

Processing Temperatures & Mass Loss of Vapor Corrosion Inhibitors

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ABSTRACT

Vapor corrosion inhibitors can be more volatile during elevated processing temperatures. It is critical that amount of VCI mass loss is engineered into the final product design. This paper focuses on a study where different vapor corrosion inhibitors are tested for mass-loss at different temperatures by use of TGA; and how this may affect corrosion inhibition level of the end-product. The paper also provides some critical considerations for manufacturing steps to improve application processes and final product quality.

Key words: Vapor corrosion inhibitors (VCIs), processing temperature, mass-loss, thermal gravimetric analysis (TGA), quality assurance, quality control

INTRODUCTION

Engineering metals are all unstable on the earth in the environment of oxygen, water, and warm temperatures, because they tend to form more stable compounds to lower their energy by spontaneously reacting with the surrounding environmental species.¹ The damage or deterioration of metal due to this reaction is called corrosion. Additional accelerating factors to this process may include rain, snow, wind, dirt, UV, heat, etc.² According to the 2016 NACE IMPACT study, the global cost of corrosion is ~ US\$2.5 trillion in 2013. However, 15%~30% of the corrosion cost could be saved by

utilizing nowadays available corrosion control technologies, which means US\$375 ~ US\$875 billion could be saved globally.³

One of the traditional corrosion protection methods for metals during transport and storage is to use coating or oils. But it has its disadvantages and limitations. The oily coating on metal surfaces needs to be removed before painting or welding, which is an extra step for end-users, rather time-consuming, and raising the cost. There are also some hard to reach spaces such as crevices and surfaces of complex-shaped articles that are difficult to apply coatings.⁴ Additionally, coating systems could fail from prolonged environmental exposure and deterioration through UV radiation, moisture, chemical or biological agents, abrasion, water freezing and thaw cycle, etc.⁵ New technologies that involve volatile corrosion inhibitors (VCIs) packaging materials keep evolving over the past decades to meet these challenges.

Corrosion inhibitors (CIs) are substances or chemicals that could drastically reduce the corrosion rate when added to the corrosive environment in small amounts.¹ VCIs are corrosion inhibitors that could sublimate or vaporize from a condensed phase under ambient conditions, then transport in the atmosphere to reach and condense on the metal surfaces in the enclosed system (according to NACE international standard TM0208)⁶. VCIs can penetrate those inaccessible spaces by coatings or oils, such as the crevices in metallic structures. Recently, considerable attention has been drawn to the corrosion protection of electronic equipment by VCIs. Electronic components are more susceptible to galvanic corrosion because they typically consist of various metals. Due to the miniaturization of electronic devices, slight moisture or a drop of water may cause severe damages.⁷ VCI packaging materials, such as VCI covers, could be used to protect not only the surfaces of the equipment, but also the electronics that are contained inside.

VCIs are typically mixtures of several volatile compounds that could be customized to different formulations to protect ferrous, nonferrous, or multi-metals. At the same time, they must provide not only immediate protection at the beginning of the packaging, but also long-term protection. Numerous VCIs and structures, along with their effective protecting metals, had been listed in review papers.² They are typically amines, amine nitrites, carboxylic acid amines, heterocyclic compounds (triazole, imidazoline, pyrazole, etc.), carboxylic acid esters, mixtures, and reaction products of these substances.⁸

VCI molecules do not need direct contact to reach surfaces, instead through sublimation and condensation process they can reach to the surface to be protected. So, they must have volatility, which is the ability of a substance to form vapor by evaporation or sublimation. The temperature is the major factor that affects the rate of volatility. VCIs, when in use, would experience a phase transition and the vapor pressures could be estimated by the Clausius-Clapeyron equation. It has been widely used to estimate the saturated vapor pressure of VCIs at specific temperatures.⁹

$$\ln P = -\frac{\Delta H}{RT} + C$$

where P is the saturated vapor pressure, ΔH is the specific latent heat, R is the specific gas constant, T is the temperature, C is a constant. Due to a weak dependence of ΔH on T, $\ln P$ is linear to $-(1/T)$. As T increases, P increases, more VCI vapors would release from its resources.

VCIs have been used in many industries: oil and gas, automotive, electronics, concrete structures, military, and packaging. They come in different applications, from VCI manufacturers, such as powders, solutions, additives, paints, emitters, pellets, aerosols etc. They could be further processed and impregnated into papers, fabrics, plastic sheets, and adhesives. Some of these processing may require higher temperatures, which would cause more VCI evaporation during manufacturing, negatively affecting their protection effectiveness when in use. It is important to monitor VCI losses to make sure

enough VCIs have been conserved during processing and manufacturing. Quality assurance at different stages plays a critical role in preventing corrosion failures shown in the field.

Covers made of VCI fabrics have been approved to be an effective, low-cost, and easy-to-apply approach to combat atmospheric corrosion for many valuable equipment and assets. Examples are shown as below. VCI fabric technologies have been developed over the past two decades. US 6,444,595, US 8,883,284, US 8,828,487 and US 9,718,998, were some granted patents on this new technology. These patented VCI fabrics were laminates of a film or fabric with a nonwoven layer by an exterior grade block copolymer hot melt adhesive. VCI additives, were compounded into the adhesive composition. This adhesive was used in a lamination type production, as nozzle-sprayed on the surface of the nonwoven layer to secure the top and bottom layers of a fabric.



Figure 1: VCI covers for tank



Figure 2: VCI cover for weapon system on navy ship



Figure 3: VCI cover for aviation application



Figure 4: VCI cover for industrial application

Figure 5 is a schematic of the twin-screw adhesive compounding process and Figure 6 is a schematic of the fabric lamination process. Both processes need to increase temperatures to lower the adhesive viscosities to the extent that allow it to flow through the twin-screw extruder and could be sprayed out of the dispenser respectively. The higher the temperature, the more VCIs would get lost. Lowering the operating temperature or selecting the VCI product that is more stable at an elevated temperature

would help more VCIs to be conserved in the final product.

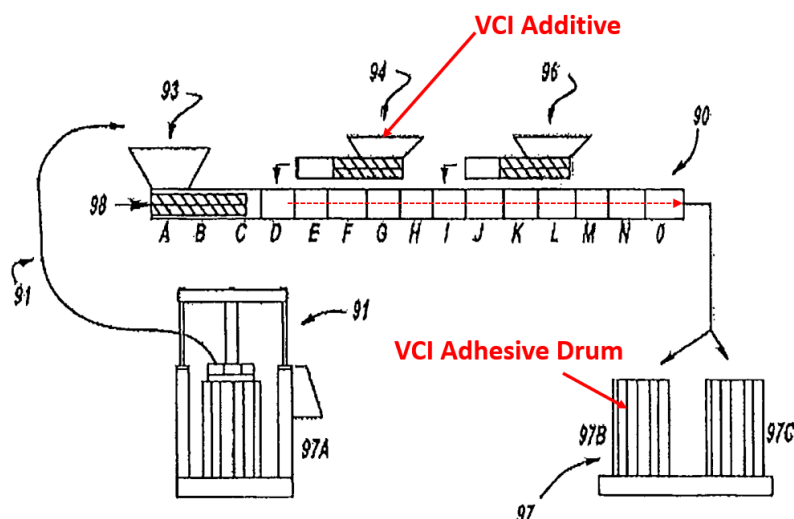


Figure 5: Schematic of a twin-screw adhesive compounding process¹⁰

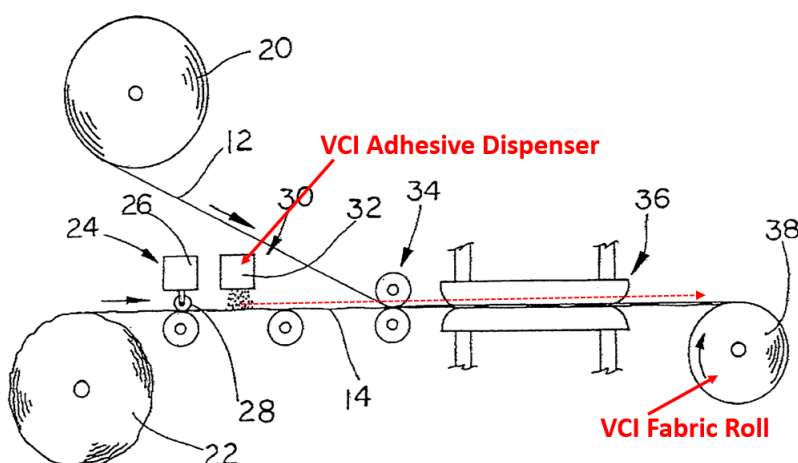


Figure 6: Schematic of a fabric lamination process with VCI compounded adhesive¹⁰

Coupling agents (CAs), such as Zirconate and Titanate, were applied to enhance the dispersion of VCI additives in the adhesive matrix. CAs allowed a higher loading of VCI particles in the adhesive matrix. Certain types of VCIs significantly increase the viscosity of base adhesives they are compounded with. CAs also help reduce the negative affect on the viscosity, allowing lower processing temperatures.¹¹

The VCI adhesive was stored in drums after compounding, then shipped to the lamination plant. The adhesive in drums was first melted in a drum melter, then sprayed on top of the substrate to laminate either a film with a nonwoven layer or a multi-layered fabric construct. The laminated VCI fabrics could be cut and sewn into corrosion protective fitted covers. The VCI loss in these processes must be considered. To lower the processing temperatures, increase the amount of CAs or lower the load

of VCIs would work, but they had their limits. A new VCI additive product that is relatively more stable at higher temperatures could be considered.

In the past several years, we have evaluated several VCI additives that are available on the market by applying the following approaches. Herein, we would focus on one of the candidates (VCI-1) and current additive (VCI-0) to demonstrate how we typically evaluate new VCI products for process applications. Compositions of these VCI additives were proprietary to the authors. We have completed the initial evaluation and are optimistic about introducing VCI-1 to our existing production system in the future.

List of the test methods and their purposes:

- German TL8135-0002: to test the anti-corrosive effect of VCI packaging materials
- Rheometer: to measure the hot melt adhesive viscosity
- Thermal gravimetric analysis (TGA): to measure mass loss of VCIs over time as the temperature changes
- Gas chromatography-mass spectrometry (GC-MS): to identify unknown substances within a test sample. More details could be found in NACE 2021 paper” Study of Vapor Corrosion Inhibitors Built into Corrosion Control Covers: Do VCIs Last the Life of the Covers?”

EXPERIMENTAL PROCEDURE

Vapor Inhibiting Ability (VIA) test: German TL8135-0002

This test is an accelerated corrosion testing to examine the vapor inhibiting ability on steel, which is commonly used for quality control of VCI films and VCI paper. A high humidity level in the air and condensation inside an enclosed system can lead to corrosion quickly. For this investigation, steel cylindrical samples with a diameter of 16mm were used. The steel sample with a high sensitivity to corrosion was packed with two strips of VCI adhesive coated polyester (PET) clear film samples in a jar. Condensation was forced on the surface of the steel samples. A blank, with the same setup structure except no VCI sample, was used to determine whether the conditions inside the flask was enough to cause corrosion on the unprotected test sample. Datalogger was used to monitor temperature (T) and relative humidity (RH) inside the flask occasionally. Test setup and a typical RH and T profile were shown in figure 7. For each test, 4 test sets were required.

Preparation of sample for this test is a quality control step prior to fabric lamination. The VCI adhesive is a solvent coated onto PET film, in a way that uses no heat application. This method tests the corrosion inhibition of the VCI containing adhesive prior to lamination heat history.