

Study of Vapor Corrosion Inhibitors Built into Corrosion Control Covers

Do VCIs Last the Life of the Covers?

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ABSTRACT

Vapor corrosion inhibitors (VCI) are volatile chemistries and eventually they diminish at the source to provide the necessary protection on valuable assets. Shipping and Storage Covers with vapor corrosion inhibitors are used to protect military equipment, wind energy assets and other high value industrial goods. This paper provides gas chromatography-mass spectrometry (GC-MS) testing and data on corrosion inhibitors. New and used protective covers with corrosion inhibitors; were tested to answer the end users concerns; if the VCIs last as long as the covers do; or do they deplete before the covers need replacement?

Key words: Vapor corrosion inhibitors, military equipment, GC-MS, Life cycle of VCIs

INTRODUCTION

Military equipment must be mission ready at all times. These military assets may include military ground vehicles, weapon systems, support equipment and other deck equipment on naval ships. Metal parts contained in such equipment are subject to the effects of corrosion, a natural process.¹ To mitigate corrosion damage on this equipment and meet readiness requirement, significant amount of efforts have been put by the armed forces. According to United States Government Accountability Office (GAO) report GAO-19-513 in May 2019; the cost impact of corrosion to Department of Defense (DoD) assets in fiscal year 2016 was \$20.6 billion.²

Some of the traditional corrosion mitigation methods for these assets may include general-purpose warehouses, shed storage facilities, controlled humidity preservation (CHP) storage facilities, or heavy-

duty tarps. However, they have their limitations in terms of accessibility and day-to-day use. Warehouses and storage facilities are not always available and accessible in every location. To build one requires a lot of capital and sometimes it is not even practical considering the size of the equipment. Heavy-duty tarps may be applicable on some cases, but custom fitted covers may be better suited on complex items.

Corrosion control covers have been used in all branches of the U.S. Armed Forces including, USMC, Army, Navy, Airforce and National Guard, in various climates. In 2000, the US Navy started a small business innovation research (SBIR) funding to study and develop “Flexible Corrosion Preventative Coverings”. The first-generation of protective covers with VCI technology was patented as US 6,444,595 in 2002.³ According to a United States Airforce (USAF) report published in 2008, after a year-long study of different corrosion protection methods, the first-generation advanced protective covers with VCI could provide up to 10 times better asset protection comparing with the traditional protective methods.⁴ Naval Sea System Command (NAVSEA) approved the use of these protective covers for a variety of equipment ranging from weapon systems to deck equipment in 2003.⁵ With the rapid technology developing in this field, a new generation of VCI covers emerged as providing more breathability, flexibility and durability against rough surfaces of military equipment in 2012. Two US patents, US 8,883,284 and US 8,828,487, were granted on this new technology.⁶ According to a paper on this new technology presented at Fleet Maintenance & Modernization Symposium (FMMS) in 2016;⁷ the US Navy was the first to use these protective covers and demand has steadily increased across the other military branches.

Table below is from a business case analysis on equipment covers for Army Ground Systems presented in DoD-Allied Nations Technical Corrosion Conference 2017.⁸ The presentation compared several corrosion prevention and control (CPC) methods: equipment covers, storage facilities with or without environmental control, shed storage, and contractor corrosion service teams (CSTs). The study showed a 19:1 return of investment (ROI) by using covers with 90% corrosion protection efficiency and assuming 2 years cover service life. The equipment cover method received a high-grade rating, which was a little better (or comparable) than existing controlled humidity preservation (CHP) storage spaces; having a 17:1 ROI. However, a CHP storage space is not always available near the equipment, while covers can be purchased beforehand and readily available to use anytime; anywhere. In addition, service life of new generation VCI covers may exceed 2 years, increasing the ROI.

Solution	Corrosion Prevented	Purchase Cost (\$K)	Service Life (years)	Operating Cost (\$K/year)	Benefit (\$K/year)	ROI	Grade
(Baseline) Open Storage	0%	0	N/A	0	0	0	N/A
Covers	90%	0.5	2	0	136.1	19:1	High
CHP Storage Space							
Existing	92%	0	20	8.3	139.1	17:1	High
New	92%	750.0	20	8.3	139.1	3:1	Moderate
Leased	92%	100.0	1	8.3	139.1	1:1	Low
GP Warehouse							
Existing	90%	0	20	3.8	136.1	36:1	High
New	90%	618.0	20	3.8	136.1	3:1	Moderate
Leased	90%	75.0	1	3.8	136.1	2:1	Low
Shed Storage							
Existing	40%	0	20	1.9	60.5	32:1	High
New	40%	100.0	20	1.9	60.5	8:1	Moderate
Leased	40%	50.0	1	1.9	60.5	1:1	Low
CSTs	66%	0.3	1	7.0	99.8	13:1	High

Table 1: Comparison of Different Corrosion Prevention and Control Methods⁸

A corrosion inhibitor is a substance, or mixture thereof, that will significantly reduce corrosion rate of the material when introduced in a small amount into the environment.⁹ According to NACE standard TM0208¹⁰: VCI is corrosion inhibitors that could sublime or vaporize from a condensed phase source under ambient conditions, then transport into the atmosphere and condensate onto the metal surfaces in the enclosed system. The VCI corrosion inhibiting mechanism may include adsorption, dissolution or hydrophobic effects of metal surfaces depending on the chemistry of the VCIs. VCIs come in various forms such as coatings, films, oils, adhesives, etc. and often are formulated to provide protection for ferrous, nonferrous, or multi-metal applications. By its definition, VCI vapor can reach narrow spaces such as crevices in metallic structures that are typically inaccessible by other means.

Even though literature has listed numerous VCIs and their chemical structures,¹¹ compositions of the VCI products on the market are almost all proprietary. They are typically mixtures of several chemicals that are unknown to the end user. Before implementing a VCI application, the end users are advised to consult with the VCI suppliers. Implementation is a challenging process that requires input from the end user and the user assumes all risks. A consultative style of implementation is typically desired, because it must be proven that the proposed VCI technology and the end user application are compatible. A common question that has been continuously presented was if the vapor corrosion inhibitors lasted the life of the covers? In 2019 a research agreement was signed to utilize the Material Characterization Facility at the University of Notre Dame to answer this common question.

The covers used in this study were manufactured under several different patents US6875712, US7074288, US8828487, and US8883284. The adhesive system with VCI composition was manufactured according to US9718998 and a paper was previously presented on C2018-10986.¹² The fabrics were manufactured by applying VCI containing adhesive between the top and bottom layers of the fabric at various amounts.¹³⁻¹⁴ The initial goal of our study was to identify presence of corrosion inhibitor chemistry within the cover after their service life. We used the Gas Chromatography-Mass Spectrometry (GC-MS) analytical technique to investigate VCI covers having different field service period vs. a brand-new fabric containing VCIs. The process of mapping the presence of VCI started with raw VCI powder. We identified the peaks of the powder. Next, we tested the VCI adhesive, and new fabric containing VCI adhesive. These levels of testing helped us create a baseline for comparison, because the amount of inhibitor chemistry was less concentrated at each level. The used covers or samples cut from used covers were sent to our lab for evaluations. After running the GC-MS method we were able to compare the used fabric results to our baseline graph. We were also able to compare these results quantitatively.

GC-MS has numerous applications such as drug detection, fire investigation, environmental analysis, explosives investigation, health and safety, packaging, and many others.¹⁵ This paper has demonstrated GC-MS is a powerful and effective tool in terms of understanding behavior of VCI chemistries in industrial applications. This technique helped us generate fast, reproducible, and effective results to answer the following questions:

- Were VCIs left in the used covers?
- Can we quantify the remaining amount?
- How much VCI loss takes place on manufacturing steps?

EXPERIMENTAL PROCEDURE

Material



Figure 1: Used VCI Cover, made in 2013



Figure 2: Used VCI Cover, made in 2017

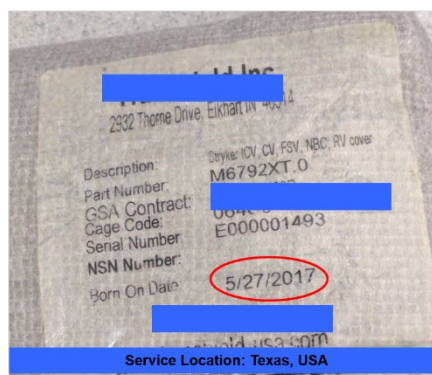
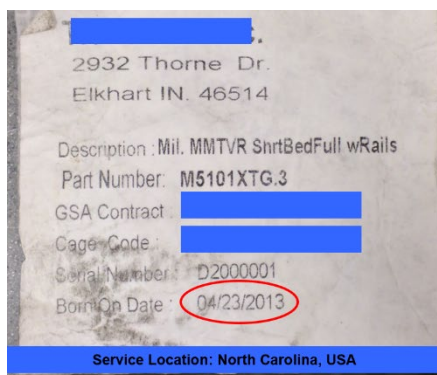


Figure 3: Used VCI cover labels

The samples in this study included used military covers with VCI, which were shipped to our lab from the field. These covers were not test covers; they were randomly selected from a pool of sold covers on the given year. One from North Carolina and one from Texas were shipped back from the end user. To have full understanding of the vapor corrosion inhibitors from pure form to fabric and to a cover we wanted to have meaningful comparisons; and we grouped our testing as follows:

Group 1 – Compares different VCIs available on the market for baseline comparison;

- VCI Product 2: Industrial Grade VCI (CTS)
- VCI Product 3: Powder VCI (C)

Group 2 – Compares the quantitative amount of VCI through different stages of production for baseline;

- VCI Product 1: Powder Form
- VCI Product 1: Adhesive Compounded VCI
- VCI Product 1: Adhesive Compounded VCI in Fabric Form

Group 3 – Compares new fabric with VCI to used cover fabrics with VCI;

- VCI Product 1a: Used Cover Fabric from Field, service use started in 2017.
- VCI Product 1b: Used Cover Fabric from Field, service use started in 2013.
- VCI Product 1c: New VCI fabric from production, manufactured in 2020, as Control

Methods

The GC-MS instrument applied was a Thermo Scientific Trace 1300 TSQ 9000. ⁽¹⁾For GC-MS detection, an advanced electron ionization energy system with an ionization energy of 70eV was used. The carrier gas was helium. The sample agitator temperature was set at 150°C for 10min. The oven temperature was programmed from an initial temperature 35°C for 0.5 min, ramp at 10°C/min to 275°C, hold 3 min. Total GC running time was 28~35 min. The relative percentage amount of each substance was calculated by comparing its peak area to the total areas. The spectrum of the unknown substances was compared with the spectrum of known substances stored in libraries. The name of the substance, retention time, and percentage were recorded.

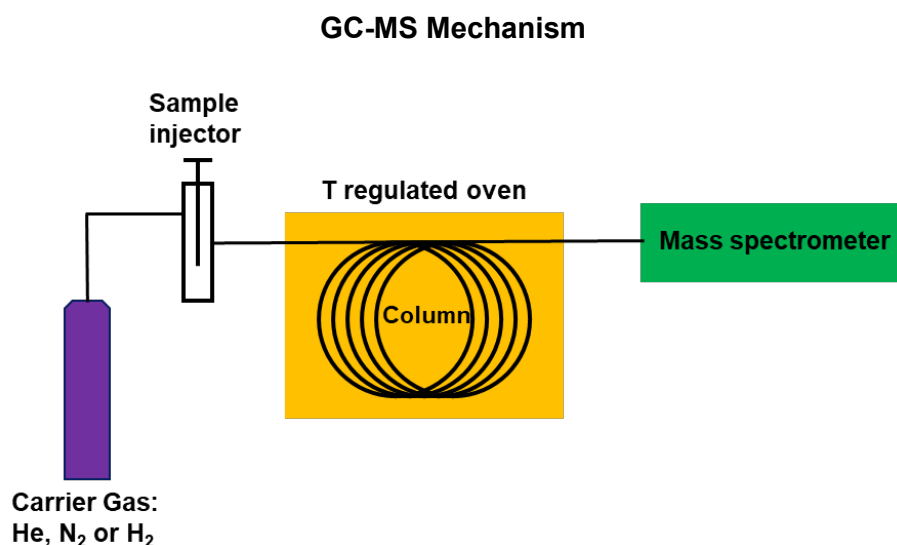


Figure 4a: GC-MS Schematic Diagram

Figure 4a shows a schematic diagram of GC-MS. An inert gas (typically He, H₂ or N₂) flows through the sample injector to carry the sample vapors to the gas chromatography, which uses a capillary column to separate molecules in the mixed gases. Different molecules will have a different affinity with the stationary phase in the column, which promotes the separation. The column is held in an oven with a program to increase temperature gradually to further facilitate separation of different molecules. As the temperature increases, the molecules having lower boiling points would elute first, then the ones with higher boiling points. The time that different molecules have been retained in the column is called retention time. As the different gas molecules are separated, they enter the mass spectrometer, which will capture, ionize, accelerate and detect the ionized separately. The MS detector can create an electronic signal whenever a molecule is detected. The intensity of the signal roughly corresponds to the relative percentage of each substance.¹⁵ Therefore, the stronger the signal, the more substances contained in the mixture. The GC-MS has a library of spectra of known substances, which will be used to compare with the spectrum of the unknown substance in the sample to identify it. Since most VCI suppliers intend to keep their compositions proprietary, the identified VCI components in their products were coded with a generic name and mass spectrum was not disclosed in this paper.

¹ Trade name.