Pre-Demonstration Development of Controlled-Release Corrosion Inhibitors and Healing Agents as Alternatives to Hexavalent Chromium

WP18-E1-1531

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14. ABSTRACT
The technical objectives of this project are listed below:
● Conduct pre-demonstration development of chromate alternatives as proposed to ESTCP in “Controlled-Release Corrosion Inhibitors and Healing Agents as Alternatives to Hexavalent Chromium” (WP18-B6-5249), following the direction from the Weapons Systems and Platforms Technical Committee:
● Scale-up of materials that can meet MIL-PRF-23377 (solvent-based primer).
● Provide evidence of resistance to aircraft alkaline cleaners and deicing fluids.
● Provide formulation for initial ecological and toxicity screening.
● Submit an interim report that will provide the basis for a future ESTCP demonstration effort.

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Corrosion, repair technologies, passivation, primers, topcoats, chromium, chrome, Cr6, hexavalent, soft coating

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Project Team

- Dr. Wenyan Li, URS Federal Services, Inc.
- Dr. Gerald Wilson, Autonomic Materials, Inc.
- Mr. Mike Mayo, PPG Coatings Innovation Center
- Mr. Mike Spicer, AFRL/MLSSO

Background

- **Project initiation date**: March 1, 2018
- **Original Statement of Need: (ESTCP, Topic B6 January 5, 2017)**

  Projects are sought to demonstrate and validate alternative materials and processes to hexavalent chromium (Cr^{6+}) containing primers that are currently used on a variety of weapons systems
- **Originally proposed under ESTCP (WP18-B6-5249) but placed on HOLD and funded, as a Limited Scope SERDP one-year effort under SON “FY 18 SERDP Pre-Demonstration Development (Invitation Only)”**

Technical Objectives

Conduct pre-demonstration development of chromate alternatives as proposed to ESTCP in "Controlled-Release Corrosion Inhibitors and Healing Agents as Alternatives to Hexavalent Chromium" (WP18-B6-5249), following the direction from the Weapons Systems and Platforms Technical Committee:

- Scale-up of materials that can meet MIL-PRF-23377 (solvent-based primer).
- Provide evidence of resistance to aircraft alkaline cleaners and deicing fluids.
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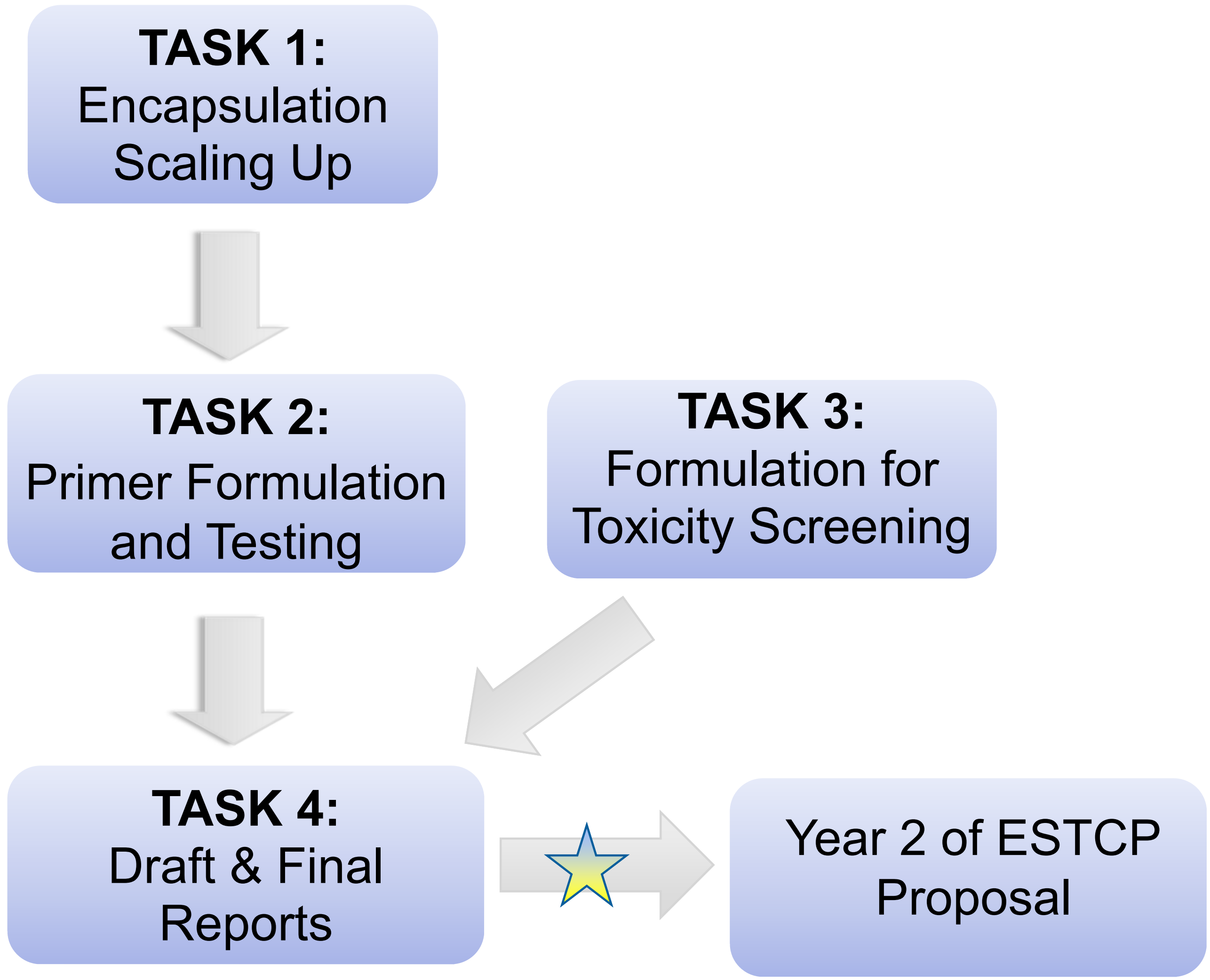
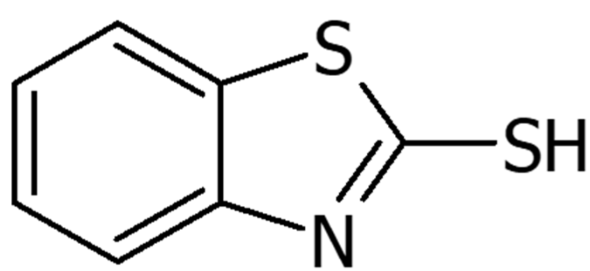
Technical Approach



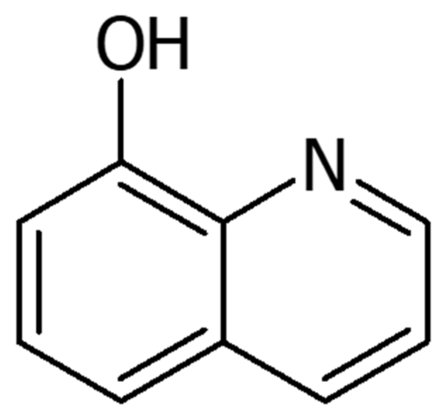
Technical Approach (contd.)

Task 1. Encapsulation Scaling-up

- Work on scaling-up the microencapsulation process of corrosion inhibitors, in collaboration with Autonomic Materials Inc. (AMI), to demonstrate producibility to accommodate a follow on field demonstration effort.



2-Mercaptobenzothiazole (2-MBT)



8-Hydroxyquinoline (8-HQ)

Technical Approach (contd.)

- **Task 2. Primer Formulation and Testing**
  - Incorporate encapsulated corrosion inhibitor and healing agent into primer coating formulations, provided by PPG.
  - Test primer coating properties and performance, using MIL-PRF-23377 to evaluate the material compatibilities of encapsulated inhibitors and healing agent.
  - Test resistance to aircraft alkaline cleaners and deicing fluids.

Technical Approach (contd.)

Task 3. Formulation for Toxicity Screening

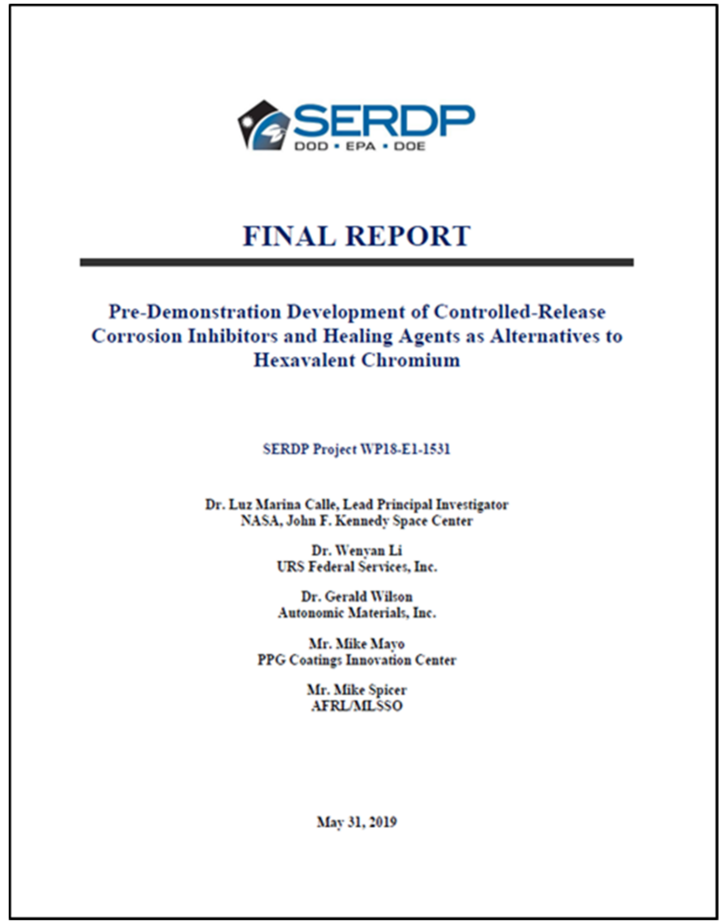
- Provide formulation information to the Army Public Health Center (APHC), to conduct an initial ecological and toxicity screening.

Formulation compounds included in toxicity screening			
2-Mercaptobenzothiazole	Melamine	Formaldehyde	Gum arabic
Pentaerythrytol tetrakis(3-mercaptopropionate)	Sodium dodecyl sulfate	Tetrahydrofuran	p-Toluenesulfonic acid

Technical Approach (contd.)

Task 4. Draft & Final Reports

Interim report to provide the basis for a follow-on year 2 of ESTCP demonstration/validation proposal.



FINAL REPORT

Pre-Demonstration Development of Controlled-Release Corrosion Inhibitors and Healing Agents as Alternatives to Hexavalent Chromium

SERDP Project WP18-E1-1531

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May 31, 2019

Results - Task 1. Encapsulation Scaling Up

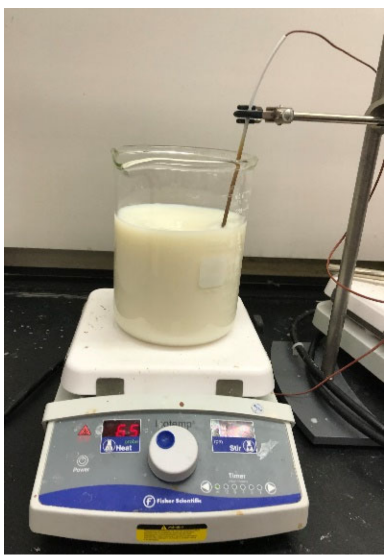
Methods and Techniques:

- Thorough assessment of laboratory scale encapsulation procedure.
- Evaluation of process parameters: surfactant type and concentration, temperature, reaction time, and micro particle yield.
- Optimization of reaction conditions for scaled up encapsulation process for 2-MBT and 8-HQ.
- Testing product for compliance with key quality specifications and characteristics.

Results - Task 1. Encapsulation Scaling Up (contd.)

Results: Successful scaling up of the encapsulation process of both inhibitors to the small pilot scale.

Go/No-go Decision: Go (Producibility)



Lab scale:
Less than100g

Small pilot scale: 4.0 kg (2-MBT); 2.0 kg (8-HQ)

Results - Task 2. Primer Formulation and Testing

Method and Techniques:

- Primer coating formulation selection: a solvent-based epoxy and a flexible polythioether primer.
- Substitute commercial inhibitor package with encapsulated corrosion inhibitor (2-MBT) and self-healing microcapsules.
- Test primer formulations for MIL-PRF-23377 compliance and for resistance to aircraft alkaline cleaners and deicing fluids.
- Evaluate material compatibilities of encapsulated inhibitor and healing agents.
- Use non-chromate pretreatment to address the risk of combining Cr(VI)-free primer with Cr(VI)-free pretreatment.

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Task 2 Test Matrix

MIL-PRF-23377 Requirement	Test	Coating Systems	Panel/Pre-treatment per MIL-PRF-23377	Panel/Pre-treatment Tested with Epoxy	Panel Pre-treatment Tested with Polythioether
Physical properties: Paint before and after mixing	Fineness of grind	Primer Paint	None	None	None
	Accelerated storage stability	Primer Paint	None	None	None
	Viscosity	Primer Paint	None	None	None
	Pot life	Primer Paint	None	None	None
Physical properties: Film	Surface appearance	Primer	A	A	E
	Drying time	Primer	A	A	E
	Adhesion	Primer only Topcoated	C	F	E
	Flexibility	Primer	B	B	B
Resistance	Water	Primer only with topcoat	A	A and E	E
	Salt-spray corrosion	Primer only with topcoat	A	A and E	E
	Filiform corrosion	with topcoat	D	D	D
	Solvent (cure)	Primer only	A	A	E
	Fluids: Lubricating oil hydraulic fluid	Primer only	A	A and E	E
Working Properties	Mixing/ dilution	Primer Paint	None	None	None
	Application	Primer Paint	None	None	None
Toxicity	Health Hazard Assessment	Primer Paint	None	None	None
Strippability	Strippability	Primer only	A	A and E	E

Four types of test panels are required per MIL-PRF-23377:

A = 2024-T3/Alodine
B = 2024-0/Anodize
C = 2024-T3/Alclad/ deoxidized
D = 2024-T3/Alclad/ Alodine

Two new types of test panels were included in this study:

E = 2024-T3/PreKote
F = 2024-T3/Bare

Results - Task 2. Primer Formulation Initial Screening

Primer	Primer Label	Description
Polythioether	1	Polythioether Control: Polythioether chrome-free primer (with PPG inhibitor package).
	5	Polythioether chrome-free primer with encapsulated inhibitor and healing agent (2.5 wt%/2.5 wt%)
Epoxy	10	Epoxy Control: Epoxy chrome-free primer (with PPG inhibitor package)
	14	Epoxy chrome-free primer with encapsulated inhibitor and healing agent (4.5 wt%/4.5 wt%)

Results - Task 2. Primer Formulation Initial Screening

MIL-PRF-23377 Requirement	Test	Coating System	Test Results			
			1	5	10	14
Physical properties: Paint before and after mixing	Fineness of grind	Primer	N	N	Y	Y
	Accelerated storage stability	Primer (10 only)	N/A	N/A	Y	N/A
	Viscosity	Primer	N	N	Y	Y
	Pot life	Primer	N	N	Y	Y
Physical properties: Film	Surface appearance	Primer	Y	Y	Y	Y
	Drying time	Primer	N	N	Y	Y
	Adhesion	Primer: 1, 5 Primer and Topcoat: 10, 14	Y	Y	Y (primer) N (topcoated)	Y (primer) N (topcoated)
	Flexibility	Primer	Y	Y	Y	N
Resistance	Water	Primer: 1, 5 Primer and Topcoat: 10, 14	Y	Y	Y	Y
	Salt-spray corrosion	Primer: 1, 5 Primer and Topcoat: 10, 14	N	N	Y	Y
	Filiform corrosion	Primer only: 1, 5 Primer and Topcoat: 10, 14	Y	Y	Y	Y
	Solvent (cure)	Primer	Y	Y	Y	Y
	Fluids: Lubricating oil hydraulic fluid	Primer	Y	Y	Y	Y
Working Properties	Mixing/dilution	Primer	Y	Y	Y	Y
	Application	Primer	Y	Y	Y	Y
Toxicity	Health Hazard Assessment	Primer	Y	Y	Y	Y
Strippability	Strippability	Primer	Y	Y	Y	Y

Results - Task 2. Primer Formulation Initial Screening

Polythioether Primer Coating:

- As expected, the flexible polythioether primer did not meet several of the MIL-PRF-23377 requirements. This is due to resin chemistry (fineness of grind, viscosity, pot life, drying time) and pretreatment (salt fog).
- However, the polythioether primer with encapsulated inhibitor/healing agents performed equally or better than the commercial primer.
- Encapsulated inhibitor/healing agents showed excellent material compatibility with the polythioether resin. However, further paint formulation is needed to improve its corrosion protection with non chromate pretreatment.
- **Go/no-go Decision: Go** (Material Compatibility)

  Additional Work: Corrosion protection with non chromate pretreatment

Results - Task 2. Primer Formulation Initial Screening

Non-chromate epoxy primer:

- The non-chromate epoxy primer met the MIL-PRF-23377 requirements except those for flexibility and adhesion (topcoated).
- Both the epoxy control and the epoxy with encapsulated inhibitor/healing agents failed the adhesion test when topcoated (as expected), as they were tested with no pretreatment.
- The epoxy primer with encapsulated inhibitor/healing agents performed equally or better than the commercial primer, with one exception: the flexibility requirement. This is most likely due to the higher pigment loading.
- **Go/no-go Decision:** **Go** (Material Compatibility)

Additional Work: Minor paint formulation adjustment to improve flexibility.

Results - Task 3. Formulation for Toxicity Screening

Encapsulated Inhibitor

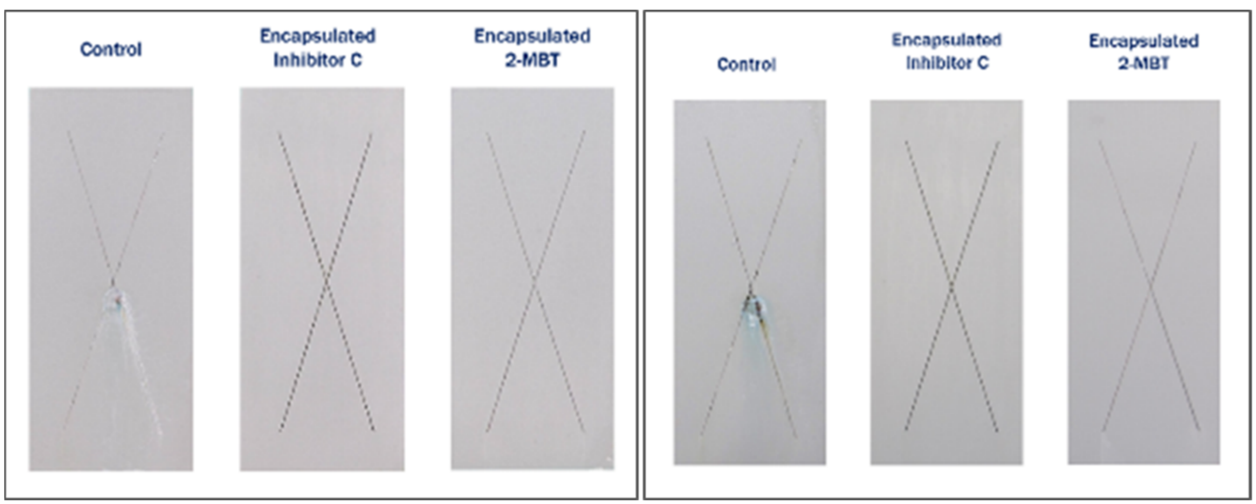
- An initial ecological and toxicity screening, on the encapsulated inhibitor formulation, concluded that most of the proposed components are of low to moderate toxicity and that there are no significant concerns.
- **Go/no-go Decision: Go**

Results (Summary)

- **Task 1**: The scale-up of the inhibitor encapsulation process for two corrosion inhibitors to the 4.0 kg scale (2-MBT) and 2.0 kg scale (8-HQ) was achieved successfully.
- **Task 2:** The epoxy primer formulation met most of the MIL-PRF-23377 requirements and showed sufficient resistance to alkaline cleaners and aircraft deicing fluids; the flexible polythioether primer failed several of the requirements. However, the polythioether primer with encapsulated inhibitor/healing agents performed equally or better than the commercial primer.
- **Task 3**: An initial ecological and toxicity screening, on the encapsulated inhibitor formulation, concluded that most of the proposed components are of low to moderate toxicity and that there are no significant concerns.
- **Task 4:** Report submitted and reviewed.

Next Steps

Instead of using a MIL-PRF-23377-compliant epoxy primer, the epoxy paint formulation, for which salt fog test results are shown below, will be used to formulate the non-chromate primer. Further primer formulation efforts will be focused on improving flexibility and adhesion of a paint formulation that is ready for field demonstration.



Salt fog test results for epoxy-amine coating on aluminum alloy (no pretreatment) with encapsulated corrosion inhibitors: 4500 hours (left three panels) and 6000 hours (right three panels).

Remaining Activities Schedule

Tasks	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
1. Encapsulation Scaling Up (inorganic micro particle)												
2. Non-chromate primer formulation, testing, and optimization												
3. Field demonstration plan development												
4. Pilot scale production of micro particles												
5. Atmospheric exposure testing												
6. Accelerated corrosion testing												
7. Report												

Technology Transfer

Issued Patents:

- U.S. Patent No. 7,790,225 (NASA Case No. KSC-12723) for an invention entitled "Coatings and Methods for Corrosion Detection and/or Reduction," which issued on September 7, 2010;
- U.S. Patent No. 8,859,288 (NASA Case No. KSC-13592) for an invention entitled "pH-Sensitive Micro particles with Matrix-Dispersed Active Agent," which issued on October 14, 2014;
- U.S. Patent No. 9,108,178 (NASA Case No. KSC-13278) for an invention entitled "Elongated Microcapsules and their Formation," which issued on August 18, 2015;
- U.S. Patent No. 9,227,221 (NASA Case No. KSC-13167) for an invention entitled "Hydrophilic-Core Microcapsules and their Formation," which issued on January 5, 2016; and
- U.S. Patent No. 9,233,294 (NASA Case No. KSC-13161) for an invention entitled "Hydrophobic-Core Microcapsules and their Formation," which issued on January 12, 2016.

Technology Transfer (contd.)

Patent Applications (patents pending):

- U.S. Patent Application Serial No. 12/792,238 (NASA Case No. KSC-12723-DIV) for an invention entitled "Coatings for Corrosion Detection and/or Reduction," which was filed on June 2, 2010 and
- U.S. Patent Application Serial No. 15/055,247 (NASA Case No. KSC-13907) for an invention entitled, "Controlled Release Materials for Anti-Corrosion Agents," which was filed on February 26, 2016.

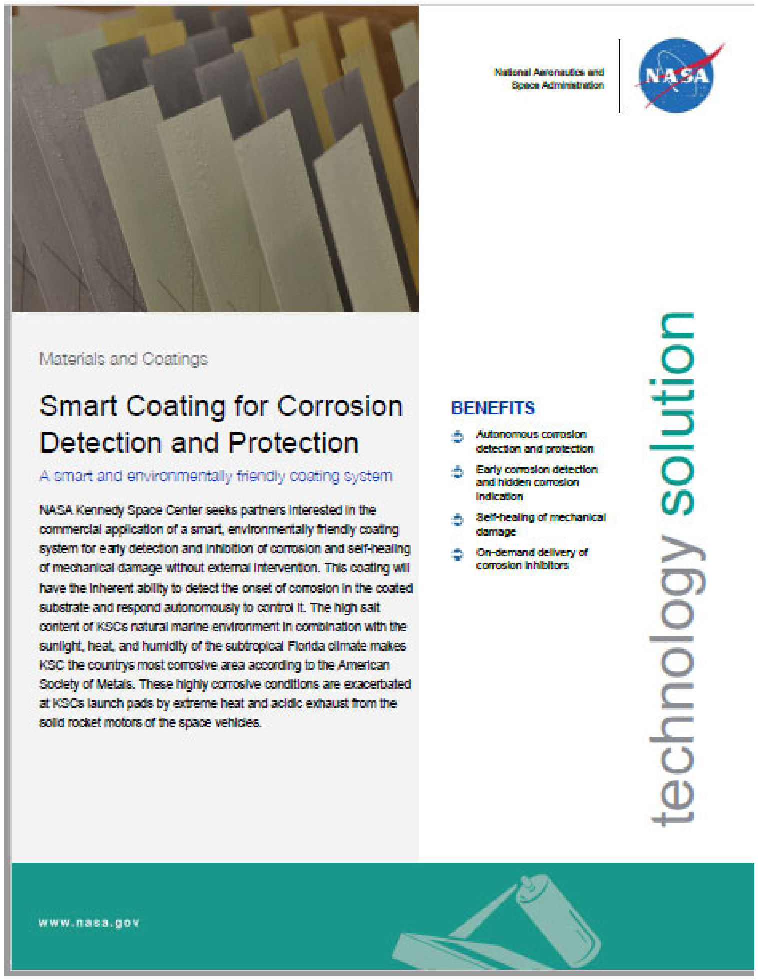
Technology Transfer (contd.)

- Current NASA Evaluation Licenses with Autonomic Materials Inc. (AMI) and PPG Industries.
- The technical team at NASA participates in market infusion by generating peer-reviewed papers and participating in SERDP & ESTCP workshops.
- AFRL participation will facilitate transition throughout the DoD services.

Technology Transfer Examples

- Presentations at key conferences and symposia such as: DoD-Allied Nations Corrosion Conference, Smart Coatings, and SERDP and ESTCP Symposium (2018 and 2019)
- NASA Technology Transfer Program Website:
  https://technology.nasa.gov/patent/KSC-TOPS-1
- NASA Technology fact sheet: https://ntts-prod.s3.amazonaws.com/t2p/prod/t2media/tops/pdf/KSC-TOPS-1.pdf
- NASA Technology Transfer Booth at relevant conferences.

Technology Transfer Examples (contd.)



National Aeronautics and Space Administration

Materials and Coatings

Smart Coating for Corrosion Detection and Protection

A smart and environmentally friendly coating system

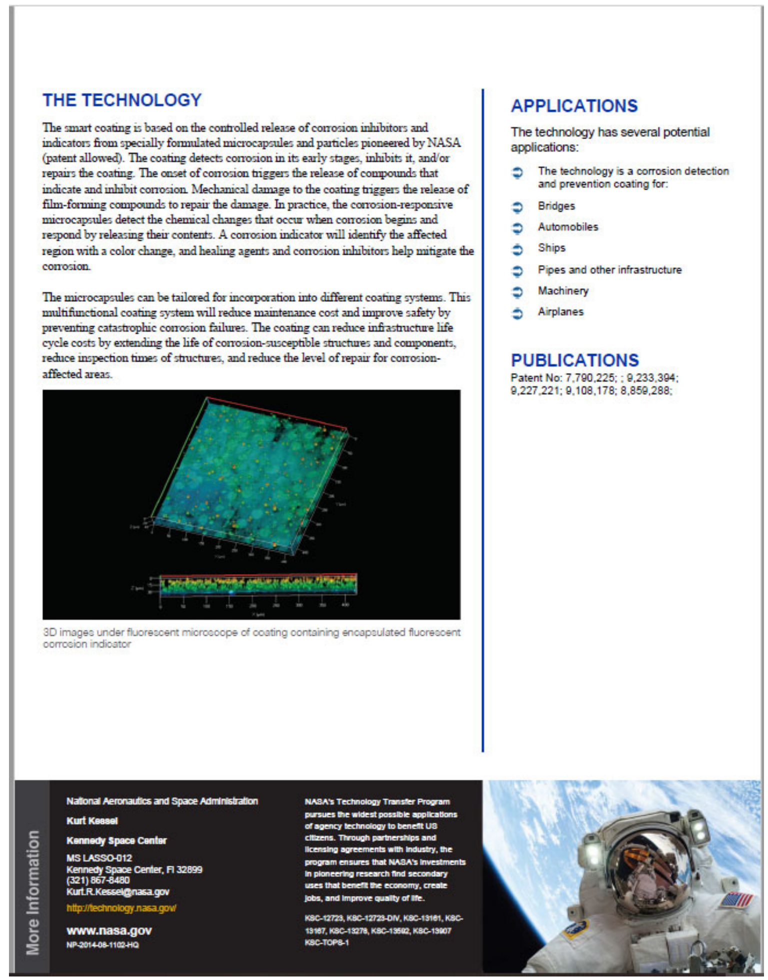
NASA Kennedy Space Center seeks partners interested in the commercial application of a smart, environmentally friendly coating system for early detection and inhibition of corrosion and self-healing of mechanical damage without external intervention. This coating will have the inherent ability to detect the onset of corrosion in the coated substrate and respond autonomously to control it. The high salt content of KSCs natural marine environment in combination with the sunlight, heat, and humidity of the subtropical Florida climate makes KSC the countrys most corrosive area according to the American Society of Metals. These highly corrosive conditions are exacerbated at KSCs launch pads by extreme heat and acidic exhaust from the solid rocket motors of the space vehicles.

BENEFITS

- Autonomous corrosion detection and protection
- Early corrosion detection and hidden corrosion indication
- Self-healing of mechanical damage
- On-demand delivery of corrosion inhibitors

technology solution

www.nasa.gov



THE TECHNOLOGY

The smart coating is based on the controlled release of corrosion inhibitors and indicators from specially formulated microcapsules and particles pioneered by NASA (patent allowed). The coating detects corrosion in its early stages, inhibits it, and/or repairs the coating. The onset of corrosion triggers the release of compounds that indicate and inhibit corrosion. Mechanical damage to the coating triggers the release of film-forming compounds to repair the damage. In practice, the corrosion-responsive microcapsules detect the chemical changes that occur when corrosion begins and respond by releasing their contents. A corrosion indicator will identify the affected region with a color change, and healing agents and corrosion inhibitors help mitigate the corrosion.

The microcapsules can be tailored for incorporation into different coating systems. This multifunctional coating system will reduce maintenance cost and improve safety by preventing catastrophic corrosion failures. The coating can reduce infrastructure life cycle costs by extending the life of corrosion-susceptible structures and components, reduce inspection times of structures, and reduce the level of repair for corrosion-affected areas.

3D images under fluorescent microscope of coating containing encapsulated fluorescent corrosion indicator

APPLICATIONS

The technology has several potential applications:

- The technology is a corrosion detection and prevention coating for:
- Bridges
- Automobiles
- Ships
- Pipes and other infrastructure
- Machinery
- Airplanes

PUBLICATIONS

Patent No: 7,790,225; ; 9,233,394; 9,227,221; 9,108,178; 8,859,288;

More Information

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NP-2014-08-1102-HQ

NASA's Technology Transfer Program pursues the widest possible applications of agency technology to benefit US citizens. Through partnerships and licensing agreements with industry, the program ensures that NASA's investments in pioneering research find secondary uses that benefit the economy, create jobs, and improve quality of life.

KSC-12723, KSC-12723-DIV, KSC-13161, KSC-13167, KSC-13278, KSC-13592, KSC-13907
KSC-TOPS-1

https://ntts-prod.s3.amazonaws.com/t2p/prod/t2media/tops/pdf/KSC-TOPS-1.pdf

Key Points

New controlled-release corrosion inhibitors and healing agents are a viable option as alternatives to hexavalent chromium:

- Self-healing microcapsules are currently commercially available.
- Encapsulation process for two corrosion inhibitors has been scaled up to the small pilot scale.
- Industry partners (AMI and PPG) hold evaluation licenses for the NASA patented technology.
- This effort advanced the field demonstration readiness of the technology.
- Further optimization of the chromate-free primer formulation is needed.

Future Research

- Additional primer formulation optimization (pigment loading) is needed to improve the adhesion (when topcoated) and flexibility of the hexavalent chromium alternative primer, prior to field demonstration.
- Although the chromate-free alternative primer passed the 2000 hour salt spray test on Alodine (chromate) pretreated panels, additional primer formulation, using a primer for which prior salt spray testing showed greater than 6000 hours of corrosion protection performance (without pretreatment), will be done (as described on the original proposal).

Future Research (contd.)

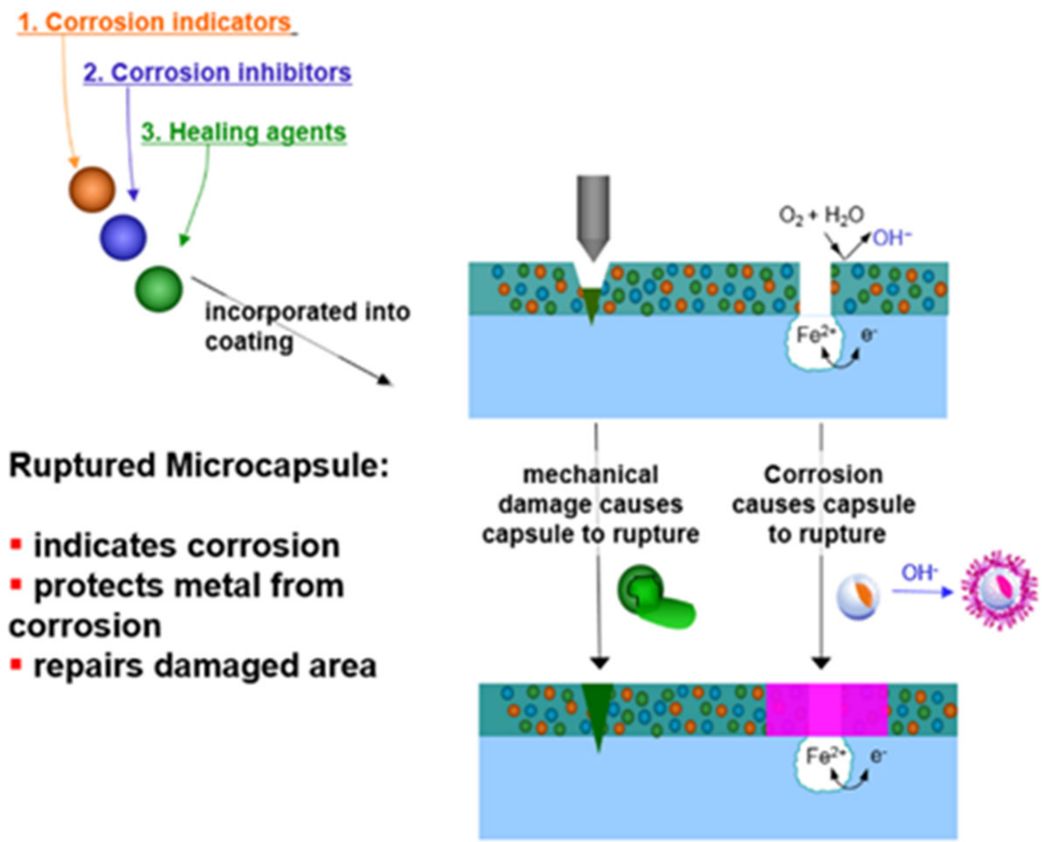
- Scaling up of the inorganic micro particle process for the new primer will be carried out.
- MIL-PRF-23377 will be used as a guide to optimize this new “real” non-chromate primer system: substrate, pretreatment, primer, and topcoat.
- Accelerated corrosion testing will be performed using the AFRL ACES (accelerated combined-effects simulation) method.
- Atmospheric exposure testing will be initiated.
- A field demonstration plan will be developed.
- A final report will be submitted.

BACKUP SLIDES

Publications

- L. M. Calle, W. Li, J. W. Buhrow, G. O. Wilson, M. Mayo, and M. Spicer, “Controlled-Release Corrosion Inhibitors and Healing Agents as Alternatives to Hexavalent Chromium,” SERDP/ESTCP Symposium 2018: Enhancing DoD’s Mission Effectiveness, Washington, DC, November 27-29, 2018.
- L. M. Calle, W. Li, G. O. Wilson, M. Mayo, and M. Spicer, “Pre-Demonstration Development of Controlled-Release Corrosion Inhibitors as Alternatives to Hexavalent Chromium [Cr(VI)] (Chromate)-containing Primers,” SERDP/ESTCP Symposium 2019: Enhancing DoD’s Mission Effectiveness, Washington, DC, December 3-5, 2019.

Supporting Material



Schematic Illustration of the Smart Multifunctional Coating Concept.

WP18-E1-1531: Pre-Demonstration Development of Controlled-Release Corrosion Inhibitors and Healing Agents as Alternatives to Hexavalent Chromium

Performers: NASA, AFRL, APHC, AMI, and PPG

Technology Focus

- *Alternatives to hexavalent chromium primers*

Research Objectives

- *Scaling up of encapsulation process, chromate-free primer formulation and testing,* initial *ecological and toxicity screening, and report*

Project Progress and Results

- *Corrosion inhibitor encapsulation scaled up and screened for ecological and toxicity concerns*
- *Chromate-free primer formulation developed and tested*
- *Further optimization of chromate-free primer needed*

Technology Transition

- *5 issued patents, 2 patents pending, NASA evaluation licenses to industry partners, webinars, presentations at relevant symposia and conferences, NASA Technology Transfer Program website, NASA on Twitter*