

AIR COMMAND AND STAFF COLLEGE

AIR UNIVERSITY

**THE ELIMINATION OF CORROSION . . . IS
NANOTECHNOLOGY THE ANSWER TO THE USAF's #1
AGING AIRCRAFT DILEMMA?**

by

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A Research Report Submitted to the Faculty

In Partial Fulfillment of the Graduation Requirements

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Maxwell Air Force Base, Alabama

April 2009

Report Documentation Page		Form Approved OMB No. 0704-0188
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.		
1. REPORT DATE APR 2009	2. REPORT TYPE N/A	3. DATES COVERED -
4. TITLE AND SUBTITLE The elimination of corrosion . . . is nanotechnology the answer to the USAFs #1 aging aircraft dilemma?		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER	
	5e. TASK NUMBER	
	5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Command And Staff College Air University Maxwell Air Force Base, Alabama		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited		
13. SUPPLEMENTARY NOTES The original document contains color images.		
14. ABSTRACT United States Air Force aircraft currently average 30 years old. As this aircraft fleet continues to age, the cost of corrosion maintenance, both in terms of dollars spent and lost operational readiness, increases correspondingly. Corrosion maintenance cost the Air Force over \$1.5 billion in 2004, and trends show that number quickly rising, as it cost only \$800 million in 1998. These rising costs must be reversed before Air Force operations suffer serious detrimental effects. Nanotechnology offers one possible solution for creating new revolutionary anticorrosion coatings capable of adapting to environmental damage and conditions. Nanoscience research and development aims to discover new properties and behaviors of materials at the nanoscale (1 to 100 nanometers (nm); 1 nm = 10⁻⁹ m). Nanotechnology, subsequently, is the application of nanoscale discoveries toward accomplishing specific functions. The proposed nanotechnology-enhanced corrosion control coating, or NEC3, will prevent and combat corrosion degradation by directly targeting the thermodynamic enablers to corrosion, namely the galvanic cell formed between the anode, cathode, and electrolyte. Specifically, it will detect and repair small coating damage, detect and signal maintainers of moisture intrusion, detect corrosion and signal maintainers of its presence, release inhibitors to combat corrosion, replenish its corrosion inhibitors from the environment, and integrate needed repairs to the coating. Though significant technological hurdles remain, such as developing successful self-assembly methods and efficient nanocomponent manufacturing and integration processes, a trend forecast based on microelectromechanical systems (MEMS) development indicates that an integrated approach to research and development should make the NEC3 possible by 2029.		
15. SUBJECT TERMS		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 57	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

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Preface

I have spent most of my time in the Air Force around aging aircraft. My career began in the Materials and Manufacturing Directorate's Adhesives, Composites, and Elastomers team at Wright-Patterson AFB, OH. There we researched methods and techniques to bond composite structural repair patches onto aging aircraft structures. Next, I worked as an A-10 Thunderbolt II structural engineer at Hill AFB, UT. I learned a great deal there about aging aircraft, specifically how corrosion and fatigue are the main limiting factors in aircraft service life. I then "took some time off" and taught engineering mechanics at the US Air Force Academy in Colorado Springs, CO. While there, I directed a course on failure analysis and prevention and worked in the Department of Engineering Mechanics' Center for Aircraft Structural Life Extension (CAStLE). CAStLE studies aging aircraft issues and helps to determine how best to mitigate the two main concerns—fatigue and corrosion. All of these experiences led me to this research topic, which has definitely broadened my horizons, for which I am grateful.

The best part about working with Air Force aging aircraft experts during my career is that I know who to call when I need help. I would like to thank CAStLE's amazing Dr. Sandeep Shah for giving me feedback and advice on my topic. Also, LtCol Frank Dement, Mr. David Ellicks and the rest of the Air Force Corrosion Prevention and Control Office staff for providing invaluable support for my research on Air Force corrosion issues and impacts. Thanks also go to Mr. Danny Anderson and Mr. Paul Clark for providing valuable insight on aging aircraft issues. My special thanks to the Blue Horizons staff and my advisors, Colonel Brett Morris and Major Paul Hoffman, for their guidance and patience throughout this project. Lastly, to my family—wife Andie, son Joe, and daughter Lilly—thanks so much for your support every time this paper kept me from doing what I really wanted to do—spend more time with all of you.

Abstract

United States Air Force aircraft currently average 30 years old. As this aircraft fleet continues to age, the cost of corrosion maintenance, both in terms of dollars spent and lost operational readiness, increases correspondingly. Corrosion maintenance cost the Air Force over \$1.5 billion in 2004, and trends show that number quickly rising, as it cost only \$800 million in 1998. These rising costs must be reversed before Air Force operations suffer serious detrimental effects. Nanotechnology offers one possible solution for creating new revolutionary anticorrosion coatings capable of adapting to environmental damage and conditions. Nanoscience research and development aims to discover new properties and behaviors of materials at the nanoscale (1 to 100 nanometers (nm); $1 \text{ nm} = 10^{-9} \text{ m}$). Nanotechnology, subsequently, is the application of nanoscale discoveries toward accomplishing specific functions. The proposed nanotechnology-enhanced corrosion control coating, or NEC³, will prevent and combat corrosion degradation by directly targeting the thermodynamic enablers to corrosion, namely the galvanic cell formed between the anode, cathode, and electrolyte. Specifically, it will detect and repair small coating damage, detect and signal maintainers of moisture intrusion, detect corrosion and signal maintainers of its presence, release inhibitors to combat corrosion, replenish its corrosion inhibitors from the environment, and integrate needed repairs to the coating. Though significant technological hurdles remain, such as developing successful self-assembly methods and efficient nanocomponent manufacturing and integration processes, a trend forecast based on microelectromechanical systems (MEMS) development indicates that an integrated approach to research and development should make the NEC³ possible by 2029.

Introduction

United States Air Force aircraft currently have an average age of 30 years. Fighter aircraft average 21 years; bombers average 30 years; while tankers average an amazing 47 years old!¹ Another way to estimate the age of an aircraft involves the operational age, or number of flight hours, combined with the severity of the operating environment. This provides the best estimate of an aircraft's true "age" and corresponding remaining service life, much like comparing a car's highway versus city driving miles. The harsher the environment the more it causes "aging" of the vehicle. As this operational age increases so do the number of aircraft maintenance issues. Of these, fatigue cracking and corrosion damage prove to be the two most common and detrimental issues affecting Air Force aircraft operations and maintenance costs.² While fatigue cracking damage proves slightly more common, corrosion produces the single largest siphon of maintenance cost and man-hours, bleeding over \$1 billion annually from the Air Force budget.³ As the aircraft fleet continues to age, the cost of corrosion maintenance, both in terms of dollars spent and lost operational readiness, will increase correspondingly.

The Air Force has historically combated corrosion in two ways—through the use of coatings to protect materials from environmental effects, and through the development of better metals to reduce susceptibility to corrosion. Materials science research and development (R&D) aimed at engineering new metals less prone to corrosion has proven very successful. This paper, though, targets the development of new "adaptive" coatings capable of better preventing, detecting, and combating corrosion. Specifically, it investigates the potential to leverage nanoscience to create adaptive corrosion coatings that combat the environmental conditions that enable corrosion.

Nanoscience involves research and development aimed at discovering new properties and behaviors of materials at the nanoscale (1 to 100 nanometers (nm); $1 \text{ nm} = 10^{-9} \text{ m}$).

Nanotechnology is the application of nanoscale discoveries toward accomplishing specific functions.⁴ Nanoscience and technology R&D sprouted largely over the last two decades of the 20th century as a result of transistor technology advances in the computer industry. Nanoscale materials are already in use and having profound effects in certain industries. Examples include nanostructured coatings applied to cutting tools and wear-resistant components, the controlled manufacturing of silicon transistors on the nanoscale, and a computer's nano-thin magnetic film on the spinning disk.^{5,6} The recent increased world-wide focus on nanotechnology research will serve to advance this industry farther and faster than ever before.

This paper argues that nanotechnology can be leveraged to create new revolutionary anticorrosion coatings capable of adapting to environmental damage and conditions, effectively eliminating the AF's #1 aging aircraft concern. To accomplish this, it first outlines the main Air Force corrosion issues and impacts, along with a brief discussion of the science behind corrosion degradation. From this, it derives the corresponding historical and current AF corrosion prevention methods. Next, the paper lays out the relevant basics of nanotechnology, highlighting relevant areas that offer potential corrosion prevention and control solutions for the future. The paper then turns to focus specifically on what relevant technological and social advances need to occur before an adaptive corrosion prevention nanocoating can be realized, specifically by looking at technological, support, and military suitability hurdles. Finally, it leverages an overview of the technological development of microelectromechanical systems (MEMS), the last effort to miniaturize technology and the closest for comparison with nanotechnology, to extrapolate a nanotechnology future trend portraying how a corrosion prevention coating may develop over the next 20 years.

Chapter 1. Air Force Corrosion Issues and Resulting Impacts

Industry manufactures Air Force aircraft on the leading edge of the design envelope, utilizing mostly advanced aerospace aluminums with high strength-to-weight ratios. Military spending cuts, and the resulting reductions in aircraft acquisition projects, have forced the Air Force to utilize its fleet of aircraft well beyond their original design service lives.^{7,8} Managing this aging aircraft fleet to ensure structural integrity for operations has therefore become a main focus of AF sustainment engineers and maintainers.⁹ Fatigue cracking and corrosion degradation inflict the most damage on the aging aircraft fleet. While these two issues can occur separately, they often have a synergistic effect, with corrosion damage acting as an initiation point for fatigue cracking. The most notable example of this was the 1988 catastrophic failure of Aloha Airlines Flight 243, where 18 feet of fuselage exploded off in flight, causing numerous injuries and the death of a flight attendant. The resulting investigation showed that the combined effects of corrosion and fatigue cracking caused the accident.¹⁰ This chapter summarizes the main Air Force corrosion issues and impacts beginning with an overview of the main corrosion types and followed by a look at both the operational and financial costs of corrosion.

Corrosion Types

Corrosive degradation takes on many forms dependent on the materials being utilized, the type of loading involved, and environmental factors. The Center for Aircraft Structural Life Extension (CAStLE) at the USAF Academy displayed this well in a graphic published in 2007 as part of their failure analysis course, shown in Figure 1.¹¹ While the graphic shows seven different variants of corrosive attack, the four that the AF most commonly confronts are pitting, intergranular attack, exfoliation, and stress corrosion cracking (SCC).

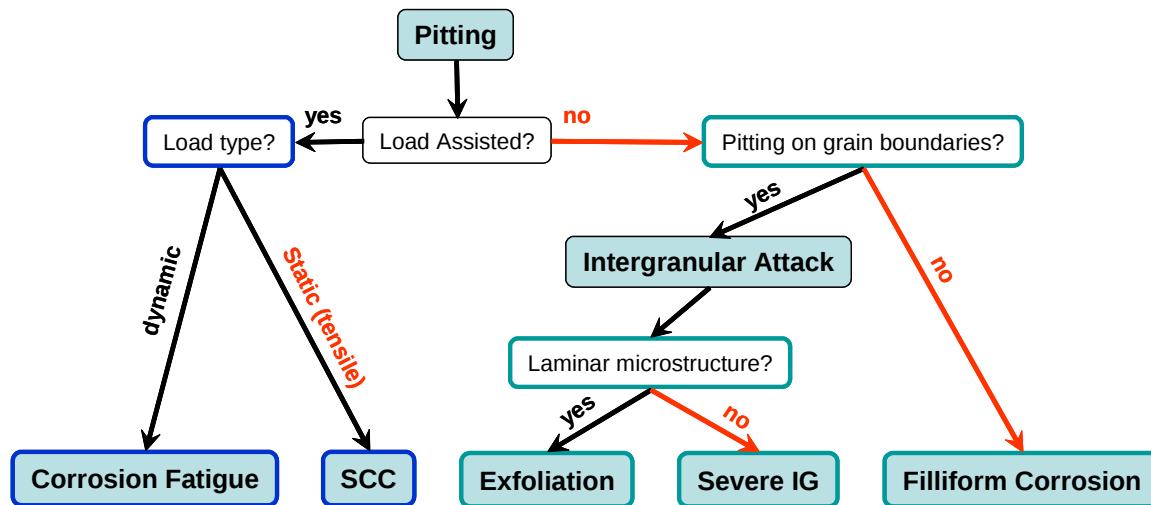


Figure 1 Types of Corrosion Common to Aerospace Aluminum Structure

Pitting—a localized inhomogeneity that causes a “pit” in the material surface—is the origin for all other forms of corrosion. Severe pitting also risks fatigue crack initiation. If pitting is not in conjunction with an applied load, it is common for continued corrosion to propagate along the aluminum’s grain boundaries. All metals are crystalline and consist of an ordered network of “grains”, the microscopic portions of the material with identical atomic structure.¹² Depending on the orientation of the grains, corrosion can either be intergranular, where the corrosion propagates into the depth of the material, or exfoliation, a variant where corrosion runs parallel to the metal surface and causes metal to flake off in thin sheets. Figure 2 shows examples of all three non-stress related corrosion types.¹³

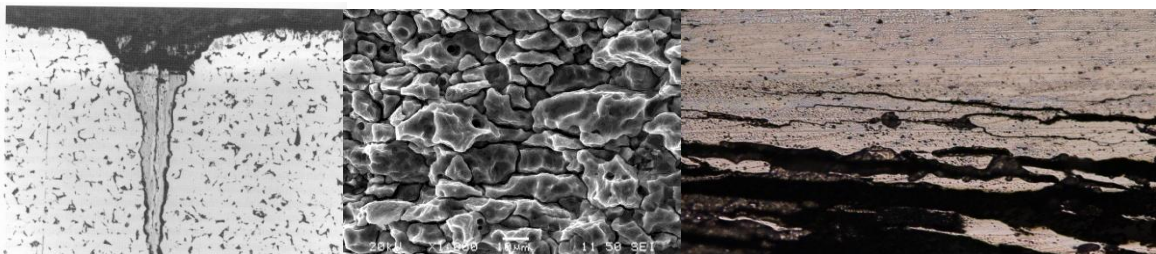


Figure 2 Photographic Examples of Pitting, Intergranular, and Exfoliation Corrosion, respectively

When aircraft loading exists in combination with a corrosive environment, SCC acts as the main corrosion mechanism. This presents a large problem for the Air Force because it occurs with even mild corrosive environments and seemingly negligible static loading—far below maximum design loads. Consequently, large cracks can occur unpredictably and take maintainers by surprise. As with other types of corrosion, the risk that SCC might transition into a fatigue crack and continue to propagate to dangerous lengths subsists. Figure 3 shows an example of SCC.¹⁴



Figure 3 Photographic Evidence of a Stress Corrosion Crack in Aluminum Aircraft Structure

Operational Costs of Corrosion

Corrosion damage profoundly impacts AF operations and maintenance costs and unless the AF develops better corrosion control and prevention methods the historical trends do not bode well for future operations. According to an Air Force Air Logistics Center, the number of additional maintenance man-hours required to repair corrosion damage afflicting one specific fighter/attack fleet had increased from 3,500 hours in 2005 to more than 5,000 hours in 2008. In just this four-year time span unexpected maintenance due to corrosion damage increased by more than 45%.¹⁵ This general trend of a worsening corrosion problem is present throughout the AF, with the worst effects felt in the tanker and transport communities. Historically, tanker and transport fleets suffer even more serious corrosion degradation problems, with fighter/attack fleets tending to suffer more from fatigue damage.¹⁶ Fighter aircraft are designed much closer to

the limits of the aeronautical design envelope than tanker and transport aircraft, with smaller margins of safety. This allows them to be more agile and maneuverable, exposing them frequently to high operational fatigue loads that often lead to fatigue crack initiation. Tanker and transport aircraft, on the other hand, operate in safer and less harsh environments. As a result, tanker and transport aircraft do not develop aggressive widespread fatigue damage as quickly and operate in service much longer, where corrosion plays a larger role. To reinforce this view, the average age of AF fighter aircraft is 21 years old, while the age of tankers is 47 years old.

While aircraft depots perform a majority of corrosion maintenance, operational field units also perform extensive amounts.¹⁷ As the AF aircraft fleet continues to age, corrosion maintenance will become an even larger part of both depot and field unit maintenance operations. This increase in overall corrosion maintenance required causes a corresponding impact on AF operational readiness due to the loss of aircraft availability. This impact on operational readiness can easily be visualized, but actual corrosion maintenance operation statistics are more readily available in terms of financial costs, as opposed to operational costs.

Financial Costs of Corrosion

Along with substantial impact to operational readiness, aircraft corrosion degradation also significantly burdens the AF financially. According to the 2004 Cost of Corrosion report, the AF spent \$1.5 billion dollars on corrosion maintenance alone, with almost \$1.2 billion directly related to aircraft fleet maintenance. The costs of corrosion includes not only direct aircraft repairs, but also corrosion prevention, detection, and engineering support, which make up a sizeable portion of the overall cost. In fact, approximately 29%, or \$354 million, of the cost goes toward corrosion prevention (painting, washing and inspection).¹⁸ Appendix A contains more specific information regarding aircraft corrosion maintenance cost.

Additionally, corrosion maintenance is a growing portion of the overall USAF annual maintenance budget. According to the 1998 Cost of Corrosion report, the AF spent less than \$800 million on corrosion. That is an 87.5 percent increase in corrosion maintenance costs in the six years leading up to 2004's estimate of \$1.5 billion.¹⁹ This growing corrosion cost will continue to worsen as AF weapon systems are utilized past their designed service lives. As of 2004, three of the four most expensive corrosion maintenance air frames—the XC-135 fleet (\$351 million annually), the C-130 fleet (\$121 million annually), and the A-10 fleet (\$75 million annually)—have no planned replacement and will continue to be significant contributors to the AF mission past 2025.^{20,21,22,23}

Chapter 2. The Science Driving Corrosion and Corrosion Prevention Methods

Clearly corrosion degradation is a legitimate problem affecting Air Force operations. Therefore, developing better methods to prevent and control aircraft corrosion needs to be addressed as a crucial need. In order to understand how best to combat the corrosion problem, one must first understand the basics of why components corrode. Combining understanding of the corrosion process with experiences gained through historical Air Force corrosion control methods and research results on potential future prevention methods allows the best opportunity to develop successful nanotechnology-based corrosion prevention coatings.

Corrosion Degradation Based on Thermodynamics and Kinetics

Thermodynamics drives the corrosion process, which requires each of the following actors to be present: an anode, a cathode, an electrolyte, and susceptible materials. When two dissimilar materials become connected to each other by an electrolyte (an electrical-conducting liquid medium), one material acts as the anode, or material more prone to give up its electrons and corrode, and the other acts as the cathode, or material more prone to receive electrons in the

specific circuit, based on their relative position in the Galvanic Series.²⁴ The Galvanic Series rank-orders different alloys based on their anodic or cathodic tendencies in a specific electrolytic environment, such as seawater.²⁵ Appendix B shows an example of this series.

Thermodynamics answers the question, “Will corrosion happen?”, based on the difference in Gibbs free energy, or ΔG , of a system.²⁶ ΔG measures a closed system’s (fixed mass and composition; constant temperature and pressure) tendency toward stable equilibrium. Gibbs free energy is defined mathematically by the expression, $G = H - TS$, where H is enthalpy, T is absolute temperature, and S is the entropy of the system.²⁷ Appendix C includes a more detailed description of Gibbs free energy and the specific properties used to define it. ΔG is known for many reactions and can be looked up in charts, like the one shown in Appendix C. When a negative ΔG exists for a chemical reaction between two materials, corrosion will occur. Electrical current flows between the anode and the cathode causing negatively charged metal ions (anions) to be emitted as corrosive by-product, causing degradation. Reference the following representation for a better understanding.

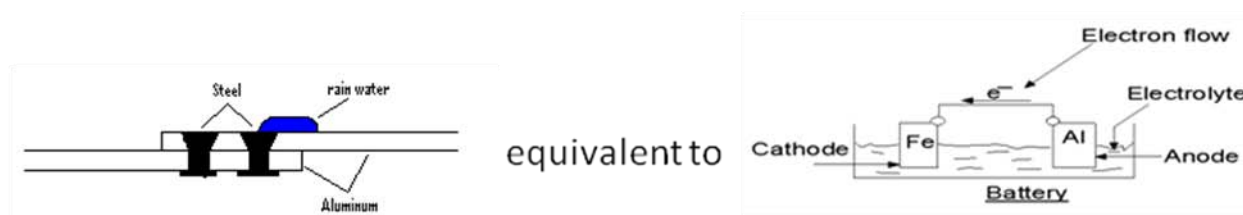


Figure 4 Graphic Showing Corrosion Process²⁸

Kinetics, as opposed to thermodynamics, answers the question “How fast will corrosion occur?” An Arrhenius equation defines this rate, expressed as, $\text{rate} = A^{(-Q/RT)}$, where A is a material constant, Q is a material activation energy (free energy required to drive a specific reaction), R is the universal gas constant, and T is absolute temperature.²⁹ Outside of choosing

materials wisely to control the applicable properties (A and Q), temperature remains the only variable that can be manipulated to reduce corrosion rate. Per the equation, higher temperatures result in more rapid corrosion, and vice versa.

AF Historical Prevention Methods

Thermodynamic and kinetic processes play main roles in every corrosive reaction. Slowing the kinetic process or eliminating the thermodynamic process correspondingly affects the corrosion process. As already stated, outside of material properties, manipulating temperature remains the only variable that can slow the kinetic reaction of corrosion. Unfortunately, while reducing the temperature would slow down corrosive reactions, it is not feasible to control the temperature over the entire surface of an aircraft. Also, while material science research has been very successful in minimizing corrosion susceptibility, new generations of aluminums still experience corrosion. More importantly, the current aging aircraft dilemma does not benefit from these new materials. As a result, the Air Force's most viable corrosion prevention and control methods for aging aircraft aim to reduce or eliminate the thermodynamic corrosion enablers, specifically the galvanic cell formed between the anode, cathode, and electrolyte.

According to Technical Order (T.O.) 1-1-691, "*Cleaning and Corrosion Prevention and Control, Aerospace and Non-Aerospace Equipment*," a successful corrosion prevention and control program includes "thorough cleaning, inspection, preservation, and lubrication, at specified intervals."³⁰ *Cleaning* removes accumulations of condensation that might combine with surface sediments of dirt, salt, or dissolved engine exhaust gases to form highly corrosive electrolytic solutions. This is a crucial step, as testing has shown that sea water (highly corrosive) accelerates the corrosion rate by up to 1000 times over distilled water (inert).³¹

Lubrication of moving aircraft components reduces the chance of wear, reduces contact between dissimilar materials, displaces water and other possible electrolytes, and reduces the local operating temperature.³² Component wear breaks down surface corrosion prevention coatings, so eliminating it is critical. Additionally, reducing effective surface temperature reduces the rate of corrosion. *Preservatives* provide corrosion preventive compounds (CPCs) that protect metallic aircraft, missile, and other component parts by preventing corrosive materials from contacting and corroding metallic surfaces.³³ The Air Force utilizes both water displacing and non-water displacing CPC's, depending on the specific application.

Lastly, *inspection* provides a crucial corrosion deterrent for the Air Force's corrosion prevention and control program. Detection of corrosion early allows any corresponding damage to be minimized. Otherwise, severe damage can ensue causing aircraft downtime and substantial maintenance costs, or even loss of an asset. Maintainers utilize both visual inspection and non-destructive inspection (NDI) methods to search for corrosion symptoms. The maintainers eyes remain the main tool used for visual inspection, but magnifying glasses, boroscopes, videoscopes, and fluorescent dye penetrant aid greatly in the process. NDI involves utilizing equipment and methods to detect corrosion damage below metal surfaces without damaging the aircraft. The main tools used for NDI are eddy current and ultrasonic testers, and radiographic (X-ray) equipment.³⁴ Any corrosion found is repaired in accordance with Air Force T.O. 1-1-691 and other specific aircraft repair manuals.

Future Trends in Corrosion Prevention and Control

Engineers aim to better manage corrosion degradation by designing in corrosion prevention through better material selection in the acquisition process. Aerodynamics, structures, avionics, fuel systems, and hydraulics design make up just a few of the iterative design efforts ongoing at

any given time during airframe design. Within these efforts, designers tend to focus more on performance-based aspects of the product, as opposed to life-cycle aspects, like corrosion control. This attitude may be engrained in engineers from their educational experiences, as one professional noted, “the instruction we received in this class discussed *what* corrosion is, and not *how* to select materials and technologies to prevent its occurrence.”³⁵ In reality, much of DOD’s corrosion degradation could be avoided with smarter design.³⁶ The DOD’s recently established Office of Corrosion Policy and Oversight ensures that new acquisition programs now plan for corrosion prevention and control from the beginning of a system’s life-cycle through proper material selection.³⁷

Air Force efforts also aim to utilize superior processes and inspection techniques to better manage fleet corrosion. Detection of corrosion early limits material degradation and ensures that it does not transition into more serious problems, such as fatigue crack initiation. As such, Battelle® is working to apply coating-embedded sensors that provide qualitative information on coating viability and also detect corrosion occurring under the coating.³⁸ Additionally, the Air Force develops and utilizes better processes to manage specific corrosion concerns. For instance, R&D specifically targeted sand and dust intrusion in the Southwest Asia operating environment and resulted in more effective sealants, sealing tapes, and gasket materials that provided better corrosion prevention and control to deployed units.³⁹ They also make strides with fleet modernization efforts. One study covering a 10-year span showed that more corrosion-resistant aluminum, better sealants, wet installation of fasteners, and more corrosion-resistant coatings applied to the C-5 Galaxy and C-130 provided a 53 percent and 82 percent reduction in total corrosion maintenance cost, respectively.⁴⁰

Lastly, the Air Force teams with industry and academia to develop more technologically advanced corrosion prevention coatings. University of Pittsburgh researchers are working with AFRL to develop new novel corrosion inhibition methods, specifically targeting aluminum surfaces.⁴¹ Also, researchers at several leading universities collaborated R&D efforts to develop corrosion-resistant metallic coatings. These coatings would provide on-demand release of corrosive ionic inhibitors (positively charged ions, called cations, to counter the negatively charged anions released by the corrosion process), a local barrier to corrosive environments, and sacrificial cathodic prevention to protect against corrosive degradation.⁴² Finally, University of Virginia researchers, funded by the DOD, researched an environmentally compliant, multi-functional coating for aerospace application. This new coating would combine corrosion inhibitors, embedded sensors, and a nanotechnology-enhanced coating layer to sense both corrosion and mechanical damage and actively combat corrosive degradation.⁴³

Chapter 3. Nanotechnology Overview

While all of the AF's efforts to prevent and control corrosion degradation have merit, the considerable size and cost of the corrosion dilemma calls for even more aggressive efforts at stemming this problem. Nanotechnology interest as a potential solution has risen, as the University of Virginia research indicates. According to the National Nanotechnology Initiative (NNI), nanotechnology is the “ability to work—to see, measure, and manipulate—at the atomic, molecular, and supra-molecular levels, in the length scale of approximately 1-100 nm range, with the goal of understanding and creating useful materials, devices, and systems that exploit the fundamentally new properties, phenomena, and functions resulting from their small structure.”⁴⁴ More simply put, nanotechnology aims to apply newly discovered material properties at the nanoscale toward developing capabilities across fields of science, engineering, and medicine.⁴⁵

Nanotechnology Background

Advances in scientific instruments related to computer and information technology development first enabled manipulation of objects more than 1,000 times smaller than a microcircuit.⁴⁶ The earliest applications of nanoscale materials involved free-form use of nanoscale powders for cosmetics, reflective paints, and wear-resistant coatings.⁴⁷ The military soon realized the potential of nanotechnology and became a main driving force in R&D in the 1980's with programs like the Ultra Submicron Electronics Research program, the Navy's interfacial nanostructures research for coatings technology, and the Army's Institute for Soldier Nanotechnology.⁴⁸ Federal coordination on nanotechnology research efforts began informally in 1996, but started officially in 1998 with the establishment of the Interagency Working Group on Nanotechnology (IWGN). Support for nanotechnology reached the highest levels of government in 2001 when then-President Clinton recognized nanoscale science and technology as a national initiative, establishing the NNI with the goal of coordinating national R&D efforts.⁴⁹

Since the establishment of the NNI in 2001 nanotechnology research has resulted in numerous new military and industrial capabilities. The US oil industry saves approximately \$12 billion a year using nanoparticles called zeolites that extract up to 40 percent more gasoline from crude oil.⁵⁰ Also, nanoparticle filters remove "viruses, bacteria, and protozoa such as Hepatitis A, E-coli and Giardia from water."⁵¹ In 2002, the US Navy started using a nano-coating on ship air intakes and exhaust valves, resulting in an estimated \$20 million savings over the next 10 years.⁵² More than 1200 companies currently conduct nanotechnology research and development and sales of products incorporating nanotechnology amounted to \$32 billion in 2005.⁵³ Along with applications already available for military and industrial use, numerous R&D programs exist that show promise for future applications. Nanostructured coatings for

detection of chemical and biological warfare agents, carbon nanotube-reinforced composite structures, antibiotics based on peptide nanotubes, and metallic iron nanoparticles used to filter groundwater contaminated with heavy metals are just a few examples.⁵⁴

Hurdles to Nanotechnology Development

Nanotechnology, like other developing advanced technologies before it, must overcome technological and social challenges to realize its full potential. The largest technological hurdle lies in nano-manufacturing. The size and negligible mass involved at the nanoscale makes the process and equipment for manufacturing more challenging to develop and produce. Widely used microchip-based top-down construction methods have inherent scale limitations. Self-assembly is a bottom-up construction method where individual atoms and molecules are organized by energy minimization and/or selective affinity of the substructures into specified nanocomponents.⁵⁵ This method does not suffer from scale limitations and must be fully understood and developed. Additionally, integrating molecular components into higher-order working machines and systems presents a large challenge.⁵⁶ Nanoparticles, with their inherent increased surface volume, cause difficulties with friction, stiction, surface tension, etc. during operation. Finally, there are challenges associated with making nano-manufacturing economical for industrial use.⁵⁷

Technological hurdles provide the most obvious challenges to nanotechnology progress, but a lack of sufficient funding and support can also derail nanotechnological advancement. With only limited funds available, projects with the most chance of being successful—as opposed to *more challenging yet feasible* research projects with larger technological payoffs—have the best chance of getting funded.⁵⁸ Additionally, the new field of nanotechnology is highly dependent on a full understanding of many science and engineering fields—physics, chemistry, biology,

mechanics of materials, etc. Without national interagency partnerships, along with international cooperation, nanotechnology advancement could stall.⁵⁹ Scientific transparency and cooperation will allow nanotechnology to advance more quickly with less wasted effort, making a nanotechnology-enhanced corrosion control coating a realizable near-term reality, as opposed to simply a distant pipe-dream.

Chapter 4. Nanotechnology Applied to Corrosion Prevention and Control

At 0500 hours, the sun is just starting to peak over the mountains in Tucson, AZ. As TSgt Smith and his maintenance crew approach his A-10 Thunderbolt II at Davis-Monthan AFB, he cannot help but reflect back on how much maintenance has changed over the course of his 14-year AF career since he took the oath in August, 2012. He yells to SrA Duffy to hit the ultraviolet lights in the hangar. During the walk-around, three small areas on the plane jump out at him—two glowing purple and one glowing yellow. The AF has been using a new aircraft coating—one that combines paint scheme and corrosion prevention/control—for the last few years, and it has truly revolutionized aircraft maintenance. When the coating glows purple under ultraviolet light, it means that a form of corrosive attack has occurred at the metal surface. This isn't necessarily a disaster, as the coating now actually fights the corrosion itself by releasing metal cations to counter the anions released through the corrosion process. As the coatings supply of cations is depleted, it replenishes them by taking hydrogen electrons out of water vapor in the air through an electrochemical process, with the only by-product into the atmosphere being negligible amounts of pure oxygen. After a quick ultrasonic inspection of the area, TSgt Smith's team determined no significant corrosion damage requiring repair at either spot was indicated.

Now TSgt Smith's team moves to a closer inspection of the glowing yellow spot, which indicates some form of moisture at the coating/metal surface interface. It is essential that this be eradicated as quickly as possible, as moisture acts as a corrosive-enabling electrolyte. After a thorough NDI inspection of the area, the team verifies the presence of moisture, so a repair will need to be done. To accomplish this, TSgt Smith puts SrA Duffy and AIC Folley in charge of removing the coating, drying out the metal surface, and re-applying the coating to re-seal the area. The new coating and old coating integrate perfectly as the repair is baked on with minimal applications of heat. TSgt Smith thinks back to how it took a team an entire day just to inspect the aircraft when he first arrived on station. With the small size of the corrosion and moisture damage, they wouldn't even have found these spots until significant corrosion damage had occurred, requiring much more time and manpower-intensive repairs. Thanks to the new coating, his team required only 2.5 hours to not only inspect the aircraft, but determine the extent of corrosion and moisture infiltration and process all repairs. What a savings to the AF!

Nanotechnology-Enhanced Corrosion Control Coating Relevance Tree

The previous scenario describes a potential application and the corresponding advantages of the nanotechnology-enhanced corrosion control coating (NEC³) in preventing and combating corrosion degradation. The NEC³ concept possesses the ability to detect and self-repair coating damage; detect moisture at the coating/metal interface and signal maintainers; detect metal anions, the product of corrosion; release metal cations to inhibit the corrosion process, while signaling maintainers for a more thorough human inspection; sustain itself by absorbing electrons from the atmosphere to replenish deficiencies in metal cations; and automatically integrate repairs to the coating. This capability would greatly enhance the Air Force maintainer's ability to combat corrosion, while freeing up their time and resources for other

operational challenges. In order to make this scenario a reality, however, many developmental hurdles must be targeted, investigated and overcome.

A relevance tree breaks down a significant problem into successively smaller parts to highlight those steps that must be accomplished to move an idea from a mere concept to an actual capability.⁶⁰ As already discussed, there are numerous hurdles between the concept of a nanotechnology-enhanced corrosion prevention coating and its application. Appendix E shows the relevance tree developed to break down this problem.

Relevance Tree Key Node Analysis

The NEC³ relevance tree has over 140 branches; hence it is not feasible to analyze every branch in the tree specifically. This key node analysis, therefore, highlights the main hurdles to technological advancement of nanotechnology from its potential capabilities to actual application in fighting aircraft corrosion. This analysis provides a broad survey of three of the branches: the technological branch, the support branch, and the military suitability branch.

Technological Key Node Analysis

The technological branch has three main sub-branches: nano-manufacturing, corrosion control, and coating maintainability. Each branch contains significant hurdles to be overcome before this technology will be viable. First, nano-manufacturing poses the largest technical hurdle to the advancement of nanotechnology. Researchers point out the inherent problems associated with equipment utilized to manufacture atomic- or molecular-sized components—they will be the same size or larger than the atoms they are attempting to manipulate. Also, atoms, especially carbon, bond to almost everything. This “fat” or “sticky fingers” argument presents one of the key proposed dilemmas facing nanomanufacturing.⁶¹ Researchers have proposed an atomic force microscope (AFM) with a “gripper” able to manipulate single atoms or molecules

(see Figure 10 in Appendix E), but further development must be accomplished.⁶² Bottom-up self-assembly methods, such as block copolymer-directed assembly, dielectrophoretic assembly, or tailored adhesion, have been proposed as future solutions to this problem, but more research needs to be accomplished (Table 7 in Appendix E lists leading self-assembly methods with corresponding applications).⁶³ Integrating atomic or molecular nanocomponents into higher order working systems, hence overcoming surface volume effects of friction, stiction, surface tension, and electrostatic forces, also poses technical hurdles and requires significant research.^{64,65} Once nanomanufacturing has been more fully developed, industrial manufacturing processes must be developed to ensure feasible, efficient, repeatable and cost effective production of nanocomponents.⁶⁶

Along with nanotechnology development, specific corrosion control hurdles exist in developing a nanotechnology-enhanced corrosion control coating. For the coating to be adaptable to corrosion it must detect the metal anions released by the corrosion process, automatically release cations to combat the corrosion, and then be able to replenish its supply of cations to be prepared for the next “corrosion battle.”^{67,68} This electrochemical process will require an electrical power source to drive this process. The electric field created by corrosion could potentially fill this role.⁶⁹ An energy source built into the coating, such as solar energy, or a nano-battery sheet, provides another potential power option. A nano-battery film has already been demonstrated using nano-engineered viruses.⁷⁰ The ability to signal maintainers, saving countless hours of inspection time on each aircraft, is an essential capability of the proposed coating. Nanomaterials show interesting light emitting properties, such as cadmium nanocrystals fluorescing color dependent on the crystal size.⁷¹ Research can further develop these properties to utilize them for flagging corrosion, moisture, or other issues pertinent to aircraft maintenance.

The final technological branch includes coating maintainability, a key issue to AF maintainers because aircraft live and operate in harsh environments. The ability to “self-heal” small damages which might occur from foreign object damage (FOD) strikes, hail damage, or other normal wear and tear would greatly benefit the Air Force. Although a large technical hurdle, the benefits of reducing the routine maintenance burden and protecting the integrity of the corrosion prevention coating make the R&D effort worth it. Ease of application and the ability to repair small areas with complete integration in the nanocoating system are also essential requirements for coating maintainability. Lastly, the coating must not inhibit NDI capabilities of maintainers. The NDI methods utilized to detect corrosion, delamination, disbonding, fatigue cracking, etc. are visual inspection using the naked eye and fluorescent dye penetrant, eddy current inspection, ultrasonic inspection, and radiographic (x-ray) inspection.⁷² The NEC³ must be compatible with these inspection methods.

Support Key Node Analysis

The second main branch in the NEC³ relevance tree key node analysis is the support branch, which contains two main sub-branches: funding support and institutional support. For nanotechnology development, and hence the NEC³, to progress efficiently across the spectrum of design challenges and applications, hurdles in both of these areas need to be overcome. First, funding support can be further broken up into two broad areas: research and development, and institutional development. With only limited dollars available to fund nanotechnology R&D, much competition exists. The tendency to fund programs that have a high chance of success, yet overlook the potentially revolutionary, high risk projects, dominates the funding process. While the NNI realizes this and moves to support revolutionary initiatives, limited funding often results in one-year “proof-of-concept” grants. For very challenging R&D problems, like revolutionary

nanocomponent self-assembly methods or a nanotechnology-enhanced corrosion control coating, one year is often not enough time to prove a concept.⁷³

Funding must also be allocated for development of nanotechnology research and manufacturing facilities. Two of the NNI's five funding themes—*Centers and Networks of Excellence* and *Research Infrastructure*—focus on setting up R&D research facilities and coordinating efforts between government, industry, and academia.⁷⁴ In September of 2001, the NNI announced plans to spend \$65 million over 5 years establishing six university-based nanotechnology R&D centers, with the caveat that each of the centers collaborated with industry.⁷⁵ Efficient nanotechnology assembly and nanocomponent manufacturing facilities and processes must be in place before the NEC³ can be realized. This goal requires early collaboration of all research entities.

Along with funding, institutional support for nanotechnology research and development efforts across the spectrum of sectors—government, industry, academia, and international—is critical to the continued development of the technology and makes up the second main area of the NEC³ relevance tree support branch. “Nanotechnology is highly interdisciplinary. It is not just chemistry, molecular biology, medicine, physics, engineering, information science and metrology; it is all of these fields at once.”⁷⁶ The NNI has traditionally done a good job coordinating R&D across all of the sectors.⁷⁷ In 2001, the NSF chaired a conference reporting on over 65 nanotechnology Small Business Innovative Research (SBIR) awards funded at more than \$11 million. The DOE's Nanoscale Science Research Centers are open to US industry researchers, either for free or for a modest fee. Along the same lines, the NSF works specifically with academia by providing nanofabrication research infrastructure at five US universities, available for academic or industrial research.⁷⁸

Along the same lines, support for the development of nanotechnology education and training opportunities, starting at K-12 and going through post-graduate opportunities, is vital to the progression of the technology.^{79,80} This will help ensure that scientists and engineers synergistically focus on technology hurdles and that trained technicians exist to produce the new technology once it is available. Government agencies, like DOD, DOE, DOT, NASA, and NSF, are leading multi-disciplinary, multi-agency efforts across the spectrum of the NNI's nine Grand Challenge Areas.⁸¹ State and local nanotechnology research must be monitored and coordinated with these efforts to ensure transparency and coordination of R&D efforts. Nanotechnology support and funding hurdles must be overcome to ensure general nanotechnology R&D efforts continue to progress and build toward technology breakthroughs. General nanotechnology breakthroughs, such as developing atomic self-assembly methods or nanocomponent integration processes, are essential to the successful development of the NEC³ in the face of its many technological hurdles. For reference, Appendix D further details the NNI's initiatives to support nanotechnology development

Military Feasibility Key Node Analysis

The last main branch in the NEC³ relevance tree key node analysis reviewed in this paper is the military feasibility branch. This branch attempts to break down the hurdles to the efficient, successful military utilization of this coating by specifically looking at coating application, environmental protection, and integration into military maintenance manuals. Attempts should be made during R&D of the new coating to ensure its compatibility with current Air Force coating application equipment. If necessary, should NEC³ requirements force the issue, new Air Force-appropriate application equipment will be developed. New equipment must be compatible with Air Force standards and interoperable with existing maintenance equipment, both for

utilization at home-base and at deployed locations. Also, all new maintenance equipment must be maintainable, with adequate industrial support, both for repair operations and for spare parts.

Along with ensuring feasibility of application, the NEC³ must also comply with regulations prohibiting use of chromate conversion coatings for environmental and personnel protection. Chromium is listed as a hazardous material and must be eliminated from Air Force operations and installations in accordance with Executive Orders 13148 and 13423 and OSHA requirements per Hexavalent Chromium Standard 29 CFR 1910.1026.^{82,83} Chromium has been the mainstay of Air Force corrosion control coatings and there is still no completely chromium-free coating system available, so this is a significant hurdle to military suitability of the NEC³ system.⁸⁴

Lastly, processes for application of the NEC³ must be in accordance with Air Force standards. Testing on the new corrosion coating must be coordinated with weapon system corrosion managers, to ensure oversight and compliance with standards. This would also allow the most conservative testing to be accomplished, i.e. the harshest environments and flight spectrums. To minimize the risk to Air Force assets, testing will be implemented in the field by aircraft size, corrosiveness of the materials, and by aggressiveness of the operational environment.⁸⁵ Once processes have been fully developed and accepted, they must be added to the appropriate technical orders (AF T.O. 1-1-8, Application and Removal of Organic Coatings; T.O. 1-1-691, Cleaning and Corrosion Prevention and Control, Aerospace and Non-Aerospace Equipment; etc.) and job guides. Maintenance personnel must then be trained to apply the coatings, both initially and for repair operations.^{86,87}

Chapter 5. Nanotechnology Forecasting

Technological forecasting attempts to predict how future technology will develop and what timeline of development might be expected. One way to accomplish this is a method called extrapolation, which uses technological patterns observed from the past to project developmental trends into the future.⁸⁸ For this forecast, historical technological development observed for microelectromechanical systems (MEMS) will be utilized as an example to illustrate what can be expected for the nanotechnology development timeline, and subsequently for the NEC³.

MEMS Definition and Developmental History

To paraphrase one definition, MEMS is the integrated microsystem which converts physical stimuli to electrical, mechanical, and optical signals and vice versa; performs actuation, sensing, and other functions; comprises control, diagnostics, signal processing, and data acquisition features; and comprises microscale features of electromechanical, electromagnetic, electronic, electro-optical, optical, electrochemical, and biological components, architectures, and operating principles.⁸⁹ More plainly, MEMS aim to utilize the combined effect of micro-devices to achieve specific effects in a macro-world. MEMS development began in the 1960's and has evolved steadily since then as needs arose in the integrated circuit (IC), auto, audiovisual, and other industries. This discussion is not meant to be an exhaustive study of MEMS development, but rather will focus on general technological development, with specific mention of fundamental advances that led to the three biggest MEMS success stories: pressure/acceleration sensors, ink jet print-heads, and Texas Instruments' Digital Light Processor.⁹⁰

Microtechnology is an evolutionary technology with origins in the IC industry, beginning in the 1960's with simple strain gages fabricated from single-crystal silicon. Further development yielded new etching techniques that led to combining strain and pressure sensing mechanisms on

a single microsensor. Expense limited their usefulness to the aerospace industry in the early 1970's, but the technology reaped benefits in the late 1970's and 1980's with the auto industry. Implementation of automotive pollution control legislation forced development and implementation of manifold pressure sensors to reduce emissions and increase automobile fuel efficiency. High volume production of micromachined sensors ensued, which also resulted in parallel applications, such as disposable blood pressure sensors for medical use. Ultimately, it took approximately 15 years to develop micromachined sensor technology adequately enough to lead to high-volume production and application in the automobile industry.⁹¹

At roughly the same time as micromachined sensor research, parallel efforts into new etching techniques led researchers to explore two other new microdevices: acceleration sensors (accelerometers) and microfluidic structures. Combined academia and industry research efforts ensured the necessary infrastructure was in place to grow the technology. Texas Instruments' R&D efforts showed significant promise, as they produced micromachined thermal print-heads for dot-matrix printers. In the mid 1980's, the poly-silicon sacrificial layer etching process began being used to micromachine silicon carbide (SiC). This breakthrough, in particular, was an essential step in making MEMS technology possible.⁹² Then, in 1988 the first electrostatic micromotor, the crucial ingredient that made microactuators possible, became operational at UC Berkeley. In turn, microactuators are the "key device for MEMS to perform physical functions."⁹³ Around the same time, parallel design efforts resulted in the development of silicon fusion bonding which allowed direct silicon-to-silicon bonding without any melting alloys, glass layers, or polymer glues. This greatly reduced thermal residual stresses on micromachined surfaces.⁹⁴

Years of MEMS research and development paid off in the early 1990's when MEMS devices entered high-volume production in the automobile and computer-based industries.⁹⁵ MEMS accelerometers were installed on cars, for instance, to signal air bags to deploy during accidents. Also, MEMS-based ink jet nozzles are now the single largest MEMS product area in the computer industry.⁹⁶ As with micromachined sensors, it required approximately 20 years of R&D to advance the initial technology to the point where high-volume production and use by industry could commence. One final example of MEMS technology development and transfer to industry is Texas Instrument's DLP (Digital Light Projector) projection system, which has a MEMS chip that contains a "rectangular array of up to 2 million hinge-mounted microscopic mirrors." This array of mirrors, coordinated with a digital signal, reflects a high-definition digital image.⁹⁷ This technology came to market in 1996 following 20 years of incremental technological development and is now a greater than \$1 billion per year business.⁹⁸

Lessons learned from MEMS technological development suggest that new technology requires vast amounts of basic R&D, with small incremental advancements combining to precede large technological breakthroughs. For MEMS, the process took approximately 15 to 20 years from initial research to high-volume production. This benchmark provides a solid foundation from which to make a nanotechnology development prediction, although differences between MEMS and nanotechnology must be explored first.

Correlation between MEMS and Nanotechnology Development Timelines

Studying the historical development of MEMS provides good correlation to nanotechnology development because many of the technological hurdles are similar. As with nanosystems, MEMS suffer from scaling effects, where frictional and stictional forces play more dominant roles than inertia. This presents a hurdle to component manufacturing, as well as system

integration on both the micro- and nanoscale. Also, integration of many scientific disciplines was crucial for MEMS development to continue, as it is with nanotechnology.⁹⁹ Finally, as MEMS technology was the next step in miniaturizing technology to continue Moore's Law (the prediction that the number of transistors on a microchip would double every two years, resulting in exponential growth in IC technology), nanotechnology is the natural next step in miniaturizing technology, following in the footsteps of the IC boom and MEMS development, in an attempt to continue the exponential growth in technological advancement.

While there are similarities between MEMS and nanotechnology, there are also some significant differences. MEMS utilized top-down assembly techniques that were relatively established in the IC industry. Nanotechnology advancement, however, is contingent on the development of new, bottom-up self-assembly techniques. Along the same lines, while MEMS researchers utilized established equipment, nanotechnology advancement depends on the development of equipment that can manipulate atomic- and molecular-sized components. As evidenced by these two technology hurdles, nanotechnology requires larger leaps in technology than MEMS did, which will tend to extend the general development timeline in comparison to MEMS. However, the NNI provides nanotechnology R&D more widespread support and funding than MEMS experienced initially. Plus, though it is a relatively young technology, nanotechnology R&D already has a 20 year history. National and international efforts with ties to government, academic, and industrial support will tend to shorten the development timeline of nanotechnology when compared to MEMS. Taken as a whole, it seems reasonable to assume a similar 15- to 20-year developmental cycle for nanotechnology as was observed for MEMS.

Predicted NEC³ Technological Development Timeline

In order to make a reasonable technological forecast for NEC³ development, two main assumptions were required. The *first main assumption* is that successful development of bottom-up self-assembly techniques will occur within the next 10 years. Although this is aggressive, two facts support the probability that this will occur. First, there is much support and significant research and development ongoing in this area, as detailed in the previous chapters. Second, 10 years is a significant amount of time in this age of exponential technology growth, as detailed historically in Figure 5 for both the IC and MEMS industries.

The *second main assumption* is that the supporting nanotechnology R&D successes required to enable the NEC³'s development and application on AF weapon systems will be developed incrementally leading up to five major nanotechnology advances: 1) proven nanotechnology self-assembly methods; 2) proven nanocomponent integration methods; 3) ability to replenish cations from the atmosphere; 4) "self-healing" ability of nanotechnology-enhanced coatings; and 5) development of efficient nanotechnology production techniques. Each of these five developmental areas is crucial to the NEC³ becoming operational and will require smaller technology advances to be realized. This assumption is supported by observing the numerous incremental technology advances that led up to each major MEMS breakthrough.

Following a conservative 20-year developmental timeline, and applying these two main assumptions, it is reasonable to forecast that the NEC³ should be available for AF use by 2029. One possible developmental timeline showing the five major nanotechnological advances required to make the NEC³ a reality is provided in Figure 6.

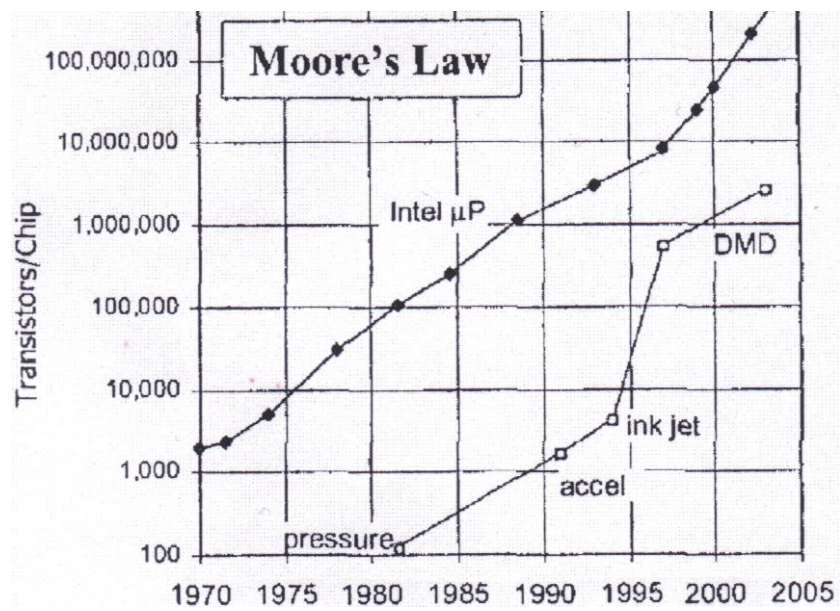


Figure 5 Approximation of Moore's Law for Intel Microprocessors and MEMS devices¹⁰⁰

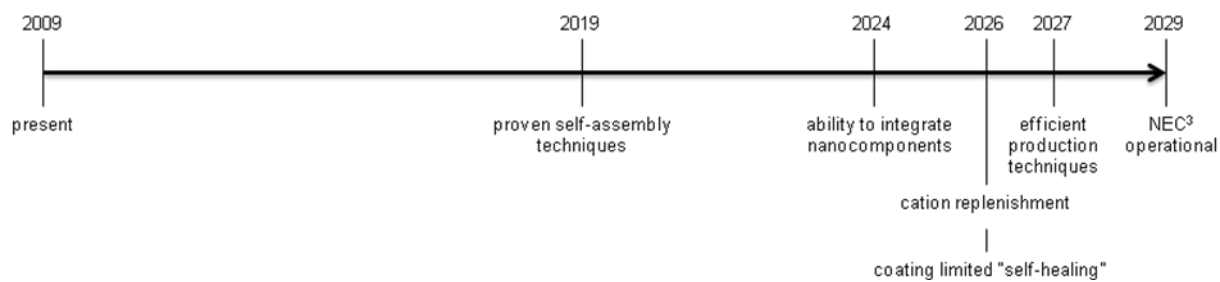


Figure 6 Possible Timeline of NEC3 Development

Conclusions

This paper argued that nanotechnology can be leveraged to create new revolutionary anticorrosion coatings capable of adapting to environmental damage and conditions, effectively eliminating the Air Force's #1 aging aircraft concern. It outlined Air Force corrosion issues and impacts, the science behind corrosion degradation, and corrosion prevention methods. It then overviewed the basics of nanotechnology, focusing on areas relevant to future corrosion prevention and control solutions. Next, relevant technological and social advances required to allow development of an adaptive corrosion prevention nanocoating were discussed, specifically looking at technological, support, and military suitability hurdles. Finally, the paper developed a trend forecast to predict when a nanotechnology-enhanced corrosion control coating might be realized by drawing conclusions based on an overview of MEMS technological development, the last effort to miniaturize technology and the closest for comparison with nanotechnology.

The nanotechnology-enhanced corrosion control coating, or NEC³, aims to prevent and combat corrosion degradation by detecting and self-repairing aircraft coating damage; detecting moisture at the coating/metal interface and signaling maintainers; detecting metal anions, the product of corrosion; releasing metal cations to inhibit the corrosion process, while signaling maintainers for a more thorough human inspection; sustaining itself by absorbing electrons from the atmosphere to replenish deficiencies in metal cations; and automatically integrating repairs to the coating. In short, it directly targets the thermodynamic enablers to corrosion, namely the galvanic cell formed between the anode, cathode, and electrolyte. Though significant technological hurdles remain, such as developing successful self-assembly methods and efficient nanocomponent manufacturing and integration processes, a trend forecast based on MEMS

development indicates that an integrated approach to research and development should make the NEC³ possible by 2029.

Air Force aircraft average approximately 30 years old, and this age will continue to increase as aircraft operate well beyond their design service lives. This trend leads to increasing maintenance costs, most notably in the areas of fatigue cracking and corrosion degradation. Corrosion is the most costly, especially for the tanker and transport fleet who's less harsh operational environment leads them to remain in service much longer than fighter/attack aircraft, making them more prone to severe corrosive attack. Corrosion maintenance currently costs the Air Force over \$1.5 billion annually, but the trend over the last eight years shows that number quickly rising, as the cost in 1998 was only \$800 million. This severe trend of rising costs must be stopped and reversed, or Air Force operations, which are vital to the United States' national security, may become restricted. Utilization of better corrosion prevention methods, such as adaptable, resilient, self-inspecting coatings, will not only diminish the annual cost of prevention, but could also substantially reduce the nearly \$900 million directly attributable to aircraft corrosion repairs each year. The NEC³ will help enable the US Air Force to better manage their aging aircraft fleet and continue to dominate the skies as the world's best air force.

Appendix A: Cost of Corrosion Specifics

Table 1 Cost of Aircraft Corrosion Maintenance (millions)¹⁰¹

	Aircraft	Fleet Costs
OC - ALC Aircraft	C-135	\$351
	B-1	17
	B-2	1
	B-52	45
	E-3	35
	CLS	31
	Misc	4
OO - ALC Aircraft	A-10	75
	F-16	62
	F-117	1
	T-37	2
	T-38	16
WR - ALC Aircraft	C-5	109
	C-17	20
	C-130	121
	C-141	3
	F-15	75
	Helo	24
	U-2	3
	J-Stars	3
Other Aircraft related Costs	Sub Total	998
	Landing Gear	104
	Backshops	56
	Aircraft Total	\$1,158

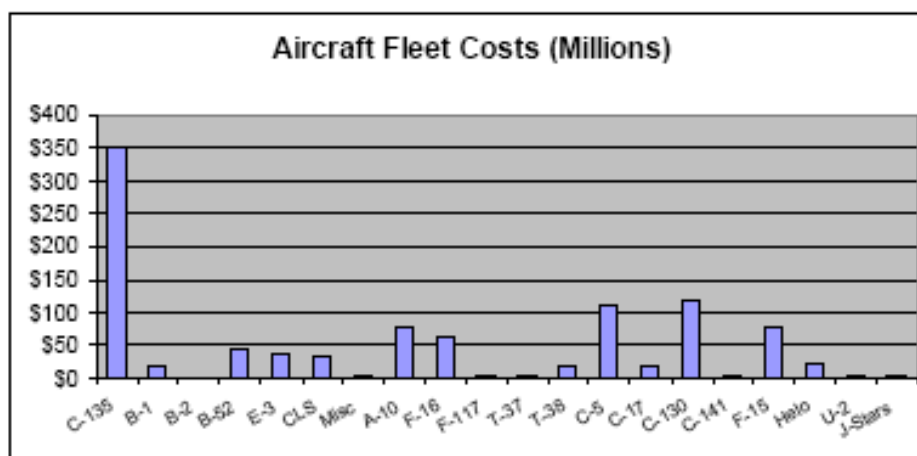


Figure 7 Cost of Aircraft Corrosion Maintenance (millions)¹⁰²

Table 2 Aircraft-Specific Corrosion Maintenance Cost, by Category (thousands)¹⁰³

	Wash	Inspect	Paint	Repair	Total
C-135	\$8,727	\$656	\$91,337	\$250,350	\$351,070
B-1	1,427	61	13,912	1,647	17,047
B-2	364	13	629	11	1,016
B-52	1,038	275	13,316	30,546	45,174
E-3	790	3	10,200	24,102	35,096
CLS	852	717	13,956	15,544	31,070
Misc	499	373	850	2,150	3,872
A-10	2,131	583	22,853	49,798	75,365
F-16	5,018	620	28,799	27,447	61,885
F-117	-	395	575	232	1,202
T-37	214	99	421	1,173	1,907
T-38	389	195	607	15,230	16,401
C-5	2,118	125	37,596	69,376	109,215
C-17	1,219	-	14,077	4,366	19,662
C-130	10,507	502	22,086	87,481	120,576
C-141	416	7	201	1,998	2,622
F-15	4,207	357	17,938	52,496	74,999
Helo	1,194	84	1,589	21,219	24,086
U-2	135	-	1,969	435	2,540
J-Stars	462	43	1,286	974	2,765
Total	\$41,688	\$5,109	\$294,198	\$656,575	\$997,570

Appendix B: Galvanic Series in Seawater

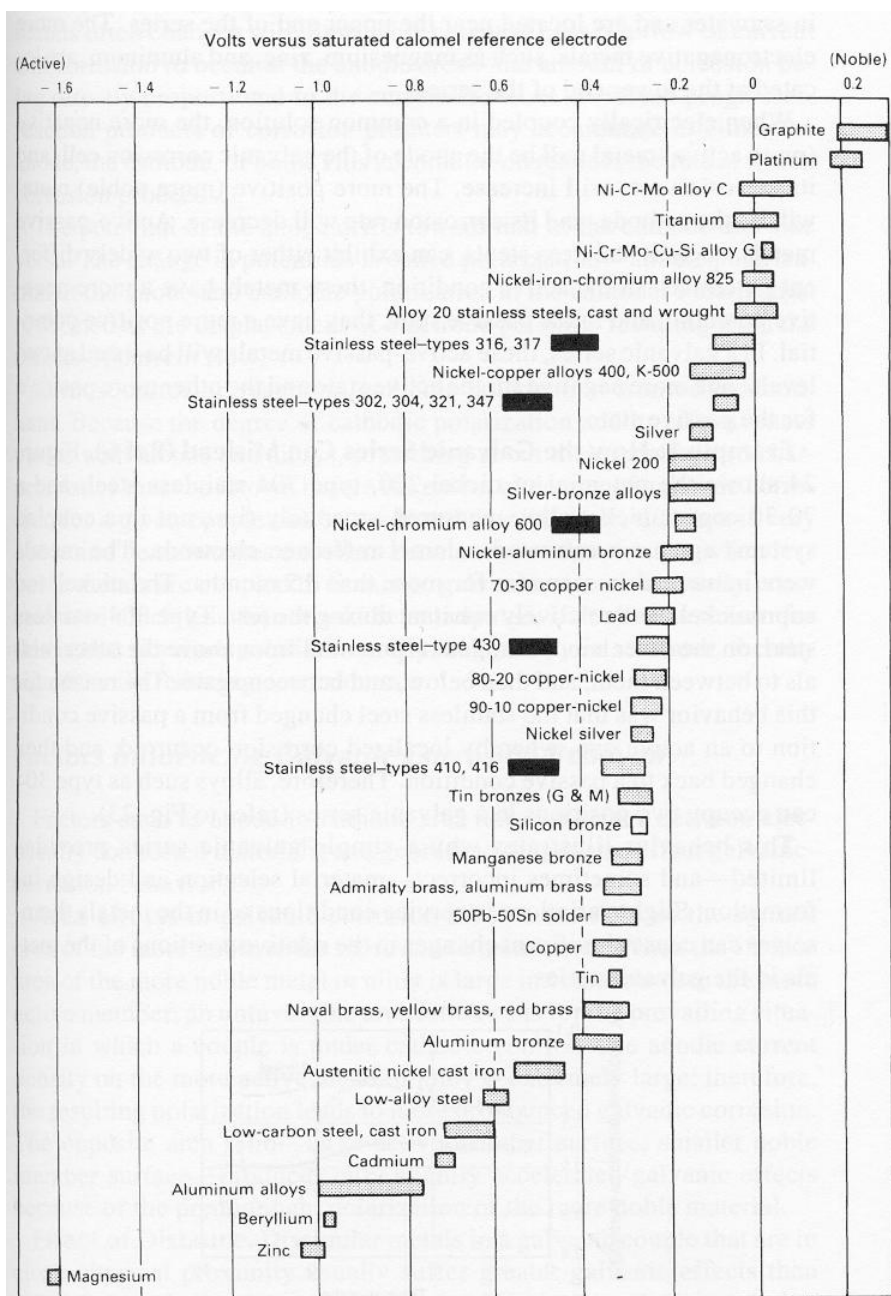


Figure 8 Graphic of Corrosion Potentials in Flowing Seawater (8-13 ft/s), Temperature Range 50-80 F (10-27 C)¹⁰⁴

Table 3 Detailed Galvanic Series of Selected Metals in Seawater¹⁰⁵

Active (Anodic)	Nickel (pl.)
Magnesium (Mg)	Chromium (pl.)
Mg Alloy AZ-31B	Tantalum
Mg Alloy HK-31A	Stainless steel 350 (active)
Zinc (pl. hot-dip, die cast)	Stainless steel 310 (active)
Beryllium (hot pressed)	Stainless steel 301 (active)
Aluminum (Al) 7072 cl. on 7075	Stainless steel 304 (active)
Al alloy 2014-T3	Stainless steel 430 (passive)
Al alloy 1160-H14	Stainless steel 410 (passive)
Al alloy 7079-T6	Stainless steel 17-7 pH (active)
Cadmium (pl.)	Tungsten
Uranium (depl.)	Niobium (Columbium) 1% Zr
Al alloy 218 (die cast)	Brass, yellow, 268
Al alloy 5052-O	Uranium (depl.) 8% Mo.
Al alloy 5052-H12	Brass, Naval, 464
Al alloy 7131-T6	Yellow brass
Al alloy 5456-O, H353	Muntz metal 280
Al alloy 5052-H32	Brass (pl.)
Al alloy 1100-O	Nickel-silver (18% Ag)
Al alloy 3003-H25	Stainless steel 316L (active)
Al alloy 6061-T6	Bronze 220
Al alloy 7071-T6	Everdur 655
Al alloy A360 (die cast)	Copper 110
Al alloy 7075-T6	Red brass
Al alloy 1100-H14	Stainless steel 347 (active)
Al alloy 6061-O	Molybdenum, Comm pure
Indium	Copper-Nickel 7151
Al alloy 2014-O	Admiralty brass
Al alloy 2024-T4	Stainless steel 202 (active)
Al alloy 5052-H16	Bronze, phosphor 534 (B-1)
Tin (pl.)	Stainless steel 202 (active)
Stainless steel 430 (active)	Monel
Lead	Stainless steel 201 (active)
Steel 1010	Steel alloy Carpenter 20 (active)
Iron, cast	Stainless steel 321 (active)
Stainless steel 410 (active)	Stainless steel 316 (active)
Copper (pl.)	Stainless steel 309 (passive)
	Stainless steel 17-7 pH (passive)
Stainless steel 304 (passive)	
Stainless steel 301 (passive)	
Stainless steel 321 (passive)	
Stainless steel 201 (passive)	
Stainless steel 286 (active)	
Stainless steel 316L (passive)	
Steel alloy AM355 (active)	
Stainless steel 202 (active)	
Steel alloy, Carpenter 20 (passive)	
Steel alloy AM350 (passive)	
Steel alloy 286 (passive)	
Titanium 5Al, 2.5 Sn.	
Titanium 13V, 11Cr, 3Al. (annealed)	
Titanium 6Al, 4V (h.t + aged)	
Titanium 6 Al, 4V (annealed)	
Titanium 8Mm.	
Titanium 3 Al, 13V, 11Cr (h.t + aged)	
Titanium 75A	
Stainless steel 350 (passive)	
Graphite	
Noble (Less Active-Cathodic)	

Appendix C: Thermodynamic Principles and Gibbs Free Energy

The following is a brief explanation of Gibbs free energy, the corresponding chemical properties used to define it, and how the change in Gibbs free energy, or ΔG , is used to determine if a chemical phase transformation will occur or not. “Phase Transformations in Metals and Alloys,” 2nd edition, by D.A. Porter and K.E. Easterling was utilized solely as source material for this discussion.¹⁰⁶

Thermodynamics applied to physical metallurgy provides a means to determine whether a given alloy is in equilibrium or not. A system reaches the state of equilibrium when it reaches its most stable state, i.e. when it shows no desire to change to another phase or state. In other words, thermodynamics is a tool that can predict whether or not a phase transformation will occur in a given system (alloy, pressure, temperature, etc.). A phase can be defined as “a portion of the system whose properties and composition are homogeneous and which is physically distinct from other parts of the system.” Corrosion is simply a phase transformation from a less stable phase—i.e. metal alloy—to a more stable, ore-like phase, which is the corrosion by-product. “The reason why a transformation occurs at all is because the initial state of the alloy is unstable relative to the final state.”

Gibbs free energy provides a measure of a given system’s relative stability at a constant pressure and temperature, and is defined by the equation:

$$G = H - TS$$

where H is the enthalpy, T is the absolute temperature, and S is the entropy of the given system.

Enthalpy is a measure of the heat content of the given system, defined by the equation:

$$H = E - PV$$

where E is the internal energy of the system, P is the pressure, and V is the volume. When dealing with incompressible solids and liquids, there is negligible change in volume, meaning the enthalpy of the system is approximately equal to the internal energy for most reactions ($H \cong E$). The other term that helps define G , entropy (S), is a measure of the randomness of the system.

The laws of thermodynamics show that a closed system in a steady environment (constant temperature and pressure) reaches stable equilibrium when it has the lowest value of G possible. For each material system, there may be, and probably is, more than one phase with a relatively stable G . However, there is only one minimum G for a given material system. Given time and the appropriate conditions, the laws of thermodynamics will drive the system toward the most stable equilibrium state with the lowest G . “Any transformation that results in a decrease in Gibbs free energy is possible.” Therefore, a necessary criterion for any phase transformation to occur, including corrosion, is:

$$\Delta G = G_2 - G_1 < 0$$

where G_1 and G_2 are the free energies associated with the initial and final states of any potential phase transformation, respectively. See Table 4 for a list of common material systems and associated thermodynamic properties.

Table 4 Thermodynamic Values at Standard State (298K)¹⁰⁷

Species	Name	Enthalpy " $\Delta H^{0\prime\prime}$ " (kJ/mol)	Entropy " $S^{0\prime\prime}$ " (J/mol*K)	Gibbs energy " $\Delta G^{0\prime\prime}$ " (kJ/mol)
<i>Aluminum</i>				
Al(s)	Aluminum solid	0	28.3	0
AlCl ₃ (s)	Aluminum Chloride	-705.63	109.29	-630.0
Al ₂ O ₃ (s)	Aluminum Oxide	-1675.7	50.92	-1582.3
<i>Chromium</i>				
Cr (s)	Chromium solid	0	23.62	0
Cr ₂ O ₃ (s)	Chromate	-1134.7	80.65	-1052.95
CrCl ₃ (s)	Chromium Trichloride	-556.5	123.0	-486.1
<i>Copper</i>				
Cu (s)	Copper solid	0	33.17	0
CuO (s)	Copper Monoxide	-156.06	42.59	-128.3
CuCl ₂ (s)	Copper Chloride	-220.1	108.07	-175.7
CuSO ₄ (s)	Copper Sulfate	-769.98	109.05	-660.75
<i>Iron</i>				
Fe (s)	Iron solid	0	27.78	0
FeO (s)	Iron (II) Oxide	-272	----	----
Fe ₂ O ₃ (s)	Hematite	-825.5	87.40	-742.2
Fe ₃ O ₄ (s)	Magnetite	-1118.4	146.4	-1015.4
FeCl ₂ (s)	Iron (II) Chloride	-341.79	117.95	- 302.30
FeCl ₃ (s)	Iron (III) Chloride	-399.49	142.3	-344.00
FeS ₂ (s)	Pyrite (fool's gold)	-178.2	52.93	-166.9
Fe(CO) ₅ (l)	Iron Pentacarbonyl	-774.0	338.1	-705.3
<i>Titanium</i>				
Ti (s)	Titanium solid	0	30.72	0
TiCl ₄ (l)	Titanium Tetrachloride liquid	- 804.2	252.34	- 737.2
TiCl ₄ (g)	Titanium Tetrachloride gas	-763.16	354.84	-726.7
TiO ₂ (s)	Titanium Dioxide	- 939.7	49.92	- 884.5

Appendix D: National Nanotechnology Initiative Specifics

National and worldwide interest in advancing nanotechnology beyond major scientific hurdles has raised support and funding to the highest levels in history. From 1999 to 2000, nanotechnology federal research funding increased by 6 percent. From 2001 to 2003, following the inception of the NNI, funding increased by an average of 40 percent annually, from \$464M to \$709.9M.¹⁰⁸ The Bush Administration requested \$1.447B for FY2008, a \$56M increase over the previous year, and a 467 percent increase since 1999.^{109,110} Numerous federal organizations support nanotechnology research, with the majority of funds since 2005 going to the NSF (\$360M average), the DOE (\$260M average), and the DOD (\$365M average).¹¹¹ See Appendix D for more complete information on NNI funding.

NNI funding is organized around five research areas: long-term fundamental research; Grand Challenges; centers and networks of excellence; research infrastructure; and ethical legal and social implications. Funding and research in the Grand Challenges is aimed at solving problems essential for the advancement of nanotechnology.¹¹² Two of the Grand Challenges—nanostructured materials by design and manufacturing at the nanoscale—directly impact corrosion control. The NSF is leading these areas, with complimentary efforts from the DOD, DOE, Department of Transportation (DOT), Food and Drug Administration (FDA), NASA and the National Institute for Science and Technology.¹¹³

Many non-federal organizations, including state, academic and industry-sponsored, are involved in nanotechnology funding and support as well. California committed \$100M over a four year span to fund development of the California Nanosystems Institute (CNSI). CNSI received another \$46.7M in funding from corporations in just the first year¹¹⁴. Penn State, along with other Pennsylvania universities, formed a partnership with the Commonwealth of

Pennsylvania to establish both 2- and 4-year nanofabrication manufacturing technology degrees aimed at preparing the future workforce for the nanotechnology industry.¹¹⁵ Lastly, worldwide nanotechnology research and development investments tripled between 1997 (\$432M) and 2001 (\$1.619B). More than 30 countries now have national nanotechnology R&D initiatives of their own resembling the U.S. NNI.¹¹⁶ These international partnerships will hasten the development and application of nanotechnology, providing more efficient solutions to technology hurdles and more rapid application of nanotechnology to every day challenges.

Table 5 Estimated Funding for Nanotechnology from FY 1999 to FY 2003 (million dollars)¹¹⁷

Organization^a	FY 1999	FY 2000	FY 2001	FY 2002 (estimate)	FY 2003 (request)
NSF	85	97	150	199	221
DOD	70	70	123	180	201
DOE	58	58	88	91	139
DOJ			1	1.4	1.4
DOT				2	2
NIH^b	21	32	40	41	43
NASA	5	5	22	46	51
NIST^c	16	8	33	38	44
EPA			5	5	5
USDA			2	1.5	2.5
Total	255	270	464	604.9	709.9

^aFunding figures for four additional entities (the Departments of State and Treasury, the CIA, and the Nuclear Regulatory Commission) that are also joining the NNI are not yet available; ^bIn the Department of Health and Human Services; ^cIn the Department of Commerce

Table 6 Estimated Funding for Nanotechnology FY2008 (\$ millions)¹¹⁸

	FY 2005 Enacted	FY 2006 Enacted	FY 2007 Estimate	FY 2008 Request
NNI Total	1,200	1,303	1,391^a	1,447
NSF	335	344	373	390
DOE	208	207	293	332
NASA	37	45	25	24
DOC (NIST)	63	79	89	97

EPA	5	7	9	10
DOD	315 ^c	352 ^d	417	375
DHS (TSA)	1	1	1	1
USDA	1	3	7	6
USDA/FS ^b	0	0	2	2
NIOSH ^e	3	3	3	3
Department of Justice	2	2	1	1
Transportation	0	0	1	1
HHS (NIH)	80	165	170	205

^aThe revised FY2006 funding levels are contained in President's Supplement to the FY2007 budget request released in July of 2006; ^bU.S.D.A./Forest Service; ^cIncludes \$148 million in earmarks, according to DOD; ^dIncludes \$130 million in earmarks, according to DOD; ^eNational Institute of Occupational Safety and Health (within CDC)

Appendix E: NEC³ Relevance Tree Key Node Analysis

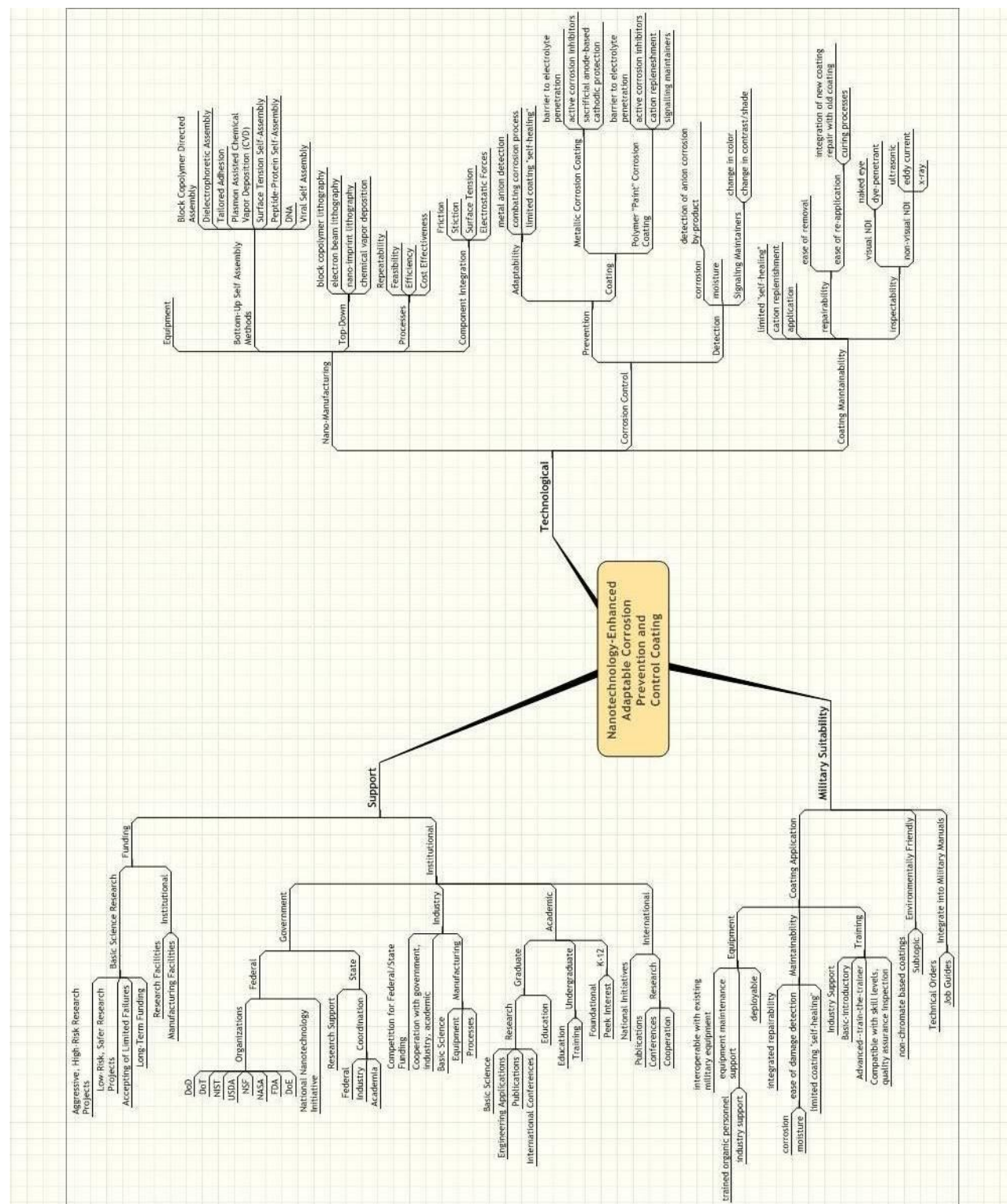
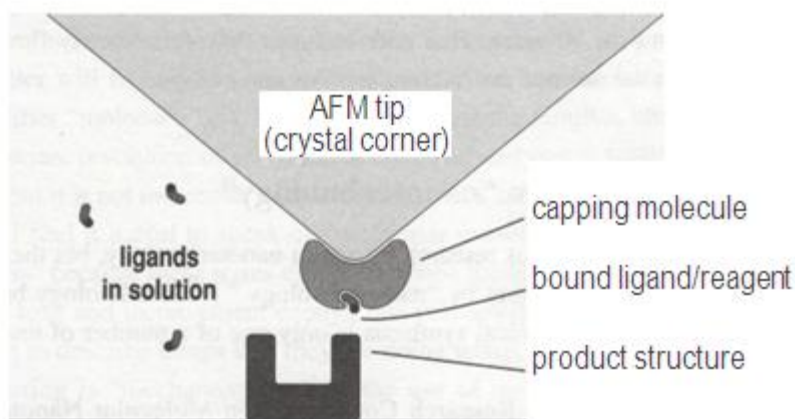


Figure 9 Nanotechnology-Enhanced Corrosion Control Coating Relevance Tree

Figure 10 Atomic Force Microscope Atom “Gripper”¹¹⁹Table 7 Leading Self-Assembly Methods and Corresponding Applications¹²⁰

METHOD	SOURCE/USER	CONVENTION	APPLICATIONS
Block Copolymer Directed Assembly	Univ of Wisconsin-Madison & Lab for Micro and Nanotechnology, Switzerland	Uses thin film templates at the 5 to 50 nm scale	Quantum dots, nanowires, magnetic storage media, nanopores and silicon capacitors
Electron Beam Lithography	Ecole Polytechnique Federale De Lausanne, Switzerland, Univ of Heidelberg, Germany; Inst. For Molecular Biophysics, Maine; Univ of Bielefeld, Germany; Chinese Academy of Sciences, China	Uses irradiation of monolayers with electrons	Potential application for ultrasensitive sensor materials
Dielectrophoretic Assembly	Inst of Robotics and Intelligent Systems, Switzerland; Zhejiang Univ, China	Uses Composite AC-DC electric field	Lateral emitters with potential use in vacuum sensing applications
Plasmon Assisted Chemical Vapor Deposition	Caltech, Stanford Univ, and NYU	Uses low-power laser beam	Si nanowires and single-walled carbon nanotubes
Tailored Adhesion	IBM Research, Zurich	Uses forces inherent	60 nm gold

	Research Lab, Switzerland	from large surface-to- volume ratio	nanocrystals
Surface Tension Self-Assembly	Univ of Michigan, MI	Uses forces inherent from large surface-to- volume ratio	Scalable biomimetic actuators
Peptide-Protein Self- Assembly	Univ of Washington, Seattle; New York Univ, NY, University of Leeds Centre for Nanotechnology, United Kingdom	Uses amino acid sequences	Materials and medical related applications
DNA Self-Assembly	Arizona State Univ; California Inst. Of Technology	Uses DNA as “scaffolding”	Molecular printboards
Viral Self-Assembly	MIT	Uses viruses as “scaffolding”	Nanowires, Batteries

¹ Kinzie and Jett, “DOD Cost of Corrosion,” pg 5

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³ “Cost of Corrosion, Final Report,” C² Technology, Inc., 3 March 2005, pgs 2-3

⁴ “Small Wonders, Endless Frontiers—A Review of the National Nanotechnology Initiative,” pg 4

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⁶ *ibid*, pg 6

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⁸ Bell and Shelton, “Corrosion Management—A Statistical Approach,” pg 1

⁹ Clark, et al., “Observations from the Inspection of an Aged Fuselage Panel,” *Journal of Aircraft*, pg 1403

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¹¹ Shoales, “Failure Analysis and Prevention for the Air Logistics Center Engineer: CASTLE Course Development Summary”

¹² Askeland, “The Science and Engineering of Materials,” pg 85

¹³ Shoales, “Failure Analysis and Prevention for the Air Logistics Center Engineer: CASTLE Course Development Summary”

¹⁴ *ibid*

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¹⁶ Anderson, Chief, 538 ACSG/ENC, Hill AFB, UT, email to Maj Jason Avram, 24 November 2008

¹⁷ “Cost of Corrosion, Final Report,” C² Technology, Inc., 3 March 2005, pg 7

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²⁰ “Cost of Corrosion, Final Report,” C² Technology, Inc., 3 March 2005, pgs 2-3

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https://www.dodmantech.com/successes/DLA/dla_A-10_SLEP_SS.pdf
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- ²⁸ <http://www.seaguard.co.nz/images/battery.gif>
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- ³¹ *ibid*, pgs 2-2 to 2-4
- ³² *ibid*, pg 3-50
- ³³ *ibid*, pg 3-53
- ³⁴ *ibid*, pg 4-2
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- ³⁶ Rose, "Selecting Materials for Improved Corrosion Resistance," *AMPTIAC Quarterly*, Volume 9, Number 3, 2005, pg 5
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- ⁵⁰ Teague, "Statement Before the Committee on Commerce, Science, and Transportation, U.S. Senate," pg 4
- ⁵¹ *ibid*
- ⁵² Murday, "Status Report on the (various) National Nanotechnology Initiative(s)," slide 26
- ⁵³ *ibid*
- ⁵⁴ Teague, "Statement Before the Committee on Commerce, Science, and Transportation, U.S. Senate," pgs 4-5
- ⁵⁵ Jovene, "Next Generation Assembly Fabrication Methods: A Nanotechnology Trend Forecast," pg 10
- ⁵⁶ Reif, "The Challenge of Self-Assembly of Molecular Scale Structures," conference motivation, 3rd Conference on Foundations of Nanoscience: Self-Assembled Architectures and Devices, Snowbird, UT, 23-27 April 2006.
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- ⁷⁵ *ibid*, pg 23
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- ⁷⁷ Davey, "Manipulating Molecules: Federal Support for Nanotechnology Research," pg 4
- ⁷⁸ *ibid*, pgs 5-6
- ⁷⁹ *ibid*, pgs 28-30
- ⁸⁰ *ibid*, pg 4
- ⁸¹ "Investment Mode 2: NNI Grand Challenge Areas," National Nanotechnology website, http://www.nano.gov/html/res/fy04-pdf/fy04%20-%20small%20parts/NNI_FY04_K_mode2_part1.pdf
- ⁸² Moran, "AF Compliance with OSHA (Hexavalent Chromium)," May 2008
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- ⁹⁷ DLP Texas Instruments website, <http://www.dlp.com/tech/what.aspx>
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¹¹⁵ *ibid*, pg 33

¹¹⁶ *ibid*, pgs 29-30

¹¹⁷ *ibid*, pg 12

¹¹⁸ Davey, “Manipulating Molecules: Federal Support for Nanotechnology Research,” pg 3

¹¹⁹ Drexler, “Introduction to Nanotechnology,” *Prospects in Nanotechnology Toward Molecular Manufacturing*, pg

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