16th Middle East CORROSION CONFERENCE & EXHIBITION

NACE Paper No.
MECCFEB16-8358

A Novel Material for Microbiologically Influenced Corrosion Protection

Benton Allen
Advanced Nano Solutions
LBJ Fwy, STE 240
Dallas, TX 75240
USA

Trent Kelly
Advanced Nano Solutions
LBJ Fwy, STE 240
Dallas, TX 75240
USA

Emily M. Hunt, Ph.D., P.E.
West Texas A&M University
2401 Russell Long Blvd
Canyon, TX 79015
USA

Paige Earl
West Texas A&M University
2401 Russell Long Blvd
Canyon, TX 79015
USA

ABSTRACT

It is well recognized that chemical and microbiological mechanisms both contribute to corrosion and that an estimated 40% of all internal pipeline corrosion in the oil and gas industry can be attributed to microbiologically influenced corrosion (MIC). When this degradation is combined with MIC in storage tanks, pumps, and subsurface equipment and tooling, it is apparent that any significant advancement in MIC mitigation would prove invaluable to asset protection programs. Researchers at West Texas A&M University[(1)] have developed a new material that can function as a coating additive to protect assets from MIC. Experiments were conducted to evaluate the antimicrobial performance of material, and mechanical characteristics of coatings doped with the material. Results from microbiological testing showed that coatings doped with the material resisted and deactivated over 99% of bacteria exposed to the surface while results from mechanical testing indicated that the additive has no significant impact on the corrosion or abrasion resistance of host coatings. These results are significant because the additive material eliminates the primary source of MIC while maintaining the mechanical and thermal properties of the existing coating system. This technology provides transformative change in treatment and prevention methods for the oil and gas industries.

Key words: microbiologically influenced corrosion, protective coatings, MIC, antibacterial coatings, antimicrobial coatings

[1] West Texas A&M University (WTAMU), 2401 Russell Long Blvd, Canyon, TX 79015, USA

INTRODUCTION

As technology continues to advance oil and gas production, engineers are faced with challenges induced by indigenous microorganisms that reside in hydrocarbon and secondary water injection systems. Microbiologically influenced corrosion rates can be significantly greater than general corrosion rates and can lead to the rapid development of pitting (Figure 1). Studies done by Delft[1, 2] demonstrate that an increase of 8% in biomass growth can affect oil and natural gas production by as much as 50% by inhibiting the production flow and engineered fluid properties.

Figure 1: Pitting on a steel pipe due to microbiologically influenced corrosion.

Pipe failure is a main component of the operating and maintenance costs of oil and gas industry pipelines. Currently, oil and gas companies do not have many choices in the prevention of internal pipe corrosion. Literature shows that many producers spend significant amounts of money each month to flush systems with various chemicals and biocides to kill off the sulfur-producing bacteria[3, 4]. There is a strong need to mitigate microbial colonization by engendering materials with properties that include surface chemistry[5-7] and surface roughness[3, 8-9] which are unfavorable for bacterial attachment and growth.

Unlike other paints or chemicals that are currently on the market (research and commercial), the coating additive in this study, AntiMicrobial NanoAlloy (ANA)[†], is activated through combustion synthesis and forms a structural metallic alloy that can then be incorporated into a traditional coating system. Several key outcomes from previous research conducted by the authors have established a basis for the development of the material, the most impactful of these being a method to create highly porous, antibacterial solid materials through combustion synthesis.[10] By combining nanoscale particles into a reactant mixture and providing an energy source for ignition, the reaction produces a self-propagating heat wave that will synthesize metallic structures made of pores only nanometers wide that inherently exhibit antibacterial properties. The extraordinarily high surface areas these materials possess serve as

[†] Trade Name.

an excellent platform for the neutralization of bacteria. These newly synthesized alloys can be incorporated into coatings, which can be applied to metal, ceramic, plastic or composite surfaces. This type of coating system presents a novel approach to microbiological neutralization, or more specifically, microbiologically influenced corrosion protection.

Figure 2 shows an antimicrobial coating applied to the sucker rod and interior of a well tubing. The tubing is the conduit that allows flow of hydrocarbons from the sub-surface rock to the surface. High costs are associated with tubing failure in wells by either replacing the tubing or continuously injecting chemicals into the string to prevent failure. Packers are common tools used to isolate the intermediate and surface sections of casing and tubing from hydrocarbon induced corrosion by filling the volume between the surface and packer with an anti-corrosive fluid called packer fluid. Although many oil and gas companies have adopted this process to protect their piping, it is not universal. A coating doped with the novel material not only resists microbiological growth and reproduction, but also actively kills microbes that encounter the coating. This prohibits any biofilm development or buildup allowing for an uninhibited flow through the pipe.

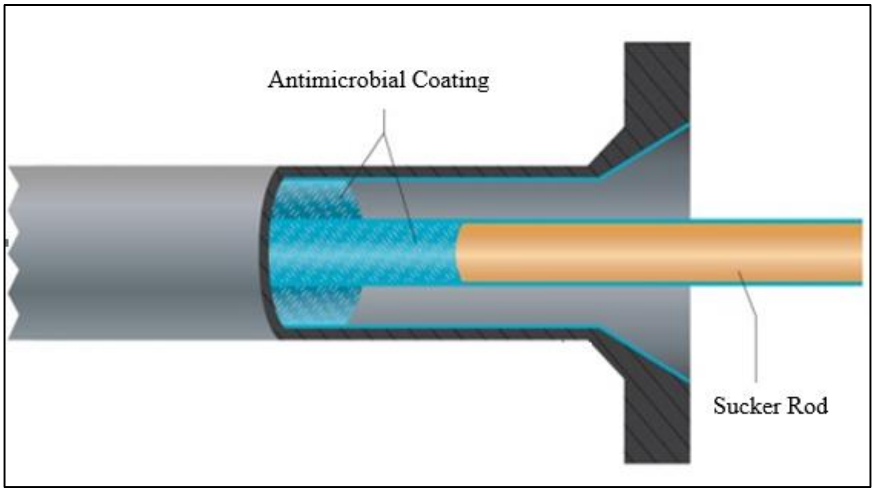


Figure 2: Antimicrobial coated well schematic.

EXPERIMENTAL PROCEDURE

Microbiological Procedure

Experiments were performed to demonstrate the effect the antimicrobial material had on microbiological growth kinetics. A preliminary series of diffusion tests were designed to test the antimicrobial efficacy of the material in powder form. In these tests, varying amounts of powder were inserted into cylindrical voids within agar plates. The plates were then introduced to various bacteria strains and examined for zones of inhibition produced by the antimicrobial powder.

To test the antibacterial efficacy of the powder when incorporated into a coating, a polymer based paint was doped 20% (by weight) with the powder. The doped coating was then applied to the internal surface of a 250ml Erlenmeyer flask. The flask was filled with inoculated water and incubated in a shaker incubator at 37°C and 200 rpm. Samples were taken and plated at various time intervals. By coating the internal surfaces of a vessel, the tests seek to confirm the effectiveness of the coating when applied internally to pipes or storage vessels to prevent microbiological activity.

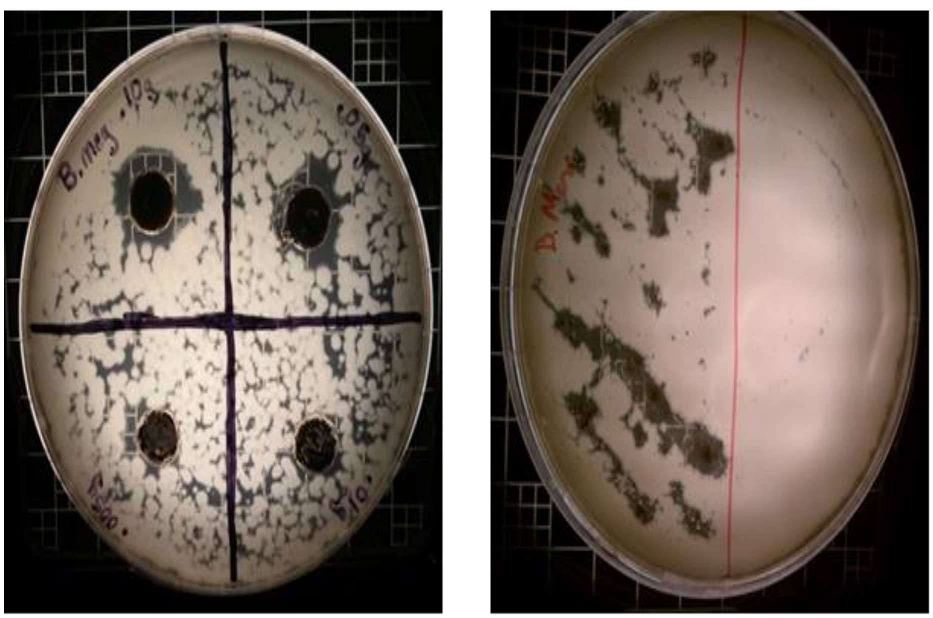
Bacillus Subtilis is a spore-forming bacterium like anthrax but benign and used for this study.[11] Experiments were also conducted with Escherichia coli, Bacillus megaterium, and Staphylococcus aureus because they represent the behavior and reproduction characteristics of several common types of bacteria found in nature. The antimicrobial powder (5mm) was procured from Advanced Nano Solutions†. Standardized cultures of Staphylococcus aureus, Bacillus megaterium, and Escherichia coli in 20% glycerol were used as the sample cultures throughout the tests. To prepare a standardized sample of the bacteria, a sample taken from an isolated colony on a stock plate was incubated overnight in 10 mL of LB broth at 37°C. The next morning the LB broth was inoculated into 100 mL of LB broth in a nephlo flask. The flask was then incubated in a shaker incubator at 37°C and 200 rpm. The O.D. (optical density) was read every half hour using a spectrophotometer at 600 nm. When the O.D. reached 0.6 the cells were then harvested by taking 40 ml of the culture and adding 10 mL of glycerol for a final concentration of 20%, aliquots of 1 mL were then prepared and stored at -80°C. To quantify bacterial concentration, a standard plate count was conducted and the VC/mL was determined.

RESULTS

Microbiological Results

Powder Diffusion Tests Results.

The following results were obtained from third party microbiological testing. Figure 3A displays zones of inhibition created by the coating with S. aureus. The top left quadrant was introduced with 0.10g of the antimicrobial powder, the top right quadrant had 0.05g of powder, the bottom left had 0.005g of powder, and the bottom left had 0.01 g of powder. Figure 3B displays the zones of inhibition created by the powder after it was distributed on half of the agar plate.

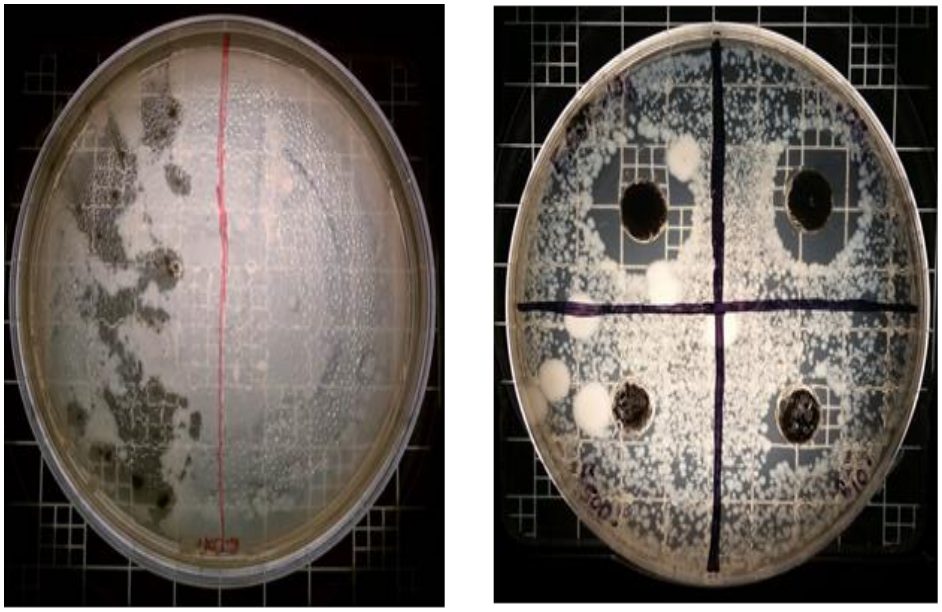


A B

Figure 3: Staphylococcus aureus diffusion test results.

† Trade Name.

Figure 4A displays the zones of inhibition created by the antimicrobial powder after it was distributed on half of the agar plate. Figure 4B displays zones of inhibition created by the powder with E.coli. The top left quadrant was introduced with 0.10g of the powder, the top right quadrant had 0.05g of powder, the bottom left had 0.005g of powder, and the bottom left had 0.01 g of powder.



A B

Figure 4: Escherichia coli diffusion test results.

<u>Flask Coating Test Results.</u>

Figure 5 shows plated samples from the flasks coated with doped and standard paint. The flasks were coated then filled with inoculate.

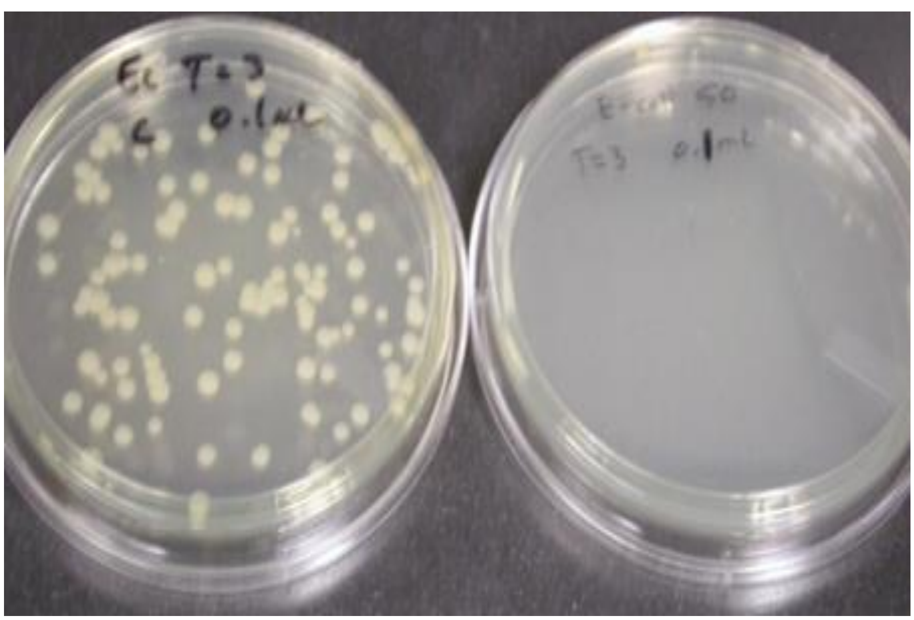


**Figure 5: Escherichia coli flask coating test results after 3 hours of exposure.
The control flask result is shown on the left while the test flask result is shown on the right.**

Table 1 shows the colony counts of three samples taken from the test flask, which was coated with 20% (by weight) antimicrobial doped paint.

Table 1
Colony Counts of Escherichia coli after Exposure to Coated Flasks

Time (hr)	Control Flask (0% weight antimicrobial powder)		Test Flask (20% weight antimicrobial powder)	
	Colony Count	Average VC/mL	Colony Count	Average VC/mL
0	TNTC (too numerous to count)		85, 11, 3	850
1	TNTC		0,0,1	33
2	156, 212, 176	1813	0,0,0	0
3	86,87,100	910	0,0,0	0
4	52,78,93	710	0,1,9	33

Interpreting the data collected with the tests, the antimicrobial powder shows an ability to kill bacteria. The plate counts in Figures 3 to 5 show that there was a decrease of over 99% in viable cell counts within the bacteria that was exposed to the antimicrobial material in contrast to the control. The data collected show efficient killing of all tested organisms, suggesting the coating is very quick and complete. The diffusion tests also show a very effective neutralization of the organisms. The quadrant plates show zones of inhibition against E.coli and S.aureus even at the lowest concentration. All three organisms show a significant zone of inhibition when the coating is applied to the agar.

Mechanical Results

To examine how the addition of addition of the antimicrobial material effects the mechanical properties of the host coatings, several standardized tests were employed. Assured Testing Services† was independently contracted to perform ASTM[2] standard testing on thermally sprayed coatings doped with the antimicrobial material. To test the doped coatings for corrosion resistance, ASTM B117-11 standards, commonly referred to as salt spray testing, were employed along with ASTM D610 (scribe testing) to coated steel panels. Salt spray testing is well known in many industries as a reliable method for evaluating the corrosion resistance of coatings. Though exposure to salt spray is not a typical hazard to oil and gas industry coatings, salt spray testing is a method of evaluating any change in the anticorrosive properties of the coating due to the addition of the antimicrobial material. The panels were subjected to 190 hours of salt-water spray and were then evaluated for rust and blister using ASTM D610 and D714 standards. The doped coatings were found to perform equivalent to coatings that were not doped.

A Taber Abrasion Device† was employed to measure the wear resistance of the coatings per ASTM D4060. The device utilizes a weighted CS-10F abrading wheel that rotates at a constant speed to determine the resistance of a coating to abrasion and wear. A 1000g weight was placed on a CS-17 Taber Abrasion wheel per ASTM D4060. Results are given in wear cycles per mil of coating. Results from the testing showed thermally sprayed aluminum oxide (Al_20_3) coatings to lose 202mg of mass per 1000 cycles while aluminum oxide coatings doped with 50% antimicrobial powder lost 139mg of mass

† Trade Name.
[2] ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

per 1000 cycles. This demonstrates that, for some coatings, addition of the antimicrobial powder increases the abrasion resistance of the host coating. This result indicates that the antimicrobial material can increase the wear resistance of standard coatings while simultaneously rendering them antimicrobial.

DISCUSSION

Many of the unique characteristics demonstrated by the antimicrobial material in the study stem from the synthesis process used to make the material along with the subsequent surface morphology of the product powder. Figure 7 demonstrates the high surface area and porosity gained through the activation process. Increasing the porosity of a material will effectively decrease the overall thermal conductivity. The effective thermal conductivity (k_{eff}) is a local volume-averaged conductivity used for reactant matrices along with the assumption of a local thermal equilibrium between the solid, fluid, and gas phases.[12]The effective thermal conductivity is a function of the material, porosity, temperature, and microstructure. Kaviany[12] presents correlations to determine an effective thermal conductivity for given phase distributions of a representative elementary volume, V. Equation 1 uses the concept of a geometric mean to determine an effective thermal conductivity for porous media.[12]

$$\frac{k_{eff}}{k_g} = \left[\frac{k_{\max}}{k_g}\right]^s \left[\frac{k_{\min}}{k_g}\right]^{1-s} \tag{1}$$

In this equation k_{eff} is calculated based on the limiting thermal conductivities of the material, where k_{min} is the minimum thermal conductivity of the material, k_{max} is the maximum thermal conductivity based upon the reactants and k_g is the thermal conductivity of the gas in the pores (assumed to have properties similar to air at 2000 K). The s in the equation is described as a wetting parameter and an inverse function of the porosity of the products.[12] Figure 6 shows the data for effective thermal conductivity based on the porosity measurements and a corresponding power law curve fit.

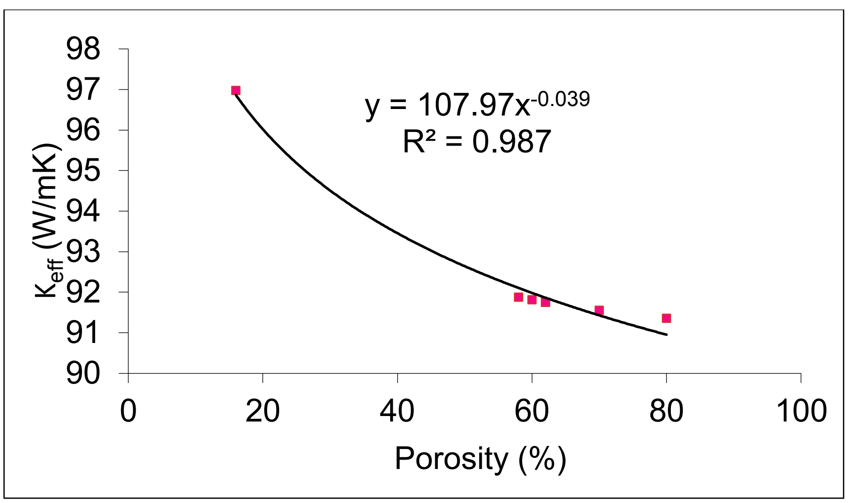


Figure 6: Effective thermal conductivity as a function of porosity (%).

The thermal conductivity continues to decrease as the porosity of the material increases leading to the improved property of heat resistance for the coating. The averaged conductivity term typically used for a metal-based alloy similar to the material in this study is 194 W/mK.[13-14] Increasing the porosity from 0% to 16% reduces the thermal conductivity to 97 W/mK. Increasing the porosity to 80% reduces the effective thermal conductivity by a factor of two (i.e. 194 to 91 W/mK).[13-14]

Because the material has good high temperature and structural properties, the material is ideal for hot, corrosive applications in the oil and gas industry. Tremendous effort has been devoted to developing new thermal barrier coating materials and processing methods in order to decrease the thermal conductivity.[15] The results from this study are significant because they show the production of coating that offers the superior hardness inherent from metallic nanoparticles and the oxidation and hot corrosion resistance associated with materials developed through combustion synthesis, as well as a reduction in thermal conductivity by a factor of two. This material could then be used as an improved thermal barrier coating in a variety of industries.

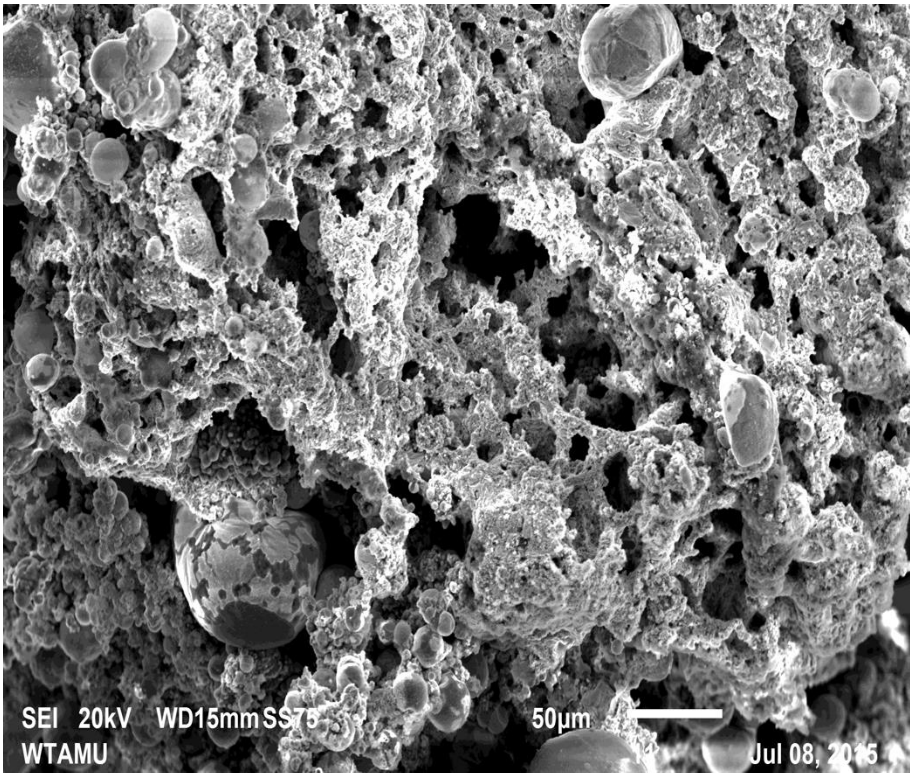


Figure 7: SEM image of antimicrobial material microstructure at 20kV.

CONCLUSIONS

The overall conclusion from a microbiological standpoint is that the material used in the study is a very potent antimicrobial material capable of being incorporated into a variety of coatings to render them antimicrobial. Coatings doped with the material provide a control strategy for microbial attachment and will have great potential in alleviating pipeline and equipment corrosion due to MIC. Testing demonstrated that the material can be incorporated into existing coatings without detrimental effects to the mechanical properties of the host coating. This technology provides a novel and promising alternative for mitigating microbiological corrosion and presents an innovative engineering solution for both external and internal protection of piping systems for the oil and gas industry. The reduction in thermal conductivity based upon increase porosity has significant implications for industrial applications. The extraordinarily high surface areas these materials possess serve as an excellent platform for the neutralization of bacteria. These newly synthesized alloys can be applied as a coating to existing surfaces such as metal, ceramic, or plastic and present a novel approach to bacterial neutralization, or more specifically, MIC.

ACKNOWLEDGEMENTS

The authors are thankful for the support of the Aggie Venture Fund, Advanced Nano Solutions, Dr. Carolyn Bouma and Valeria Rodriguez, and West Texas A&M University as well as DTRA (HDTRA-1-08-10-BRCWMD) and program officer Dr. Suhithi Peiris and NSF (CBET-0914382) and program officer Dr. Phil Westmoreland.

REFERENCES

1. A. Heyer. et al, "Ship ballast tanks a review from microbial corrosion and electrochemical point of view." *Ocean Engineering* 70 (2013): 188-200.
2. KJ Martin, C. Picioreanu, R. Nerenberg, Assessing Microbial Competition in a Hydrogen-Based Membrane Biofilm Reactor (MBfR) using Multidimensional Modeling. *Biotechnology and Bioengineering*, 112(9), 1843-1853.
3. L. Kenar, et al. "Comparative Sporicidal Effects of Disinfectants after Release of a Biological Agent." *Military Science* 172(6) 2007.
4. Understanding Biocides, Biocides: What they are, what they do, and why they matter, Dow Microbial Control, http://iogcc.publishpath.com/Websites/iogcc/Images/Tucson/Love%20ERRT.pdf. (May 16, 2015).
5. K. Vasilev, J. Cook, and H. Griesser, "Antibacterial surfaces for biomedical devices," *Expert Review of Medical Devices*: 6, (5), 553-567; (2009).
6. C. Trapalis, M. Kokkoris, G/ Perdikakis, and G. Kordas, "Study of Antibacterial Composite Cu/SiO2 Thin Coatings," *Journal of Sol-Gel Science and Technology*," 26, 1213-1218, (2003).
7. J.R. Morones, J.L. Elechiguerra, A. Camacho, K. Holt, J.B. Kouri, J.T. Ramirez, J. Yacaman, The bactericidal effect of silver nanoparticles, *Nanotechnology* 16: 2346-2353 (1998).
8. G. Zhao, E. Stevens, Multiple parameters for the comprehensive evaluation of the susceptibility of Escherichia coli to the silver ion, *Biometals* 11: 27-32 (1998).
9. C. Faille. et al. "Adhesion of Bacillus Spores and Escherichia coli Cells to Inert Surfaces: Role of Surface Hydrophobicity." *Canadian Journal of Microbiology* 48; 2002.
10. EM Hunt, ML Pantoya, and R J Jouet, "Combustion Synthesis of Metallic Foams from Nanocomposite Reactants," *Intermetallics* vol. 14 (6), pp. 620-629 (2006).
11. E. Whitney, et al. "Inactivation of Bacillus anthracis Spores." *Emerging Infectious Diseases* 9(6); 2003.
12. M. Kaviany, Principles of Heat Transfer In Porous Media, Springer-Verlag, New York (1991).
13. EM. Hunt, K. Plantier, M. Pantoya, "Nano-scale Reactants in the Self-Propagating High-Temperature Synthesis of Nickel Aluminides," Acta Materialia Vol. 52 No. 11 pp. 3183-3191, 2004.
14. EM Hunt, J.J. Granier, K.B. Plantier, ML Pantoya, "Nickel Aluminum Superalloys Created by the Self-propagating High-temperature Synthesis (SHS) of Nano-particle Reactants," Journal of Materials Research, Vol. 19, No. 10 pp.1-9 (2004).
15. V.A. Shcherbakov, and A.G. Merzhanov, "Self-propagating High-Temperature Synthesis of Cermet Foam Material," Translated from Doklady Akademii Nauk, Vol. 354, No. 3 p. 346-349, (1997).