson, Gas and Liquid Transmission Pipelines, Alaska, www.dnvusa.com/binaries/gasliquid, *Retrieved* 7/11/2014.
- [20] D. Shchukin, H. Möhwald, M.G. S. Ferreira and M. Zheludkevich, Corrosion Inhibiting Pigment Comprising Nanoreservoirs of Corrosion Inhibitor, WO2007104457A1 (2009).
- [21] D.G. Shchukin and H. Möhwald, Angewandte Chemie International Edition, 18(13), 1672-1678 (2006).
- [22] R. Abdel Hameed, H. Abd-Alhakeem, Abu-Nawwas and H. Shehata, Advances in Applied Science Research 4(3), 126-129 (2013).
- [23] V.S. Saji, Recent Patents on Corrosion Science 2, 6-12 (2010).
- [24] R. S. Abdel Hameed, A. H. Abu-Nawwasb and H. A. Shehataa, Advances in Applied Science Research 4(3), 126-129 (2013).
- [25] NanoTech Metal Coating, Metal Coating, www.nanotechcoatings.com, Retrieved on 10/11/2014.
- [26] C.G. Munger, Corrosion Prevention by Protective Coatings, 2nd Ed (National Association of Corrosion Engineers, Houston, 1999), p. 317.
- [27] O. Tikkurila, Industrial Coating of Metal Surfaces, 2nd Ed (Vantaa, Finland, Tikkurila Oyj Industries, 2011), pp. 19-24.

- [28] M. Xylem Dewatering Pump Hand Book, Canada, <u>www.flygt.com</u>, Retrieved on 7/11/2014.
- [29] A. Mathiazhagan and J. Rani, Int J of Chemical Eng and Applications **2**(4), 225-237 (2011).
- [30] H. Devold, Oil and Gas Production Handbook, An Introduction to Oil and Gas Production, (ABB ATPA Oil and Gas, Oslo, 2006), p. 16.
- [31] K. Harishanand, H. Nagabhushana, B. Nagabhushana, P. Panda, A. Adarsha, M.

Benal, N. Raghavendra and K. Mahesh, Int J of Eng Res and Applications 3(1), 1569-1576 (2013).

- [32] A.Y. Badmos, H.A. Ajimotokan and E.O. Emmanuel, New York Science Journal 2(5), 36-40 (2009).
- [33] G. McCraw and A. Dierdorf, Functional Coatings and Ceramic Composites, New Dimension Materials (Clariant International Ltd, Rothausstrasse, 2007), pp. 21, 61.