CONTRACT NUMBER: FA8532-17-C-0008 (CDRL A001)

Evaluation of the Commercial off-the-shelf (COTS) Low Temperature Powder Coating (LTPC)

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Date: 15 November 2017

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1.0 Introduction

1.1 Background

Traditional military coating systems formulated with Volatile Organic Compounds (VOCs) and Hazardous Air Pollutants (HAPs) burden the Air Force and other DoD agencies with environmental compliance, permitting, tracking, storage, operations, disposal, and reporting requirements. In addition, the handling and disposal of toxic hazardous wastes associated with the removal and reapplication of the hexavalent chromium containing primers in traditional coating systems is costly, time consuming, and represents a risk to health, safety, and the environment.

Powder coatings represent a mature technology that eliminates the hazardous waste streams (e.g., air emissions, contaminated booth filters, unused admixed paints and cleaning solvents) associated with conventional wet painting operations. Additionally, use of powder coatings also reduces employee exposure and liabilities associated with wet painting. Advantages over conventional wet painting include greater coating durability, elimination of VOCs and HAPs, improved transfer efficiency, and the elimination of drips, runs, and blistering defects. Low temperature powder coatings (LTPC) offer the advantage of reduced energy consumption by being able to process at lower temperatures.

In 2014, Battelle completed a comprehensive evaluation of three commercially available LTPCs. The coatings manufacturers were required to supply test specimen/coatings panels applied per the project's experimental plan. Hentzen's Crosslink LTPC was ranked the best performing powder coating during Phase I evaluation and recommended for reformulation / modification to improve its resistance to Ultraviolet (UV) light and microbiologically influenced Corrosion (MIC).

This technical report is CDRL A001 of the Phase II (PWS paragraph 4.2) and it summarizes the limitations/deficiencies identified during Phase I for improvements to be undertaken during this Phase II work. Provided in this report are lists of materials that inhibit microbial growth and UV degradation. The lists are identified based on structure activity relationship that are reported earlier in the coating literature. The list will be further consolidated with additional materials through the duration of the project.

1.2 Scope and Objectives

The scope of this report is to list the performance gaps of the Commercial-Off-The-Shelf (COTS) Hentzen (Crosslink) Low Temperature Powder Coatings (LTPC) No. 6191-61003.

The objective of the task is to provide COTS solution for the two key performance gaps using known practices or standards, that are known or already practiced in the coating industry namely;

1. Addition of suitable UV stabilizers to improve weathering performance,
2. Addition of relevant biocides to mitigate against MIC

We accomplished this objective by performing literature review, use of anecdotal information from in-house subject matter experts (SME), consultation from the COTS LTPC manufacturer (Hentzen), as well as knowledge gleaned from previous studies performed by Battelle.

2.0 Analysis of Phase I COTS LTPC Performance Results

The report submitted by Battelle[1] along with analytical testing and industry accepted test methods were reviewed. The following considerations will be discussed with Hentzen to meet the desired UV and MIC performance of the modified LTPC under this Phase II of the project.

2.1 Considerations to Improve Weathering Performance

Xenon-Arc Accelerated Weathering Testing (ASTM D 6695) of the coating on aluminum panels had a color difference (ΔE average) of approximately 1.0. This value is considered high and for a coating with high UV resistance the color difference value is typically far less than 1. It should be noted that that the COTS LTPC passed the color difference (ΔE average) specification when applied on steel substrate. The results were discussed with the manufacturer and it is mutually agreed to add UV stabilizer to the current LTPC composition. Battelle identified additives (Table 1) that are used in the coating industry to improve UV performance. It should be noted additives listed in Table 1 is preliminary; Battelle and Hentzen will discuss the chemistry of the LTPC resin and the crosslinker in detail and down select the top UV additives. The rationale of the candidate selection will be based on the structure of the UV additive and its interaction with the ingredients present in the LTPC composition.

Table 1: Typical UV absorbers and HALS used in powder coatings[2]

Class	Name	CAS	Melting range (°C)	Notes
Hindered amine class (HALS)	Bis (1, 2, 2, 6, 6-pentamethyl-4-piperidinyl)-[[3, 5-bis (1, 1-dimethylethyl)-4-hydroxyphenyl]methyl]butylmalonate	63843-89-0	146 - 150	May interact with acid catalyst
	Polymer of 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-dispiro [5.1.11.2]-heneico-san-21-on and epichlorohydrin	202483-55-4	>148°C (softening point)	
	Tetramethyl-7-oxa3,20-diazadispro[5.1.11.2]-henicosan-21-one	64338-16-5	>225°C	
UV Absorber	2-Ethyl,2'ethoxy-oxalanilide	23949-66-8	126-128°C	Good heat stability
UV Absorber	95% Benzenepropanoic acid, 3-(2H-benzotriazol-2-yl)-5-(1, 1-dimethylethyl)-4-hydroxy-, C7-9-branched and linear	127519-17-9, 108-65-6	73 - 77°C	Does not interact with amine-and/or metal-catalyzed coating systems or coatings applied on base coats or

[1] Battelle's report: Qualification Testing of Low Temperature, Commercial-off-the-Shelf (COTS) Powder Coatings for Aerospace Applications Contract W911NF-11-D-0001/Delivery Order 0125/TCN 12-041 February 29, 2016
[2] George Wpych, e. (2015). Handbook of UV Degradation and Stabilization 2nd edition. Toronto: Chemtech publishing.

Class	Name	CAS	Melting range (°C)	Notes
	alkyl esters, 5% 1-methoxy-2-propyl acetate			substrates containing such catalysts.
UV absorber	2-Hydroxyphenyl-s-triazine	137658-79-8	73 - 77°C	Ideal for acrylic powder coatings.
UV absorber	2-(2H-benzotriazol-2-yl)-4, 6-bis (1-methyl-1-phenylethyl)phenol	70321-86-7	137 – 141°C	

2.2 Considerations to Improve Microbiologically Induced Corrosion (MIC)

Battelle conducted outdoor exposure studies of the LTPC was conducted at Battelle's Florida Materials Research Facility (FMRF) for 12 months during the Phase 1. Varying amounts of localized mold and mildew were observed on all wet control panels. It is of paramount importance to control these microbe's formation on the coatings substrate as these microbes contribute to the corrosion of the coatings. Battelle identified preliminary list of biocides (Table 2) that are typically added to coatings to reduce or eliminate microbial growth. Activities undertaken under the task described in paragraph 4.3 of the performance work statement (PWS) will generate the required information such as (a) the types of microorganisms present in the environment (b) chemical and physical properties of the LTPC and (c) environmental and regulatory aspects of the biocides. The list of biocides presented in Table 2 and the task results will be taken into consideration for the modification of the COTS LTPC.

Table 2: Microbicides used in coating formulations[3]

Name	CAS	Melting Point	Boiling Point	Vapor Pressure	Chemistry, Mode of Action
3-Iodo-2-propynylbutylcarbamate (IPBC)	55406-53-6	~65-67°C		2.4-4.5x10^{-3} (25°C)	**Carbamate; Mode of Action:** Disturbs the cell membrane permeability and affects the fatty acids metabolism
Thiabendazole (TBZ)	148-79-8	~297-298°C		4.6-5.3x10^{-7} (25°C)	**Benzimidazole; Mode of Action:** Contact and systemic fungicide; interferes with the assembly of microtubules (components of fungal exoskeleton)

[3] Shauer, F. (2017). Microbicides in Coatings. European Coatings Library.

Name	CAS	Melting Point	Boiling Point	Vapor Pressure	Chemistry, Mode of Action
Carbendazim (BCM)	10605-21-7	~302-307°C		$1.5x10^{-4}$ (25°C)	**Benzimidazole, Carbamate; Mode of Action:** Interferes with DNA synthesis, mitosis, cytokinesis or related processes
Zinc Pyrithione (ZnP)	13463-41-7	≥240°C		$1x10^{-6}$ (25°C)	**Pyridine-N-oxide; Mode of Action:** Membrane-active substance with chelating properties; influence on ATP levels, protein synthesis and nutrient transport
2-n-octyl-4-isothiazolin-3-one (OIT)	26530-20-1		120°C	$4.9x10^{-3}$ (25°C)	**Isothiazolinone; Mode of Action:** Electrophilic active agent. Reacts with nucleophiles (e.g. amines or thiols); enzyme
4 5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT)	64359-81-5	~41-42°C		$9.8x10^{-2}$ (25°C)	**Isothiazolinone; Mode of Action:** Electrophilic active agent with activated N-S bond and vinyl activated halogens; reacts with nucleophilic elements of cell proteins resulting in interruption of important metabolic processes
2-Butyl-1,2-benzisothiazolin-3-one (BBIT)	4299-07-4		Decom. before boiling	$1.5x10^{-2}$ (25°C)	**Isothiazolinone; Mode of Action:** Electrophilic active agent
Tebuonazole	107534-96-3	105°C		$1.7x10^{-6}$ (20°C)	**Azole; Mode of Action:** Inhibition of ergosterol biosynthesis in fungal membranes; at lower azole concentration, retardation of fungal growth, at higher azole conc. Disruption of fungal membranes
Propiconazole	60207-90-1		>250°C	$5.6X10^{-5}$ (25°C)	**Azole; Mode of Action:** Inhibition of ergosterol biosynthesis in fungal membranes; at lower azole concentration, retardation of fungal growth, at higher

Name	CAS	Melting Point	Boiling Point	Vapor Pressure	Chemistry, Mode of Action
					azole conc. Disruption of fungal membranes

3.0 Conclusions

This report summarizes limitations/deficiencies in the LTPC formulation tested during the Phase I with respect to UV light decomposition and MIC. It also provides with the list of potential additives for modification of the LTPC during the project. These candidates will be downselected based on the results generated from the samples collected during the inspection of the aircraft ground equipment (AGE) at the three PACAF locations earlier this month. The analysis of the samples will primarily focus on the types of microorganisms present in the environment as well as the degradation of the coatings from the UV exposure recorded on the inspected AGE. Additional factors will include; chemical and physical properties of the LTPC and the environmental and regulatory aspects of the biocides and UV additives.