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Development of Sustainable Vapor Corrosion Inhibitors for Industrial Applications

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Chapter 1

1. INTRODUCTION

1.1 • Background and Context

Corrosion is a significant concern in various industrial applications and leads to substantial economic losses and potential safety risks (Sastri, 2015). Corrosion is a natural process that transforms metals and their alloys such as wrought iron into chemically stable products, like oxides, hydroxides, or sulfides (Frank & Martínez-Vázquez, 2015). Corrosion can affect the performance of metallic equipment and buildings, thereby reducing their longevity.

Vapour corrosion inhibitors (VCIs) have emerged as a promising solution for reducing corrosion, particularly in confined spaces where conventional contact inhibitors are ineffective. VCIs are chemicals released into the atmosphere that polarise the steel surface to form a thin protective layer that prevents corrosion (Sastri, 2011). The use of VCIs is advantageous because no direct application is required, thereby reducing labour costs, associated potential risks, and the need to handle perishables.

In the current VCI technologies, the development of sustainable VCIs is of utmost importance. Increasing environmental concerns and stringent regulations necessitate the development of VCIs that are not only effective in terms of corrosion control but also environmentally friendly (Ducheyne & Hastings, 2018). Strategies explored for the development of sustainable VCI include utilisation of biodegradable materials, waste reduction, and recycling.

However, there are obstacles to the creating of environmentally friendly VCIs. Balancing corrosion prevention with minimizing environmental impact is a key challenge. Ensuring that VCIs are compatible with different types of metals and remain stable under various environmental conditions is crucial (Ducheyne and Hastings, 2018). The advancement of VCIs is an area of study with extensive implications across various industrial sectors.

In conclusion, the development of sustainable VCIs is a critical area of research with significant implications for various industrial applications. This thesis aims to contribute to the field by developing sustainable vapour corrosion inhibitors for industrial applications.

1.2.1 Overview of VCI (Vapour Corrosion Inhibitor) Products

Vapour corrosion inhibitors are widely used and highly effective in preventing corrosion in various industries. In addition, they are available in different formulations, each tailored to specific requirements and adapted to diverse conditions. Paper-based VCIs stand out, particularly among these formulations, because of their ease of use and cost-effectiveness. This paper is integrated with carefully selected corrosion-inhibiting compounds, providing a practical method for safeguarding metal parts during storage and transit. Furthermore, VCIs release corrosion inhibitors into the surrounding environment, creating a protective atmosphere that prevents metal parts from rusting and damaging due to corrosion. This makes them especially well-suited for the automotive, electronics, and metalworking industries, where preserving metal parts is crucial (Cheng et al., 2018; Vuorinen et al., 2004).

Film-based VCIs are notable formulations in the VCI family. Moreover, these innovative products utilise thin polymeric films that contain corrosion-inhibiting compounds. In addition, VCI films are flexible and adaptable for wrapping and covering metal surfaces. Furthermore, the versatility of these films allows them to adhere to the contours of metal components, providing reliable protection against corrosion. Film-based VCIs are highly effective in various environments, ranging from outdoor exposure to harsh industrial conditions. Their versatility makes them a preferred solution for industries that require reliable corrosion protection in challenging environments (Granath, 2010).

Emitters have become popular for corrosion prevention. Furthermore, these products utilise volatile corrosion inhibitors enclosed in a diffusive medium, such as foam or plastic (Sastri, 2011). Additionally, the gradual release of inhibitors creates a protective environment that prevents the corrosion of the exposed metal surfaces. Moreover, emitters are especially useful in applications where long-term corrosion protection is desired, such as storage containers, cabinets, and electrical enclosures. In addition, by maintaining a stable and corrosion-inhibiting environment, emitters provide a reliable and efficient solution for preserving the integrity of the metal components over extended periods (Cheng et al., 2018).

In addition to papers, films, and emitters, VCI coatings have emerged as a versatile and direct approach for protecting metal surfaces from corrosion (Sastri, 2011). Moreover, they can be applied using various methods, such as spraying, dipping, or brushing, to form a robust barrier that inhibits corrosion initiation and propagation. Additionally, their chemical resistance makes them suitable for use in industries such as automotive manufacturing, infrastructure maintenance, and marine engineering. Furthermore, by using VCI coatings, metal structures and equipment can be protected from direct contact with corrosive environments, ensuring their longevity and reliability, even under the toughest conditions.

In recent years, the development of sustainable VCIs has emerged as a crucial area of focus, driven by the growing emphasis on environmental stewardship and regulatory compliance. Researchers and industry experts are actively exploring eco-friendly alternatives to traditional VCI formulations, such as the use of natural products and bio-derived compounds as potential corrosion inhibitors (Raja & Sethuraman, 2008). Furthermore, this approach aims to minimise the environmental impact while maintaining the effectiveness of the corrosion protection. Moreover, by embracing sustainable practices and innovative technologies that leverage renewable and nontoxic resources, the VCI industry is poised to meet the evolving needs of modern industries while contributing to a greener and more responsible future.

Industries now have access to a diverse range of VCI products, including paper, films, emitters, and coatings, which provide them with a complete toolkit to prevent corrosion effectively. Furthermore, these formulations offer flexibility, versatility, and cost-effectiveness for protecting valuable metals from the harmful effects of corrosion. Moreover, as the demand for sustainable and environment-friendly solutions continues to grow, the development of eco-friendly VCIs is set to shape the future of corrosion prevention. This ensures the long-term integrity and performance of metal components while minimising their environmental footprint. Furthermore, progress in VCI technology, combined with the growing recognition of the significance of corrosion prevention, has led to the implementation of these cutting-edge approaches in multiple sectors.

1.2.1 Importance of Studying the Development Process

Corrosion is a widespread issue that affects businesses and causes significant economic loss and potential security risks. According to a NACE International study, the global cost of corrosion is estimated at US$2.5 trillion per year, equivalent to 3.4% of the global GDP (Sastri, 2015). Vapour corrosion inhibitors (VCIs) protect against corrosion in confined spaces such as packaging, storage, and transportation and are emerging as effective and environmentally friendly solutions (Bastidas et al., 2005).

The study of VCI development process is important for several reasons:

- **First**, understanding the mechanisms of VCI will allow researchers to design and formulate inhibitors that are more effective. VCIs adsorb volatile chemicals on metal surfaces and protect them from corrosive agents that attack the metal. By investigating the adsorption behaviours, chemical structure, and diffusion properties of VCIs, researchers can enhance their efficiency and broaden the applications of these inhibitors (Valente et al., 2020).
- **Second**, the development of sustainable and environment-friendly VCIs is a major concern. Conventional corrosion inhibitors often contain toxic compounds that harm the environment and pose health risks to humans (Valente et al., 2020). Thus, there is an increased demand for sustainable VCIs derived from nature, such as plant extracts and biodegradable polymers (M. Chigondo & F. Chigondo, 2016). Research and development of sustainable VCIs is necessary to ensure their efficiency, stability, and compatibility with various metallurgical applications.
- **Third**, the study of VCI development enables the formulation of inhibitors for specific industrial applications. Different industries face unique corrosion challenges, which require appropriate solutions. For example, the electric and electronics industries require VCIs that can protect sensitive electric and microelectronic components without affecting or leaving residuals on electrical installations and devices (Granath, 2010). Similarly, the aerospace industry requires a VCI that can withstand large temperature fluctuations (Pieterse et al.,

2006). By investigating application-specific VCIs, researchers can optimise their formulations to satisfy the stringent requirements of these industries and ensure effective corrosion protection under extreme operating conditions.

- **Finally**, studying the development process of volatile corrosion inhibitors (VCIs) encourages collaboration between academia and the industry. The partnership between researchers and industrial stakeholders facilitates knowledge transfer, enabling the translation of laboratory findings into practical solutions (M. Chigondo & F. Chigondo, 2016). This collaboration accelerated the development of innovative VCI formulations that cater to the specific needs of various industries. Consequently, corrosion control strategies have been developed to reduce economic losses while preventing negative social and environmental impacts.

In conclusion, the study of VCI development is of paramount importance for advancing corrosion protection technologies. By understanding the mechanisms of VCI, developing sustainable and eco-friendly formulations, creating application-specific inhibitors, utilising advanced characterisation techniques, and promoting academia-industry collaboration, researchers can develop highly effective VCIs that meet the diverse needs of various industries. Continued research in this field will not only mitigate the economic impact of corrosion but also contribute to the development of sustainable and environmentally friendly corrosion protection solutions.

1.2 Research Questions and Objectives

1.2.1 Main Research Question and Complementary Questions

The main research question is as follows:

How can sustainable vapour corrosion inhibitor (VCI) formulations be developed to meet industrial performance requirements while minimising the environmental impact?

The complementary questions are:

1. Which other sustainable materials can be successfully used in VCI chemistry?
2. How do the corrosion control methods differ between durable and conventional VCIs?
3. What are the best criteria for sustainable, high-performance VCI products?

4. How do designed VCIs perform in terms of corrosion protection, durability, and compatibility?
5. What are the potential environmental advantages and disadvantages compared to traditional solvents?

1.2.2 Objectives of the Study

1. Explore and identify sustainable VCI products.
2. Enhance efficiency by understanding preventive measures.
3. Perform tests on the efficiency, sustainability, and environmental impacts of all industries.
4. Design strategies to overcome challenges in business development and adoption.
5. Supports sustainable crop protection technologies and responsible industrial practices.

1.3 Scope and Limitations

The scope of this study was to investigate long-term corrosion inhibitors (VCI) and their mechanical performance. However, there are limitations to the effectiveness and acceptability of the formulations.

1.3.1 Definition of VCI Product and Related Terms

Vapour corrosion inhibitors (VCIs) are a group of chemicals that form molecules in the vapour phase, which can adsorb onto metal surfaces, thereby forming a protective barrier against the corrosive environment. These materials can be produced in various forms, such as paper, films, powders, and emitters. Related terms include volatile corrosion inhibitors (VCIs), which refer to the vapour pressure or volatile properties of the chemical substances used as inhibitors, and vapour phase inhibitors, which refer to the mode of action of the vapour phase.

1.3.2 Scope of the Research Project

This research project focuses on the development of sustainable vapour corrosion inhibitors for industrial applications. This project aimed to explore new environmentally friendly materials and enhance their performance in various VCI products. This research includes corrosion prevention strategies using the new VCIs developed, which are evaluated through laboratory and field tests in accordance with industry partners in the automotive, aerospace, electronics, oil, and gas industries requirements. As well as the development of more effective products for the packaging industry to minimise environmental impact.

An important limitation of this study was the current market dominance of traditional VCIs. Sustainable alternatives can face challenges, such as high production costs, availability of specialised raw materials, and poor industry conditions for the use of new materials. Traditional systems are well-established, cost-effective, and compatible with existing methods, making the industry reluctant to switch to sustainable VCIs owing to potential risks

Chapter 2

2. HISTORY AND EVOLUTION OF VCI PRODUCTS

Corrosion, a naturally occurring process that reduces the integrity of metal components, has long been a significant challenge in various industries. The development of vapour corrosion inhibitors (VCIs) has emerged as one of the most important solutions for combating the effects of corrosion, which have been developed since the late 19th century has become an indispensable tool in automobiles, aerospace, and electronics (Sastri, 2011). This technology leverages the ability of volatile compounds to create a protective environment and protect metallic surfaces from corrosion. The history and development of VCI products are characterised by unprecedented progress owing to the pioneering work of early researchers and subsequent innovations that took the field to new heights. This chapter examines a wide variety of important developments and improvements that have characterised the growth of the VCI industry and highlights pioneers who have paved the way for ongoing efforts to improve the effectiveness and long-term viability of these durables.

2.1 Early developments and pioneers

The early development of volatile corrosion inhibitors (VCIs) can be traced back to the early 1900s when volatile compounds were first employed to protect the steam boiler and condensate lines of heating systems from corrosion. These compounds, such as ammonia, ethylenediamine, morpholine, and cyclohexylamine, were found to prevent or significantly retard corrosion in both immersed and exposed parts of the boiler system (Baker, 1954).

This early application of volatile compounds to prevent corrosion in confined spaces laid the foundation for developing more advanced VCIs in the following decades. The discovery of VCIs dates back to the early 1900s, when they were developed to protect ferrous metals in tropical environments. However, it was not until the 1940s that VCIs gained widespread use in protecting ferrous and non-ferrous metals from atmospheric corrosion during storage and transportation (M. Chigondo & F. Chigondo, 2016).

The Shell Oil Company played a crucial role in developing and commercialising VCIs in the 1940s. The driving force behind Shell's work on vapour-phase inhibitors during this period was the need to protect precision military equipment from corrosion damage during storage or transportation during World War II. In the early 1940s, Shell introduced its first commercial vapour corrosion inhibitor (VCI), which marked a pivotal moment in corrosion protection technology. This innovation represents a transition from using volatile corrosion inhibitors to the practical and commercially feasible applications of VCIs. The first compound used by Shell Development Co., isopropyl-ammonium nitrate (Dipan), was subsequently superseded with dicyclohexylammonium nitrite (DICHAN) (Rowden, 1958). Figure 2-1 shows VCI compounds used by Shell Development Co., such as isopropyl-ammonium nitrate (Dipan) and dicyclohexylammonium nitrite (DICHAN)

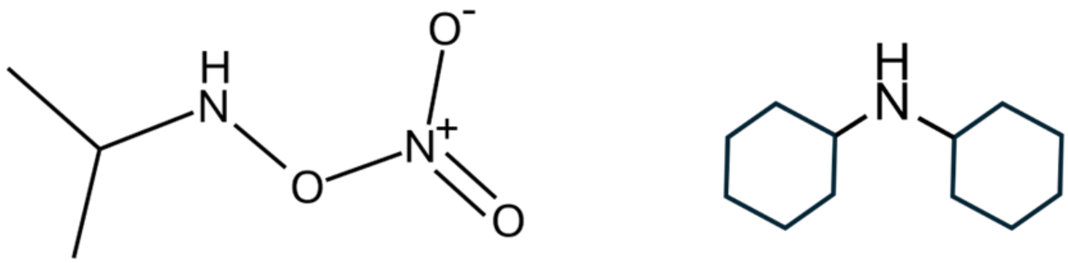


Figure 2-1: VCI compounds used by Shell Development Co., such as isopropyl-ammonium nitrate (Dipan) and dicyclohexylammonium nitrite (DICHAN)

Shell's patent for DICHAN, issued in 1947, was a significant milestone in the history of the VCIs. This compound was eventually commercialised as VPI 260 and became the first widely used VCI product (Baker, 1947). The success of DICHAN has paved the way for the development and application of various VCIs in the following decades.

During World War II, the requirement for an inhibitor to protect ferrous metal corrosion in the exposed areas of hydraulic systems became evident while researching the development of non-flammable aqueous hydraulic fluids. Compounds such as ammonia, ethylenediamine, morpholine, and cyclohexylamine were evaluated but showed only moderate success. In 1944, disopropylammonium nitrite was identified as a promising vapour-phase corrosion inhibitor, and several amine nitrites were synthesised and found to provide adequate vapour-phase corrosion inhibition in aqueous hydraulic fluids (Rowden, 1958).

The war also highlighted the need to protect military equipment and parts from corrosion during storage, as existing packaging procedures were inadequate, and desiccants proved insufficient in many cases. The vapour-phase inhibition of amine nitrites opens up a new approach to address these packaging problems. In 1945, impregnated paper tubes containing disopropylammonium nitrite were found to effectively prevent the corrosion of rocket bodies during storage without the cleaning difficulties of oil-based preservatives. Dicyclohexylammonium nitrite, which is less volatile and more water-soluble than disopropylammonium nitrite, is a more suitable paper impregnant, and military specifications have been issued for the procurement of impregnated paper tubes (Rowden, 1958).

Since the 1970s, various amine-carboxylate salts, typically based on mixtures of amines such as dicyclohexylamine and carboxylic acid, have been patented and used as VCIs to protect ferrous metals. After World War II, Naval Research detailed the properties of amine nitrites and their effects on non-ferrous metals. Applications in electrical equipment are limited because of the undesirable coatings formed on some metals. Since then, volatile corrosion inhibitors have been extensively tested and used for packaging and protecting a wide variety of military and industrial equipment, machinery, instruments, and parts, allowing the immediate use of items without tedious cleaning procedures (Gangopadhyay & Mahanwar, 2018).

In conclusion, the early development of vapour corrosion inhibitors began with investigating ammonia and its derivatives as potential volatile corrosion inhibitors before World War II. The wartime needs for effective corrosion protection in hydraulic systems and during the storage of military equipment has driven the development and application of amine nitrites as vapour phase corrosion inhibitors. Shell's pioneering work in developing and patenting dicyclohexylammonium nitrite (DICHAN) in the 1940s laid the foundation for the commercial use of VCIs. The success of these compounds in preventing corrosion without direct contact has paved the way for their widespread use in various industries for protecting metal parts and equipment during storage and transportation. Currently, VCIs continue to play a vital role in corrosion prevention, with ongoing research and development aimed at improving their effectiveness and expanding their application.

The field of corrosion research has been significantly influenced by several pioneering figures, notably I.L. Rozenfeld, H. R. Baker, W. A. Zisman, R. H. Herrmann, and E. E. Becker. Their collective contributions have shaped our understanding of vapour corrosion inhibitors (VCIs) and their applications in protecting metal surfaces. I.L. Rozenfeld, a prominent figure in corrosion research, is instrumental in elucidating the complexity of corrosion inhibition. His research emphasised that no single substance could entirely prevent corrosion, a revelation that has guided contemporary corrosion protection strategies. These strategies often combine methods to achieve a passive state in iron materials (Koehler & Reinhard, 2014).

In 1951, H. R. Baker and W. A. Zisman from the Naval Research Laboratory (NRL) published a report titled "Liquid and Vapor Corrosion Inhibitors.” The findings of their study on the use of polar-type corrosion inhibitors for steel in non-aqueous fluids offer valuable insights into the function of soaps and amine-acid complexes as corrosion inhibitors in oils. (Koehler & Reinhard, 2014). This study further advances the understanding of VCI technology and its potential applications.

Concurrently, R.H. Herrmann and E.E. Becker, researchers at the Shell Development Company, studied the use of volatile organic compounds as corrosion inhibitors. In the early 1940s, the Shell Corporation developed dicyclohexylammonium nitrite (Dichan) for U.S. military use. This marked a significant milestone in the development of the VCIs.

Shell's pioneering work in VCIs continued with the introduction of the first vapour corrosion inhibitor (VCI) under the trademark "VPI" in 1944. VPI, an acronym for "Vapor Phase Inhibitor”, is a groundbreaking development in corrosion protection. The first product, Shell VPI 260, was used by the military to protect equipment and weapons from corrosion during World War II (Baker, 1947).
Shell's pioneering role has extended the study of VCIs' effects on non-ferrous metals. For instance, Shell VPI 260 was found to be corrosive to cadmium, zinc, magnesium, and certain aluminium alloys, providing valuable data for developing more effective and compatible VCIs.

In conclusion, the pioneering work of Rozenfeld, Baker, Zisman, Herrmann, and Becker significantly advanced our understanding of VCIs and their applications. Their contributions continue to inform contemporary corrosion protection strategies, underscoring the enduring relevance of their research.

2.2 Milestones in VCI technology

Developing effective corrosion prevention methods is crucial for ensuring the longevity and reliability of metallic components and structures. Vapour Corrosion Inhibitors (VCIs) have emerged as a promising solution, offering a unique approach to corrosion protection through the release of vapour-phase inhibitors that form a protective barrier on metal surfaces.

Vapour Corrosion Inhibitors (VCIs) work by releasing vapour-phase inhibitors that form a protective barrier on metal surfaces. This process is crucial for preventing corrosion without the need for direct contact with the metal. Figure 2-2 provides a schematic illustration of the VCI mechanism of action on metal surfaces.

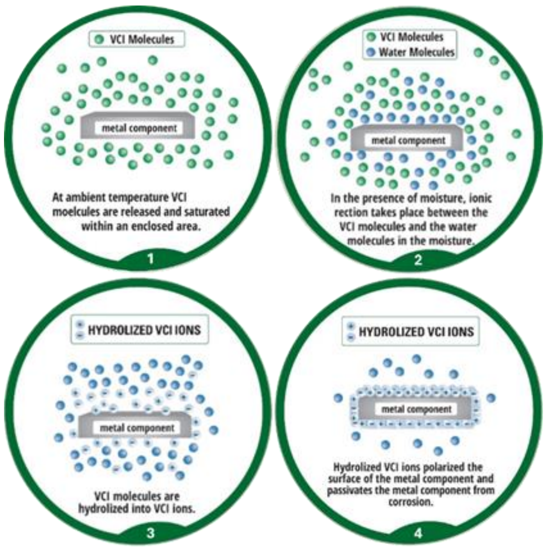


Figure 2-2 : Schematic illustration of VCI mechanism of action on metal surfaces.

2.2.1 Early Developments (1930s-1940s)

The origins of VCI technology can be traced back to the 1930s, when Shell Oil Co. introduced the first Vapour Corrosion Inhibitor, Isopropyl-ammonium nitrate (Dipan), which was later replaced with Dicyclohexylammonium Nitrite (Dichan) (Rowden, 1958;

Pieterse et al., 2006). During World War II, the widespread use of VCIs proved invaluable for safeguarding military equipment and spare parts from corrosion, regardless of the harsh weather conditions. This early success paved the way for the further exploration and development of VCI formulations. Figure 2-3 illustrates a timeline of key milestones in the development of VCI technology.

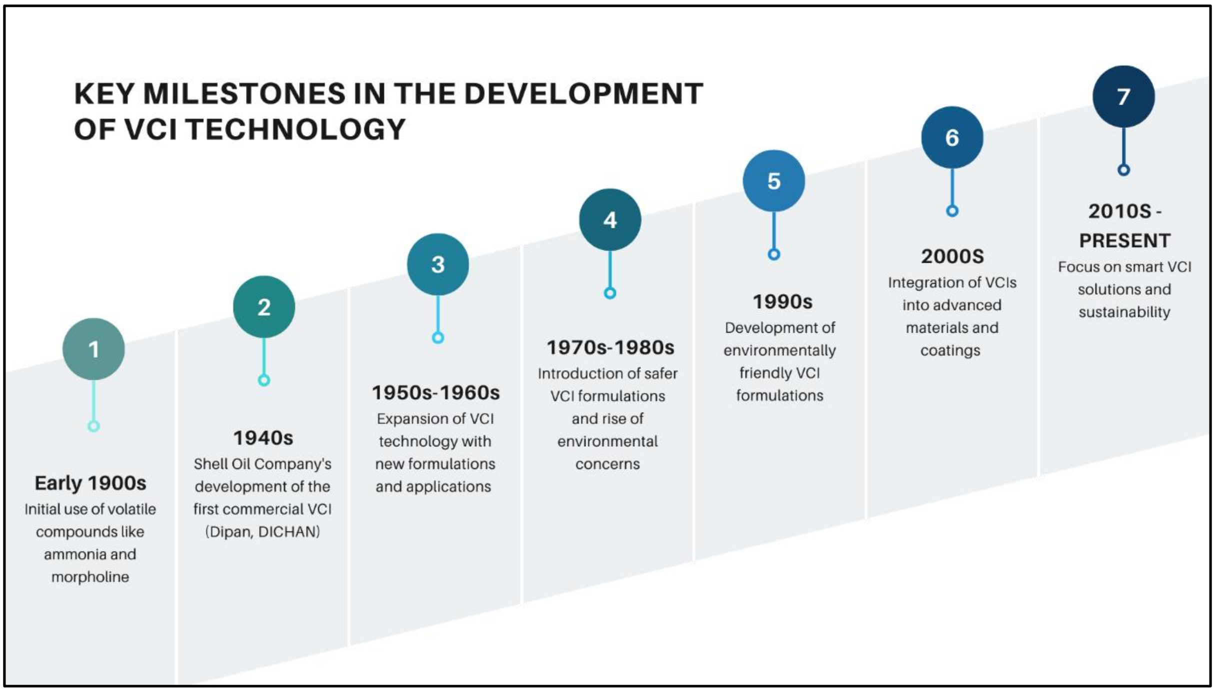


Figure 2-3: Timeline of key milestones in the development of VCI technology.

2.2.2 Expansion and Diversification (1950s-1960s)

The 1950s and 1960s witnessed significant advancements in VCI technology, with research focused on developing safer and more versatile formulations that are suitable for various applications. Coating compositions that combine binders and corrosion-inhibiting agents have been introduced to provide dual-purpose protection for metallic materials (Cooper & Woods, 1950). VCIs have also been incorporated into wrapping materials to offer additional protection during storage and transportation (Krieg, 1958). Specialised formulations have been developed for specific applications such as hydraulic fluids (Celanese Corporation of America, 1957) and high-humidity environments (Denman, 1959). The versatility of the VCI technology has expanded with the introduction of transparent heat-sealable sheets impregnated with VCIs (Fessler et al., 1960) and packaging materials tailored for non-ferrous metals (Daubert Chemical Company, 1964).

2.2.3 Safety Concerns and Nitrite-Based Systems (1970s-1980s)

The adaptability of VCI has led to its expansion and diversification, thanks to the development and commercialisation of safer and more effective formulations. VCIs have been widely used in automotive, aerospace, and electronics industries, demonstrating their potential for various applications. Effective VCI chemistries such as amine carboxylates and benzotriazole derivatives have also been introduced (Lynch & Henderson, 2004). In the late 1970s, the use of dicyclohexylamine-nitrite, a common component of volatile corrosion inhibitors (VCIs), raised concerns about the safety of VCI technology because of its potential to form nitrosamines, which are known to be carcinogenic.

Figure 2-4: Various packaging materials impregnated with VCIs to protect against corrosion during storage and transportation

Nitrosamines are compounds that can form when nitrite-containing chemicals react with amines under specific conditions, limiting the expansion of VCI technology (Meiners et al., 1980). To address these safety issues, Northern Technologies International Co. (NTIC) introduced a new VCI chemical system based on common food additives, relying on nitrites, specifically sodium nitrite, as the foundation for corrosion inhibitor systems (Lynch & Henderson, 2004). The 1980s witnessed a significant expansion in the use of VCIs across various industries, with new formulations being developed using various compounds. This period was marked by a growing awareness of the benefits of VCIs in protecting metallic components and equipment from corrosion during the storage, transportation, and operational phases, particularly in packaging materials such as papers, films, pouches, and emitters. Various packaging materials impregnated with VCIs are shown in Figure 2-4 to protect against corrosion during storage and transportation.VCIs have been incorporated into polymer coatings and metalworking liquids, and benzotriazole and tolyltriazole mixtures have been shown to be effective for copper and copper alloys (Andreev et al., 2013). Figure 2-5 depicts the molecular structures of benzotriazole and tolyltriazole, which are commonly used in these applications.

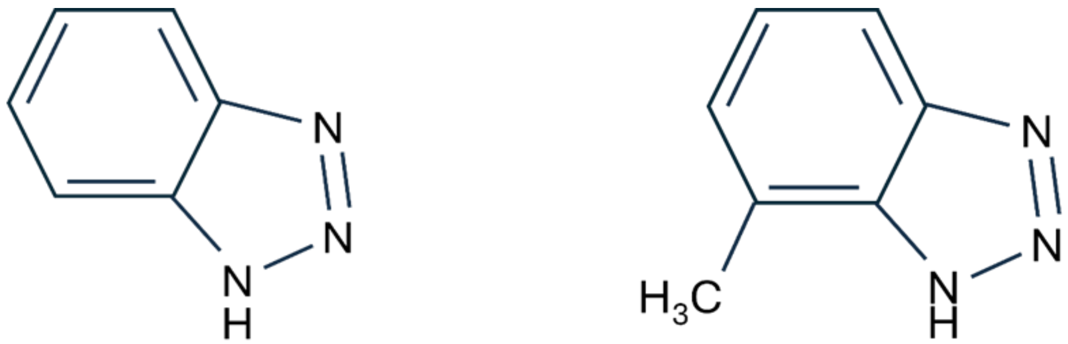


Figure 2-5: Benzotriazole and tolyltriazole for copper and copper alloy corrosion protection

2.2.4 Environmental and Safety Improvements (1990s)

The 1990s focused on developing environmentally friendly VCI formulations to address previous health concerns (David Sharman., 2017). Ongoing research aims to create safer and more effective VCI formulations, such as water-based amine complex salts of carboxylic acids (Reinhard et al., 2009). Advancements in VCI packaging materials and methods have enabled their integration into paint coatings and other delivery systems. This period saw a high interest in and extensive research on vapour-phase protection methods (Inzunza et al., 2013).

2.2.5 Integration into Advanced Materials and Coatings (2000s)

In the 2000s, the use of vapour-phase corrosion inhibitors (VCIs) expanded significantly. VCIs have been integrated into advanced materials and coatings to improve their corrosion protection efficiency. This integration was made possible by using innovative microencapsulation techniques, which allow VCIs to be embedded in coatings and films. Patents have been granted for the composition of vapour-phase corrosion inhibitors that can protect challenging environments through sublimation (Georg et al., 2009).

However, concerns have arisen about the safety of these formulations. It has been found that using secondary amines without nitrites is still unsafe due to the formation of carcinogenic N-nitrosamines when combined with nitrogen oxides in the air. German researchers have confirmed that some N-nitrosamines, including those generated by dicyclohexylamine-nitrite, are carcinogenic and genotoxic. As a result, German regulations, such as TRGS-615, have prohibited the use of metalworking products containing secondary amines or hidden secondary amines owing to their potential health hazards (Westphal et al., 2001).

Consequently, the focus has shifted towards developing environmentally friendly, more efficient, and compatible VCI materials. Expansion to the electronics and aerospace industries has led to the development of non-toxic, residue-free VCIs (Rehioui, 2023).

2.2.6 Smart VCI Solutions and Sustainability Focus (2010s-Present)

Recent developments in the 2010s and beyond have focused on creating "micro VCIs that respond to environmental changes such as humidity and temperature, reducing unnecessary chemical release, and enhancing sustainability (Lynch & Henderson, 2004). Biodegradable VCI materials that offer adequate corrosion protection and break down into non-toxic byproducts after their useful life have been introduced (Bottcher et al., 1999). Continued research is being conducted to optimise the VCI combinations to protect specific metals and alloys in harsh environments. Integrating VCIs with other corrosion-mitigation technologies, such as coatings and inhibitors, has created robust multilayered protection approaches (Gangopadhyay & Mahanwar, 2018).

In the 2020s and present, the focus on sustainability and biodegradability has significantly influenced the development of VCIs (Hossain et al., 2021; Verma et al., 2021). Environmentally friendly alternatives derived from natural resources can replace traditional toxic chemicals, and biodegradable VCIs synthesised using green solvents are considered to be more sustainable. The demand for less harmful and more sustainable green corrosion inhibitors is increasing, reflecting the growing emphasis on their sustainability and biodegradability of corrosion inhibitors.

2.2.7 Conclusion

The evolution of the Vapour Corrosion Inhibitor (VCI) technology has been marked by continuous innovation driven by the need for effective corrosion protection solutions while addressing environmental and safety concerns. From its early beginnings to the current focus on sustainable and biodegradable formulations, the VCI technology has undergone significant advancements, expanded its applications, and improved its efficiency and compatibility. As the demand for corrosion prevention continues to grow across various industries, ongoing research and development efforts are crucial to further optimise VCI technology and address emerging challenges sustainably and responsibly.

2.3 Evolution of VCI products over time

Vapour corrosion inhibitors (VCIs) have undergone significant advancements over the years to meet the diverse corrosion protection requirements of various industries. Figure 2-6 illustrates the various application methods for VCIs in modern industrial practices.

Figure 2-6: VCI products used in various industries

This evolution can be traced back to the historical progression of VCI products, from their initial formulations to the contemporary environmentally friendly solutions that are currently available.

2.3.1 Early Developments and Expansion to Multi-Metal Protection

The concept of vapour phase corrosion inhibition dates back to the late 1940s when the United States Navy first explored using amine nitrites as VCIs to preserve military equipment. These early VCIs, such as dicyclohexylamine nitrite (DICHAN), were primarily oil-soluble inhibitors designed to protect ferrous metals, such as steel and cast iron, during storage and transportation (Bastidas et al., 2005; Lynch & Henderson, 2004; Rowden, 1958).

As the demand for corrosion protection grew, VCI formulations were developed to protect non-ferrous metals, including aluminium, copper, brass, bronze, and their alloys. This led to the introduction of multi-metal protection VCIs, which incorporate a blend of organic and inorganic inhibitors, such as benzotriazole, tolyltriazole, and amine salts targeting specific metal types (Finšgar & Milošev, 2010; Koehler & Reinhard, 2014).

2.3.2 Transition to Water-Soluble VCIs

With growing environmental concerns and tightening regulations for volatile organic compounds (VOCs), the demand for water-soluble VCI formulations has noticeably increased. These formulations offer advantages over oil-soluble VCIs, including better compatibility with various industrial processes, and improved safety during handling and disposal.

A significant outcome of water-soluble VCI development is the amine-carboxylate-based formulation, known for its exceptional corrosion inhibition properties towards ferrous metals. This formulation laid the groundwork for further advancements in water-soluble VCI technology (Cheng et al., 2019).

2.3.3 Environmentally Friendly and Sustainable VCIs

As environmental awareness grew and regulations became stricter, the focus shifted towards developing environmentally friendly and sustainable VCI formulations. Traditional VCIs, such as amine nitrites and chromates, have been investigated for their potential toxicity and environmental impacts (Popoola, 2019).

Efforts have been directed towards using biodegradable and non-toxic materials as VCI components, leading to the development of eco-friendly VCI products that exhibit encouraging outcomes in safeguarding metal objects from corrosion (Gece, 2011). These formulations often incorporate plant-based extracts, amino acids, and ionic liquids as corrosion inhibitors (Sastri, 2011).

2.3.4 Advanced VCI Technologies

Ongoing research efforts have focused on enhancing the performance and sustainability of VCI products. Current and future trends in VCI technology include the following.

1. Nanotechnology-based VCIs: The incorporation of nanoparticles or nanocomposites into VCI formulations can provide enhanced barrier properties and sustained release of inhibitor molecules (Liao et al., 2022).
2. Smart and responsive VCIs: Efforts have focused on developing smart VCI systems that can respond to environmental conditions or provide real-time monitoring of corrosion status (Makhlouf, 2014; Kendig et al., 2010; Shchukin & Möhwald, 2007).
3. Hybrid VCI systems: VCIs are combined with other corrosion protection techniques, such as coatings or surface treatments, to create hybrid systems with synergistic effects and improved durability (Koehler and Reinhard, 2014).
4. Self-healing VCIs: Innovative VCI formulations with self-healing properties have been developed, enabling the repair and regeneration of protective layers on metallic surfaces even after exposure to corrosive environments (Qian et al., 2017).
5. Encapsulated VCIs: Encapsulation techniques have been employed to enhance the controlled release and targeted delivery of VCI compounds, customise the release pattern, and enhance the efficiency of the corrosion protection process (Raja et al., 2020).
6. Bio-based VCIs: A significant advancement in environmentally friendly VCIs is the formulation of bio-based VCIs derived from renewable resources, such as plant extracts and agricultural byproducts (Njoku et al., 2024). These formulations offer a sustainable alternative to traditional VCIs while providing comparable or superior corrosion inhibition performance.

As the demand for sustainable and effective corrosion protection solutions continues to grow, the evolution of VCI products is likely to continue, driven by advancements in material science, nanotechnology, and computational techniques.

Chapter 3

3. FUNDAMENTAL PRINCIPLES OF VCI TECHNOLOGY

3.1 Overview of Common Raw Materials

Selecting the right raw materials for vapour corrosion inhibitors (VCIs) is crucial for effective metal corrosion protection. This section provides an overview of the common organic and inorganic compounds used in VCI formulations and highlights their role in corrosion prevention. Figure 3-1 provides a visual summary of these common raw materials, and Table 3-1: Common Raw Materials Used in VCI and their roles in corrosion protection details their specific roles in corrosion protection.

3.1.1 Organic Compounds

Organic compounds are widely used in VCI formulations due to their ability to form protective films on metal surfaces. They are considered adsorption inhibitors, and film-forming inhibitors. Organic compounds such as amines, oils, and waxes are adsorbed onto the steel surface, forming a thin protective film and preventing metal dissolution (Bastidas et al., 2005). These compounds include:

- **Amines and Their Salts**
  Amines and their salts, such as dicyclohexylamine nitrite, cyclohexylamine benzoate, and monoethanolamine benzoate, are commonly used in VCI formulations to protect ferrous metals. These compounds release protective vapours that form a barrier on the metal surface, thereby preventing corrosion (Subramanian et al., 2000).
- **Carboxylic Acids and Their Salts**
  Carboxylic acids and their salts such as sodium benzoate and sodium caprylate, are used in VCI formulations because they can form protective films on metal surfaces. These compounds are often combined with amines to enhance corrosion protection (Rammelt et al., 2009).
- **Heterocyclic Compounds**
  Heterocyclic compounds, such as benzotriazole and tolytriazole, are effective VCI raw materials for protecting copper and its alloys. These compounds form a protective film on the metal surface, inhibiting corrosion (Valdez et al., 2018).

3.1.2 Inorganic Compounds

Inorganic compounds play a significant role in VCI formulations by providing various mechanisms of corrosion inhibition:

- **Anodic Inhibitors**

  Anodic inhibitors retard anodic corrosion by forming passive films. There are two types of passivation inhibitors.

  1. **Oxidising Anions**: Compounds, such as chromate, nitrite, and nitrate, can passivate steel without oxygen.
  2. **Non-oxidising Ions**: Compounds such as phosphate, tungsten, and molybdate require oxygen to passivate the steel.

- **Cathodic Inhibitors**

  Cathodic inhibitors suppress the cathodic reaction by reducing the dissolved oxygen (DO). They can be inhibited through the following three mechanisms:

  1. **Cathodic Poisons**: Substances such as arsenic, antimony, sulphur, selenium, tellurium, and cyanide ions prevent the formation of hydrogen gas.
  2. **Cathodic Precipitates**: Compounds, such as polyphosphate, calcium, and magnesium, precipitate as oxides to form a protective layer on the metal surface.
  3. **Oxygen Scavengers**: Chemicals, such as hydrazine and sodium sulphite, react with oxygen, preventing cathodic depolarisation.

- **Mixed Inhibitors**

  Mixed inhibitors interact with both the anodic and cathodic reactions, providing comprehensive protection (A. Al-Amiery et al., 2023; Palanisamy, 2019).

3.1.3 Plant-based and biomass-derived Substances

Plant-based wastes and biomass-derived substances have shown great potential as sustainable VCIs for industrial applications and considered as green corrosion inhibitors. Peels, rinds, and other plant byproducts contain organic compounds with corrosion-inhibiting properties. Lignins from oil palm fronds, sugar beet molasses, raffinate, and plant extracts rich in alkaloids have demonstrated excellent vapour corrosion inhibition capabilities. These renewable and biodegradable resources offer promising avenues for the development of eco-friendly and cost-effective VCIs aligned with the principles of green chemistry and sustainability in various industrial sectors (Marzorati et al., 2018; Ansari et al., 2018).

Developing sustainable VCIs requires careful selection and combination of organic and inorganic raw materials to provide effective corrosion protection while minimising environmental impact. As the demand for eco-friendly corrosion protection solutions grows, bio-based and biodegradable raw materials in VCI formulations will likely increase.

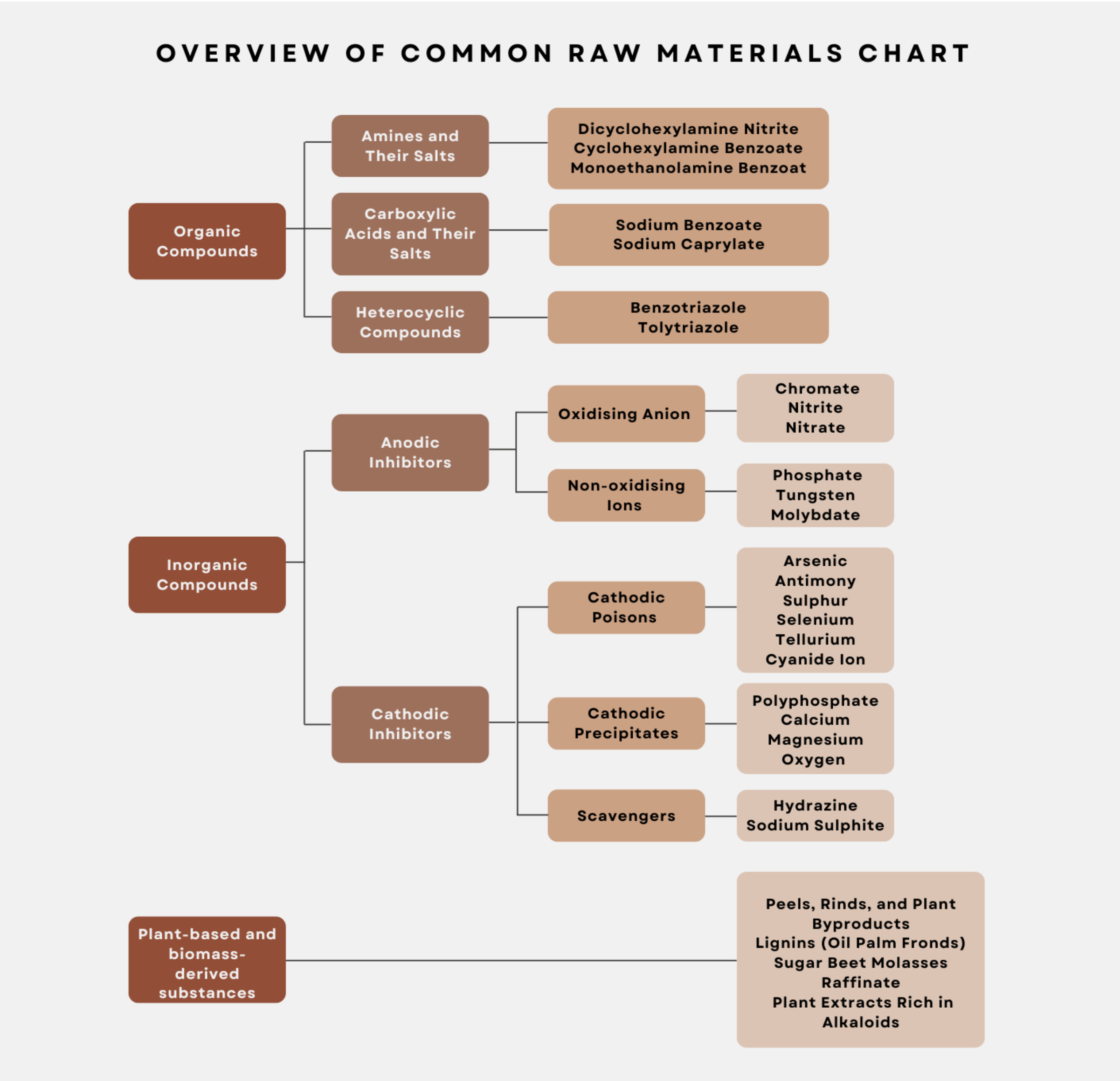


Figure 3-1: Overview of Common Raw Materials Used in VCI

Table 3-1: Common Raw Materials Used in VCI and their roles in corrosion protection

Inhibitor Type	Sub-Type	Role in Corrosion Protection
Organic Compounds	Adsorption Inhibitors	Adsorb onto metal surfaces to form thin protective films, preventing metal dissolution (Bastidas et al., 2005).
	Mixed Inhibitors	Interact with both anodic and cathodic reactions, providing comprehensive protection (A. Al-Amiery et al., 2023; Palanisamy, 2019).
Inorganic Compounds	Anodic Inhibitors	Form passive films to retard anodic corrosion (Substech, 2023).
	Cathodic Inhibitors	Suppress cathodic reaction by reducing dissolved oxygen and forming protective layers (Substech, 2023).
Plant-Based Compounds	Adsorption Inhibitors	Adsorption and film formation mechanisms provide eco-friendly corrosion protection (Marzorati et al., 2018; Ansari et al., 2018).

3.2 Properties and Characteristics

VCIs possess unique properties that make them effective and versatile for corrosion protection in various industries. Their key properties, such as volatility, adsorption behaviour, and film formation, provide long-lasting protection to the metal surfaces. Additionally, VCIs exhibit desirable characteristics, such as compatibility with different metals, efficiency at low concentrations, and environmental friendliness, making them a preferred choice over traditional corrosion inhibitors.

3.2.1 Volatility and Vapour Pressure

One of the critical properties of VCIs is their volatility, which allows them to evaporate and diffuse through the air to reach and protect metal surfaces. Effective VCIs typically have vapour pressures ranging from 10^{-2} to 10^{-7} mmHg at room temperature, ensuring optimal volatilisation and protection without rapid dissipation. This optimal vapour pressure ensures that the inhibitor can volatilise and provide protection but is not so high that it dissipates too quickly. Vapour pressure also influences the transport mechanism and ability of VCI molecules to reach and adsorb onto metal surfaces (Altsybeeva et al., 2012).

3.2.2 Adsorption and Film Formation

VCI molecules adsorb onto metal surfaces through physical or chemical interactions, typically through heteroatoms (e.g., nitrogen, oxygen, and sulphur) and π-electron systems (Betti et al., 2023; Bijapur et al., 2023; Chung et al., 2019). The resulting protective film is usually a monomolecular layer that maintains the appearance and functionality of the metal parts (Gangopadhyay & Mahanwar, 2018).

The thickness of the VCI film plays a crucial role in its corrosion protection ability. For example, a 3µm film remained intact after 240 hours in a Neutral Salt Spray (NSS) chamber, while a 1µm film deteriorated completely within the same period. The NSS chamber replicates harsh wet conditions that typically induce metal corrosion, allowing the testing of the VCI film performance (Valdez et al., 2006).

3.2.3 Compatibility and Versatility

VCIs are compatible with ferrous and non-ferrous alloys, making them versatile for diverse industrial applications, including automotive, offshore/onshore, water, military, marine, manufacturing, oil and gas, electronics, and concrete structures. They can be incorporated in different forms, such as packaging materials, lubricants, coatings, and emitters, offering a flexible and targeted approach to protect against corrosion. VCIs can be incorporated into coatings, foams, adhesives, powders, sprays, and plastics. They are also compatible with other additives and can be formulated to meet specific requirements, such as FDA approval or environmental regulations (Ansari et al., 2018).

3.2.4 Efficiency and Long-term Protection

VCIs are highly efficient and often provide protection at low concentrations (e.g. less than 1 wt% in VCI products like VCI plastics). (Gangopadhyay & Mahanwar, 2018). They offer long-term protection, providing up to 24 months of corrosion inhibition. The efficiency of VCIs depends on the type of metal, environmental conditions, and properties of the inhibitor, such as water solubility, volatility, and active components (Gangopadhyay & Mahanwar, 2018). Appropriate selection and application of VCIs are crucial for optimal performance.

3.2.5 Environmental and Health Considerations

VCIs provide a safer and more environmentally friendly alternative to traditional toxic inhibitors like chromates and nitrites. These 'green inhibitors' are sustainable and non-toxic, derived from plant extracts or other bio-based materials. They provide effective corrosion protection while minimising environmental impact (Asmara et al., 2017; Devarayan et al., 2012; Shehata et al., 2018).

In conclusion, the unique properties and characteristics of VCIs, including their volatility, adsorption behaviour, compatibility, efficiency, and environmental benefits, make them valuable tools for corrosion protection in various industries.

3.3 Selection Criteria for Optimal Performance

Selecting the most suitable VCI for a specific application is crucial for achieving optimal corrosion protection. Several key factors must be considered when choosing a VCI to ensure its effectiveness and compatibility with metal substrates, environmental conditions, and application methods. The decision-making framework illustrated in Figure 3-2 provides a step-by-step guide to help in selecting the appropriate VCI.

3.3.1 Metal Substrate Compatibility

The compatibility of the VCI with a metal substrate is a primary consideration. Different metals and alloys exhibit varying susceptibilities to corrosion, necessitating specific types of VCIs. For example, amines and their salts are commonly used to protect ferrous metals, whereas heterocyclic compounds, such as benzotriazole and tolytriazole, are more effective against copper and its alloys (Valdez et al., 2018; Subramanian et al., 2000; Ansari et al., 2018). Ensuring that the chosen VCI is compatible with the metal substrate is essential for achieving optimal performance.

3.3.2 Environmental Conditions

Environmental conditions, such as storage and transportation environments, are crucial factors in VCI selection. Humidity, temperature, and corrosive agents, such as hydrogen sulphide, chloride, and sulphur dioxide, can significantly influence the effectiveness of VCIs. For example, amine-based VCIs are required to protect steel in high-humidity environments and efficiently protect it against corrosion. The pH of the environment can also affect the stability and performance of certain VCIs. Most VCI molecules show their best activity in the pH range of 5.5–8.5 (Gangopadhyay & Mahanwar, 2018; Ansari et al., 2018).

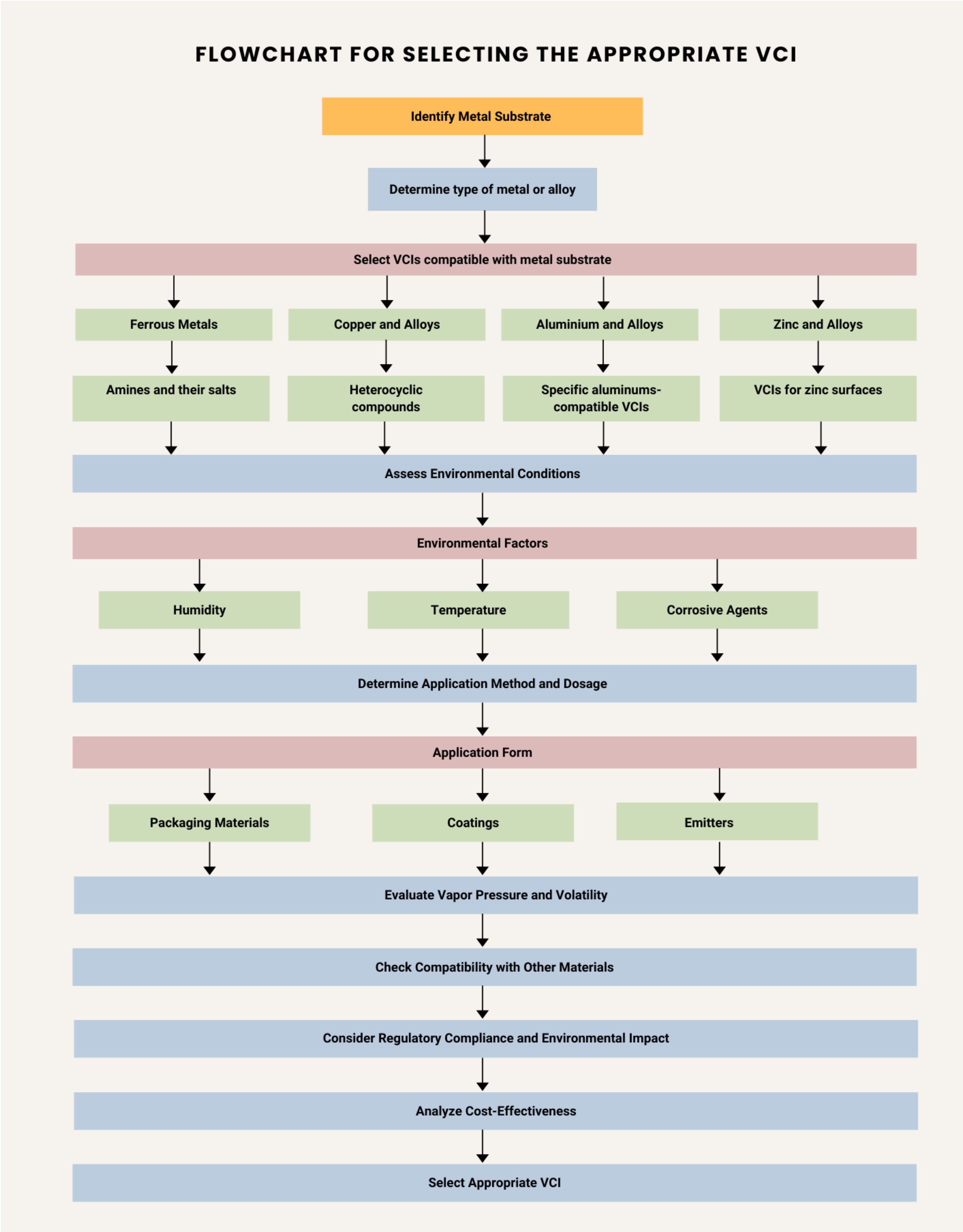


Figure 3-2: Flowchart for Selecting the Appropriate VCI

Note. This flowchart illustrates the decision-making process for selecting the most suitable vapour corrosion inhibitor (VCI) based on metal substrate compatibility, environmental conditions, application method, vapour pressure, compatibility with other materials, regulatory compliance, and cost-effectiveness.

3.3.3 Application Method and Dosage

The application method and dosage of VCI are essential for achieving optimal performance. VCIs can be incorporated in various forms, such as packaging materials, coatings, and emitters, each requiring specific application techniques (Cheng et al., 2018). The dosage of VCI should be carefully determined based on the metal surface area, enclosed space volume, and protection duration. Insufficient dosage may lead to inadequate corrosion protection, whereas excessive dosage can result in unnecessary costs and potential compatibility issues.

3.3.4 Vapour Pressure and Volatility

The vapour pressure and volatility of VCI are critical factors in their ability to provide effective corrosion protection. VCIs with optimal vapour pressure can readily vaporise and form a protective layer on the metal surface. However, if the vapour pressure is too high, VCI may dissipate too quickly, leading to a shorter protection period. However, VCI may not provide sufficient protection if the vapour pressure is too low. Balancing the vapour pressure and volatility of VCI is essential to achieve long-lasting and efficient corrosion protection (Gangopadhyay & Mahanwar, 2018; Koehler & Reinhard, 2014).

3.3.5 Compatibility with Other Materials

VCIs should be compatible with other materials present in the application environment, such as plastics, elastomers, and other packaging materials. Some VCIs may adversely affect certain materials, leading to discolouration, embrittlement, or loss of mechanical properties (Subramanian et al., 2000; Ansari et al., 2018). To avoid potential issues during storage or transportation, it is crucial to select VCIs that do not interfere with the integrity and functionality of the surrounding materials.

3.3.6 Regulatory Compliance and Environmental Impact

Regulatory compliance and environmental impacts are increasingly important factors in VCI selection. Some traditional VCIs, such as those containing secondary amines, chromates, or nitrites, are being phased out owing to their toxicity and environmental concerns (Patrick Lynch & James Henderson, 2004; Balejčíková et al., 2020). Eco-friendly VCIs derived from plant extracts or other bio-based materials are gaining popularity as sustainable alternatives (Asmara et al., 2017). When selecting VCIs, it is essential to consider local and international regulations regarding the use of certain chemicals and prioritise environmentally friendly options whenever possible.

3.3.7 Cost-Effectiveness

Another important consideration is the cost-effectiveness of the VCI. While the primary goal is to achieve optimal corrosion protection, the cost of VCI should be balanced against their performance and the value of the assets being protected. Factors such as the duration of protection, ease of application, and potential for reuse or recycling should be considered when evaluating the cost-effectiveness of a VCI solution (Papavinasam, 2000).

If corrosion protection is insufficient, it can lead to costly repairs and equipment failure, which can have severe consequences for industry and the environment. Therefore, it is crucial to carefully evaluate the criteria and understand the application's specific requirements before selecting a VCI to ensure the best possible corrosion protection for assets.

3.4 Mechanisms of Corrosion Inhibition

The corrosion inhibition mechanism involves complex interactions at the metal/environment interface, which is often dictated by the type of inhibitor used, nature of the metal and environmental conditions.

VCIs protect metals from corrosion through various mechanisms, including synergistic effects, mixed inhibition, alteration of the corrosive environment, film formation, passivation, and adsorption. Understanding these mechanisms is crucial for effectively selecting and applying VCIs to industrial settings.

3.4.1 Synergistic Effects and Mixed Inhibition

In many cases, corrosion inhibitors do not act through a single mechanism but rather through a combination of different mechanisms. This is particularly true for mixed inhibitors, which can influence anodic and cathodic reactions in the corrosion process (Chen et al., 2023). They are typically film-forming compounds that cause the formation of precipitates on the surface, indirectly blocking both the anodic and cathodic sites (Cui et al., 2023; De Souza Morais et al., 2023). For instance, benzohydrazide derivatives were found to be mixed-type inhibitors of carbon steel in HCl solution (Fouda et al., 2013).

Moreover, the efficiency of corrosion inhibition can often be enhanced by using a combination of different inhibitors that act synergistically. A synergistic effect occurs when the degree of inhibition in the presence of both inhibitors is higher than the sum of individual effects. This can be achieved by using inhibitors with complementary mechanisms of action or by combining inorganic and organic inhibitors (Papavinasam, 2011). These synergistic effects can be attributed to the formation of denser and more stable protective films on the metal surfaces (Hu et al., 2019). For example, a mixture of 5-methyl benzotriazole (MBT) and trisodium 2-hydroxypropane-1,2,3-tricarboxylate (TSPC) demonstrated enhanced inhibition efficiency of brass in aqueous environments (Gowrani et al., 2014).

3.4.2 Alteration of the Corrosive Environment

VCIs alter the corrosive environment primarily through pH modification and scavenging of aggressive species. By releasing alkaline compounds, VCIs alter the pH of the environment to more basic levels, significantly reducing the corrosion rate of metals, such as iron and steel. VCI also neutralises corrosive surrounding reagents, such as H_2O, SO_2, H_2S, and CO_2 (Gangopadhyay & Mahanwar, 2018; Saini & Kumar, 2014; Ansari et al., 2018). Certain VCIs, such as oxygen and chlorides, can scavenge aggressive species. VCIs react with dissolved oxygen, reducing their availability for oxidation. VCI can modify the environmental parameters of seawater, such as the pH, total hardness, and total alkalinity, to prevent metal corrosion through colloidal formation (Cheng et al., 2018).

These pH modifications, scavenging, and colloidal formation mechanisms create a less corrosive environment, enhancing the longevity of metal structures in industrial applications.

3.4.3 Film Formation and Passivation

The protection mechanism of VCIs involves a combination of passivation, adsorption, and precipitation.

- **Adsorption:** VCIs protect the metal surfaces through adsorption. This process involves VCI molecules either adsorbing in their molecular form or dissociating and then adsorbing onto a metal surface. The adsorbed VCI molecules form a thin monomolecular film that shields the metal from corrosive agents (Papavinasam, 2011).

- **Passivation:** Passivation is another key mechanism for corrosion inhibition by VCIs. This involves the formation of a protective oxide film on the metal surface, which acts as a barrier to prevent further corrosion. An example of passivation is the use of salts of weak carboxylic acids to protect mild steels from corrosion caused by dissolved oxygen in aerated solutions under nearly neutral conditions (Rammelt et al., 2008).
- **Precipitation Films:** These films form through the precipitation of insoluble compounds on the metal surface. They seal the defects in the oxide layer and provide additional protection. This method is particularly effective in environments with fluctuating humidity and temperatures (Roberge, 1999).

3.4.4 Adsorption Mechanism

Adsorption is a fundamental mechanism for corrosion inhibition by VCIs. Inhibitor molecules adsorb onto the metal surface through physical or chemical interactions, forming a protective barrier that prevents access to corrosive species (Subramanian et al., 2000). Physical adsorption occurs via electrostatic interactions between the oppositely charged metal surface and corrosion inhibitor components. The chemical adsorption of corrosion inhibitors on metal surfaces occurs via heteroatoms such as nitrogen, oxygen, sulphur, phosphorus, and π-electron systems in the inhibitor molecules. The adsorption behaviour of VCIs can be described using different isotherms, such as the Langmuir adsorption isotherm or the Temkin adsorption isotherm. These isotherms represent the relationship between the surface coverage of corrosion inhibitor species and their concentration in the solution (Fateh et al., 2020). The adsorption mechanism is influenced by factors such as the molecular structure of the inhibitor, the nature of the metal surface, temperature, and moisture content (Rammelt et al., 2011).

The corrosion inhibition mechanisms of VCIs are complex and multifaceted. These involve synergistic effects, mixed inhibition, alteration of the corrosive environment, film formation, passivation, and adsorption. Understanding these mechanisms is essential to develop and apply effective VCI systems in various industrial settings.

3.5 Principles of Vapour Phase Corrosion Protection

Vapour phase corrosion inhibitors (VCIs), also known as volatile corrosion inhibitors, are chemical compounds that protect metals from atmospheric corrosion by forming a protective molecular layer on the metal surface.

Metal Type	Inhibition Mechanism	References
Ferrous Metals	Adsorption of VCI molecules onto the metal surface, forming an adsorbed monolayer that covers imperfections in the oxide layer, reinforcing it and preventing penetration by corrosive agents. VCIs also act as pH buffers inside defect sites, limiting localised proton accumulation. In some cases, VCI molecules can chelate with Fe atoms, forming a complex film.	Zhang et al., 2006; Rammelt et al., 2011
Copper and Alloys	Formation of an adsorption layer or a complex polymeric film that reacts with copper and copper alloy ions on the surface, resisting oxidation and acting as a barrier to prevent corrosion.	Yi et al., 2018
Aluminium and Alloys	Adsorption onto the naturally formed oxide layer, preventing anodic dissolution and slowing the corrosion rate.	Semiletov, 2017; Altsybeeva et al., 2012
Zinc and Alloys	Formation of a hydrated oxide or hydroxide film in dry atmospheres. In high humidity and the presence of aggressive components, VCIs adsorb onto the surface, forming a protective film through chemical bonding.	Goncharova et al., 2019; Subramanian et al., 2000

Note. * This table summarises the specific inhibition mechanisms of VCIs for different metals, highlighting the adsorption and film formation processes that protect against corrosion.

Table 3-2: Specific Inhibition Mechanisms for Different Metals

The principles of vapour phase corrosion protection involve several steps: volatilisation, diffusion, adsorption, and the formation of a protective barrier film. These steps alter the corrosive environment and provide specific inhibition mechanisms tailored to different metal substrates.

3.5.1 Specific Inhibition Mechanisms for Different Metals

VCIs work with different metals through various specific inhibition mechanisms. Table 3-2 summarises these mechanisms for ferrous metals, copper and its alloys, aluminium and its alloys, and zinc and its alloys.

- **Ferrous Metals (Steel, Iron):** VCIs adsorb onto the metal surface and attach to the outer surface of a metal oxide through weak chemical bonding. This forms an adsorbed monolayer that covers imperfections in the oxide layer, reinforcing it and preventing penetration by corrosive agents, such as water and ions (Cl^- or SO_4^{2-}). VCIs also act as pH buffers inside defect sites, limiting localised proton accumulation, especially in alkaline environments. In some cases, VCI molecules can chelate with Fe ions forming a complex film (Zhang et al., 2006; Rammelt et al., 2011).
- **Copper and Copper Alloys (brass):** VCIs form an adsorption layer or a complex polymeric film that reacts with copper and copper alloy ions on the surface, resisting oxidation and acting as a barrier to prevent corrosion (Yi et al., 2018).
- **Aluminium and its alloys:** Aluminium naturally forms a surface oxide film. VCIs adsorb onto the oxide layer, preventing anodic dissolution and slowing the corrosion rate (Semiletov. ,2017; Altsybeeva et al., 2012).
- **Zinc and its alloys:** Zinc forms a hydrated oxide or hydroxide film in dry atmospheres but corrodes quickly in high humidity and in the presence of aggressive components. VCIs adsorb onto the surface, forming a protective film through chemical bonding (Goncharova et al., 2019; Subramanian et al., 2000).

3.5.2 Volatilization and Transport of Inhibitor Molecules

The principle of vapour phase corrosion protection involves several steps:

- **Volatilisation**: VCIs volatilise owing to their inherent volatility or through hydrolysis products. The required volatility typically ranges from 1.33 to 1.33 x

10^{-5} Pa at room temperature. Factors such as temperature, humidity, and air currents influence the volatility (Ansari et al., 2018).

- **Diffusion**: In an enclosed area, the VCI vapour fills the entire volume by diffusion. The transportation of VCI molecules to the metal surface is determined by gas permeability, which is the product of the vapour pressure and diffusion coefficient (Pieterse et al., 2006). VCI molecules are adsorbed onto the metal surface, forming a protective film. The diffusability of the inhibitor vapour determines the protection radius and passivation time (Andreev & Kuznetsov, 2005).

3.5.3 Adsorption of Inhibitor Molecules on the Metal Surface

The adsorption of VCI molecules onto metal surfaces is influenced by several factors (Roberge, 1999).

- **Surface Charge on the Metal**: The electric charge on the metal surface determines the adsorption of the ionic or dipolar species.
- **Functional Group and Structure of the Inhibitor**: Inhibitors with loosely bound electrons form stronger coordinate bonds with metals, leading to greater adsorption.
- **Interaction with Water Molecules**: VCI molecules often displace the adsorbed water molecules from the metal surface.
- **Interaction of Adsorbed Inhibitor Species**: The behaviour of adsorbed inhibitor molecules can be affected by their interactions with each other.
- **Reaction of Adsorbed Inhibitors**: In some cases, the adsorbed inhibitor undergoes a reaction to form a new substance that can also inhibit corrosion.

3.5.4 Formation of a Protective Barrier Film

The effectiveness of VCIs depends on the formation of a protective barrier film on the metal surface. This involves:

1. **Transport of VCI Molecules**: VCI molecules volatilise and are transported to the metal surface via diffusion and natural convection.
2. **Adsorption and Film Formation: V**CI molecules adsorb onto the metal surface, forming a thin protective film. The types of protective films include

passivation films, adsorption films, and precipitation films (Roberge, 1999; Bastidas et al., 1990)

3.5.5 Factors Influencing Film Formation

Several factors influence the formation and effectiveness of protective barrier films (Roberge, 1999; Skinner, 1993; Bastidas et al., 1990).

- **Vapour Pressure of the VCI**: VCIs with suitable vapour pressures can effectively volatilise and transport to the metal surface.
- **Environmental Conditions**: Moisture enhances the adsorption of VCI molecules, and temperature affects the volatility and adsorption kinetics.
- **Chemical Nature of VCIs**: The structure of VCIs, including their functional groups, determines their adsorption behaviour and the stability of the formed film.

In summary, VCIs protect metals through volatilisation, diffusion, surface adsorption, and formation of protective films. These processes are influenced by the chemical nature of VCIs, environmental conditions, and specific metal substrates. Understanding these mechanisms is crucial for optimising the use of VCIs in various industrial applications.

3.6 Factors Influencing Effectiveness

Several key factors influence the effectiveness of VCIs in protecting metals from corrosion. Understanding these factors is crucial for selecting the appropriate VCI and optimising its performance for various industrial applications.

3.6.1 Types of VCI and Application Methods.

The effectiveness of VCIs is highly dependent on the correct use of specific types and application methods. VCIs are available in various forms including emitters, pellets, powders, films, paints, aerosols, and aqueous and solvent solutions. Each form is tailored to specific applications based on its chemical composition, which can be organic or inorganic. They can be applied through impregnation on paper or plastics, enclosure in pouches and sachets or added to greases, coatings and paints to form a protective barrier against corrosion agents.

For instance, VCI foam emitters are ideal for protecting electrical and electronic instruments within enclosures, whereas VCI coatings are effective in safeguarding the external surfaces of equipment stored outdoors. VCI powders are particularly useful for hydro-testing and long-term storage on sealed internal surfaces, as demonstrated by their successful use in offshore pipeline maintenance by a major oil and gas company (Figure 3-3).

Figure 3-3: Use of VCI powders in offshore pipeline maintenance for hydro-testing and long-term storage.

Additionally, VCI paper and plastic are effective in preventing the corrosion of spare parts during shipping and storage, ensuring that these parts remain pristine until use (Figure 3-4). VCI greases and oils derived from petroleum- or vegetable-based oils offer corrosion protection and lubrication for metallic surfaces and are suitable for short- and long-term idle periods (Cheng & Valdez Salas, 2021).

Figure 3-4: VCI plastic used to prevent corrosion of spare parts during shipping and storage.

Industries can optimise their corrosion protection strategies by selecting the appropriate VCI form and application method, reducing maintenance and replacement costs.

3.6.2 Metal Type and Surface Conditions

The effectiveness of VCIs varies significantly depending on the type of metal being protected. An effective inhibitor of one metal may either stimulate corrosion or be ineffective against other metals and alloys (Singh & Banerjee, 1984).

This variation is due to the different surface properties of metals, such as surface energy and roughness, which influence the adsorption and distribution of VCI molecules. For example, VCIs that are effective in protecting steel may not offer the same level of protection for copper or aluminium alloys. Therefore, selecting a VCI that is compatible with a specific metal type is crucial to ensure optimal corrosion protection (Andreev & Kuznetsov, 2005).

Moreover, contaminants such as fingerprints, dirt, oil, and existing corrosion products on the metal surface can impede the adsorption and film formation of VCI molecules, thereby reducing their effectiveness. Consequently, VCIs are the most effective when applied to clean metal surfaces (Lyublinski et al., 2015).

3.6.3 Impact of Environmental Conditions and Concentration of VCIs

The effectiveness of VCIs is significantly influenced by environmental factors such as temperature, humidity, pH, and the presence of contaminants such as hydrogen sulphide (H_2S), sulphur dioxide (SO_2), and carbon dioxide (CO_2). As shown in Figure 3-5, when the relative humidity is below 50%, the corrosion rate is generally very low. On the other hand, RH values higher than 80%, permits the formation of wet layers on the metal surface, which is under time of wetness conditions (TOW).

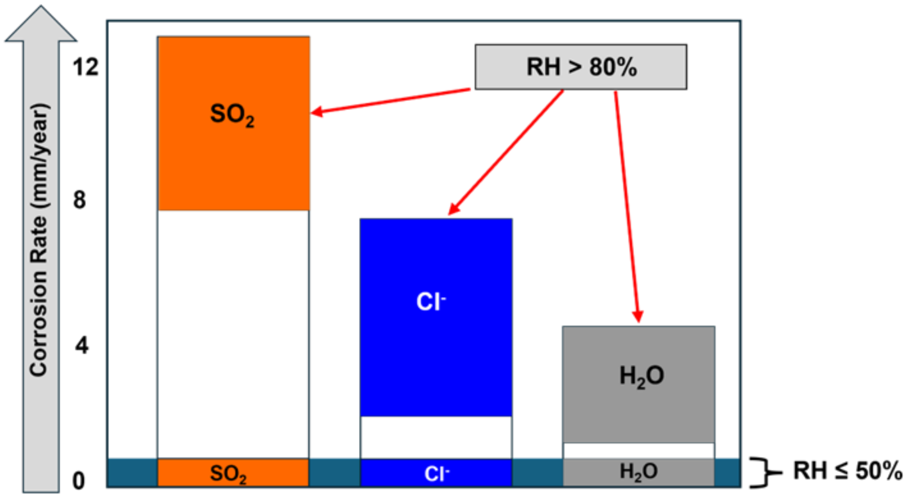


Figure 3-5: Corrosion rate depends on environmental compositions

Note. At relative humidity >80%, contaminants increase the corrosion rate. From "Application experience and new approaches for volatile corrosion inhibitors" by E. Lyublinski, P. Lynch, I. Roytman, & T. Yakubovskaya, 2015, International Journal of Corrosion and Scale Inhibition, 4(2), 176–192. Reprinted from Results section, Figure 1 (https://doi.org/10.17675/2305-6894-2015-4-2-176-192).

High temperatures can accelerate the evaporation of VCIs, reducing their effectiveness over time. Additionally, temperature increases elevate the kinetic energy of VCI molecules, enabling more molecules to enter the vapour phase and increasing vapour pressure, as explained by the Clausius-Clapeyron equation (Perry & Green, 2008).

The Clausius-Clapeyron equation in its differential form is

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

Where:

- $\frac{dP}{dT}$ = is the rate of change of pressure P with respect to temperature T
- *L* is the latent heat of the phase transition (positive for vaporisation and sublimation),
- *T* is the absolute temperature,
- ΔV is the change in volume during phase transition.

This increased vapour pressure leads to more vapour molecules dissolving into the liquid, as described by Henry's law for dilute solutions (Lide, 1985; McConnell, 2008).

Henry's Law states:

$C = k_H \cdot P$

Where:

- C is the concentration of gas in the liquid.
- k_H is Henry's law constant, which depends on the gas-liquid pair and temperature.
- P is the partial pressure of gas above the liquid.

Thus, higher temperatures can enhance the concentration of VCIs in the vapour phase within an enclosed area.

Humidity plays a crucial role in the adsorption of VCI molecules on metal surfaces, generally enhancing their protective effect at higher levels. However, excessive humidity, particularly beyond the critical relative humidity of 60%, can lead to condensation and the formation of a corrosive electrolyte, accelerating corrosion.

Contaminants, such as chlorides or sulphur dioxide, can interfere with the adsorption of VCI molecules and reduce their efficacy (Vigdorovich et al., 2018; McConnell, 2008).

Furthermore, the concentration of VCIs is pivotal for their effectiveness. Insufficient concentrations may not provide adequate protection, whereas excessive concentrations can lead to wastage and potential compatibility issues with the metal or other materials in contact. In some cases, low inhibitor concentrations can increase the corrosion rate or cause dangerous pitting corrosion (Lyublinski et al., 2015).

Proper control of these factors is crucial to ensure effective corrosion protection and minimise the risk of corrosion in enclosed environments.

3.6.4 Inspection and Maintenance

Inspection and maintenance during equipment or plant protection periods involve periodic examinations and necessary repairs. Regular inspection of VCI-protected equipment is essential to detect any changes in the applied protection, such as damaged VCI packaging materials, leaks, wet insulation, or damaged VCI coatings, which may indicate ongoing corrosion. The performance of VCIs relies on maintaining a sufficient concentration of inhibitor vapour within the packaging or enclosure. Any leaks or breaches can allow VCI vapours to escape, reducing the protection level over time. Therefore, regular inspection and maintenance of packaging integrity are necessary to maintain the effectiveness of VCI systems.

Most inspections involve visual examinations to detect deterioration. However, non-destructive evaluation techniques, such as ultrasonic thickness measurements, can augment visual inspection.

The equipment sealed and protected with VCI should be examined monthly to ensure that the sealing is intact. If any signs of moisture are found or the equipment is opened for inspection, the protection system should be replaced, as required. Additionally, areas draped over electrical panels, switchgear, and control consoles should be checked monthly for collected moisture. Moisture-laden sheets should be removed, cabinets should be opened to promote drying, and protection should be reapplied as necessary.

VCI-coated steel should be inspected monthly in warm climates and biannually in temperate climates. Any coating breakthrough should be repaired, typically by hand cleaning and paint reapplication.

All inspection and maintenance activities should be documented to create a comprehensive history of work and repair.

In conclusion, the effectiveness of VCIs depends on various factors, such as VCI type, environmental conditions, metal type, application method, concentration, and monitoring. Optimising these factors is crucial for achieving reliable corrosion protection for industrial applications (Cheng & Valdez Salas, 2021)

Chapter 4

4. EXPERIMENTATION, TESTING, APPLICATION, AND PERFORMANCE OF THE DEVELOPED VCI'S

4.1 Types of VCI Formulations

Volatile corrosion inhibitors (VCIs) represent a significant advancement in corrosion-protection technology. These specialised compounds are designed to protect metal surfaces from atmospheric corrosion using various delivery methods and formulations. Each type of VCI formulation offers unique advantages for different corrosion protection scenarios, from long-term storage to the shipping and handling of metal parts and equipment. The main categories of VCI formulations are as follows:

1. VCI Emitters: These devices release corrosion-inhibiting vapours into enclosed spaces. They typically consist of VCI compounds encapsulated in permeable containers, such as flexible polyurethane foam
2. VCI Films: Specialised packaging materials that incorporate corrosion inhibitors directly into polymer films. These are produced by compounding amino-carboxylate corrosion inhibitor (ACCI) masterbatch powder with polyethylene resin
3. VCI Papers: Kraft paper impregnated or coated with volatile corrosion inhibitors. Two main production methods are impregnation and flexographic printing
4. VCI Powders: Dry formulations of corrosion-inhibiting compounds that can be dispersed in enclosed spaces or incorporated into other materials
5. VCI Coatings: Liquid or semi-liquid formulations designed to be applied directly to metal surfaces. These often include metal sulfonates for barrier protection and water displacement, along with volatile corrosion inhibitors for vapour phase protection

Each of these formulation types plays a crucial role in modern corrosion-prevention strategies, offering tailored solutions for various industrial applications and environmental conditions. The choice of VCI type depends on the specific protection requirements, the metals being safeguarded, and the challenges of the storage or transportation environment.

4.1.1 VCI Emitters Formulation

Vapour corrosion inhibitor (VCI) emitters are crucial in modern corrosion prevention strategies. These devices are designed to release corrosion-inhibiting vapours into enclosed spaces, protecting the metal components without direct contact. VCI emitters are particularly valuable in industries where traditional corrosion prevention methods may be impractical or insufficient, such as storage and shipping of sensitive equipment, automotive parts, and military hardware (Cheng et al., 2018). The VCI emitters (Figure 4-1: VCI emitters) were designed to release corrosion-inhibiting vapours into the enclosed areas.

Figure 4-1: VCI emitters

The production and formulation of VCI emitters involve a series of meticulous steps, each contributing to the unique properties and effectiveness of these devices.

4.1.1.1 Encapsulation

Encapsulation involves enclosing VCI powder in a permeable container, such as flexible polyurethane foam, an open-cell isocyanate-derived polymer. This foam is highly resistant to chemical and physical degradation in hostile environments and has a large available volume to hold multiple corrosion inhibitors with different vapour pressures. These foams are compatible with many chemicals and exhibit stable physical properties including compression, deflection, tensile strength, tear resistance, and elongation. They also provide excellent stability and resistance under various environmental conditions, whether exposed to moisture or dry conditions, ensuring consistent performance. The most critical attribute of these foams is their permeability, which is measured by the airflow. With a minimum airflow rate of 2.0 cubic feet per minute (cfm), the open-cell structure allowed for the controlled release of VCI vapours.

The foam should have a medium density ranging from 20 to 27 kg/m³ (Polyurethane Foam Association (PFA), 2016).

Compared to other potential encapsulating materials such as closed-cell foams or solid polymers, flexible polyurethane foam offers a superior balance of permeability and structural integrity, making it ideal for VCI emitter applications.

4.1.1.2 Impregnation

The open-cell isocyanate-derived polymer foam was impregnated with the volatile corrosion inhibitor cyclohexylamine benzoate. The inhibitor, in powdered form, was first dissolved in solvent and then introduced into the foam. After impregnation, the solvent evaporated, leaving cyclohexylamine benzoate uniformly distributed within the foam. The impregnation of the foam carrier with a volatile corrosion inhibitor (VCI) facilitated the efficient distribution and deposition of the inhibitor throughout the numerous cavities of the foam, thereby increasing the effective surface area. VCI, which is retained within these extensive cavities, achieves and sustains an effective vapour pressure level more rapidly and over a longer duration. This unique combination of foam carrier and impregnated VCI ensures that the surfaces of the inhibitor remain cleaner, with each cavity maintaining a slight positive pressure. Consequently, this enhanced the efficiency and effectiveness of the foam carrier in hostile environments, improving its overall performance.

4.1.1.3 Selecting VCI Inhibitors Based on Vapour Pressure

To achieve optimal corrosion protection in various environments with different temperature and humidity levels, VCI inhibitors with varying vapour pressures were utilised:

1. VCI inhibitors with a vapour pressure of less than 10^{-4} mm Hg at 20°C are used in environments where a slower, more sustained release of the inhibitor is needed. Cyclohexylamine Chromate, Cyclohexylamine M-Mononitro-Benzoate, and Dicyclohexylamine Chromate are classified as low vapour pressure inhibitors and are used in vapour-phase corrosion protection. Their relatively low vapour pressure allows for a slower and more sustained release of inhibiting compounds into the environment.

2. VCI inhibitors with vapour pressure between 10^{-4} mm Hg and 10^{-3} mm Hg at 20°C are employed in conditions requiring a moderate rate of inhibitor release. Cyclohexylamine Benzoate, Diethanolamine Benzoate, and Benzotriazole are classified as intermediate vapour pressure inhibitors because their vapour pressure falls within the specified range at 20°C. They are used in corrosion protection applications, where a moderate rate of inhibitor release is desired.
3. VCI inhibitors with a vapour pressure above 10^{-3} mm Hg at 20°C were applied in situations demanding rapid inhibitor dispersion. Monoethanolamine Benzoate and Tolyltriazole are classified as high vapour pressure inhibitors due to their vapour pressure exceeding 10^{-3} mm Hg at 20°C. They are typically used in corrosion protection applications where a rapid rate of inhibitor release is required.

The following Table 4-1 summarises the categories of VCI inhibitors based on their vapour pressure, along with examples of compounds and typical applications.

Table 4-1: VCI Inhibitor Categories Table

Category	Vapour Pressure at 20°C	Example Compounds	Typical Applications/ Conditions
Low Vapour Pressure	Less than 10^{-4} mm Hg	Cyclohexylamine Chromate, Cyclohexylamine M-Mononitro-Benzoate, Dicyclohexylamine Chromate	Long-term storage, high-temperature environments, sealed containers
Intermediate Vapour Pressure	10^{-4} mm Hg to 10^{-3} mm Hg	Cyclohexylamine Benzoate, Diethanolamine Benzoate, Benzotriazole	Short-term protection, low-temperature environments, frequently opened enclosures
High Vapour Pressure	Above 10^{-3} mm Hg	Monoethanolamine Benzoate, Tolyltriazole	Short-term protection, low-temperature environments, and frequently opened enclosures.

4.1.1.4 Conclusion

The selection of VCI inhibitors based on their vapour pressure allows for tailored corrosion protection under various environmental conditions. Low vapour pressure inhibitors offer sustained protection, intermediate vapour pressure inhibitors provide balanced release, and high vapour pressure inhibitors ensure rapid dispersion. This range of options enables effective corrosion prevention strategies that are suited to diverse industrial and storage needs. When properly formulated and applied under appropriate environmental conditions, VCI emitters can provide protection for periods of up to two years, making them a versatile and long-lasting solution for corrosion prevention.

4.1.2 VCI Film Formulation

Volatile corrosion inhibitor (VCI) film formulations are specialised packaging materials designed to prevent corrosion of metal surfaces through the release of corrosion-inhibiting compounds. These formulations typically involve a two-stage process: first, converting an Amino-Carboxylate Corrosion Inhibitor (ACCI) masterbatch powder into a VCI masterbatch polyethylene resin and then extruding this resin into various types of VCI films, such as standard polyethylene, shrink, and stretch films.

4.1.2.1 VCI Film Production: From Masterbatch Powder to Final Film

The production of the ((VCI) films began with the amino-carboxylate corrosion inhibitor (ACCI) Vappro VBCI MBP 3000 masterbatch powder. This masterbatch powder is crucial for ensuring the effectiveness of the final VCI films, including shrink films and stretch films. The primary objective of utilising the ACCI masterbatch powder is to eliminate the formation of carcinogenic N-nitrosamines using nitrite-free raw materials, thus ensuring a safer and more environmentally friendly product (Cheng & Salas, 2020).

4.1.2.2 Stage 1: Conversion of Amino-Carboxylate Corrosion Inhibitor (ACCI) Masterbatch Powder to VCI Masterbatch Polyethylene Resin

The initial stage of the production process involves compounding, which is the process of melting-blending plastics with other additives, such as Amino-Carboxylate Corrosion Inhibitor (ACCI) Masterbatch Powder, into VCI Masterbatch Polyethylene

(PE) resin. This process was performed during the molten stage to obtain a homogenous blend. Compounding changes the physical characteristics of plastics. Compounding is generally performed using a twin-screw extruder (Patel and Shin, 2011).

4.1.2.2.1 Selection of Raw Materials

The production process begins with the careful selection of raw materials. The required primary components include the following.

- **Amino-Carboxylate Corrosion Inhibitor (ACCI) masterbatch powder**: This core additive provides corrosion-inhibiting properties at 20% usage.
- **Polyethylene (PE) Resin**: This is the base polymer matrix.
- **Pigments**: Various pigments are added, depending on the desired colour of the final film.
- **Other Additives**: These additives may include stabilisers, processing aids, and other performance enhancers.

4.1.2.2.2 Mixing

The compounding process begins by carefully mixing the amino-carboxylate corrosion inhibitor (ACCI) masterbatch powder with polyethylene resin and pigments to create a masterbatch that can be readily used in the extrusion processes. Mixing the ingredients into the polymer matrix should be uniform and homogenised, including dispersive and distributive components (Figure 4-2). This ensured that the additives no longer formed agglomerates and reached their primary particle size.

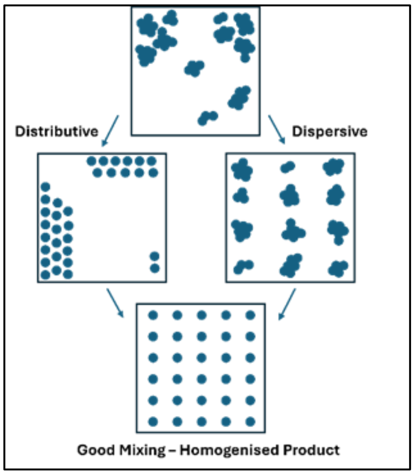


Figure 4-2: Mixing process

4.1.2.2.3 Compounding

The mixed raw materials were fed into a Twin-Screw Compounding Extruder (Figure 4-3). The compounding process involves the following steps.

1. **Feeding**: The mixed components were fed into a twin-screw extruder for melt compounding.
2. **Melting and Mixing**: The materials were subjected to controlled heating inside the extruder at approximately 115–120°C. The Low-Density Polyethylene (LDPE) resin melts and forms a homogeneous blend with the amino-carboxylate corrosion inhibitor (ACCI) masterbatch powder and other additives. This was achieved through mechanical shear and mixing provided by the rotating screws in the extruder.
3. **Extrusion:** The molten mixture was forced through a die to form long strands of the master batch.

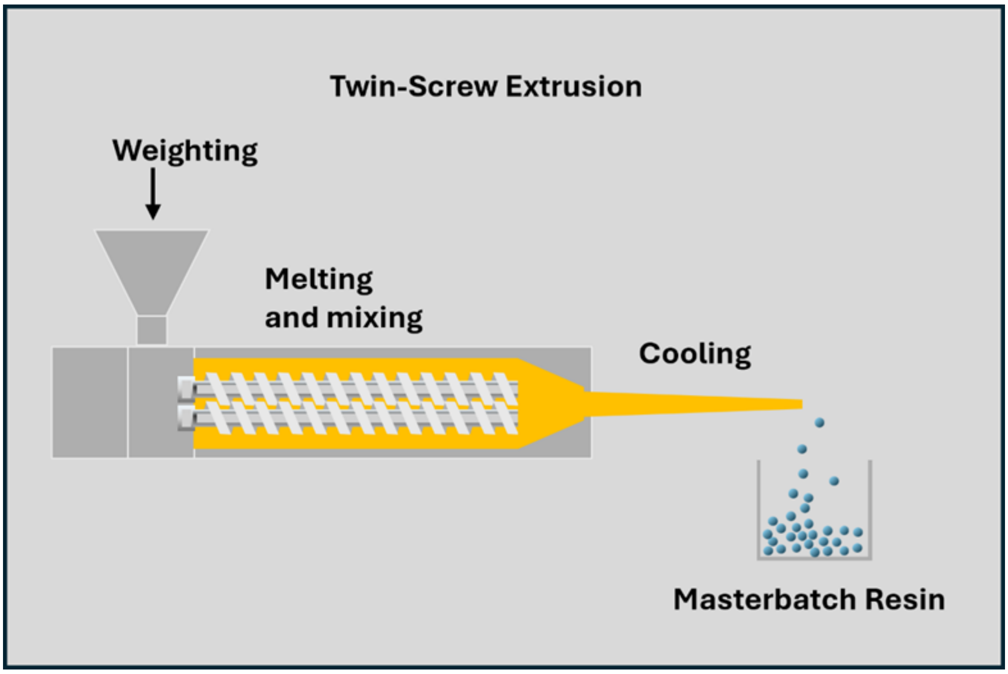


Figure 4-3: Twin-Screw compounding extruder

4.1.2.2.4 Cooling and Pelletizing

Once the molten masterbatch exits the extruder, it undergoes the following steps.

1. **Cooling**: The extruded strands were solidified using water baths or air-cooling systems.

2. **Pelletising**: Cooled strands were cut into uniform pellets and beads. This is typically performed using a pelletiser that chops the strands into small, manageable pieces.

This transformation from masterbatch powder to masterbatch resin ensures that the resin contains the necessary additives to provide excellent corrosion inhibition properties without the harmful side effects of the traditional nitrite-based products.

4.1.2.3 Stage 2: Conversion of VCI Masterbatch Polyethylene Resin to VCI Films

Once the amino-carboxylate corrosion inhibitor (ACCI) masterbatch powder was compounded into the masterbatch resin, it was extruded into various VCI film forms. These films included standard VCI polyethylene film, shrink film, and stretch films, each serving different purposes in corrosion protection and packaging.

4.1.2.3.1 Extrusion Process

The extrusion process is a critical phase, in which the compounded masterbatch resin melts and forms thin films. The preparation phase involved feeding the masterbatch resin into the extrusion machine. The resin was heated inside the machine until it reached a molten state to ensure thorough mixing. This molten resin was then extruded through a blown film extrusion process (see Figure *4-4*).

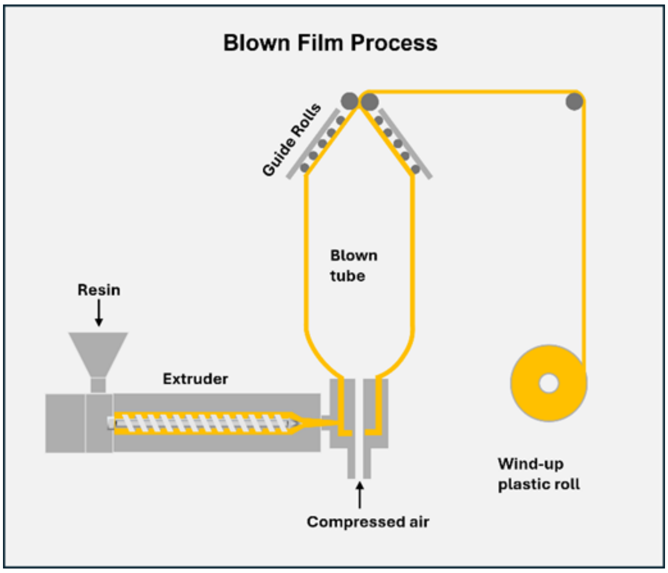


Figure 4-4: Blown film process

4.1.2.3.2 Blown Film Extrusion Process: In blown film extrusion process, the molten resin is extruded through a circular die to form a thin-walled tube. This tube was then inflated with air to create a bubble, which was continuously drawn upward while being cooled by the air rings. The bubble collapsed into a flat film through the nip rollers and wound onto the rolls. This process allows the production of films with uniform thickness and excellent mechanical properties, making it ideal for creating VCI films.

4.1.2.3.3 The types of VCI films produced were as follows:

- **VCI Polyethylene Film**: This film is extruded for general protective packaging purposes, providing a barrier against the corrosion of various metal goods.
- **VCI Shrink Film**: Designed to shrink tightly overheated objects, this film offers a secure and snug fit, ideal for protecting items during storage and transport.
- **VCI Stretch Film**: Commonly used for wrapping and securing items, stretch film provides additional mechanical strength and stability, making it suitable for protecting equipment and machinery during shipment.

4.1.2.4 Testing and Quality Assurance

VCI films produced using this method were subjected to rigorous testing to ensure their effectiveness. One of the primary tests used was the German TL 8135-002 method, which assesses the vapour-corrosion inhibition properties of the films. This test involved exposing the metal samples to the VCI film and evaluating the level of corrosion protection provided under controlled conditions. Films produced with Vappro VBCI MBP 3000 masterbatch powder have passed this test, demonstrating their ability to protect ferrous and non-ferrous metals from corrosion effectively.

4.1.2.5 Compliance and Environmental Sustainability

These VCI films effectively inhibit corrosion and conform to international standards, such as the US MIL-PRF-22019 E TYPE I and NATO Stock Number 6850-32-086-9421. This compliance indicates their reliability and quality, making them suitable for various industrial applications.

Furthermore, the production of VCI films using Vappro VBCI MBP 3000 masterbatch powder was aligned with environmental sustainability goals. The production process minimises the ecological footprint of the final product by eliminating harmful nitrites and utilising environmentally friendly materials. This commitment to sustainability addresses regulatory requirements and meets the increasing demands of consumers and industries for safer and more eco-friendly products.

4.1.2.6 Conclusion

In conclusion, producing VCI films using the amino-carboxylate corrosion inhibitor (ACCI) Vappro VBCI MBP 3000 masterbatch powder is a comprehensive process that ensures high-quality, safe, and effective corrosion-inhibiting films. By eliminating harmful nitrites and utilising environmentally friendly materials, VCI films offer excellent protection for metal goods, meet stringent international standards, and address the growing need for safer industrial products. The meticulous process of compounding and extrusion coupled with rigorous testing and quality control guarantees that the final films provide reliable and long-lasting corrosion protection, making them indispensable in various industrial applications.

4.1.3 VCI Paper Formulation

VCI paper can be produced using two methods: impregnation and flexographic printing. Both methods aim to incorporate volatile corrosion inhibitor (VCI) compounds into kraft paper; however, their application processes differ.

The impregnation method involved saturating the kraft paper with VCI solution. The optimal formulation consisted of 20% amino-carboxylate corrosion inhibitor (ACCI), which provided effective, non-toxic, and environment-friendly long-term corrosion inhibition. This VCI solution is typically dissolved in water or alcohol prior to application.

Kraft paper, which is the base paper, is commonly used because of its excellent mechanical properties and ability to absorb VCI compounds (Valdez et al., 2018).

Kraft paper production involves several key steps to transform wood materials, typically eucalyptus or pine, into strong and durable paper. The process begins with kraft pulping, in which wood chips are cooked in a digester containing a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), known as white liquor. This dissolves the lignin, which binds the cellulose fibres together, resulting in a pulp consisting primarily of cellulose fibres.

After kraft pulping, the pulp was washed to remove lignin, impurities, and any uncooked wood chips or contaminants. The pulp then undergoes mechanical treatment during the refining process to develop the desired paper properties such as strength and smoothness.

Once the pulp is refined, it is spread on a moving screen to form a continuous sheet of paper as water drains away. This sheet was then pressed to remove excess water and dried using steam-heated cylinders, resulting in the final kraft paper product (Bajpai, 2018).

4.1.3.1 Impregnation

VCI paper is produced by impregnating kraft paper with volatile corrosion inhibitor (VCI) compounds. VCI compounds are dissolved in a suitable solvent such as water or alcohol to create a solution. The optimal formulation of the VCI paper consists of 20% amino-carboxylate Corrosion Inhibitor (ACCI), which provides a non-toxic and environment-friendly solution for long-term corrosion inhibition and contributes to a greener production process (Cheng et al., 2023).

The VCI solution was then carefully impregnated into the paper using various methods such as dipping, spraying, or coating. This process ensures that the VCI compounds are evenly distributed throughout the paper, thereby maximising their corrosion-inhibiting properties. Three impregnation techniques were used.

- **Soaking:** The paper was immersed in a VCI solution bath for a specified duration of time. The paper absorbed the solution and the VCI compounds were distributed throughout the paper fibres.
- **Spraying:** A pressurised system sprays the VCI solution onto the paper surface. This method allows for a more controlled solution application, and can be used for continuous production.
- **Coating:** A coating machine, such as a rod or blade coater, uniformly applies the VCI solution to paper. This method provided a uniform coating of the VCI solution on the surface of the paper.

The goal was to ensure a uniform distribution of VCI compounds throughout the paper substrate as shown in Figure 4-5.

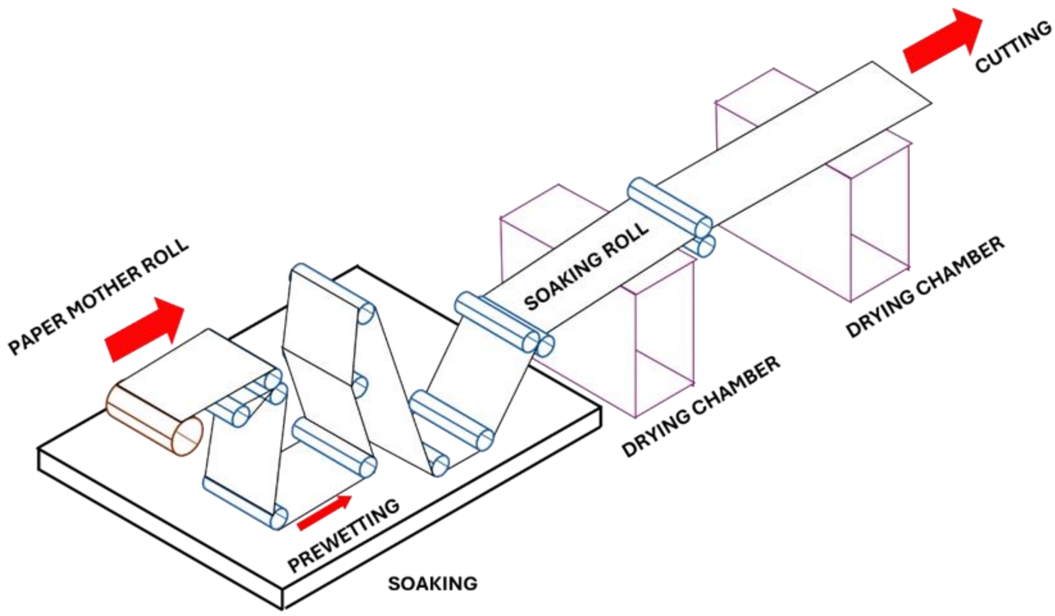


Figure 4-5: The impregnation process involved soaking the paper in a VCI solution bath

After impregnation, the paper was dried to remove the solvent and fix the VCI compounds within the paper fibres. This is typically performed using hot air or infrared lamps at temperatures ranging from 80 to 120°C for 1–5 min, depending on the paper thickness and VCI concentration.

Once dried, the VCI paper was cut to the desired size and packaged in airtight containers or bags to prevent premature loss of VCI compounds. Appropriate packaging is crucial for maintaining the effectiveness of the VCI paper during storage and transportation.

In summary, the production of VCI paper involves carefully selecting the paper substrate, preparing the VCI solution, impregnating the paper with the solution, drying, and proper packaging to ensure the optimal corrosion protection of metal parts during storage and transportation.

4.1.3.2 Flexographic Printing

Flexographic printing, also known as flexo printing, is a fast rotary printing method that utilises flexible relief plates to transfer ink onto various substrates such as paper, cardboard, and plastic films. VCI paper can be manufactured using flexo printing by incorporating a 20% amino-carboxylate corrosion inhibitor (ACCI) into fast-drying ink for flexo printing. This method allows for more precise control over VCI distribution and can be integrated into existing printing lines. Figure 4.6 illustrates the flexographic printing process, highlighting key components such as the anilox roller and flexible printing plates.

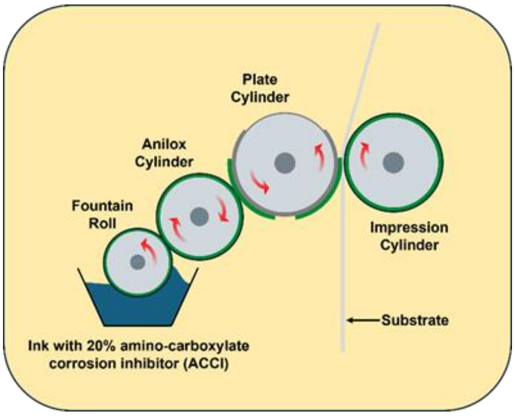


Figure 4-6: Flexographic printing

The key characteristics of flexo-printing are as follows.

- **Flexible printing plates**: Flexo printing uses flexible photopolymer plates with raised images of the design. The plates were mounted on rotating cylinders during printing.
- **Fast-drying inks**: Flexo printing typically employs fast-drying, low-viscosity inks that are water-based, solvent-based, or UV-curable. These inks allow high-speed printing and rapid drying, making Flexo suitable for high-volume production.
- **Anilox roller**: The anilox roller is a ceramic-coated cylinder with millions of tiny cells that controls the amount of ink transferred to the printing plate.
- **Substrate versatility**: Flexo printing can handle various substrates, including various types of paper, cardboard, and plastic films, making it suitable for diverse packaging applications.
- **High-speed production**: Flexo presses can operate at high speeds, making the process cost-effective for large print runs and high-volume production.

Flexo-printing is a viable and cost-effective method for producing VCI paper. It can handle suitable paper substrates, incorporate VCI compounds into the ink, and achieve high-volume production.

4.1.4 VCI Powder Formulations

4.1.4.1 Introduction

VCI technology, which has evolved significantly since its inception in the 1940s (Bastidas et al., 2005), initially relied on toxic or environmentally harmful compounds. However, the growing emphasis on sustainability has driven research towards eco-friendly alternatives. This chapter focuses on VCI powders, which represent a sophisticated approach for corrosion inhibition by combining multiple active ingredients in a comprehensive and sustainable protective system. This study aimed to analyse the composition and mechanisms of action of current VCI powder formulations, evaluate the sustainability profile of VCI components, and propose potential improvements for more environmentally friendly VCI powder formulations.

4.1.4.2 Typical VCI Powder Composition

A representative VCI powder formulation often includes the following components. (See Table 4-2)

Table 4-2: Typical composition and functions of VCI powder formulations

Component	Typical Percentage Range	Primary Function
Amine benzoate	10–20%	Vapour phase inhibitions
Sodium benzoate	30–40%	Anodic inhibition, pH buffering
Molybdates	30–40%	Anodic inhibition, synergistic effects
Azole derivative	5–10%	Film formation on non-ferrous metals
Chelating agent	2–5%	Metal ion sequestration
Alkali metal silicate	2–5%	Anodic inhibition, synergistic effects
Alkali metal phosphate	2–5%	Anodic inhibition, pH buffering

The precise ratios may vary depending on the specific application and the manufacturer's preferences. This composition provides a framework for understanding the multifaceted approach to corrosion inhibition in VCI powder.

4.1.4.3 Functional Analysis of VCI Components

4.1.4.3.1 Vapour Phase Inhibition

Amine benzoates such as Monoethanolamine benzoate and Cyclohexyl-ammonium Benzoate effectively inhibit vapour-phase corrosion (Saji, 2020; Andreev & Kuznetsov, 2012; Rammelt et al., 2009).

- These compounds are highly volatile, allowing them to reach and protect areas without direct contact with VCI powder.
- They adsorb onto metal surfaces, forming protective films that act as barriers against corrosive species.
- The alkaline nature of these amines contributed to the overall pH regulation of the system.

In addition to amine benzoate, the combination of sodium benzoate and sodium molybdate creates a vapour corrosion inhibitor (VCI) that provides comprehensive protection under various atmospheric conditions (Wang et al., 2020).

4.1.4.3.2 pH Regulation and Alkaline Environment Formation

Several components of VCI powder formulations contribute to pH regulation and create an alkaline environment, which is crucial for corrosion resistance.

- **Alkali Metal Phosphates**:
  - Primary function: pH buffering and anodic inhibition
  - Mechanism: Maintaining and stabilising alkaline conditions (To et al., 1997).
  - Secondary effects: Form protective films on metal surfaces, particularly at anodic sites
- **Alkali Metal Silicates**:
  - Primary function: Anodic inhibition and synergistic effects
  - Mechanism: Reinforces the alkaline environment created by phosphates (Lahodny-Šarc & Kaštelan, 1981; Anaee, 2013).
  - Secondary effects: Form protective layers on metal surfaces, particularly effective on ferrous metals

The combined action of these components ensures a stable alkaline environment, which significantly reduces the metal dissolution rate and promotes the formation of protective passive layers.

4.1.4.3.3 Anodic Inhibition and Film Formation

Several VCI components act as anodic inhibitors, forming protective films on the metal surfaces.

- **Alkali Metal Phosphates**:
  - Form a protective film on metal surfaces, particularly at anodic sites
  - Potent anodic inhibitors (Mohamed et al., 2022).
- **Alkali Metal Silicates**:
  - Form a protective layer on metal surfaces, particularly effective on ferrous metals
  - Acts act as barriers against corrosive species (Asrar et al., 1998; Scheetz et al., 1997).
- **Azole Derivatives**:
  - Protect copper and its alloys through chemisorption
  - Form thin protective films
  - Can act as anodic and cathodic inhibitors (Finšgar & Milošev, 2010).
  - Examples: Benzotriazole (BT), tolyl triazole (TT)
- **Sodium Benzoate**
  - Acts as an anodic inhibitor that forms protective films on metal surfaces (Subramanian et al., 2000; Al-Mashhadani et al., 2020).
  - Works synergistically with other inhibitors, particularly azole derivatives (Hosseini et al., 2003)
  - Also, contact inhibition when in direct contact with metal surfaces (Al-Mashhadani et al., 2020).
- **Molybdates**
  - Act as anodic inhibitors, forming a protective film on the metal surfaces.
  - Particularly effective in preventing pitting corrosion in various metals, including steel and aluminum alloys (Lopez-Garrity & Frankel, 2013)
  - Contribute to forming a passive layer on the metal surfaces (McGlone, 1984).
  - Remain effective over a wide pH range (Vukasovich & Farr, 1986)

4.1.4.3.4 Metal Ion Chelation

Chelating agents such as ethylenediaminetetraacetic acid (EDTA) salts have specific functions.

- Anodic Inhibition: EDTA acts as an anodic inhibitor by creating a protective film on the metal surfaces. EDTA binds to the metal ions in the solution, forming a Na-EDTA/inhibitor complex on the surface of mild steel, which reduces the metal dissolution. Na-EDTA is an effective corrosion inhibitor for mild steel. The inhibition efficiency increased with increasing Na-EDTA concentrations and temperatures. The adsorption of Na-EDTA on the mild steel surface followed Langmuir and Temkin adsorption isotherms (Azooz & Kamal, 2019).

4.1.4.3.5 Synergistic Effects

The effectiveness of VCI powder formulations lies not only in the individual properties of their components but also in their synergistic interactions:

pH Buffering and Passivation

- The combination of phosphates and silicates provides robust pH buffering, ensuring a consistently alkaline environment that promotes passivation.

Broad-Spectrum Protection

- Although some components are particularly effective for specific metals (e.g. azoles for copper), the overall formulation protects a wide range of metals and alloys.

Enhanced Inhibitor Performance

- Sodium benzoate boosts the effectiveness of other inhibitors such as azole derivatives, resulting in a stronger protective system.
- This synergistic effect allows for potentially lower concentrations of individual components while maintaining overall effectiveness.

Improved Corrosion Protection

- Molybdates enhance the performance of other inhibitors, particularly silicates and phosphates (López-Garrity & Frankel, 2014).
- This synergistic interaction improves corrosion protection under various environmental conditions and metal substrates.

4.1.4.4 Conclusion

VCI powder formulations represent a sophisticated and sustainable approach to corrosion inhibition. By leveraging the synergistic effects of various components including amine benzoates, phosphates, silicates, azole derivatives, sodium benzoate, and molybdates, these formulations provide robust and long-lasting protection against a wide range of metals and alloys.

The key points highlighted in this analysis are as follows.

1. Creating and maintaining an alkaline environment is crucial for passivation and corrosion resistance.
2. Vapour phase and contact inhibition ensure protection under diverse environmental conditions.
3. The synergistic effects between the components enhance the overall corrosion protection beyond what individual components can achieve.

The significance of the VCI powder formulations for corrosion prevention cannot be overstated. They offer several advantages over traditional corrosion prevention methods.

- Versatility in protecting a wide range of metals and alloys
- Long-lasting protection, even in sealed environments
- Ease of application and removal
- Potential for environmentally friendly formulations

As industries seek more effective and sustainable corrosion-prevention solutions, VCI powder formulations are promising. Their ability to provide comprehensive protection while potentially reducing the environmental impact of corrosion prevention makes them an important area for ongoing research and development in corrosion science.

4.1.5 VCI Rust-Preventive Coating Formulation

Rust-preventive coatings play a crucial role in temporary corrosion protection during manufacturing, storage, and shipment. These coatings are complex formulations that contain corrosion inhibitors, film-forming agents, and various additives suspended in a base fluid. Rust preventatives can be classified into three main categories based on the type of base fluid used: solvent-based, oil-based, and water-based (McGuire et al., 2016).

The effectiveness of rust-preventive coatings is primarily due to their ability to form a protective barrier on metal surfaces. This barrier prevents electrochemical reactions that cause corrosion by blocking the interactions between the metal substrate and corrosive elements in the environment.

4.1.5.1 Mechanism of Corrosion Inhibition

Rust-preventive coatings are mixed inhibitors of organic compounds. These compounds contain one or more polar groups with atoms, such as oxygen, nitrogen, phosphorus, or sulphur, as well as π electrons. These compounds adhere to the metal surfaces, forming a protective film that impedes both the anodic and cathodic reactions involved in corrosion.

The strength of adsorption of these organic compounds to the metal surface is largely determined by the electron density and polarizability of their polar groups. These characteristics make the polar groups effective reaction centres for the adsorption process, allowing them to form strong bonds with the metal substrate. [Ref]

Sulfonates, particularly metal sulfonates (typically salts of sulfonic acids with barium, calcium, or sodium), are organic compounds that have been widely used as corrosion inhibitors in rust-preventative coatings since the 1930s.

The corrosion-inhibition mechanism of metal sulfonates is noteworthy. These compounds have unique structures consisting of hydrophilic (polar) heads and hydrophobic (non-polar) tails. The polar sulfonate group has a strong affinity for metallic surfaces and chemisorbs onto them. This strong adhesion promoted long-term protection. Meanwhile, the non-polar tails are oriented and closely packed in a direction perpendicular to the metal surface, creating an effective barrier against corrosive species (See Figure 4-7: Schematic Diagram of the Corrosion Inhibition Mechanism of Metal Sulfonates and Figure 4-8: Function of Calcium Sulfonate in Corrosion Inhibition) (Tang, 2019).

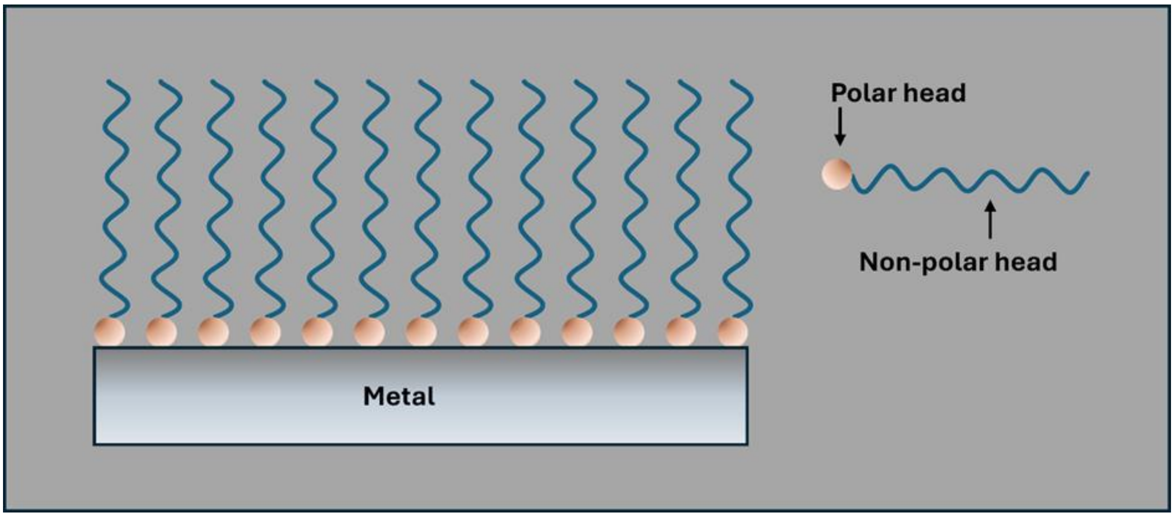


Figure 4-7: Schematic Diagram of the Corrosion Inhibition Mechanism of Metal Sulfonates

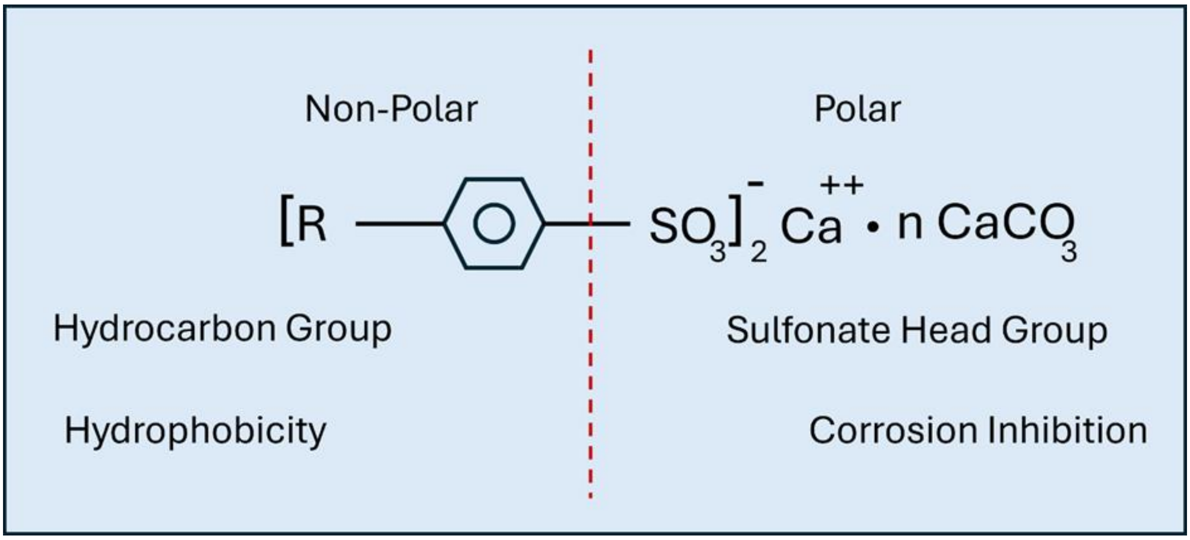


Figure 4-8: Function of Calcium Sulfonate in Corrosion Inhibition

4.1.5.2 Composition and Production

Metal sulfonates can be classified based on their feedstock (petroleum or synthetic) and the metal cations (Ba, Mg, Ca, or Na). The corrosion inhibition performance of cations generally increased in the order of Na < Mg < Ca < Ba. Barium and calcium sulfonates are widely used in industrial formulations owing to their outstanding rust prevention and water displacement properties. However, due to environmental concerns associated with barium, recent research has focused more on developing calcium sulfonate-containing compositions that provide equal or even better performance than barium-based products.

The production of sulfonates involves sulfonation, neutralisation with calcium hydroxide, and overbasing with calcium carbonate to form an overbased calcium sulfonate-calcium carbonate complex. This complex imparts thixotropic rheology, enhances the barrier properties, and ensures stability.

1. **Sulfonation**: This initial step involved mixing a major proportion of carboxylic acid with a minor proportion of sulfonic acid and an oil diluent. The mixture was then heated to 80–100°C.
2. **Neutralisation**: The sulfonic acid was neutralised with calcium hydroxide $Ca(OH)_2$. This step resulted in an exothermic reaction, producing a viscous, dark brown homogeneous fluid. The water formed during the reaction was allowed to boil off, after which the mixture was cooled and an additional solvent diluent was added to reduce the viscosity (see Figure 4.9 for the chemical equation for the neutralisation of sulfonic acid with calcium hydroxide).

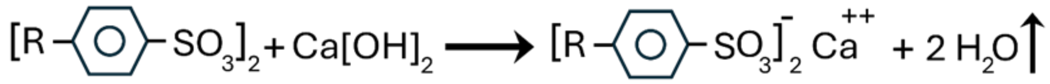


Figure 4-9: Chemical equation for the neutralisation of sulfonic acid with calcium hydroxide

3. **Overbased**: Once the mixture has cooled to about 70°C, fine particle-size calcium carbonate ($CaCO_3$) is slowly added under agitation. This process forms an overbased calcium sulfonate-calcium carbonate complex, which is crucial for the performance of the coating. The overbased calcium carbonate acts as an alkaline reserve, neutralising the acidic corrosive species that may penetrate the protective film. This over-basing process is crucial for imparting thixotropic rheology, enhancing barrier properties, and ensuring stability, which together enable superior performance (see Figure 4-10: Chemical Equation for the Formation of Overbased Calcium Sulfonate-Carbonate Complex and Figure 4-11: Simplified Diagram of Overbased Calcium Sulfonate-Calcium Carbonate Complex).

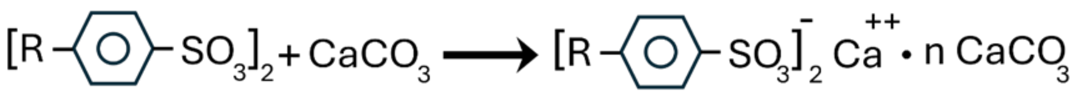


Figure 4-10: Chemical Equation for the Formation of Overbased Calcium Sulfonate-Carbonate Complex

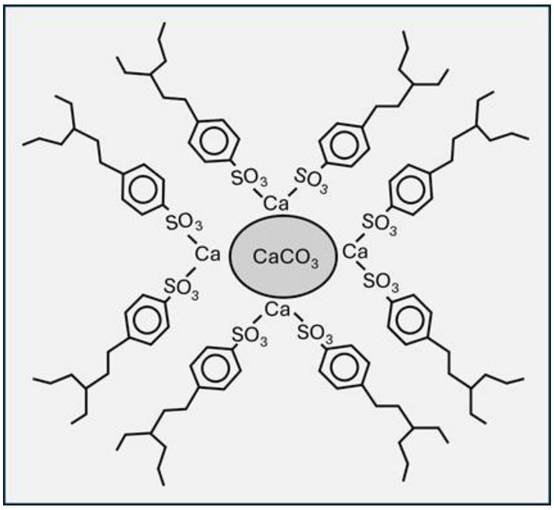


Figure 4-11: Simplified Diagram of Overbased Calcium Sulfonate-Calcium Carbonate Complex

4. **Wax Addition**: The overbased calcium sulfonate-calcium carbonate complex is mixed with microcrystalline wax. Wax dissolves at the non-polar part overbased calcium sulfonate-calcium carbonate complex and enhances the water repellent properties. (Please see Figure 4-12: Schematic diagram for wax dissolved in the non-polar tail of overbased calcium sulfonate-calcium carbonate complex).

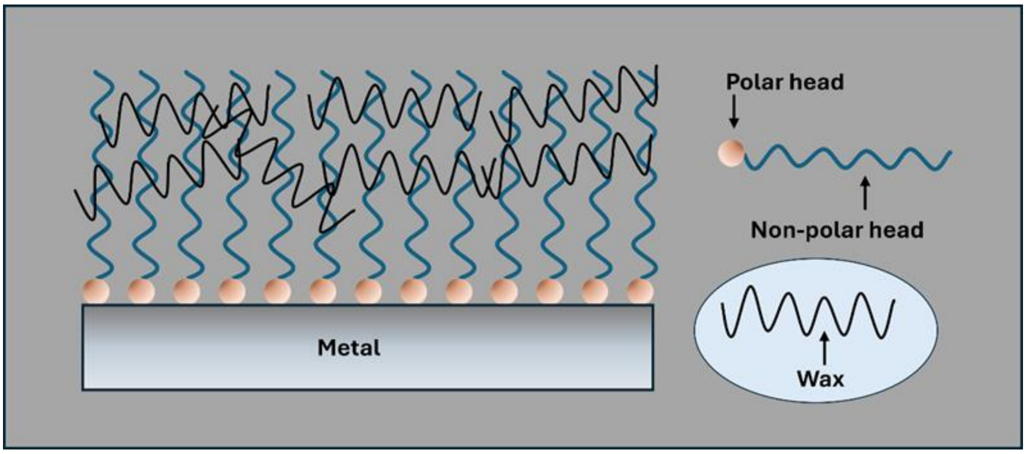


Figure 4-12: Schematic diagram for wax dissolved in the non-polar tail of overbased calcium sulfonate-calcium carbonate complex

4.1.5.3 Volatile Corrosion Inhibitors (VCIs)

While metal sulfonates provide excellent protection when they directly contact the metal surface, the addition of Volatile Corrosion Inhibitors (VCIs) enhances the protection of uncoated areas by migrating to unprotected surfaces, providing comprehensive corrosion protection.

VCIs work by evaporating and redepositing themselves on metal surfaces, including areas where the coating may have been scratched or damaged. This self-healing property significantly enhanced the overall effectiveness of the rust-preventive coating. Typically, 3–5% alkylaminoalkanol-based VCI, such as N-methylethanolamine, are added to provide this volatile corrosion protection (Prenosil, 2001).

The synergistic effect of combining VCIs with metal sulfonates results in a more robust corrosion-prevention system. This combination addresses both direct contact protection and vapour-phase protection, making these coatings particularly effective in complex geometries or enclosed spaces, where direct application may be challenging.

4.1.5.4 Thixotropic Properties and Application of Metal Sulfonates

Thixotropic versions of metal sulfonates have unique rheological properties that make them particularly suitable applications in corrosion prevention. These formulations are typically applied as single coats with thicknesses ranging from 2 to 20 µm.

The key characteristic of thixotropic compositions is their variable viscosities under different shear conditions.

1. Under high-shear conditions (such as during spraying), they exhibit lower viscosity, allowing for easy application.
2. Under low-shear conditions (such as after application), they display a higher viscosity and promote adherence to surfaces.

This behaviour is particularly advantageous in industrial settings, where spray applications are preferred. The thixotropic properties provide the following benefits:

1. Ease of Application: The low viscosity during spraying enables even coverage and penetration into complex geometries.
2. Excellent Adhesion: Once applied, the increase in viscosity helps the coating adhere well to the surface, reducing runoff and ensuring consistent protection.
3. Versatility: Most thixotropic metal sulfonate formulations are solvent based, allowing them to be applied to various surface conditions, including oily, wet, or soiled surfaces. This versatility is crucial in many industrial environments, where perfect surface preparation is not always possible.

4.1.5.5 Conclusion

In conclusion, VCI rust-preventive coatings represent a significant advancement in corrosion protection technology for industrial applications. Their ability to form protective barriers combined with the synergistic effects of metal sulfonates and VCIs provides comprehensive protection against corrosion. The thixotropic properties of certain formulations further enhance their applicability and effectiveness, making them indispensable in various industrial settings.

4.1.6 VCI Water-Based Coatings Formulation

4.1.6.1 Introduction

Volatile corrosion inhibitors (VCIs) are an important class of compounds that are used to protect metal surfaces from atmospheric corrosion. In recent years, there has been growing interest in developing water-based VCI formulations as more environmentally friendly alternatives to solvent-based systems. This paper discusses the formulation, application, and protective mechanisms of amine carboxylate water-based VCI rust-preventive coatings that achieve maximum corrosion inhibition efficiency on carbon steel substrates.

4.1.6.2 Formulation Components

The core component of an effective water-based VCI rust-preventive coating formulation is the amine carboxylate VCI compound. This compound, synthesised by neutralising long-chain carboxylic acids (18–26 carbon atoms) with a blend of organic amines at 60°C for 120 min, effectively inhibits corrosion. The effectiveness increases with an increase in the number of carbon atoms. In addition, this compound offers benefits in terms of boundary lubrication, emulsification, and detergency (Cheng et al., 2019).

4.1.6.3 Coating Application and Formation

The application method and drying conditions were crucial for forming an effective protective VCI coating. Dip coating is a common method for applying water-based VCI coatings; however, other techniques also offer advantages in certain situations.

Dip coating: This method provides good coverage and film uniformity and should be applied for at least 10 min to allow sufficient interaction between the VCI molecules and the metal surface. Optimal drying occurred for over 24 hours at room temperature (20–30°C), with studies indicating that slightly elevated temperatures (up to 30°C) can enhance the protective film formation.

- **Spray coating**: This method allows rapid application to large or complex surfaces. It can provide more uniform coverage and is particularly useful for intricate parts or for precise control over the coating thickness.
- **Brush application**: This technique is suitable for small areas, touch-ups, or when spray application is not feasible. This allows for better control in hard-to-reach areas but may result in a less uniform film thickness.

4.1.6.4 Protective Mechanism

The protective mechanism of the water-based VCI coatings involves several interrelated processes. VCI molecules chemisorb onto the steel surface through interactions of polar functional groups with the metal, forming a primary barrier against corrosive species. The chemisorbed layer and film-forming agents form a continuous protective layer. The presence of amino groups, carboxylate anions, and π bonds between carbon atoms further enhances corrosion inhibition. Additionally, the volatile nature of the inhibitor protects the areas not in direct contact through vapour-phase deposition, and maintaining a slightly alkaline pH stabilises the passive oxide film on the steel surface.

4.1.6.4 Factors Affecting Coating Performance

Several factors influence the performance of water-based VCI coatings, including the VCI concentration, drying time, temperature, and surface preparation. The optimal VCI concentration (0.25–0.5%v/v) balances the corrosion inhibition efficiency with the cost-effectiveness. Complete film formation and VCI distribution typically occur within 24 hours of drying. Slightly elevated drying temperatures (up to 30°C) can enhance protective film formation, likely by increasing the mobility and orientation of VCI molecules. Appropriate metal surface cleaning and preparation are crucial to achieve optimal coating adhesion and performance.

4.1.6.5 Conclusion

Water-based VCI rust-preventive coatings offer an effective and environmentally friendly solution for protecting carbon steel from atmospheric corrosion. The efficacy of the coating is attributed to the chemisorption of VCI molecules, vapour-phase protection, and the formation of a continuous barrier film. Achieving optimal performance requires careful control of VCI concentration, application parameters, and drying conditions.

4.2 Characteristics and Application of VCI

4.2.1 VCI Emitters

4.2.1.1 Characteristics of VCI Emitters

VCI emitters are specialised devices that release corrosion-inhibiting vapours into enclosed spaces, protecting metal components without direct contact. The key characteristics of the VCI emitters are as follows:

- **Controlled Release Mechanism**: VCI emitters are engineered to release inhibitor vapours at a controlled rate, ensuring consistent protection over extended periods. This is achieved through careful selection of inhibitor compounds with specific vapour pressures and the use of permeable encapsulation materials.
- **Versatile Formulations**: VCI emitters can be formulated with various inhibitor compounds to suit different environmental conditions and metal types. For instance, they may contain a mixture of low-, intermediate-, and high-vapour-pressure inhibitors to provide immediate and long-term protection.
- **Non-Contact Protection**: Unlike traditional corrosion prevention methods, VCI emitters do not require direct application to the metal surface. Inhibitor vapours can reach and protect intricate geometries and hard-to-reach areas.
- **Environmental Adaptability**: They designed to function effectively at various humidity levels and temperature ranges to suit diverse storage and transportation conditions.
- **Long-lasting Effect**: When properly formulated and applied under appropriate environmental conditions, VCI emitters can protect for up to two years, offering a long-lasting solution for corrosion prevention.

4.2.1.2 Applications of VCI Emitters

VCI emitters find applications across various industries where metal corrosion prevention is crucial:

- Automotive Industry: VCI emitters are extensively used for protecting vehicle parts, engines, and electrical components during shipping, storage, and between manufacturing stages.
- Electronics Sector: Sensitive electronic equipment, circuit boards, and components are protected during transport and storage using VCI emitters to prevent corrosion-induced malfunctions. Figure 4-13 illustrates the corrosion protection of a circuit board using emitters.

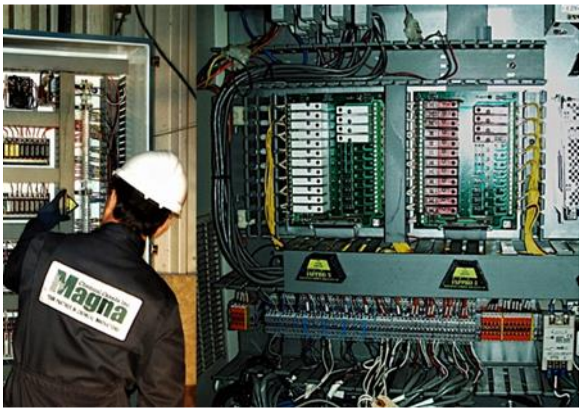


Figure 4-13: Corrosion protection of circuit board using emitters

- Military and Defense: VCI emitters play a crucial role in preserving military hardware, weapons, and vehicles during long-term storage or when deployed in corrosive environments.

Figure 4-14: Corrosion protection of military electronic components using emitters

- Aerospace Industry: Aircraft components, avionics, and spare parts are protected using VCI emitters during storage and transportation, ensuring their reliability and longevity.
- Industrial Equipment: Large machinery, tools, and industrial equipment are safeguarded during periods of inactivity or when stored in humid environments using VCI emitters.
- Marine Applications: VCI emitters are employed to protect ship components, offshore equipment, and marine structures from highly corrosive saltwater environments.

4.2.2 VCI Films

4.2.2.1 Characteristics of VCI Films

Volatile corrosion inhibitor (VCI) films are specialised packaging materials designed to protect various metal products against corrosion. These films were produced through a meticulous process involving the compounding of amino-carboxylate corrosion inhibitor (ACCI) masterbatch powder with polyethylene resin, followed by extrusion into different film forms (Cheng & Salas, 2020a).

The primary characteristic of VCI films is their ability to release corrosion-inhibiting vapours that form a protective molecular layer on the metal surfaces. This protective layer prevents electrochemical reactions that lead to corrosion and effectively preserves the integrity of metal products during storage and transportation (Bastidas et al., 2005). The films are typically transparent or translucent, allowing visual inspection of packaged items without compromising the protective barrier.

VCI films exhibit excellent mechanical properties, including a high tensile strength and elongation, which contribute to their durability and effectiveness in various packaging applications. The films were also designed to be flexible and conformable, enabling them to wrap around irregularly shaped objects and provide comprehensive protection (Cheng & Salas, 2020b).

One key characteristic of modern VCI films, particularly those produced using Vappro VBCI MBP 3000 masterbatch powder, is their environmental sustainability. These films are nitrite-free, eliminating the risk of carcinogenic N-nitrosamine formation, which is a concern for traditional nitrite-based corrosion inhibitors (Cheng & Salas, 2020a).

4.2.2.2 Applications of VCI Films

Volatile Corrosion Inhibitors (VCI) film-specialised packaging materials have widespread applications in various industries, from automotive and aerospace to electronics and heavy machinery. The versatility and effectiveness of VCI films in preserving metal integrity make them indispensable solutions for addressing the multibillion-dollar challenge of corrosion in industrial settings (Bastidas et al., 2005; Cheng & Salas, 2020a).

- Automotive Industry: VCI films are used to protect automotive parts, engines, and body components during the manufacturing, assembly, and shipping processes.
- Aerospace: Critical aircraft components and spare parts are often wrapped in VCI films to prevent corrosion during storage and transit (Bastidas et al., 2005).
- Military Equipment: VCI films are employed to protect weapons, vehicles, and other military hardware from corrosion, especially under harsh environmental conditions. Figure 4-15 illustrates the use of VCI films in military weapons.

Figure 4-15: VCI file used in military weapons

- Electronics: VCI films protect sensitive electronic components and circuit boards from oxidation and corrosion.

- Metal Processing and Manufacturing: VCI films are used to protect raw materials, semi-finished products, and finished metal goods throughout the production and distribution chains.
- Marine Applications: Ships, offshore platforms, and marine equipment benefit from the VCI film protection against saltwater-induced corrosion. This application is demonstrated in Figure 4-16, which shows VCI films used in the marine industry.

Figure 4-16: VCI file used in marine industry

- Heavy Machinery: Large industrial equipment and machinery are often wrapped in VCI films for long-term storage or overseas shipping. Figure 4-17 depicts the use of the VCI film to protect the heavy equipment.

Figure 4-17: VCI film used in heavy equipment

The versatility of VCI films is further enhanced by their availability in various forms, including standard polyethylene films, shrink films and stretch films. Each type serves specific packaging needs, with shrink films providing a tight, conforming fit around objects, and stretch films offering additional mechanical strength and stability for securing items during transport.

4.2.3 VCI Paper

4.2.3.1 Characteristics of VCI Paper

VCI paper is a specialised packaging material that protects metal products from corrosion during storage and transportation. VCI paper exhibits several key characteristics that make it suitable for various industrial applications.

- Active corrosion protection: VCI compounds continuously vaporise, forming a protective molecular layer on metal surfaces
- Barrier properties: The kraft paper base provides physical protection against moisture and contaminants
- Flexibility: VCI paper can be easily wrapped around irregularly shaped objects
- Dry protection: Unlike oils or greases, VCI paper does not leave residues on protected items

4.2.3.2 Applications of VCI Paper

VCI paper is extensively used in various industries to protect metal products from corrosion. Key applications include (Gangopadhyay & Mahanwar, 2018):

- Packaging of metal parts and components in automotive and aerospace industries
- Protection of military equipment during storage and transport
- Protect finished metal products, semi-finished goods, and raw materials in the metal processing industry during storage and transportation
- Corrosion prevention in the oil and gas industry for pipelines and equipment

Figure 4-18 Illustrates a typical application of the VCI paper, showing a machinery part wrapped for protection against corrosion.

Figure 4-18: Machinery part packed with VCI paper

The versatility and effectiveness of VCI paper in protecting various metal products across multiple industries highlight its significance in corrosion prevention strategies. Its ability to provide long-term protection without direct contact makes it an invaluable tool for preserving the integrity and functionality of metal components in diverse applications (Valdez et al., 2018).

4.2.4 VCI Powder

4.2.4.1 Characteristics of VCI Powder

VCI powders possess several unique properties that make them highly effective in corrosion protection in various industrial applications. These characteristics provide comprehensive and long-lasting protection for metal surfaces. The key characteristics of the VCI powders are as follows:

1. Volatility: VCI powders contain volatile components that sublimate at room temperature, creating protective vapour. This allows the inhibitor to reach and protect the areas without direct contact with the powder. For example, VCI vapour can penetrate small crevices and hard-to-reach areas in sealed containers with metal components.
2. Adsorption Capability: Vaporised inhibitors adsorb onto metal surfaces, forming a thin protective molecular layer. This film acted as a barrier against corrosive species. For instance, on a steel surface, VCI molecules can form a layer that repels moisture and oxygen, preventing rust formation.
3. Self-replenishing: As the protective layer is disturbed or worn away, vapour-phase inhibitors continuously replenish it, ensuring long-lasting protection. This

is particularly useful in environments with frequent temperature fluctuations and mechanical disturbances.

4. Multi-metal Protection: VCI powders are typically formulated to protect various metals and alloys, including ferrous and non-ferrous metals. For example, a single VCI product effectively protects the steel, copper, and aluminium components of an enclosed space.
5. Synergistic Action: The various components of VCI powder work synergistically, providing more comprehensive protection than individual inhibitors alone.
6. pH Regulation: Many VCI powders have components that help maintain an alkaline environment, which is crucial for corrosion resistance.
7. Non-Toxic and Environmentally Friendly: Modern VCI powder formulations are increasingly being designed to be non-toxic and environmentally friendly, addressing sustainability concerns.

These characteristics collectively make the VCI powder a versatile and effective solution for corrosion protection in various industrial settings, from small components to large storage tanks and pipelines.

4.2.4.2 Applications of VCI Powder

VCIs have emerged as pivotal solutions for mitigating corrosion in various industrial applications. The deployment of VCI powders in mothball equipment has garnered significant attention owing to their versatility and efficacy in protecting metallic surfaces under diverse environmental conditions. VCI powders can be applied through various methods suited to specific industrial needs and environments.

- **Dry Applications**

  Dry application methods involve the use of VCI powders without dissolving them in liquid medium. These techniques are particularly effective for protecting large enclosed spaces.

- **Fogging Technique**

  The fogging technique is the primary method for the dry application of VCI powders. This approach is particularly effective for protecting the interiors of large, enclosed spaces, such as

    - Tanks
    - Vessels
    - Heat exchangers

- Above storage tanks
- Cisterns
- Pipes and pipelines

Figure 4-19 shows the practical application of VCI powder to fog piping systems. In this method, VCI powder is dispersed as a fine mist or fog throughout the enclosed space, settling on all surfaces and providing comprehensive protection.

Figure 4-19: Used VCI powder to fog piping system

- **Wet Applications**
  Wet applications involve dissolving the VCI powder in a solution before application. This method is versatile and can be used in various scenarios (Cheng et al., 2018).
- **Solution-Based Protection**
  In wet applications, VCI powders are dissolved in a suitable solution that can then be used for protection.
    - Metal parts and equipment inside any enclosed space
    - The internal surfaces of the process equipment, such as
        - Cooling towers
        - Boilers
        - Ballast tanks
        - Storage tanks
- **Hydrotesting Protection**
  VCI powders are particularly useful in hydrotesting applications. Hydrotesting is critical in many industries, particularly in the oil and gas sector, for verifying

the integrity and safety of pipelines, tanks, and pressure vessels. When dissolved in the hydrotest water, they can protect

  - Equipment
  - Pipes
  - Valves
  - Tanks

This method ensures that the metal surfaces are protected during and after the hydrotesting process, preventing flash rust and long-term corrosion.

- **Integrated Systems**

  VCI powders can be integrated with other corrosion protection methods to enhance their effectiveness and broaden their applicability (Lyublinski et al., 2014).

- **DH/VCI System**

  This system combines VCI technology with dehumidification. This provides comprehensive protection through

  - Reducing ambient humidity to minimise moisture-induced corrosion
  - Utilizing VCI vapours to protect metal surfaces at the molecular level
  - Two-Layer System
  - This approach incorporates VCI technology as part of a multilayer protective strategy. It typically involves:
  - A VCI film or layer in direct contact with the metal surface
  - Additional protective layers (e.g., physical barriers, desiccants) to enhance overall protection

- **Specialised Applications**

  Concrete Reinforcement Protection

  - VCI powders are useful for protecting the reinforcing steel in concrete structures. This helps to:
  - Prevent premature concrete spalling
  - Extend the service life of concrete structures in corrosive environments (Cheng & Salas, 2020)

By leveraging these diverse application methods, VCI powders offer flexible and effective corrosion-protection solutions in various industrial scenarios. Their ability to protect both directly contacted surfaces and those in the vapour phase makes them particularly valuable for complex geometries and hard-to-reach areas.

4.2.5 VCI Rust-Preventive Coating

4.2.5.1 Characteristics of VCI Rust-Preventive Coating

Rust-preventive coatings are specialised formulations designed to protect metal surfaces from corrosion by utilising advanced chemical technologies, such as VCIs and metal sulfonates. Some of the key characteristics and applications of rust-preventive coatings are as follows.

1. **Thixotropic Properties**: The formulation exhibited variable viscosity under different shear conditions, allowing easy application and excellent adhesion.
2. **Barrier Formation**: Forms a physical barrier that protects metal surfaces from environmental corrosive agents. This barrier protects against moisture, oxygen, and other corrosive elements.
3. **Comprehensive Protection**: The combination of metal sulfonates and VCIs provides both direct contact and vapour-phase protection, making it effective for complex geometries and enclosed spaces
4. **Long-Term Protection**: Contains overbased calcium carbonate as an alkaline reserve. This neutralises the acidic corrosive species that can penetrate the protective film, extending the effectiveness of the coating for several years.
5. **Ease of removal**: Designed to be easily removed by conventional solvents, such as thinner, when protection is no longer required, often without the need for special solvents.

4.2.5.2 Applications of VCI Rust-Preventive Coatings

1. **Manufacturing and Storage**: This used to protect metal parts during storage and shipment. It is crucial to prevent corrosion during the transit and long-term storage of manufactured components.

2. **Industrial Equipment**: Apply to machinery and tools to prevent corrosion during downtime. It helps maintain the integrity of equipment that may not be in constant use but needs to be ready for operation.
3. **Automotive Industry**: Used to protect automotive components during production and storage. An asphalt-based calcium sulfonate rust-preventive coating served as an undercarriage coating.
4. **Oil and Gas Industry**: Protects pipelines and other equipment from corrosion due to harsh environmental conditions. This is particularly important for offshore installations and equipment that are exposed to corrosive substances.

Rust-preventive coatings offer unique characteristics, such as thixotropic properties, comprehensive protection, and barrier formation, making them highly effective for corrosion prevention. Their versatile applications range from protecting manufactured parts and industrial equipment to safeguarding automotive components and oil and gas infrastructure. These features position rust-preventive coatings as a valuable solution for corrosion protection across various industries, despite some limitations in specific environmental conditions or long-term use.

4.2.6 VCI Water-Based Coatings

4.2.6.1 Characteristics of VCI Water-Based Coatings

Water-based volatile corrosion inhibitor (VCI) coatings represent an innovative approach for preventing rust on metal surfaces. They combined the protective power of VCI compounds with that of environment-friendly water-based formulations. These coatings offer a unique set of characteristics and have applications in numerous industries, providing effective corrosion protection in diverse environments. The following sections outline the key characteristics and applications of water-based VCI rust-prevention coatings. Characteristics of VCI Water-Based Coatings are as follows: -

1. **Composition**: These coatings typically consisted of amine carboxylate VCI compounds, film-forming agents, and water as the primary solvent.
2. **Film Formation**: Upon application, the coating forms a thin protective film on the metal surface through chemisorption and physical barrier formation. This

film typically achieves optimal formation within 24 hours of drying at room temperature (20–30°C).

3. **Vapour Phase Protection**: VCI molecules can volatilise and protect areas not directly in contact with the coating, providing comprehensive corrosion inhibition. This unique feature enables the protection of complex geometries and hard-to-reach areas.
4. **Stability**: The formulation maintained a slightly alkaline pH to stabilise the passive oxide film on steel surfaces. This alkaline environment contributes to the overall corrosion resistance of the treated metal.
5. **Environmental Impact**: Water-based VCI coatings have significantly lower volatile organic compound (VOC) emissions than solvent-based alternatives, making them more environmentally friendly and compliant with stricter regulations.

4.2.6.2 Applications of VCI Water-Based Coatings

1. **Temporary Corrosion Protection**: Ideal for protecting metal parts during storage, shipping, or between manufacturing processes. Coatings can be easily applied and removed when required.
2. **Industrial Equipment**: Used to protect machinery, tools, and metal components in various industries, including automotive, aerospace, and marine. The versatility of these coatings makes them suitable for use in a wide range of metal substrates.
3. **Infrastructure**: Vapour phase protection protects structural steel, pipelines, and other metal infrastructures in corrosive environments. This is particularly beneficial for complex structures in the hard-to-reach areas.
4. **Construction Materials**: Can used to protect reinforcing steel in concrete, extending the lifespan of reinforced concrete structures by preventing corrosion-induced degradation.

The characteristics of water-based VCI coatings, including their composition, film-formation properties, and vapour-phase protection, significantly contribute to their effectiveness in preventing corrosion in various applications. These coatings demonstrate versatility and efficacy in various industries by protecting equipment to safeguard infrastructure components. As environmental regulations have become stricter, water-based VCI coatings are poised to play an increasingly important role in corrosion prevention strategies in multiple industries.

4.3 Advantages and Limitations

4.3.1 VCI Emitters

4.3.1.1 Advantages of VCI Emitters

VCI emitters represent a significant advancement in corrosion prevention technology, offering unique protection for metal surfaces in enclosed environments. Understanding the advantages and limitations of VCI emitters is crucial for optimising their application in industrial, military, and commercial contexts. VCI emitters offer several advantages over traditional corrosion prevention methods.

1. **Ease of Application**: VCI emitters can be simply placed within an enclosed space, eliminating the need for complex application processes or surface preparation
2. **Comprehensive Protection**: The vapour phase action allows for the protection of complex geometries, internal surfaces, and crevices that might be inaccessible to direct-contact inhibitors
3. **Clean Technology**: VCI emitters leave no residue on the protected surfaces, eliminating the need for cleaning before the use of the protected items
4. **Compatibility**: When properly formulated, VCI emitters are compatible with a wide range of metals and alloys, allowing for the protection of multi-metal assemblies
5. **Cost-Effective**: By providing long-term protection without the need for frequent reapplication, VCI emitters can be a cost-effective solution for corrosion prevention

4.3.1.2 Limitations of VCI Emitters

Despite its numerous advantages, VCI emitters have several limitations.

1. **Enclosed Space Requirement**: VCI emitters are most effective in sealed or semi-sealed environments. Their efficacy may be reduced in open or poorly enclosed spaces where the inhibitor vapours can dissipate quickly

2. **Environmental Sensitivity**: The performance of VCI emitters can be affected by extreme temperature fluctuations or very high humidity levels, potentially reducing their effectiveness
3. **Limited Protection Range**: The protective vapours have a finite range of effectiveness, which may limit their use in very large enclosures without proper distribution of multiple emitters
4. **Material Compatibility Issues**: Some VCI compounds may interact unfavourably with certain polymers or organic coatings, necessitating careful selection for specific applications

Table 4-3: Advantages and limitations of VCI emitters

Advantages of VCI Emitters	Limitations of VCI Emitters
Easy application	Requires enclosed spaces
Protects complex geometries	Sensitive to extreme environments
Leaves no residue	Limited protection range
Wide metal compatibility	Potential material incompatibilities
Cost-effective long-term protection	

As summarised in
Table 4-3, VCI Emitters offer several significant advantages; however, their limitations must be carefully considered when implementing them in corrosion-prevention strategies.

4.3.2 VCI Films

4.3.2.1 Advantages of VCI Films

VCI films are the most widely used technology for protecting equipment produced from ferrous, non-ferrous, and multi-metal alloys. They offer significant advantages including effective corrosion protection, ease of application, and long-term durability. However, VCI films also present limitations such as higher initial costs, limited reusability, and sensitivity to extreme temperatures. Table 4.4 summarises the key advantages and limitations of VCI films, which are elaborated in the following sections.

Table 4-4: Advantages and limitations of VCI films

Advantages	Limitations
Effective corrosion protection	Higher initial costs
Ease of application	Limited reusability
Dry protection	Temperature sensitivity
Visibility (transparency)	Potential for contamination
Multi-metal protection	Vapour concentration requirements
Environmental sustainability	Limitations in harsh environments
Long-term protection	Disposal considerations
	Performance variability

As outlined in Table 4-4, VCI films offer several significant advantages such as:

- Effective Corrosion Protection: VCI films provide a robust barrier against the corrosion of ferrous and non-ferrous metals. VCI form a protective molecular layer on metal surfaces, significantly reducing the risk of corrosion during storage and transportation (Bastidas et al., 2007).
- Ease of Application: VCI films do not require hermetic sealing. It can be easily applied to various shapes and sizes of metal products without requiring complex equipment or specialised training. This simplicity of application makes it a cost-effective solution for many industries (Lyublinski et al., 2015).
- Dry Protection: In most instances, VCI films protect components in a clean and dry state without the need for degreasing or cleaning before use, unlike oil-based rust preventives. This saves time and reduces additional processing costs (Cheng & Salas, 2020b; Lyublinski et al., 2015).
- Visibility: Most VCI films' transparency allows for the visual inspection of packaged items without compromising the protective barrier. This feature is particularly valuable for quality control and inventory management (Cheng & Salas, 2020a).
- Multi-metal Protection: Advanced VCI formulations, such as those using amino-carboxylate corrosion inhibitors, can protect a wide range of metals including

steel, copper, brass, and aluminium. This versatility reduces the need for multiple packaging solutions (Bastidas et al., 2007).

- Environmental Sustainability: Modern VCI films, particularly those produced with Vappro VBCI MBP 3000 masterbatch powder, are nitrite-free, eliminating the risk of carcinogenic N-nitrosamine formation. This addresses environmental and health concerns associated with traditional corrosion inhibitors (Cheng & Salas, 2020a).
- Long-Term Protection: VCI films can provide effective corrosion protection for extended periods, sometimes up to several years, making them suitable for long-term storage and overseas shipping.

4.3.2.2 Limitations of VCI Films

- Initial Cost: The upfront cost of VCI films can be higher than that of traditional packaging materials. However, this cost is often offset by long-term savings from reduced corrosion damage and simplified packaging processes (Bastidas et al., 2007).
- Limited Reusability: Most VCI films are designed for single-use applications. Once the package is opened, the protective vapours dissipate and the film may not provide the same level of protection if reused.
- Temperature Sensitivity: Extreme temperatures can affect the effectiveness of VCI films. Very high temperatures may accelerate the depletion of corrosion inhibitors, whereas very low temperatures might slow down vapour release (Cheng & Salas, 2020b).
- Potential for Contamination: In cases, residues from the VCI compounds may be transferred to the surface of the protected item. Although generally not harmful, this could be a concern in industries requiring ultra-clean surfaces, such as electronics manufacturing (Bastidas et al., 2007).
- Vapour Concentration Requirements: The VCI films require a certain level of vapour concentration within the enclosed space for optimal protection. Large air gaps or frequent package openings may reduce the effectiveness of corrosion protection.
- Limitations in Harsh Environments: While VCI films provide excellent protection under many conditions, they may have limitations in extremely corrosive

environments, such as direct exposure to saltwater or strong chemicals (Cheng & Salas, 2020a).

- Disposal Considerations: Although modern VCI films are more environmentally friendly, the proper disposal or recycling of used films may still require special consideration, particularly for films containing active corrosion inhibitors (Bastidas et al., 2007).
- Performance Variability: The effectiveness of VCI films can vary depending on factors such as the specific metal being protected, environmental conditions, and the quality of the film's application. This variability necessitates careful selection and testing of specific applications.

In conclusion, although VCI films offer significant advantages in corrosion protection across various industries, users must consider their limitations to ensure optimal performance and cost-effectiveness in specific applications.

4.3.3 VCI Papers

4.3.3.1 Advantages of VCI Papers

Vapour Corrosion Inhibitor (VCI) paper has emerged as a significant tool for corrosion prevention in various industrial applications. To better understand its capabilities and constraints, Table 4-5 presents a comprehensive overview of the advantages and limitations of the VCI paper.

While offering numerous benefits such as ease of use and the dry method, VCI paper also presents certain limitations that must be considered for optimal implementation. A comprehensive understanding of these characteristics is essential for maximising the effectiveness of VCI papers across diverse corrosion protection scenarios. The following outlines the key advantages and limitations of the VCI paper, highlighting its capabilities and constraints in corrosion protection scenarios. The Advantages of VCI paper are as follows:

- Ease of Application: VCI paper is simple to use and does not require specialised equipment or training for application. It can be easily integrated into the existing packaging processes.

- Dry Method: Unlike oils or greases, VCI paper provides dry corrosion protection, eliminating the need for cleaning before using the protected parts.
- Long-term Protection: When properly sealed, VCI paper can provide effective corrosion protection for extended periods, making it suitable for long-term storage and overseas shipping.
- Environmentally Friendly: Using amino-carboxylate corrosion inhibitors (ACCI) in VCI paper formulations contributes to a more sustainable and environmentally friendly corrosion protection solution.
- Multi-metal Protection: Many VCI paper formulations can protect various metals and alloys, including ferrous and non-ferrous metals, making them versatile for various applications.
- Cost-effectiveness: VCI paper is generally more cost-effective than other corrosion-prevention methods, especially for large-scale or long-term storage applications.
- Customisability: The VCI paper can be customised in terms of size, shape, and inhibitor concentration to suit specific application requirements.
- Compatibility with other packaging materials: VCI paper can be used with other packaging materials and methods to enhance overall protection.

Table 4-5: Advantages and limitations of VCI paper

Advantages	**Limitations**
Ease of Application	Limited Physical Protection
Dry Method	Temperature Sensitivity
Long-term Protection	Moisture Concerns
Environmentally Friendly	Potential for Residue
Multi-metal Protection	Packaging Integrity Requirements
Cost-effective	Limited Reusability
Customisability	Disposal Considerations
Compatibility with Other Packaging	

4.3.3.2 Limitations of VCI Papers

- Limited Physical Protection: While effective against corrosion, VCI paper does not provide significant physical protection against impact or abrasion. Therefore, additional packaging is necessary for fragile products.
- Temperature Sensitivity: The effectiveness of the VCI paper can be reduced at extreme temperatures. High temperatures may cause rapid depletion of the inhibitor, whereas low temperatures can slow down the vaporisation process.
- Moisture Concerns: Although VCI paper provides some moisture resistance, excessive humidity or direct water contact can compromise its effectiveness and potentially lead to degradation of the paper itself.
- Potential for Residue: In some cases, VCI compounds may leave a small amount of residue on the protected metal surface. Although generally not problematic, this could concern certain applications that require pristine surfaces.
- Packaging Integrity: The effectiveness of VCI paper relies on maintaining a sealed environment. Any breach in packaging can lead to the premature depletion of inhibitors and reduced protection.
- Limited Reusability: Once the VCI compounds are depleted, the paper loses its corrosion-inhibiting properties and cannot be "recharged" for reuse in corrosion protection.
- Disposal Considerations: While base kraft paper is recyclable, the presence of VCI compounds may require special disposal considerations, potentially limiting recycling options.

Understanding these advantages and limitations is crucial for the effective implementation of VCI papers in corrosion prevention strategies. Considering these factors, engineers and researchers can optimise the use of VCI paper in various industrial applications by balancing its benefits against potential drawbacks to achieve optimal corrosion protection.

4.3.4 VCI Powder

4.3.4.1 Advantages of VCI Powder

The volatile corrosion inhibitor (VCI) powder is an innovative solution for protecting metals from corrosion, particularly in enclosed spaces and hard-to-reach areas. This technology offers numerous benefits for industries, such as manufacturing, transportation, and storage. However, it is important to consider the limitations of the VCI powder when evaluating its use in corrosion prevention. The advantages of rust-preventive coatings are as follows.

1. **Versatile Protection:** VCI powders can protect the interior spaces of equipment, such as tanks, vessels, boilers, and piping, especially in voids and recessed areas that are difficult to reach with other methods. They can also protect various metals and alloys, including ferrous and non-ferrous metals, making them suitable for diverse applications.
2. **Long-lasting Protection:** The vapour phase inhibition mechanism allows for continuous protection, even in enclosed environments, for extended periods
3. **Easy Application and Removal:** VCI powders can be easily applied by fogging or dusting and can be removed by simply brushing or blowing off, leaving no residue
4. **Environmentally Friendly Formulations:** Modern VCI powder formulations are moving towards more eco-friendly components, reducing environmental impact
5. **Cost-effectiveness:** VCI powders are often more economical than traditional corrosion-prevention methods, especially for large-scale or long-term storage.

4.3.4.2 Limitations of VCI Powder

1. **Limited to Enclosed Spaces:** The protection level depends on the proper application and maintenance of an enclosed environment to retain the vapour concentration. However, they are unsuitable for open-air applications.
2. **Environmental Sensitivity:** Environmental factors such as temperature, humidity, and air circulation can influence the effectiveness of VCI powders.
3. **Potential for Dust Formation:** Fine VCI powders may create dust during applications, such as fogging or removal, which could be a concern in some environments.

4. **Possible Interaction with Certain Materials:** Some VCI components may interact unfavourably with certain plastics or rubbers, necessitating compatibility testing.
5. **Require Reapplication:** Owing to the biodegradability of the VCI powder, periodic reapplication might be necessary to maintain protection for long-term storage (more than 2 to 3 years) or challenging environments.
6. **Regulatory Compliance:** Some VCI powder components may be subject to regulatory restrictions in certain industries or regions, requiring careful formulation and documentation.

Table 4-6: Advantages and limitations of VCI powder

Advantages	Limitations
Versatile Protection	Limited to Enclosed Spaces
Long-lasting Protection	Environmental Sensitivity
Easy Application and Removal	Potential for Dust Formation
Environmentally Friendly Formulations	Possible Interaction with Certain Materials
Cost-effectiveness	Require Reapplication
	Regulatory Compliance

To summarise the key points discussed above, Table 4-6 provides a concise overview of the advantages and limitations of the VCI powders. In summary, the VCI powders provide significant benefits in terms of ease of application, comprehensive protection, and cost efficiency. However, their effectiveness depends on proper application within enclosed environments and regular maintenance to address environmental sensitivities and potential material interactions.

4.3.5 VCI Rust-Preventive Coating

4.3.5.1 Advantages of VCI Rust-Preventive Coating

Rust-preventive coatings offer a range of benefits in corrosion protection while also presenting certain limitations. Table 4-7 summarises the key advantages and limitations of VCI rust-preventive coatings for corrosion protection.

Table 4-7: Advantages and limitations of VCI rust-preventive coating

Advantages	Limitations
Protects complex and inaccessible parts	Environmental limitations (e.g., high temperatures)
Excellent for outdoor exposure and weathering resistance	Potential health and environmental concerns
Displaces moisture effectively	May interfere with subsequent processes
Cost-effective	Can be more expensive than traditional methods for simple applications
Versatile	May still require some level of surface preparation

The advantages of rust-preventive coatings are as follows. -

- Protection of Complex Parts: Vapour-phase protection can protect inaccessible and intricate metal parts. This allows the coating to reach areas that are difficult to directly coat.
- Outdoor Exposure: It is excellent for outdoor exposure and weathering resistance owing to the formation of physical barriers.
- Displace moisture: The calcite crystals from the rust-preventive coating form a moisture-resistant barrier. These plate-like crystals are aligned parallel to the surface, creating a difficult path for moisture, oxygen, and contaminants to reach the surface. Figure 4-20 illustrates the barrier properties of the calcite crystals.

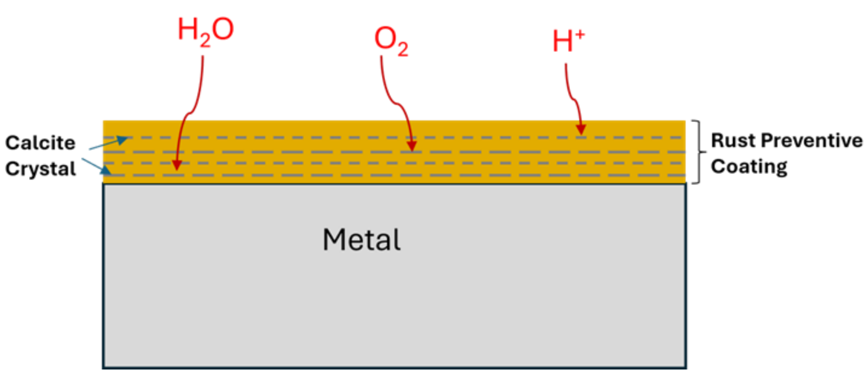


Figure 4-20: Barrier properties of calcite crystals

- Cost-Effective Alternative: In practical applications, it reduces the need for expensive alloys or protective packaging, which can lead to significant cost savings in materials and logistics.
- Versatility: Effective under various surface conditions and in different industrial settings, making it a versatile solution for diverse corrosion protection needs.

4.3.5.2 Limitations of VCI Rust-Preventive Coating

- Environmental limitations: It is unsuitable for all environmental conditions, particularly high temperatures, which limits its applicability in certain industrial settings.
- Potential Health and Environmental Concerns: Some formulations may contain harmful chemicals, raising environmental and health concerns. These include the potential presence of volatile organic compounds (VOCs).
- Process Interference: The Protected parts may interfere with subsequent processes. Therefore, they must be carefully cleaned before further processing or use.
- Cost Considerations: Rust prevention methods can be more expensive than traditional methods for simple applications. Complex formulations and specialised ingredients contribute to higher costs.
- Surface Preparation Requirements: Although versatile, optimal performance may still require some level of surface preparation. This can add to the overall time and cost of the application.

The advantages of robust preventive coatings, such as versatile protection and ease of application, make them valuable in various industrial settings. However, their limitations, including potential environmental concerns and cost factors, necessitate careful consideration of their application and selection for specific corrosion-prevention needs.

4.3.6 VCI Water-Based Coatings

4.3.6.1 Advantages of VCI Water-Based Coatings

Water-based volatile corrosion inhibitor (VCI) coatings offer several advantages over traditional solvent-based systems, such as environmental friendliness and improved safety. However, they also have certain limitations when selecting corrosion prevention solutions. The following sections outline the key advantages and limitations of water-based VCI rust-prevention coatings.

The advantages of the VCI water-based coatings are as follows: -

- **Environmental Friendliness**: Lower VOC emissions and less environmental impact than solvent-based coatings. This aligns with increasing regulatory requirements for eco-friendly coating solutions.
- **Safety**: Improved worker safety due to reduced exposure to harmful solvents. The water-based nature of these coatings minimises fire hazards and health risks associated with volatile organic solvents.
- **Versatility**: It can be applied to various metal substrates and provides contact- and vapour-phase protection. This dual-protection mechanism enhanced the overall effectiveness of the coating.
- **Easy Application and Removal**: This can be applied using standard coating techniques, such as dip coating, spray coating, or brush application, and can be easily removed when no longer needed. This flexibility simplifies maintenance procedures
- **Cost-effectiveness**: Potentially lower application and disposal costs compared to solvent-based systems. The use of water as the primary solvent reduces the material costs and simplifies waste management.

4.3.6.2 Limitations of the VCI Water-Based Coatings

- **Drying Time**: Water-based coatings may require longer drying times than solvent-based alternatives, thus affecting production efficiency. Optimal drying typically occurs over 24 hours at room temperature.
- **Temperature Sensitivity**: Extreme temperatures can affect performance and application, particularly in cold environments where freezing is a concern. Slightly elevated temperatures (up to 30°C) can enhance protective film formation.
- **Substrate Compatibility**: It may not be suitable for all metal substrates or requires specific surface preparation techniques. Appropriate metal surface cleaning and preparation are crucial for achieving optimal coating adhesion and performance.

- **Film Thickness Control**: Achieving a consistent film thickness can be challenging, especially with dip-coating methods. This may have affected the uniformity of the protection across the treated surface.
- **Long-Term Protection**: Although effective for temporary protection, it may not provide the same long-term corrosion resistance as some specialised coating systems. The duration of protection can vary depending on the environmental conditions and the coating formulation.
- **Sensitivity to Environmental Factors**: High humidity, temperature fluctuations, and contaminant exposure can affect coating performance and longevity. These factors must be considered when selecting and applying the coatings.

Table 4-8: Advantages and Limitations of VCI Water-Based Coatings

Advantages	Limitations
Environmental Friendliness	Longer Drying Time
Improved Safety	Temperature Sensitivity
Versatility	Substrate Compatibility Issues
Easy Application and Removal	Film Thickness Control Challenges
Cost-effectiveness	Limited Long-Term Protection
	Sensitivity to Environmental Factors

The advantages of water-based VCI coatings, such as low VOC emissions, improved safety, and versatility, make them an attractive option for many industrial applications. However, limitations, such as longer drying times and sensitivity to environmental conditions, must be carefully considered. As coating technologies, continue to advance, future developments may address these limitations and further enhance the effectiveness and applicability of water-based VCI coatings across various industries. For a comprehensive overview of the advantages and limitations of the VCI Water-Based Coatings, see Table 4-8.

4.4 Standardised Testing Method for VCI Products

4.4.1 Introduction to VCI Testing Standardization

Volatile Corrosion Inhibitors (VCIs), protect metal surfaces by emitting corrosion-inhibiting vapours. With their growing application in diverse industrial sectors, the need for standardised testing methods is vital. These methods guarantee consistent quality and performance and facilitate comparisons across manufacturers and applications.

Standardised testing methods for VCI products are crucial for ensuring consistent quality, performance, and comparability across different manufacturers and applications. These methods:

- Provide a common basis for comparing different VCI products
- Ensure reproducibility of results across different laboratories
- Facilitate quality control in manufacturing processes
- Support regulatory compliance and product certification

However, developing standardised tests for VCI products presents unique challenges, owing to the diverse nature of VCI formulations and their application methods. These challenges include the following.

- Simulating real-world conditions in laboratory settings
- Accounting for the volatility and distribution of VCI compounds
- Addressing the variability in metal substrates and environmental conditions
- Developing tests that are applicable across different VCI product types

Overcoming these challenges is essential for creating comprehensive and reliable standardised testing methods that accurately reflect the performance of VCI products in various industrial applications.

4.4.2 Overview of Existing Standardized Methods

Various organisations have developed standards for testing VCI products. Table 4-9 summarises the most widely recognised standards.

Table 4-9: Summary of widely recognised standards for VCI product testing

Organisation	Key Standards	Primary Focus
ASTM (American Society for Testing and Materials)	ASTM D1748, B117, D1735, D2243-95, D5894-16	Humidity resistance, salt spray resistance, water resistance, freeze-thaw resistance, cyclic exposure
NACE (National Association of Corrosion Engineers)	NACE TM0208-2008	Vapour-inhibiting ability of VCI materials
MIL-SPEC (US Department of Defense)	MIL-PRF-22019, MIL-PRF-3420, MIL-STD-3010C, MIL-I-22110C, MIL-PRF-16173, MIL-C-83933	Performance specifications for various VCI applications in military contexts
German Standards	TL 8135-0043	Technical delivery conditions for corrosion protection packaging

4.4.2.1 ASTM Standards

ASTM has established several key standards for evaluating the effectiveness of VCI, including

- ASTM D1748: Humidity cabinet test for rust protection (ASTM Standard D1748-10, 2015)
- ASTM B117: Salt spray (fog) apparatus operation (ASTM Standard B117-11, 2016)
- ASTM D1735: Water resistance testing using water fog apparatus (ASTM Standard D1735-08, 2014)
- ASTM D2243: Freeze-thaw resistance of water-borne coatings (ASTM Standard D2243-95, 2014)
- ASTM D5894: Cyclic salt fog/UV exposure of painted metal (ASTM Standard D5894-96, 2016)

These standards involve the use of specific test parameters.

- ASTM D1748: Typically conducted at 48 ± 1°C and 95-100% relative humidity for 100-1000 hours.
- ASTM B117: Continuous exposure to 5% sodium chloride solution at 35 ± 1.5°C for 24-2000 hours.
- ASTM D1735: Water fog exposure at 38 ± 1°C for 24-300 hours.
- ASTM D2243: Alternating cycles of 16 h at -18°C and 8 h at 24°C, typically for five cycles.
- ASTM D5894: Alternating one week of UV/condensation exposure at 60°C and one week of salt fog exposure at 35°C, typically for 2-12 cycles.

These standards evaluate various aspects of corrosion protection, from humidity resistance to cyclic environmental exposure.

4.4.2.2 NACE Standards

The NACE TM0208 is a widely recognised test method for evaluating the vapour-inhibiting ability of VCI packaging materials. This test was typically conducted at 22 ± 2°C and 50 ± 5% relative humidity for 20 h. VCI-treated specimens were compared with untreated control specimens to assess the ability of the VCI-treated materials to inhibit corrosion in a controlled environment, simulating real-world storage and shipping conditions (NACE International TM0208, 2008).

4.4.2.3 MIL-SPEC Standards

Military Specification (MIL-SPEC) standards set by the U.S. The Department of Defense is crucial for the VCI products used in military applications. These standards ensure that VCI products meet rigorous requirements for various challenging environments.

- MIL-PRF-22019: Performance Specification for Barrier Materials, Transparent, Flexible, Sealable, Volatile Corrosion Inhibitor Treated (MIL-PRF-22019E, 2006)
- MIL-PRF-3420: Performance Specification for Wrapping Materials, Volatile Corrosion Inhibitor Treated, Opaque (MIL-PRF-3420H, 2008)
- MIL-STD-3010, Method 4031: Test Method for Vapour Inhibiting Ability of VCI Materials (MIL-STD-3010, 2002)
- MIL-I-22110: Military Specification for Inhibitors, Corrosion, Volatile, Crystalline Powder (MIL-I-22110C, 1985)

- MIL-PRF-16173: Performance Specification for Corrosion Preventive Compound, Solvent Cutback, Cold-Application (MIL-PRF-16173E, 1993)
- MIL-C-83933: Corrosion Preventive Compounds Cold Application (MIL-C-83933, 1967)

4.4.2.4 German Testing Methods

Germany has developed several test methods to evaluate the effectiveness of VCI materials, particularly under the Technische Lieferbedingungen (TL) standards. TL 8135-0043 is a comprehensive standard that specifies the technical delivery conditions for corrosion protection packaging (TL8135-0043, 2002). Figure 4-21 illustrates the requirements of TL 8135-0043 for corrosion protection, showing the specific criteria that the VCI products must meet to comply with this standard.

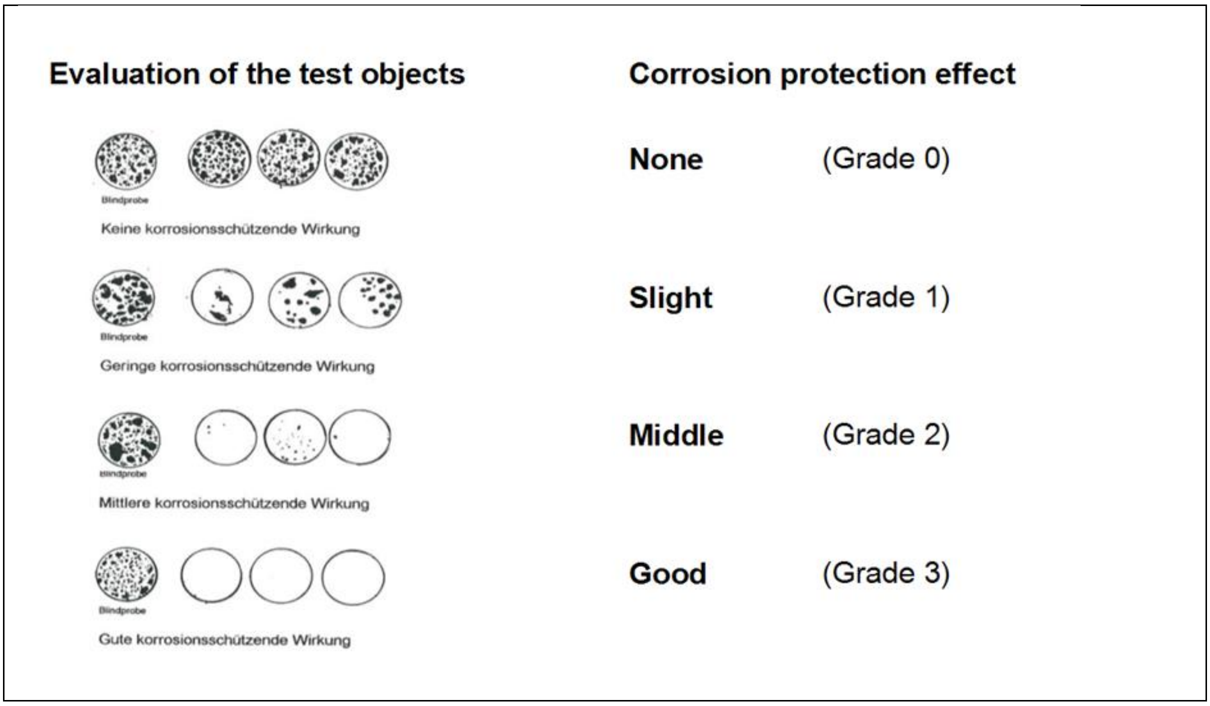


Figure 4-21: Requirements of TL 8135-0043 for the corrosion protection effect

4.4.2.5 Specific Testing Methods for VCI Product Types

Different VCI product types require specific testing methods to evaluate their performance accurately. Table 4-10 outlines the key tests for the various VCI product categories and the rationale for each test. The unique properties and application methods of each type of VCI require tailored testing.

Table 4-10: Key tests, relevant standards, and rationale for various VCI product types

VCI Product Type	Key Tests	Relevant Standards	Rationale
VCI Emitters	Vapour Inhibition Ability (VIA)	NACE TM0208-2008, German VIA Test TL 8135-002	Assesses the ability of emitters to release sufficient inhibitor vapours to protect metal surfaces in enclosed spaces.
VCI Films and Papers	Water vapour transmission rate (WVTR), Corrosion protection under cyclic humidity, Contact corrosion inhibition, VIA	MIL-P-3420E, MIL-PRF-22019D, German VIA Test TL 8135-002	Evaluate barrier properties, effectiveness in fluctuating humidity conditions, and ability to prevent corrosion through contact and vapour phase inhibition.
VCI Powders	Sublimation rate, Powder distribution uniformity, Corrosion protection in sealed environments, VIA	MIL-I-22110C, German VIA Test TL 8135-002	Measures the rate of inhibitor release, ensures even distribution for consistent protection and assesses effectiveness in confined spaces.
VCI Solvent Cutback Rust Preventive Coatings	Dry film thickness, Salt spray resistance, Humidity resistance, Adhesion testing, VIA	MIL-C-83933A, MIL-C-16173E, ASTM B117, German VIA Test TL 8135-002	Evaluates coating integrity, performance in harsh environments, and adherence to metal surfaces while maintaining vapour inhibition properties.
VCI Water-Based Non-Dry Coatings	VIA, Evaluation of corrosion protection and coating integrity	ASTM D2243-95(2008), German VIA Test TL 8135-002	Assesses the ability to provide corrosion protection without forming a dry film, focusing on vapour inhibition and direct contact protection.

4.4.3 Comparative Analysis of Different Standardized Methods

Several factors must be considered when comparing the different standardised methods.

1. Applicability to specific VCI product types
2. Correlation with real-world performance
3. Reproducibility and repeatability of results
4. Time and resource requirements
5. Sensitivity to environmental factors

Each testing method has its strengths and limitations, making it more suitable for specific industries or applications.

1. Salt Spray Test (ASTM B117):
    - Strengths: Widely accepted, easy to perform, and provides quick results.
    - Limitations: This may not accurately represent all real-world corrosive environments, especially those with cyclic wet-dry conditions.
    - Suitable for: Automotive industry, marine equipment manufacturers, and general metal finishing processes.
2. Cyclic Corrosion Tests (ASTM D5894-16)
    - Strengths: It provides a more realistic simulation of alternating wet and dry conditions and a better correlation with outdoor exposure results.
    - Limitations: Requires equipment that is more complex and extended testing periods.
    - Suitable for: Aerospace industry, architectural applications, and outdoor equipment manufacturers.
3. Humidity Cabinet Test (ASTM D1748).
    - Strengths: Simulates high-humidity environments, which are useful for evaluating the moisture resistance.
    - Limitations: Does not account for other corrosive factors such as salt or pollutants.
    - Suitable for: Electronics industry, indoor equipment manufacturers.
4. Electrochemical Impedance Spectroscopy (EIS):
    - Strengths: Provides quantitative data on corrosion rates and mechanisms, non-destructive.
    - Limitations: Requires specialised equipment and expertise to interpret results.
    - Suitable for: Evaluation on coatings for research and development in various industries, quality control in high-precision manufacturing.

5. Field Exposure Tests:
   - Strengths: Provides the most accurate representation of real-world performance.
   - Limitations: Time consumption, subject to variability in environmental conditions.
   - Suitable for: Long-term studies in specific geographical locations and validation of laboratory test results.

The choice of testing method often depends on the specific application of the VCI product and the type of corrosion protection required. For example:

- In the automotive industry, a combination of salt spray and cyclic corrosion tests is preferred to simulate the constant exposure to road salts and varying environmental conditions.
- For aerospace applications, where components are exposed to extreme temperature fluctuations and various atmospheric conditions, cyclic corrosion tests and field exposure tests may be more appropriate.
- In the electronics industry, humidity cabinet tests and electrochemical impedance spectroscopy can be used to assess protection against moisture-induced corrosion and subtle changes in protective coatings.

Furthermore, the economic implications of selecting a specific testing method should be considered. Although more comprehensive testing protocols, may require more significant initial investments in time and resources, they can lead to substantial long-term savings through improved corrosion prevention and reduced product failures in the field.

As the field of VCI technology advances, there is a growing need for standardised methods that can accurately assess corrosion inhibition efficiency and environmental impact. This is particularly crucial for industries that prioritise sustainable practices, where the balance between effective corrosion protection and environmental responsibility is becoming increasingly important.

4.4.4 Recent Developments in Standardization Efforts

Recent advancements in VCI testing standardisation include the following.

1. Development of application-specific test methods to better simulate real-world conditions

2. Integration of electrochemical techniques for quantitative corrosion rate measurement
3. Creation of accelerated testing protocols to predict long-term performance
4. Standardization of test conditions to improve reproducibility across laboratories

These developments aim to address some of the limitations of traditional testing methods and to provide more accurate and reliable results for modern VCI formulations, including sustainable options.

4.4.5 Future Directions in VCI Testing Standardization

As VCI technology continues to evolve towards more sustainable solutions, several areas require further development in testing standardisation.

1. Standardized methods for evaluating VCI effectiveness against specific types of corrosion (e.g., pitting, crevice corrosion)
2. Development of non-destructive testing methods for in-situ evaluation of VCI performance
3. Integration of computational modelling to complement physical testing
4. Harmonization of standards across different international organisations
5. Development of standardised tests specifically for assessing the environmental impact and sustainability of VCI products

4.4.6 Conclusion

Standardised testing methods for VCI products are crucial to ensure product quality, performance, and sustainability. As the field evolves, collaboration between industry, academia, and standards organisations is essential for developing and refining testing methods that accurately reflect the diverse applications and performance requirements of VCI products.

For the development of sustainable VCI for industrial applications, it is particularly important to integrate environmental considerations into standardised testing protocols. This involves assessing the biodegradability, ecotoxicity, and overall life-cycle impact of the VCI products and their corrosion inhibition performance. Thus, future VCI solutions can provide effective corrosion protection and meet the growing demand for environment-friendly industrial practices.

4.5 Parameters Evaluated for VCI Products

Volatile corrosion inhibitors (VCIs) and vapour-phase corrosion inhibitors (VPIs) protect the metal surfaces from atmospheric corrosion during transportation and storage. Several key parameters and evaluation methods have been developed to ensure the effectiveness of VCI products.

4.5.1 Corrosion Rate

Corrosion rate is a fundamental parameter for evaluating VCI products because it quantifies the effectiveness of the inhibitor in reducing metal degradation over time. Several methods have been employed to measure the corrosion rates:

4.5.2 Electrochemical Methods

Electrochemical techniques are widely used to determine corrosion rate and inhibition efficiency. These methods include the following (Roberge, 2008; Bastidas, 2020).

1. **Polarisation Resistance Measurement:** This technique involves applying a small potential perturbation to a metal sample and measuring the current response. The polarisation resistance is inversely proportional to the corrosion rate
2. **Electrochemical Impedance Spectroscopy (EIS):** EIS provides information about the electrochemical processes occurring at the metal-electrolyte interface. It can be used to determine the corrosion rate and evaluate the protective film formation by VCIs
3. **Potentiodynamic polarisation:** This method involves scanning the potential of a metal sample and measuring the resulting current. The corrosion current density, which is directly related to the corrosion rate, can be determined from the polarisation curves

4.5.3 Surface Analysis

Techniques such as Scanning Electron Microscopy (SEM) can be used to visually assess the extent of corrosion and the protective film formed by the inhibitor (Roberge, 2008; Bastidas, 2020)

4.5.4 Weight Loss Method

The weight loss method is simple and reliable for determining corrosion rates. The metal samples were exposed to corrosive environments with and without VCI, and weight loss was measured over time. The corrosion rate was calculated using the following equation (Malaret, 2022):

$$\text{Corrosion Rate (CR) [mm/year]} = \frac{(87600\ x\ C)}{(A.T.D)}$$

Where,

C = Weight loss, in gram ($W_{final} - W_{initial}$)

A = Surface area of coupon, in cm^2

T = Time of exposure, in hour

D = Density of coupon, in gcm^{-3}

4.5.5 Environmental Performance Parameters

Environmental factors significantly affect the performance of VCI products. The following tests were conducted to evaluate their effectiveness under various conditions:

4.5.5.1 Humidity Chamber Tests

Because moisture is a key factor in corrosion, VCIs must perform well under various humidity conditions. Humidity chamber tests involve exposing metal samples with VCI to a controlled humidity. The relative humidity is typically maintained at 80-100% to simulate harsh environments. The samples were periodically inspected for signs of corrosion (Vuorinen & Botha, 2013). Figure 2-1 shows a typical setup for humidity chamber tests to evaluate the VCI performance under various humidity conditions.

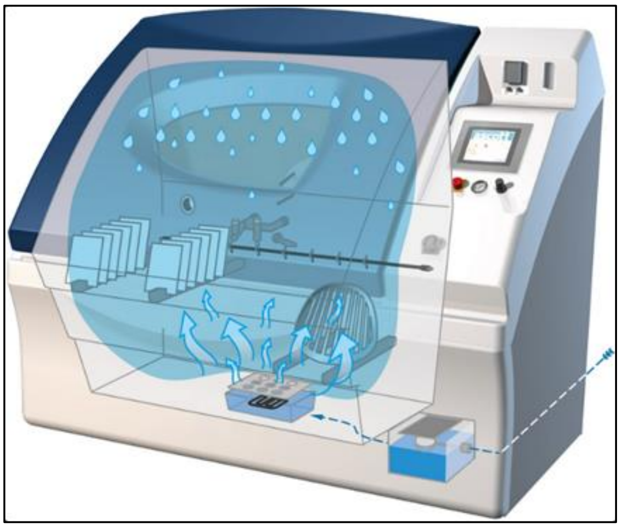


Figure 4-22: Humidity Chamber Test Setup

4.5.5.2 Salt Spray Tests

Salt spray tests evaluate the performance of VCI coating products in marine and coastal environments. The metal samples were exposed to a salt fog atmosphere, and the time until corrosion occurred was recorded. Figure 4-23 illustrates the salt spray test chamber used to assess VCI performance in salt fog atmospheres.

Figure 4-23: Salt Spray Test Chamber

4.5.5.3 Gas Phase Contaminant Tests

These tests evaluate the effectiveness of the VCI products in the presence of corrosive gases such as sulphur dioxide (SO_2) or hydrogen sulphide (H_2S). The samples were exposed to a controlled atmosphere containing these gases and the inhibition efficiency was determined (Poongothai et al., 2007).

4.5.6 Compatibility with Different Metal Substrates

VCI products should be effective for various metals and compatible with various materials used in packaging and storage.

1. **Multi-metal Corrosion Tests**

   These tests involve exposing different metal samples (e.g. steel, copper, and aluminium) to the same VCI product in order to evaluate their effectiveness across various metals.
2. **Material Compatibility Tests**

   Compatibility tests assess whether a VCI product has adverse effects on non-metallic materials, such as plastics, rubbers, or coatings, that may be present in the packaging or storage environment.

4.5.7 Adsorption Characteristics

The ability of VCI molecules to adsorb onto metal surfaces is crucial to their protective action. Several techniques can be used to study adsorption characteristics (Mohamed et al., 2022; Yi et al., 2018):

3. **Fourier Transform Infrared Spectroscopy (FTIR)**

   FTIR can be used to identify the functional groups present in VCI molecules and study their interactions with metal surfaces. This technique provides information about the adsorption mechanism and nature of the protective film formed by the inhibitor.
4. **X-ray Photoelectron Spectroscopy (XPS)**

   XPS is a surface-sensitive technique for analysing the chemical composition of the adsorbed VCI layer on metal surfaces. This provided information on the elemental composition and chemical states of the adsorbed species.

4.5.8 Vapour Pressure and Volatility

Vapour pressure and volatility are crucial for VCI performance. The effectiveness of VCIs is closely related to their vapour pressure and volatility. Vapour pressure determines the equilibrium concentration of the inhibitor in the surrounding atmosphere. Volatility, which is closely related to vapour pressure, influences the rate at which VCIs vaporise and reach the metal surfaces (Pieterse et al., 2006; Valente et al., 2020; Cheng & Salas, 2020). The key considerations include the following.

- **Balance**: VCIs must be sufficiently volatile for rapid protection but not so volatile as to be quickly depleted
- **Temperature dependence**: Volatility increases with temperature, affecting the VCI's performance across different environmental conditions
- **Molecular structure**: The chemical composition of VCIs impacts their volatility and, consequently, their effectiveness

1. **Gas Permeability**

   Gas permeability, defined as the product of vapour pressure and diffusion coefficient (S_A=$P_A D_{AB}$), is crucial for understanding the VCI transport. This parameter determines the rate at which VCI can be delivered across an air gap to a metal surface.

2. **Diffusion Coefficient**

   The diffusion coefficient (D_{AB}) is essential for estimating VCI transport through the gas phase. This parameter directly influences the rate at which VCI molecules reach and protect metal surfaces, making it crucial for understanding and optimising the VCI performance. It can be calculated using empirical methods such as Fuller's correlation:

$$\mathrm{D_{AB}} = \frac{10^{-3}\ \mathrm{T}^{1.75}\left[\frac{1}{\mathrm{M_A}} + \frac{1}{\mathrm{M_B}}\right]^{1/2}}{\mathrm{P}\left[(\sum \boldsymbol{\nu})_{\mathrm{A}}{}^{1/3} + (\sum \boldsymbol{\nu})_{\mathrm{B}}{}^{1/3}\right]^2}$$

Where,

D_{AB} = Binary gas phase diffusivity of A in B in cm^2/s

T = Absolute temperature in Kelvin

P = Absolute pressure in atmospheres

M_A, M_B = Molecular weights of A and B, respectively

$(\sum \boldsymbol{v})_A, (\sum \boldsymbol{v})_B$ = molecular volumes in cm^3/ g–mol

4.5.9 Evaluation Methods

Several techniques have been used to assess these parameters.

1. **Thermogravimetric analysis (TGA)**: Used to measure mass loss rates and estimate gas permeability at elevated temperatures
2. **Isothermal dilution**: Provides information on VCI volatility under constant temperature conditions
3. **Vapour inhibition ability (VIA) testing**: Methods such as the German Test Method TL 8135-002 were used to evaluate the effectiveness of the VCI products in protecting metal surfaces.
4. **Gas Chromatography (GC)**: The vapour composition of the VCI products was analysed and the concentration of the active components in the gas phase was determined.

Table 4-11comprehensively compares the major VCI evaluation methods discussed in this section and highlights their advantages, limitations, and applications.

4.5.10 Environmental and Safety Parameters

Environmental and safety considerations are crucial when evaluating volatile corrosion inhibitor (VCI) products. These parameters ensure that the VCI products provide effective corrosion protection, meet regulatory requirements, and minimise potential risks to human health and the environment. Figure 4-24 illustrates the key environmental and safety considerations for VCI products, summarising their impact on human health, the environment, and regulatory compliance criteria.

Table 4-11: Comparison of VCI evaluation methods

Method	Advantages	Limitations	Typical Applications
Electrochemical Methods (e.g., Polarisation Resistance, EIS, Potentiodynamic polarisation)	• High sensitivity and accuracy • Real-time measurements • Provides detailed information on	• Requires specialised equipment • May not accurately represent real-world conditions	• Laboratory evaluation of VCI effectiveness • Studying corrosion mechanisms • Rapid screening of VCI formulations

	corrosion mechanisms	• Interpretation can be complex	
Weight Loss Method	• Simple and reliable • Provides direct measurement of material loss • Applicable to various environments	• Time-consuming for long-term studies • Cannot provide real-time data • May not detect localised corrosion	• Long-term VCI performance evaluation • Field testing • Comparison of different VCI products
Humidity Chamber Tests	• Simulates real-world humid conditions • Controlled environment for reproducible results • Can test multiple samples simultaneously	• May not represent all environmental factors • Limited to specific humidity ranges • Can be time-consuming	• Evaluating VCI performance in high-humidity environments • Comparative studies of different VCI formulations
Salt Spray Tests	• Simulates marine and coastal environments • Accelerated corrosion testing • Standardised method	• May not accurately represent all corrosive environments • Can be overly aggressive compared to real conditions • Only for coating product	• Testing VCI coatings for marine applications • Evaluating VCI performance in chloride-rich environments
Gas Phase Contaminant Tests	• Evaluate VCI effectiveness against specific corrosive gases • Controlled atmosphere for reproducible results	• Limited to specific gas contaminants • May not represent complex atmospheric conditions	• Testing VCI products for industrial environments with specific gas contaminants • Developing specialised VCI formulations
Thermogravimetric Analysis (TGA)	• Provides information on VCI volatility and thermal stability • Can estimate gas permeability at elevated temperatures	• Limited to thermal properties • May not directly correlate with corrosion protection	• Studying VCI volatilisation behaviour • Optimising VCI formulations for different temperature ranges

Vapour Inhibition Ability (VIA) Testing	• Directly evaluates VCI effectiveness in vapour phase • Standardised method (e.g., German Test Method TL 8135-002)	• May not represent all environmental conditions • Limited to specific test setups	• Evaluating overall VCI product performance • Quality control in VCI production
Gas Chromatography (GC)	• Analyses VCI vapour composition • Can determine concentration of active components	• Does not directly measure corrosion protection • Requires specialised equipment	• Studying VCI vapour phase composition • Monitoring VCI product consistency

Figure 4-24: Environmental and Safety Considerations for VCI Products

3. **Toxicity**

   VCI products should have a low toxicity to humans and the environment. This can be evaluated as follows.

   - Acute toxicity tests
   - Chronic exposure studies
   - Ecotoxicity assessments for aquatic and terrestrial organisms

   Modern VCI formulations often aim to avoid harmful compounds such as nitrites, which have been traditionally used but pose health risks.

4. **Environmental Impact**

   The environmental footprint of the VCI products is a key consideration.

   - **Biodegradability**: VCIs should ideally be biodegradable to reduce long-term environmental impacts
   - **Bioaccumulation potential**: Products with low bioaccumulation potential are preferred.
   - **Volatile Organic Compound (VOC) content**: Low-VOC or VOC-free formulations are desirable to comply with air quality regulations

- **Regulatory Compliance**

  VCI products must satisfy several regulatory standards.

  - Compliance with REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) in Europe
  - Adherence to EPA (Environmental Protection Agency) guidelines in the United States
  - Conformity to other regional or industry-specific regulations (e.g., RoHS)

4.5.11 Protection Duration

The protection duration is a critical parameter for assessing the long-term effectiveness of Volatile Corrosion Inhibitors (VCIs). Although they cannot be measured directly, they can be inferred from various evaluation methods and factors.

5. **Long-term Corrosion Rate Measurements**

   Extended corrosion rate measurements using weight loss or electrochemical techniques can provide insights into the duration of the VCI protection. A sustained low corrosion rate indicates ongoing protection, whereas an increase indicates the end of the effective protection period. This approach complements the previously discussed corrosion rate evaluation methods.

6. **Environmental Performance Tests**

   Long-term environmental chamber tests were conducted to evaluate the duration of the VCI protection under specific conditions. Extended humidity chambers and salt spray tests provide valuable data on VCI longevity in controlled environments.

7. **Field Testing and Real-world Performance**

   Field testing in industrial environments is crucial for accurately assessing the protection duration. Long-term field trials with periodic inspections provide the most reliable information on the effectiveness of VCI, thus complementing laboratory evaluations.

Considering these factors and evaluation methods, it is possible to estimate the long-term effectiveness of VCI products effectively. This comprehensive approach is crucial for developing sustainable VCI solutions that ensure adequate protection throughout the service life of treated components.

4.6 Laboratory and Field Testing Protocols

4.6.1 Introduction

Vapour Corrosion Inhibitors (VCIs) are crucial for protecting industrial assets from corrosion. Developing and evaluating effective VCI products requires a holistic approach that integrates laboratory and field testing methodologies. This section explores the intricate relationship between these two testing methodologies, their significance in VCI development, and strategies employed to correlate laboratory results with real-world performance.

4.6.2 Comparative Analysis of Laboratory and Field Tests

The differences between laboratory and field-testing methodologies are substantial and influence various aspects of the VCI evaluation. Table 4-12 provides a comprehensive comparison of these two approaches.

As illustrated in Table 4.12, although laboratory testing offers high reproducibility and efficient screening, field testing provides insights into long-term performance under real-world conditions.

4.6.2.1 Environmental Control

Laboratory tests are conducted under carefully controlled conditions, allowing for the isolation and manipulation of specific variables such as temperature, humidity, and contaminant concentration (Revie, 2008). Conversely, field tests subject VCI products to the complex and dynamic conditions of industrial environments where multiple factors interact simultaneously and unpredictably (Wan et al., 2005). Moreover, real-world conditions involve multiple interacting factors that can be unpredictable and challenging to replicate in the laboratory.

Table 4-12: Comparative Table: Laboratory vs. Field Testing

Aspect	Laboratory Testing	Field Testing
Environmental Control	Highly controlled, isolation of variables	Variable, real-world conditions
Time Scale	Accelerated (weeks to months)	Real-time (months to years)
Reproducibility	High	Lower due to environmental variability
Cost	Lower, more frequent testing is possible	Higher requires significant resources
Advantages	• Precision and repeatability • Efficient screening of formulations • Controlled isolation of variables	• Comprehensive evaluation under actual conditions • Reveals long-term performance • Uncovers unforeseen interactions
Limitations	• May oversimplify real-world interactions • May not fully represent long-term performance	• Time and resource intensive Difficult to control variables • Lower reproducibility
Primary Use	Early development, rapid screening	Pre-commercialization, long-term validation

4.6.2.2 Time Scale and Acceleration

The primary distinction between laboratory tests and field tests is their temporal dynamics.

- **Laboratory Tests**: Typically accelerated to compress years of exposure into weeks or months, providing rapid results
- **Field Tests**: Operate on real-time scales, offering long-term performance data but requiring extended periods to generate conclusive results

4.6.2.3 Reproducibility and Variability

The controlled nature of the laboratory tests ensured high reproducibility, facilitating statistical analysis and comparison between different VCI formulations. This reproducibility is crucial for iterative product development and quality control. Conversely**,** field tests, which are more representative of actual conditions, often exhibit lower reproducibility because of the inherent variability in environmental factors and operational conditions (Papavinasam, 2013).

4.6.2.5 Resource Investment and Cost Considerations

Laboratory testing requires less resource investment and can be conducted more frequently, facilitating iterative product development. However, field testing, which is costly and time-consuming, provides invaluable data on real-world performance, and can reveal issues that are not apparent in laboratory settings.

4.6.3 Correlation of Laboratory and Field Results

Correlating laboratory and field test results is crucial for accurately predicting the real-world performance of VCIs based on controlled laboratory data. Therefore, this correlation enhances the reliability of laboratory tests as indicators of field success and helps to refine testing protocols for future development.

- **Scaling Factors**: Develop and apply scaling factors to adjust laboratory results to better match the field conditions. These factors often account for differences in exposure time, environmental aggressiveness, and cyclic conditions.
- **Predictive Modelling**: Develop models that translate laboratory findings into expected field performance, factoring in variables such as time, temperature, and environmental aggressiveness. Machine learning algorithms can be

particularly useful for identifying complex patterns and enhancing the predictive accuracy.

- **Parallel testing**: Simultaneous laboratory and field tests were conducted on identical materials to identify the consistent patterns and deviations. This approach allows for direct comparisons and helps to refine laboratory protocols to better mimic field conditions.
- **Comparative Analysis:** To validate laboratory methodologies and compare the corrosion rates obtained from laboratory electrochemical corrosion cells with field observations. This comparison often involves a statistical analysis to establish correlations and identify discrepancies.

4.6.4 Relative Importance in VCI Development Stages

The significance of laboratory and field tests varies depending on the stage of the product development.

- **Early Development Stage**

  Laboratory tests are crucial for the following reasons.
  - Rapid screening of formulations
  - Optimization of chemical composition
  - Refinement of application methods
- **Pre-commercialization Stage**

  As products approach commercialisation, field testing has become increasingly important for
  - Validating laboratory findings
  - Assessing long-term performance
  - Evaluating compatibility with actual service conditions

4.6.5 Application-Specific Considerations

The balance between laboratory and field testing may shift based on the specific applications. For instance, accelerated laboratory tests may suffice for temporary protection (e.g. during shipping). In contrast, extensive field testing is indispensable for long-term protection of critical industrial equipment.

The development of effective VCI products involves a systematic process that integrates laboratory and field testing at various stages. Figure 4-25 outlines this process.

As shown in Figure 4.25, the VCI development process begins with initial formulation and rapid screening in the laboratory. It progresses through various evaluation stages before final product validation, relying heavily on field testing.

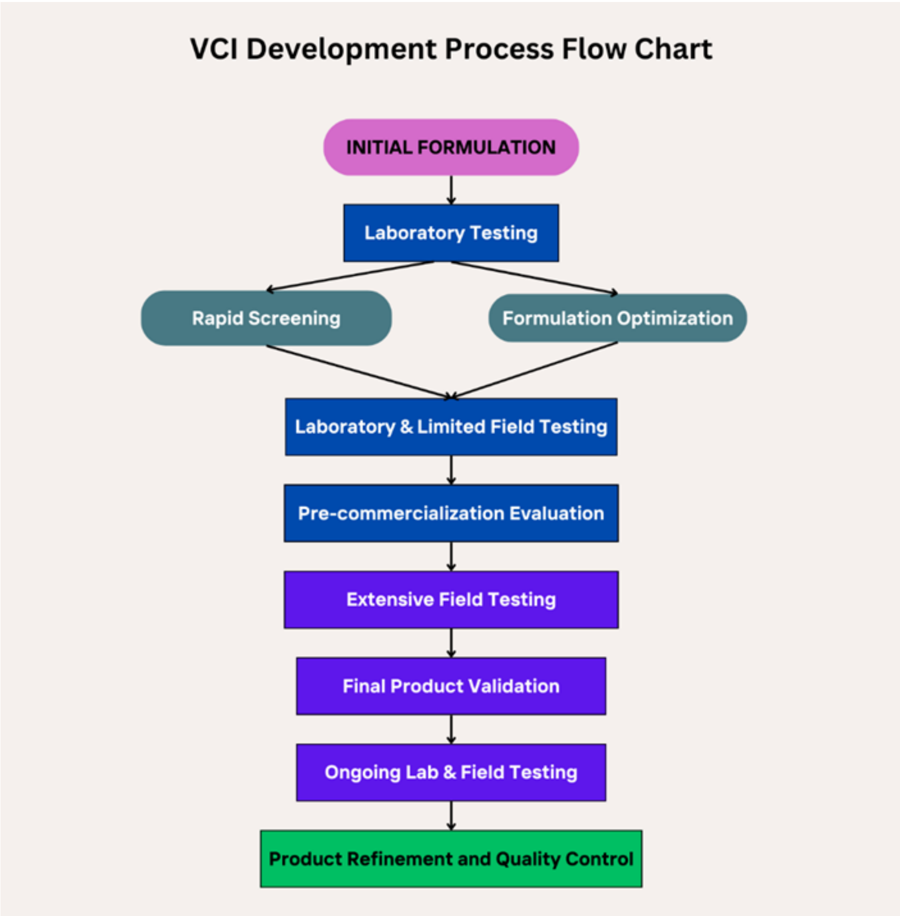


Figure 4-25: VCI Development Process Flow Chart

4.6.6 Protocols for Performing Laboratory and Field Tests

1. **Laboratory Testing Protocols**
    a. **Sample Preparation**: Standardized cleaning and preparation of metal samples (Bianchi et al., 2023)
    b. **VCI Application**: Consistent application of VCI products to samples
    c. **Exposure**: Subjecting samples to controlled corrosive environments with regulated parameters (time, temperature, humidity)

d. **Analysis**: Utilizing diverse analytical techniques to evaluate the efficiency of corrosion inhibition

2. **Field Testing Protocols**
    a. **Site Selection**: Choosing appropriate test sites representing the intended use environments.
    b. **Sample installation**: Prepare and treat the metal samples and install them in field locations.
    c. **Monitoring**: Conducting regular inspections and documentation of sample conditions over time.
    d. **Data Collection**: Gathering environmental data alongside sample performance metrics.
3. **Integration of Testing Protocols**

    To ensure a seamless transition from laboratory to field application

    a. Coordinate testing schedule
    b. Maintain consistency in sample preparation methods
    c. Establish clear criteria for evaluating performance across both settings

4.6.7 Methods to Ascertain Lab Test Results to Field Conditions

a. Correlation Studies:

Conduct parallel laboratory-accelerated corrosion tests and field exposure tests and analyse their correlation to refine the predictive models.

b. Comparative Analysis:

To validate the laboratory methodologies, the corrosion rates obtained from the laboratory electrochemical corrosion cells were compared with the field observations.

c. Realistic Environment Simulation

Enhances laboratory testing using

- Salt compositions that reflect actual environmental conditions
- Inclusion of inert dust particles, corrosive gas
- Simulation of diurnal fluctuations in temperature and relative humidity

d. Multi-environment Testing

Perform tests in diverse settings, including controlled laboratory environments, semi-field conditions, and full-field exposure. This comprehensive approach provides a more nuanced understanding of VCI performance across different scenarios.

e. **Long-term Studies:**
   Short-term accelerated lab tests have been combined with extended field exposure studies to establish the relationships between accelerated and natural corrosion processes (Bianchi et al., 2023).

f. **Extrapolation Models:**
   Develop models to extrapolate short-term corrosion test results to time-varying field atmospheric environments, enhancing the predictive power of laboratory data.

g. **Quality Control and Standardisation**
   Implementing quality control programs and adhering to standardised procedures (e.g. ASTM standards and Mil Specs) to ensure reliable and reproducible corrosion tests, facilitating the correlation between laboratory results and field performance.

h. **Documentation and Transparency**
   Finally, detailed documentation of test procedures, conditions, and deviations from standard methods is crucial for ensuring traceability and allowing the proper interpretation of results regarding field conditions.

4.6.8 Sustainability Considerations in VCI Testing

As sustainability has become increasingly crucial in industrial applications, VCI testing protocols must evolve to address environmental concerns. Therefore, it is essential to:

- Evaluate the environmental impact of VCI products during testing, considering toxicity, biodegradability, and bioaccumulation potential.
- Assess the biodegradability and eco-toxicity of VCI formulations using standardised tests, such as OECD 301, for ready biodegradability.
- Life-cycle analysis in long-term field testing was considered to evaluate the overall environmental impact of VCI use in industrial settings.

4.6.9 Advanced Techniques and Future Directions

Incorporate cutting-edge analytical methods such as

- Electrochemical Impedance Spectroscopy (EIS) for real-time corrosion monitoring

- 3D surface analysis techniques for precise quantification of corrosion damage

Big Data and Machine Learning

Leverage big data analytics and machine learning algorithms to

- Identify complex patterns in corrosion behaviour
- Enhance predictive models for VCI performance

4.6.10 Miniaturisation and In-situ Monitoring

Develop miniaturised sensors and in situ monitoring systems for continuous, non-destructive evaluation of VCI performance under field conditions (Wang et al., 2022).

4.6.11 Conclusion

The effective development and evaluation of VCI products necessitate a balanced and integrated approach to laboratory and field testing. Although laboratory tests provide rapid and controlled assessments, field tests offer irreplaceable insights into the real-world performance. By implementing robust protocols for test integration and developing sophisticated methods to relate laboratory results to field conditions, the product development process can be accelerated, performance predictions can be improved and ultimately more effective and reliable VCI solutions for industrial applications can be delivered.

Chapter 5

5. EXPERIMENTATION AND RESULTS

This chapter provides an in-intensity exploration of the performance and prevention of Volatile Corrosion Inhibitors (VCIs) throughout each laboratory and subject setting. The research is divided into two essential sections: The first examines the controlled laboratory conditions to assess the efficacy of VCIs in diverse forms along with kraft paper, movies, and coatings. The second section shifts awareness to real-global applications, assessing the overall performance of VCIs in vehicles, offshore platforms, and commercial equipment.

Through a systematic approach, this study aims to provide radical information on how VCIs are characteristic across distinctive environments and materials, presenting valuable insights into their sensible applications and barriers. Each segment is based on giving a detailed description of the look, the methods accompanied, and the outcomes acquired, presenting the effectiveness of VCIs in mitigating corrosion.

5.1 Laboratory study

5.1.1 VCI in kraft paper

5.1.1.1 Description

This experiment aims to assess the impact of MBL 2200 on ferrous steel when applied to kraft paper and to determine the minimum amount of Amino-Carboxylate required to provide effective protection to the metal.

In this experiment, a piece of MG Interleaving kraft paper with dimensions of A4 size (210 mm x 297 mm) and a weight of 57 g was selected as the test specimen. Due to the lack of data on the absorption capacity of the kraft paper, an initial quantity of 6 g of the mixture was applied using a brush to determine if it was sufficient to cover the entire surface.

After applying the 6 g, it was found that only 65% of the paper's surface was covered. Therefore, to achieve full coverage, accounting for material loss during brushing, a second application of 11 grams of the mixture was performed. This amount successfully covered the entire surface of a new piece of kraft paper (Table 5-1).

Table 5-1: Grams for brushing and percentage coverage

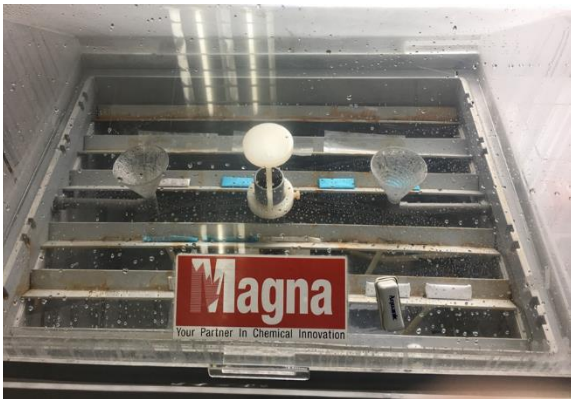
Grams used for brushing (g)	**Percentage coverage (%)**
6	65
11	100

5.1.1.2 Procedure

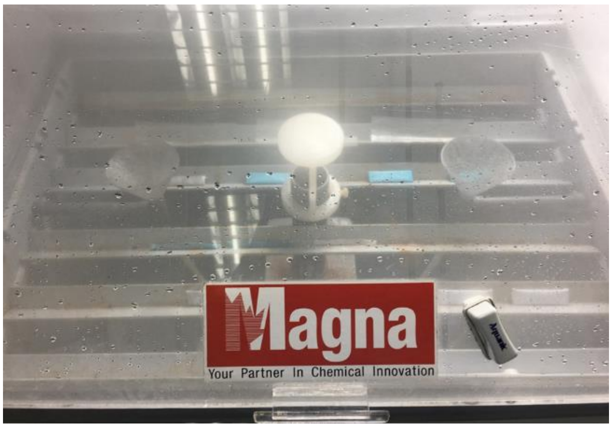
1. A size of 120mm width and 100mm length is measured and cut out from normal paper, kraft paper and kraft paper with non-diluted MBL 2200.
2. Eight steel pieces are polished and then cleansed with ethanol.
3. Images of steel pieces are taken.
4. The steel pieces are immediately wrapped by paper. The papers are normal paper, kraft paper, kraft paper with 1%, 2%, 3%, 4%, 5% and 20% (non-diluted) of Amino-Carboxylate in kraft paper.
5. The humidity chamber is turned on and the temperature is set to 35°C.
6. When the temperature inside the chamber reaches 35°C and humidity level reaches 100%, the specimens are put into it.
7. The specimens are then taken out after 1 day and the paper is carefully opened.
8. Any changes on the metals and papers are observed. Images are taken as a record.
9. The specimens are then wrapped again with the same paper and put back into the chamber.
10. Steps 8 and 10 are repeated for 5 days.

5.1.1.3 Results

From the experimental results, we observed in Figure 5-1 and Table 5-2 that 5% Amino-Carboxylate has around the same effect as 20% Amino-Carboxylate. Hence, we concluded that kraft paper with 5% Amino-Carboxylate has excellent effect in protecting metals from corrosion observed after 5 days in extreme humid condition. Hence, the process of producing VCI paper in this laboratory can be justified as success.



a) b)

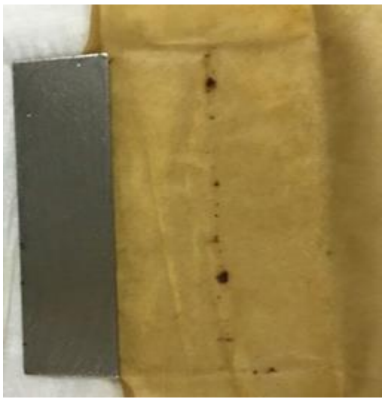
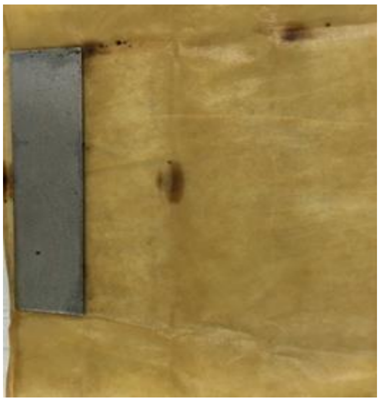


c) d)

Figure 5-1: Set-up of humidity chamber for corrosion protection test: a) before test, b) during test, c) after test, and d) temperature and pressure settings

Table 5-2: Results of humidity chamber test

Type of paper used	**Day 1 (Before putting into humidity chamber)**	**Day 3**	**Day 5**
Normal Paper			

Kraft paper			
Kraft paper with 1% Amino-Carboxylate			
Kraft paper with 2% Amino-Carboxylate			
Kraft paper with 3% Amino-Carboxylate			

Kraft paper with 4% Amino-Carboxylate			
Kraft paper with 5% Amino-Carboxylate			
Kraft paper with 20% Amino-Carboxylate			

5.1.2 VCI in films

5.1.2.1 Description

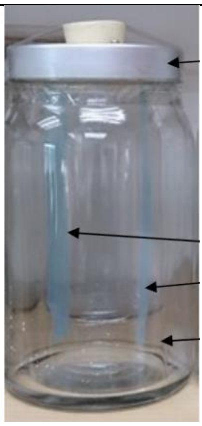
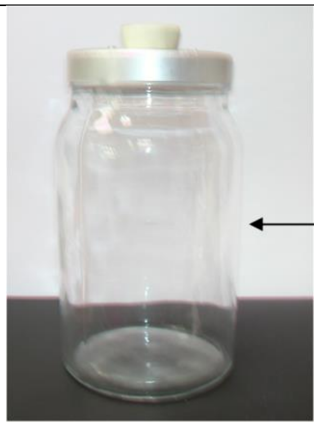
In this test, a sample highly sensitive to corrosion, due to condensation water, is packed together with VCI auxiliary packing material in a tightly sealed vessel. Condensation is then induced on the surface of the test sample. A blank trial, which is a similar setup without the VCI auxiliary packing material, is conducted to verify whether the test conditions are adequate to cause corrosion on the unprotected sample.

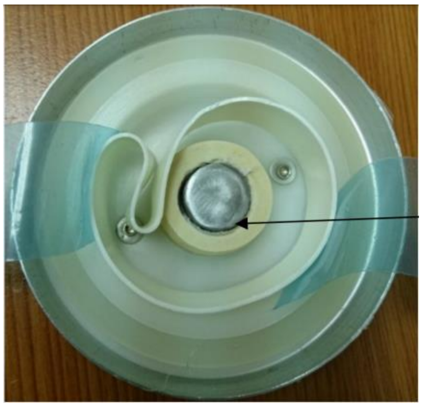
The effectiveness of the VCI packing material is assessed by comparing the level of corrosion observed on the protected sample versus the unprotected control.
The German test method TL8135-002 is utilized to evaluate the corrosion protection properties of the Vappro VBCI 826 film. This method is specifically designed to assess the effectiveness of Volatile Corrosion Inhibitor (VCI) papers and films in protecting constructional steel against corrosion.

5.1.2.2 Procedure

Four test objects were polished with 320 grit abrasive paper to remove all the grit and rust. Rinsed with ethanol and dried them. Then rubber stopper was inserted to the test jar cover. Two strips of 2.5 cm x 15 cm of test samples were attached with test jar cover. For blank sample, test jar was sealed without inserting two strips of test samples. It had no VCI chemicals and it is only used as a control/ yardstick for the experiment (Table 5-3).
The four test sets were stored for a period of (20±0.5) hours at a room temperature. At the end of the storage period, the jar covers were removed from the test jars, the freshly prepared 10 ml of test solution. Glycerine/water mixture was poured into each jar immediately after opening, and the jars were immediately closed again. After an additional 2 hours ± 10 minutes, the test jars were stored for a period of 2 hours ± 10 minutes in the heating chamber at temperature 40°C to create 90% Relative Humidity in the both test jars.

Table 5-3: Difference between unprotected and protected simple

Blanc	**With VCI**
	

5.1.2.3 Results

No sign of corrosion was found on three test objects protected with Vappro 826 VCI film. Based on above the test result, Vappro VBCI 826 Film extruded from Vappro VBCI MBR1000 Resin passed the Grade 3 German test method TL 8135-0002 (Table 5-4).

Table 5-4: Results of corrosion protection test

Blanc	**With VCI**
	

5.1.3 VCI in coating

5.1.3.1 Description

Recently, there has been a shift in using water-based VCIs, which are less hazardous to human health and are environmentally friendly, as opposed to oil-based VCIs. By substituting the organic solvent with water as the transport medium, it would lower the levels of volatile organic compounds (VOCs) emitted by VCIs. This section aims to deduce the concentration of the VCI in coating, that can offer the best corrosion protection and under what conditions can this be achieved. The effects of the concentration of inhibitors, coating time, drying time and temperature on its performance are studied and observed.

5.1.3.2 Procedure

Sample Preparation

1. The dimensions of the metal samples have been measured to calculate their surface area.
2. The metal samples have been de-rusted by hand using 600 grit abrasive paper.
3. The samples have been rinsed with deionized water and isopropyl alcohol to remove debris from the de-rusting procedure.

Corrosion Inhibitor Solution Preparation

1. Formulations of commercial VAPPRO 837C have been prepared using a concentrated corrosion inhibitor solution based on amine carboxylates.
2. The concentrated corrosion inhibitor CORPPRO has been diluted in deionized water to achieve concentrations of 0.25, 0.50, 0.75, and 1.0 ml/100 ml (v/v) for testing.
3. The prepared solutions have been allowed to stand for one day to ensure stability before use.

Application of VAPPRO 837C

1. VAPPRO 837C has been applied to clean mild steel samples by immersion using a clock glass as a coating reservoir.
2. Various immersion times for the coating process have been selected and tested: 10 min, 20 min, 30 min, 8 hr, and 24 hr.
3. After immersion, the samples have been removed using tweezers and allowed to dry.

Testing and Optimization

1. The metal samples, once dried, have been tested using a potentiostat to calculate their corrosion rates.
2. The immersion coating and drying times have been varied to determine the optimal conditions for maximum protection efficiency.

5.1.3.3 Results

Figure 5-3 illustrates the effect of drying time on corrosion reduction efficiency. The data indicates that the corrosion reduction efficiency stabilizes as the drying time increases, regardless of immersion time or inhibitor concentration. This stabilization is observed at drying times of 5 hours and 24 hours, where only minor variations in efficiency occur for 10, 20, and 30 minutes of immersion across all concentrations. However, the highest corrosion reduction efficiency (91.29%) was achieved with a 1-hour drying time, though this was inconsistent across different concentrations.

This inconsistency could be due to residual water content in the coating film, which might still promote corrosion despite appearing dry after 20 minutes. The protective inhibitor film may have partially formed with drying times shorter than 5 hours. Therefore, a drying time of around 24 hours is optimal.

From an industrial perspective, a 24-hour drying time is not only optimal for corrosion reduction efficiency, but also practical. It aligns with typical working hours, making it easier to monitor and ensure that the metals can be stored promptly once drying is complete.

Similarly, Figure 5-3 shows the effect of CORPPRO concentration on corrosion reduction efficiency. The highest efficiency was achieved with a CORPPRO concentration 0.5 when the drying time was 1, 2, and 5 hours. For a drying time of 24 hours, the highest efficiency was obtained with a concentration of 0.25 (85.07%), although the concentration of 0.5 provided a similar efficiency (82.27%).

As the coating time of CORPPRO varied, it was observed that corrosion reduction efficiency differed depending on the drying time. For 1 and 2 hours of drying, the efficiency did not exhibit a stable trend with varying coating times. However, the corrosion reduction efficiency remained stable for 5 and 24 hours of drying from 10 minutes to 8 hours of coating time. Extending the coating time beyond 30 minutes does not significantly improve corrosion reduction efficiency compared to a 30-minute coating time.

This may be because, by 30 minutes, the metal substrate’s surface becomes fully saturated with inhibitor molecules, and the metal surface-inhibitor interactions stabilize. Therefore, additional coating time does not reduce corrosion, while shorter coating times may result in incomplete substrate surface saturation with inhibitor molecules, leading to higher corrosion rates.

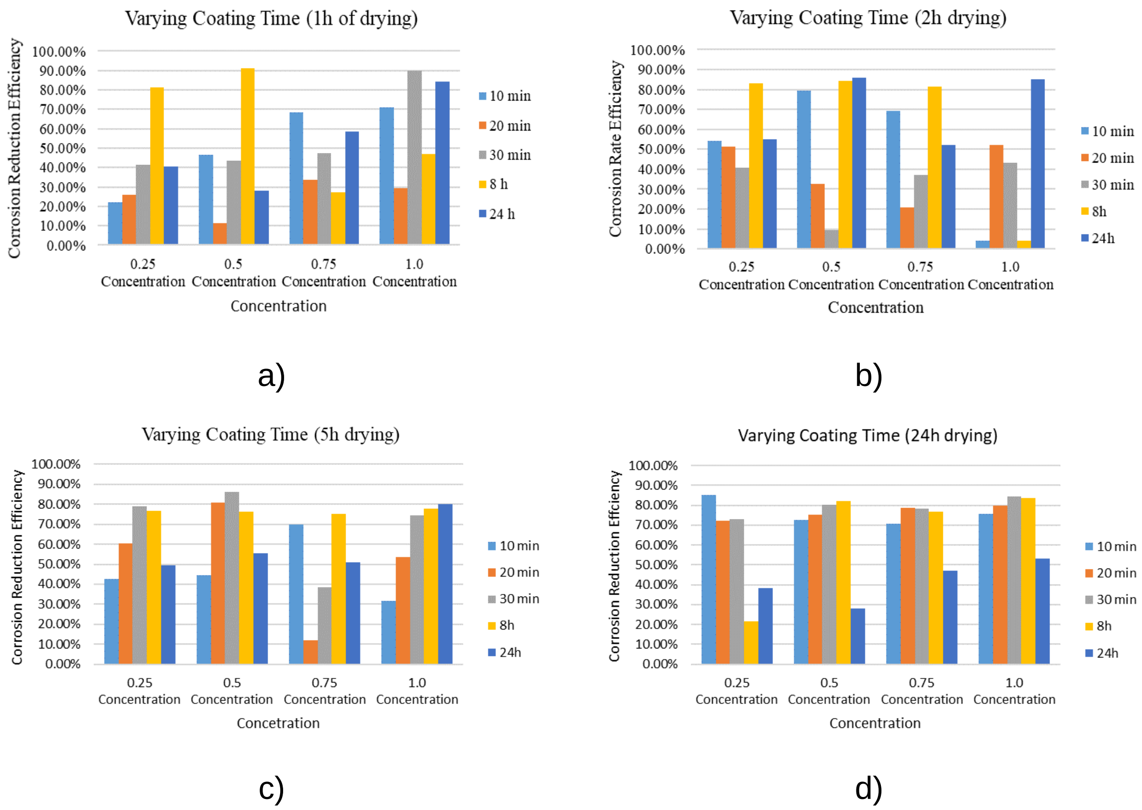


Figure 5-3: Effects of varying concentration on corrosion reduction efficiency for different coating times: a) 1h of dying, b) 2h of dying, c) 5h of dying, and d) 8h of dying

5.2 Field study

5.2.1. VCI in vehicles

5.2.1.1 Description

This section presents three case studies that demonstrate the successful application of VCIs in diverse industrial sectors. These studies illustrate the effectiveness of VCIs in protecting valuable assets from corrosion, extending their service lives, and reducing maintenance costs in military, oil and gas, and industrial equipment applications.

Armed forces worldwide face significant challenges in maintaining their armoured vehicle fleet due to downsizing and declining populations. Traditional maintenance practices, involving manual engine oil changes and periodic engine running, are labour-intensive, time-consuming, and prone to accidents. Despite these efforts, vehicles continue to suffer from corrosion and degradation of critical components, resulting in high maintenance costs and reduced operational readiness.

Environmental factors such as humidity, moisture, and temperature fluctuations cause significant deterioration in various vehicle systems, including gearboxes, engines, weapon systems, and electronics. Over time, the oils and greases degrade, further reducing the lifespan of the component. Long-term storage without proper environmental control can lead to material ageing, degradation, and system failure.

5.2.1.2 Procedure

This study focused on the application of VCIs to various systems of CM 27 armoured vehicles.
The applications of this method are as follows.

1. General preservation: VCI plastic films (polyethylene with a 1.5% w/w proprietary VCI blend) were used to wrap exterior surfaces and critical components. As shown in Figure 5-4.
2. Cooling system: As shown in Figure 5-5, a VCI coolant additive (2% v/v solution of carboxylic acid salts and azoles) was added to the coolant.
3. Engine system: A VCI engine oil additive (9% v/v amine carboxylates and thiocarbamates) was mixed with the engine oil. Figure 5-6 illustrates the process.
4. Fuel system: As illustrated in Figure 5-7, a VCI fuel additive (1500 ppm aliphatic amine derivatives) was introduced into the fuel tanks.
5. Moving mechanisms: VCI grease (lithium complex grease with 3% w/w VCI compounds) was applied to all the moving parts and bearings. Please refer to Figure 5-8 for details of this application.
6. Hydraulic system: The hydraulic fluid was treated with a VCI hydraulic oil additive (5% v/v amine carboxylates), as shown in Figure 5-9.

The preservation duration was 24 months, and inspections and tests were conducted at 6-month intervals. The VCI-treated vehicles exhibited an average reduction of 99.9% in the corrosion rate. This significant corrosion reduction demonstrates the effectiveness of VCI treatment across all vehicle systems.

Figure 5.4: Preservation of armoured vehicles with VCI plastic

Figure 5-5: Preservation of cooling system using VCI coolant additives

Figure 5-6: Preservation of engine system using VCI engine oil additive

Figure 5-7: Preservation of fuel systems using VCI fuel additives

Figure 5-8: Preservation of moving mechanisms with VCI grease

Figure 5-9: Preservation of hydraulic systems using VCI hydraulic oil additive

5.2.2 VCI in offshore platforms

5.2.2.1 Description

Offshore oil and gas platforms operate in highly corrosive environments and are constantly exposed to salt sprays, humidity, and temperature fluctuations. Traditional corrosion protection methods such as protective coatings and cathodic protection are often insufficient under harsh conditions. Corrosion results in significant maintenance cost, reduced operational efficiency, and potential safety hazards.

5.2.2.2 Procedure

This study focuses on the application of VCIs to various offshore platform systems.

1. Electrical cabinets: VCI emitters and pouches (containing a proprietary blend of amine carboxylates and azoles) were installed in the electrical cabinets to protect sensitive electronics and connections. Figure 5-10 illustrates this application. A VCI electronic spray liquid (1% v/v concentration of amine carboxylates with a fast-drying solvent) was applied to electrical circuits' relays to prevent galvanic corrosion of all commonly found metals, and alloys in electronic applications, as shown in Figure 5-11.
2. Piping systems: VCI powder (containing a mixture of amine carboxylates and azoles) was used to preserve the piping system during the layup period, as shown in Figure 5-12.
3. Hydraulic systems: A VCI hydraulic fluid additive (5% v/v amine carboxylates) was mixed with the hydraulic oil. This additive treats synthetic and hydraulic oil systems in top drives, cranes, drawworks, mud pumps, agitators, pipe-handling equipment, winches, lifeboats, davits, compressors, and air-hoists. Figure 5-13 illustrates this process.
4. Exterior equipment: A VCI water-based acrylic coating (containing 3% w/w VCI compounds) was applied to all exterior equipment and rails, drill floor areas, exterior crane cabins, housing and booms, and exposed equipment on the main deck, including transfer equipment, lifeboat equipment, air hoists, fire station locations, and winches (Figure 5-14).
5. Flanges and valves: A VCI-impregnated wrapping tape was used to protect the flanges and valves, as shown in Figure 5-15.
6. Outdoor heavy machinery: VCI plastic films (polyethylene with a 1.5% w/w proprietary VCI blend) were used to protect the heavy machinery placed outdoors, as shown in Figure 5-16.
7. Void spaces: The VCI fogging fluid (containing a 5% v/v mixture of amine carboxylates and azoles) was used to treat the void spaces and tanks during the layup periods, as illustrated in Figure 5-17.

The preservation duration was 24 months, and inspections and tests were conducted at 6-month intervals.

The VCI-treated areas exhibited an average reduction of 99.9% in corrosion rate.

Figure 5-10: VCI emitters and pouches used in large control panels, electrical power supplies

Figure 5-11: Application of VCI electronic spray to electric circuits and relays

Figure 5-12: VCI powder is fogged to preserve the piping system

Figure 5-13: Preservation of hydraulic system using VCI hydraulic oil additive

Figure 5-14: Apply VCI acrylic coating to the exterior equipment

Figure 5-15: VCI wrapping tape to protect flanges and valves

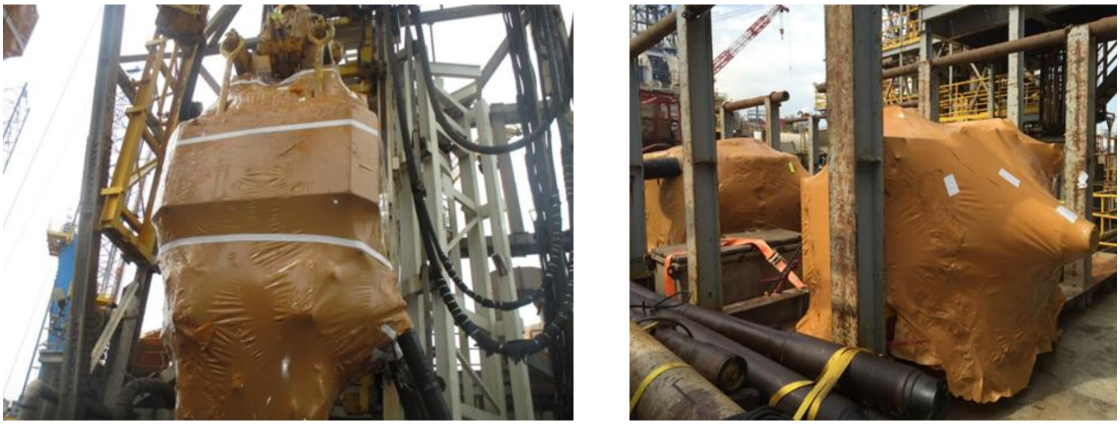


Figure 5-16: VCI plastic to preserve outdoor heavy machinery

Figure 5-17: VCI fogging fluid to treat void spaces and tanks

5.2.3 VCI in industrial equipment

5.2.3.1 Description

Industrial equipment, particularly in the manufacturing, power generation, and heavy machinery sectors, often requires long-term storage owing to seasonal operations, market fluctuations, or maintenance schedules. Traditional preservation methods, including protective coatings, desiccants, and nitrogen purging, can be costly, labour-intensive, and sometimes ineffective at preventing corrosion during extended storage periods.

5.2.3.2 Procedure

This study focuses on applying VCIs to various types of industrial equipment stored in a warehouse facility and an electrical system in an enclosed area for over 24 months. The applications include the following.

1. Preservation of LMF - 51 Series Compressor

- *Engine Treatment:* The VCI engine oil additive (9% v/v concentration of amine carboxylates and thiocarbamates) was mixed with the engine oil in an equipment engine. As shown in Figure 5-18, the existing oil was drained and refilled with the engine oil mixed with the VCI engine additive.

Figure 5-18: Drain out existing oil and re-fill with engine oil mixed with VCI engine additive

- *Coolant System Treatment:* The water in the engine coolant tank was replaced with fresh water mixed with VCI cooling additive coolant (2% v/v solution of carboxylic acid salts and azoles). Figure 5-19 shows the engine coolant tank preserved with the VCI-infused water mixture.

Figure 5-19: Engine coolant tank preserved with water mixed with VCI cooling additive

- *External Protection:* VCI pouches were attached to the machine. The compressor was then fully wrapped with a VCI film (polyethylene with a 1.5% w/w proprietary VCI blend), as shown in Figure 5-20.

Figure 5-20: VCI pouches to the compressor and wrapped with VCI film

2. Detroit engines, gearboxes, and transmissions

- *Overall Protection:* The engine was wrapped with a VCI film (polyethylene with a 1.5% w/w proprietary VCI blend), as shown in Figure 5-21.

Figure 5-21: Protection of engine with VCI film

3. Steel pipes and skid module piping systems

- *Internal Protection:* VCI fogging powder (containing a mixture of amine carboxylates and azoles) was used to preserve the inner parts of the Nippon steel pipes and skid module piping systems. Figure 5-22 shows the application of the VCI fogging powder to Nippon steel pipes, and Figure 5-23 demonstrates the preserved skid module piping system.

Figure 5-22: Preservation of steel pipes with VCI fogging powder

Figure 5-23: Preservation of piping system with VCI fogging powder

4. Electrical control panels

- A VCI electronic spray liquid (1% v/v concentration of amine carboxylates with a fast-drying solvent) was directly applied on Printed Circuit Boards (PCB) to clean and protect them from corrosion (Figure 5-24).
- The PCB was coated with a VCI electrical insulator (1% v/v concentration of amine carboxylates with an airdry insulating varnish) to achieve optimal corrosion protection (Figure 5-24).
- To fortify the VCI properties within the cabinets, VCI emitters (containing a mixture of amine carboxylates and azoles) were installed in the electrical control panels to protect sensitive electronics and connections. Figure 5-24 illustrates the installation of these VCI emitters in electrical control panels.

Figure 5-24: Application of VCI electronic spray, VCI electrical insulator, and VCI emitters in control panels

The study demonstrated significant corrosion protection across all equipment treated with VCIs. Overall, the VCI-treated equipment exhibited an average reduction of 99.9% in corrosion rate.

Chapter 6

6. CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Summary of Key Findings

This research has made significant strides in developing and evaluating sustainable vapour corrosion inhibitors (VCIs) for industrial applications. This study encompassed laboratory experiments and field trials, providing comprehensive insights into the effectiveness and applicability of various VCI formulations.

This laboratory study investigated three main types of VCI products: VCI in kraft paper, VCI in films, and VCI in coatings. VCI kraft paper experiments revealed that papers impregnated with 20% amino-carboxylate corrosion inhibitor (ACCI) provided effective corrosion protection for both ferrous and non-ferrous metals. Notably, the VCI kraft paper demonstrated superior performance compared with traditional nitrite-based VCI papers, offering comparable or better protection while eliminating the risk of harmful nitrosamine formation.

The investigation of VCI films showed that films produced using the ACCI masterbatch powder effectively inhibited corrosion on various metal substrates. These films passed rigorous testing standards, including the German TL 8135-002 method, demonstrating their ability to protect both ferrous and non-ferrous metals from corrosion under controlled conditions.

For VCI coatings, this study focused on water-based formulations containing amine carboxylate compounds. The results indicate that these coatings provide effective corrosion protection for carbon steel substrates, with optimal performance achieved at VCI concentrations between 0.25% and 0.5% v/v. The protective mechanism involves the chemisorption of VCI molecules onto the metal surface, forming a continuous barrier film and offering vapour-phase protection.

Field studies conducted across three different industrial settings - vehicles, offshore platforms, and industrial equipment–provide valuable insights into the real-world performance of the developed VCI products. In the vehicle study, VCI emitters and bags effectively protected various metal components from corrosion during extended storage periods. Offshore platform trials have demonstrated the efficacy of VCI powders in preventing corrosion in pipeline systems during hydrotesting and long-term storage. Finally, the industrial equipment study showed the versatility of VCI products in protecting large machinery and components across diverse environmental conditions.

These field trials validated laboratory findings and highlighted the practical applicability of the developed VCI formulations in challenging industrial environments. The results consistently showed that the sustainable VCI products offered comparable or superior protection to traditional corrosion inhibitors while minimising the environmental impact.

6.2 Contributions to the Field of Corrosion Protection

This study has made several significant contributions to the field of corrosion protection.

1. **Development of Sustainable VCI Formulations**: The study successfully developed and validated eco-friendly VCI formulations based on amino-carboxylate compounds. These formulations offer effective corrosion protection without environmental and health risks associated with traditional nitrite-based inhibitors.
2. **Comprehensive Performance Evaluation**: By conducting laboratory tests and extensive field trials, this research provides a holistic assessment of VCI performance across various product forms (papers, films, and coatings) and in diverse industrial settings. This comprehensive approach bridges the gap between laboratory findings and real-world applications.
3. **Optimisation of VCI Concentrations**: This study identified optimal concentrations for different VCI products, balancing corrosion protection efficacy with cost-effectiveness and environmental considerations.
4. **Elucidation of Protection Mechanisms:** The research contributes to a deeper understanding of the protective mechanisms of VCIs, particularly in water-based coating systems. Insights into chemisorption processes, film formation, and vapour-phase protection enhance the theoretical foundation of the VCI technology.

5. **Validation of Sustainable Alternatives:** By demonstrating that amino-carboxylate-based VCIs can match or exceed the performance of traditional inhibitors, this study provides strong evidence supporting the transition to more sustainable corrosion protection solutions in the industry.
6. **Application-specific Insights:** The Field studies across different industrial sectors (automotive, offshore, and general industrial equipment) offer valuable sector-specific knowledge on VCI application and performance, facilitating more targeted and effective corrosion prevention strategies.
7. **Advancement of Testing Methodologies:** This research has contributed to refining testing protocols for VCI products, particularly in correlating laboratory results with field performance, which is crucial for the future development and optimisation of VCI technologies.

6.3 Recommendations for Future Research and Development

Based on the findings and insights gained from this study, several avenues for future research and development in sustainable VCIs are recommended.

1. **Long-term Performance Studies:** While this research provided valuable insights into VCI performance over several months, long-term studies (2–5 years) would be beneficial for fully assessing the durability and sustained effectiveness of these sustainable VCI formulations in various industrial environments.
2. **Synergistic Formulations:** Future research should explore the potential synergistic effects of different types of green corrosion inhibitors. Combining amino-carboxylate compounds with other eco-friendly inhibitors (e.g. plant extracts or biodegradable polymers) could lead to more effective and versatile VCI formulations.
3. **Smart VCI Systems:** Developing smart VCI systems that can respond to environmental changes (e.g. humidity and temperature) or provide real-time corrosion monitoring could significantly enhance the effectiveness and efficiency of corrosion protection in industrial settings.
4. **Biodegradability Studies:** While developed VCIs are more environmentally friendly than traditional inhibitors, further research into their biodegradability and environmental fate would be valuable for ensuring long-term sustainability.

5. **Application Method Optimisation:** Further studies on the application methods, particularly for VCI coatings and films, could improve the performance and efficiency of inhibitors in various industrial contexts.
6. **Computational Modelling and AI Integration:** Incorporating artificial intelligence into computational chemistry and molecular dynamics simulations could accelerate VCI development:
    a. Machine Learning for Molecular Design: Predict the effectiveness of novel VCI compounds.
    b. AI-Enhanced Quantum Chemistry: Model VCI-metal surface interactions more accurately.
    c. Deep Learning for Property Prediction: Forecast key properties of potential VCIs.
    d. AI-Optimized Formulation: Optimize multi-component VCI compositions.
    e. AI-Accelerated Simulations: Enhance speed and accuracy of molecular dynamics studies.

    This AI-augmented approach could significantly improve the prediction of VCI behaviour, optimise formulations, and speed up the development of more effective, sustainable corrosion inhibitors.
7. **Recycling and Reuse Strategies:** Investigating methods for recycling or reusing VCI products after their service life could further enhance their sustainability profiles and reduce waste in industrial applications.

In conclusion, this research has made substantial progress in developing and validating sustainable vapour corrosion inhibitors for industrial applications. The findings demonstrate the effectiveness of eco-friendly VCI formulations and provide a strong foundation for future advancements in corrosion-protection technology. As industries increasingly prioritise sustainability, the continued development and refinement of VCI technologies will play a crucial role in balancing effective corrosion prevention with environmental responsibility.

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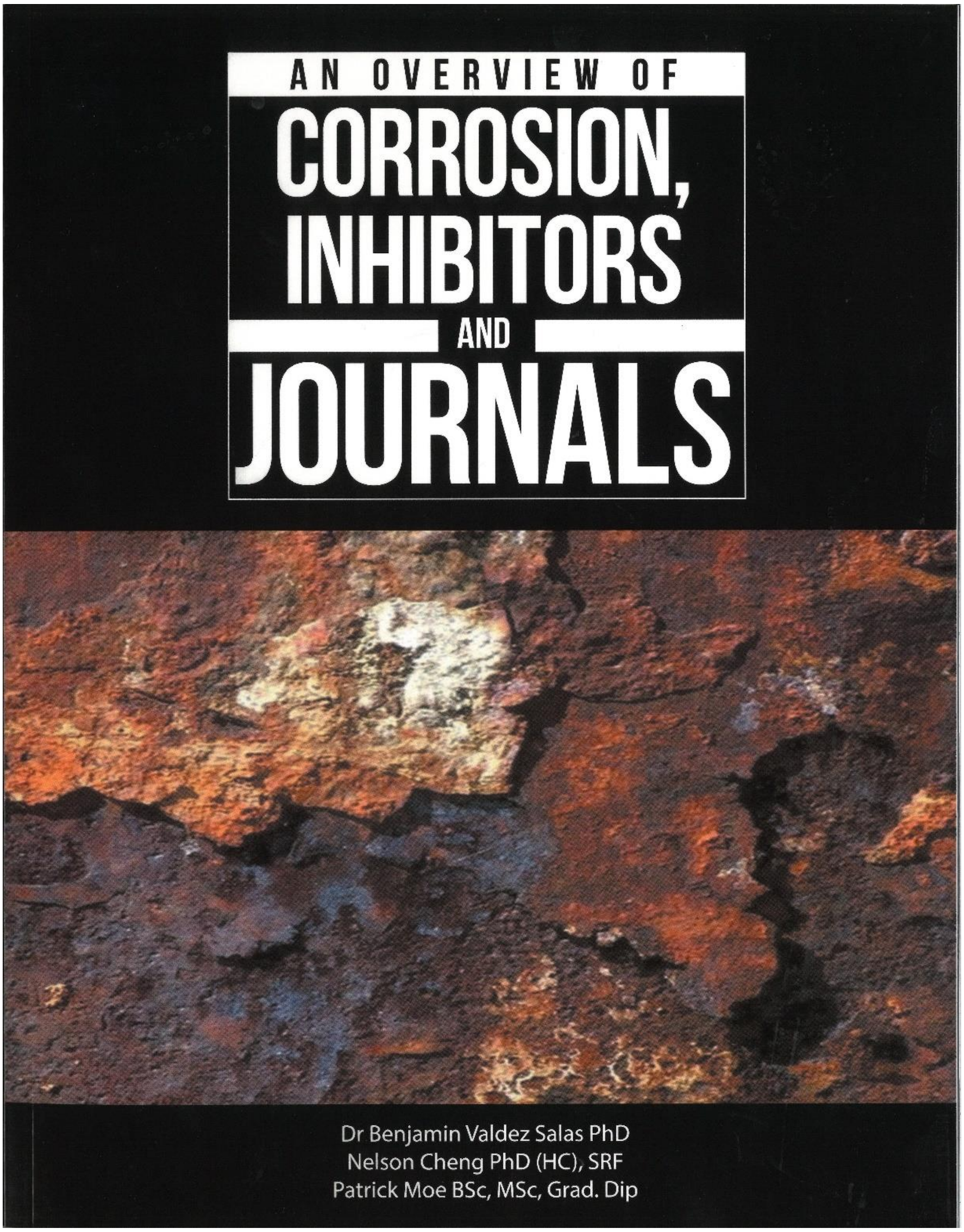
Appendix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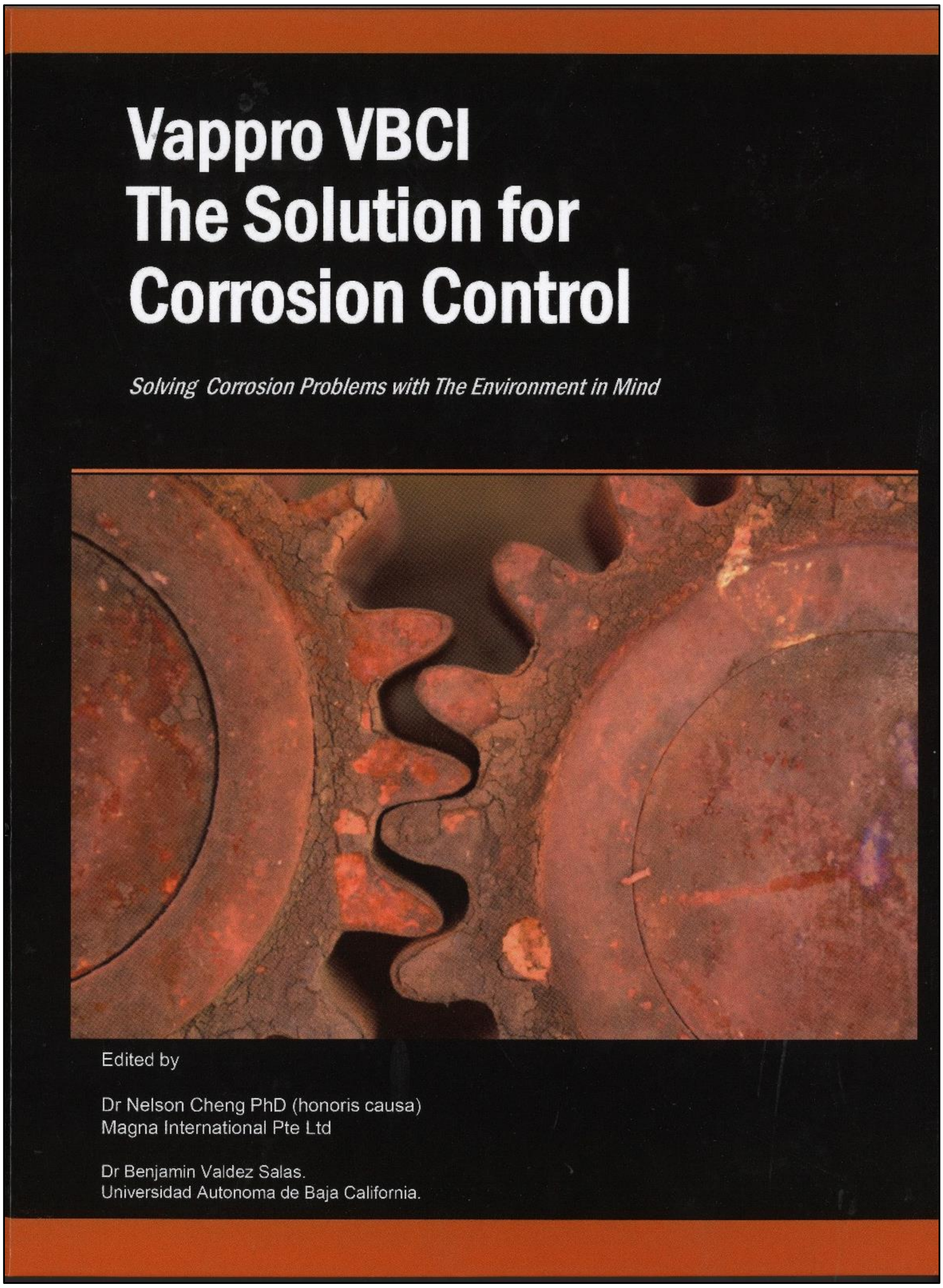
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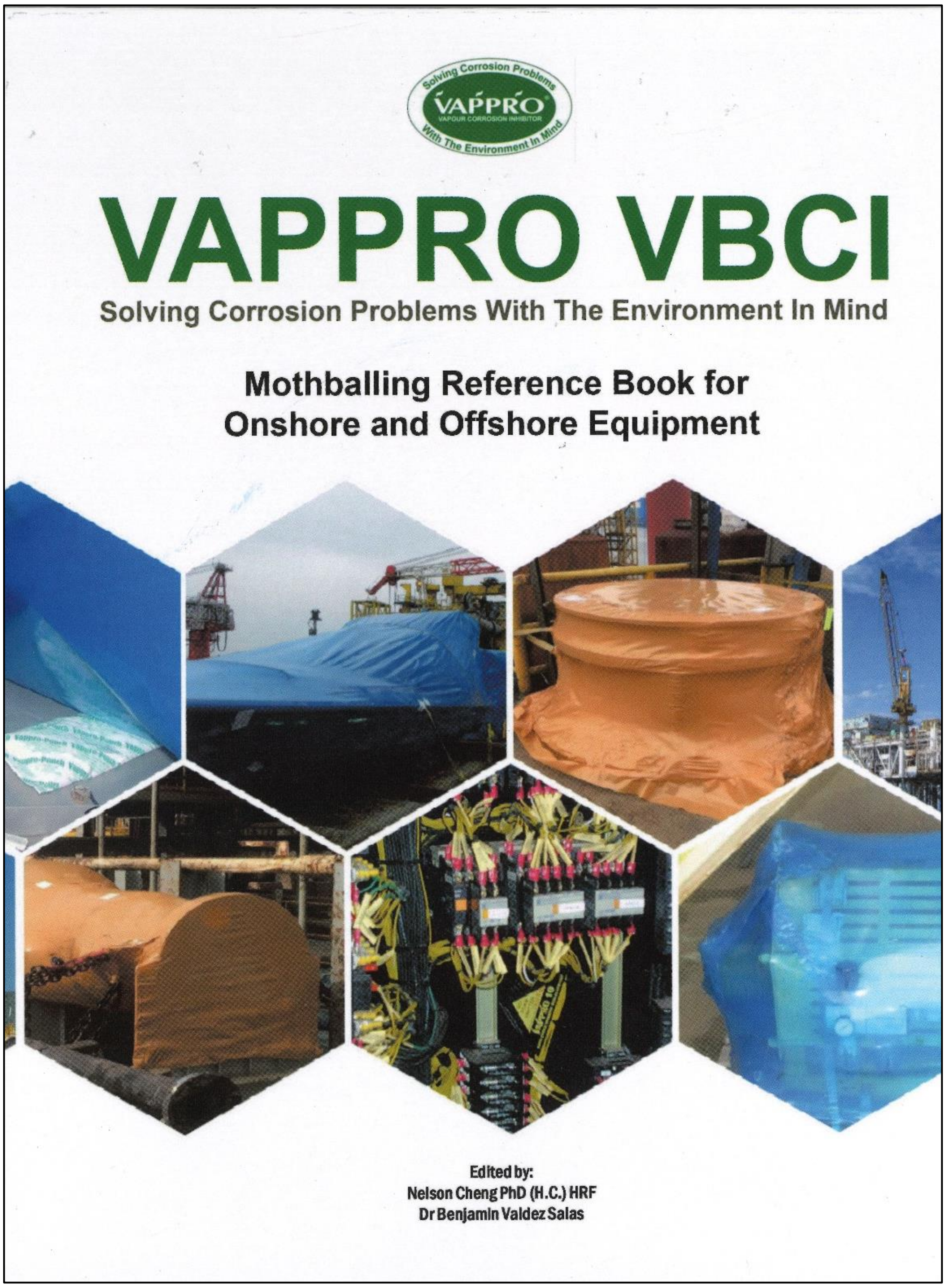
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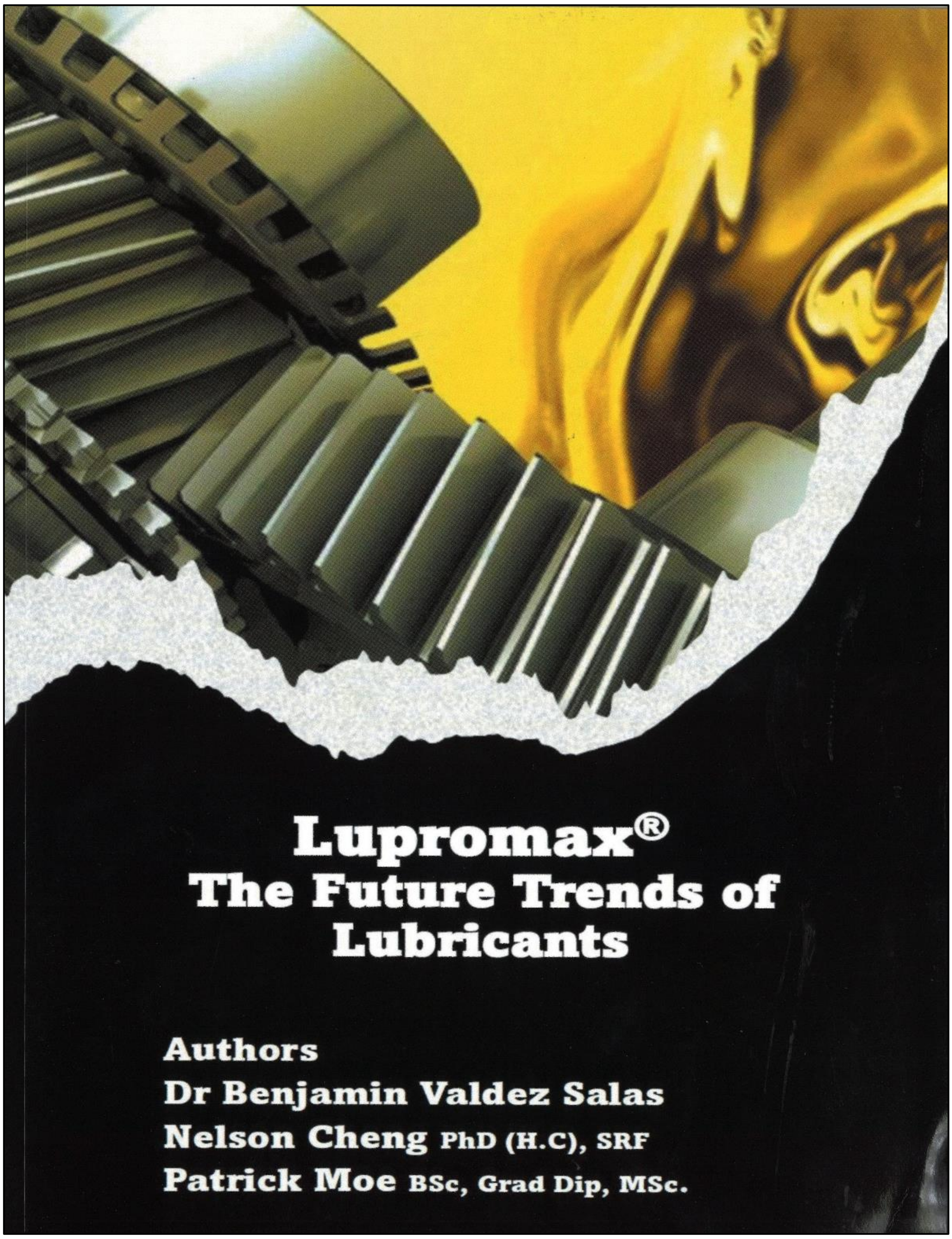
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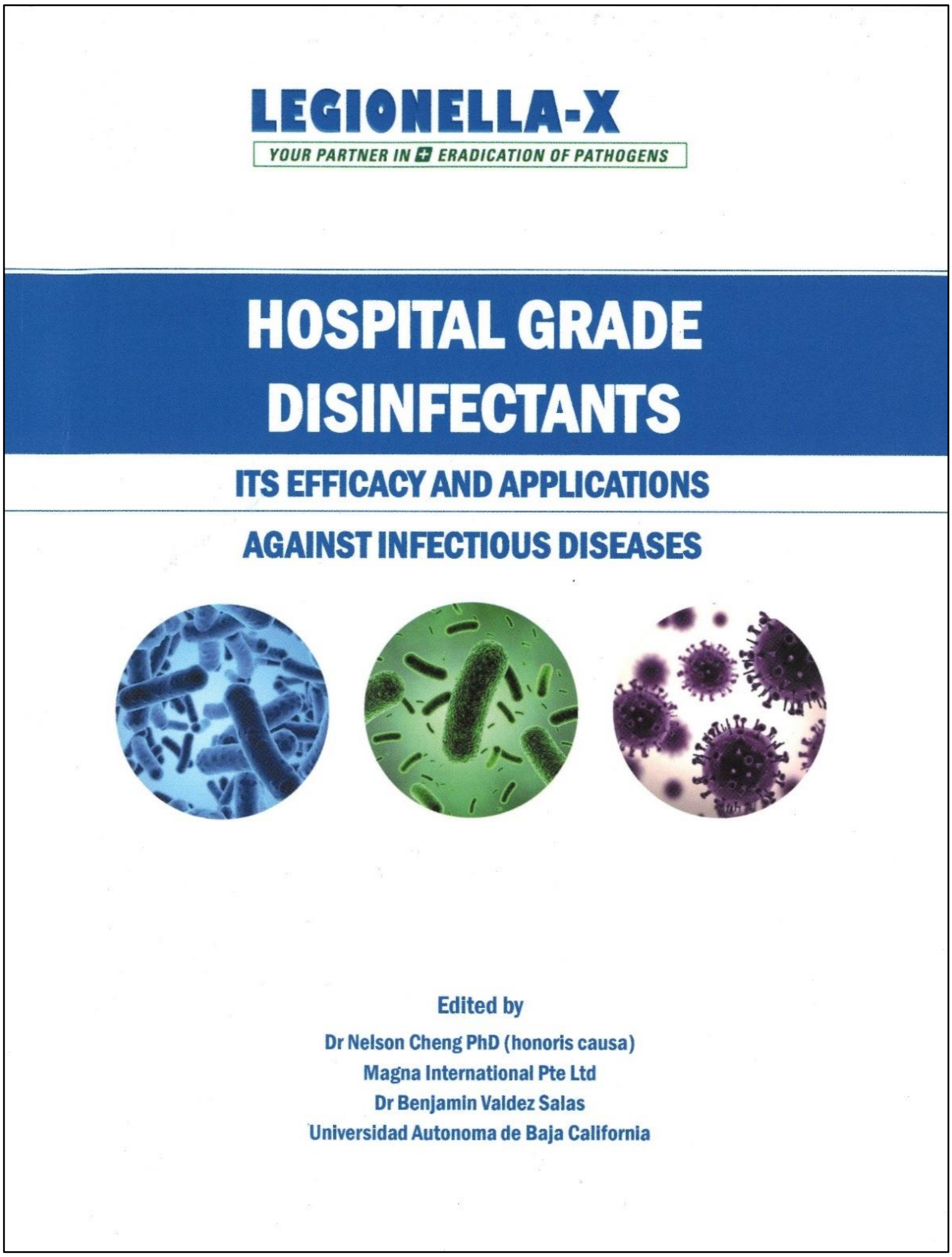

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The Essential Criteria Used for the Augmentation of Vappro VBCI-Vapour Bio Corrosion Inhibitor

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Abstract— This journal spells out the essential criteria used in the augmentation of Vappro VBCI-Vapour Bio Based Inhibitor. The gas law, coefficient of diffusion [1] and the principle of adsorption have been judiciously selected for the development of all Vappro VBCI Products.
Discerning and implementing the said criteria are fundamentals in the development good VBCI Products. Contriving the vapour pressure of VBCI Products is of the paramount importance for the said development and is foundational for all VCI manufacturers to consider, as divergent of VCI carriers are used to accommodate each particular application due to the extensive utilization of VCI products.

Keywords— Algorithm, Gas Law, Diffusion, Adsorption, VBCI, VCI.

I. Introduction

The VBCI Molecule present in the enclosed area or on the surface of the emitters such as Tyvek Pouches, P.E Packaging film, Kraft papers, Polyurethane Foam, Mineral Stone Paper, Oils, Solvents, Water, Tablets, Powders, etc. polarizes on the metal surface through sequence of steps specifically via Vapour pressure the VBCI emitters (evaporation for liquid or sublimation for solids), Diffusion and Adsorption on metal surfaces.

Establishing the Vapour Corrosion Inhibition Ability of VBCI product is predominance importance to Magna International and all VCI manufacturers. The German test method TL 8135-002 is used to evaluate the vapour inhibition ability of all Vappro VBCI products. [2][3][4][5]

Having in mind of the above, the essential criteria used for the development Vappro VBCI-Vapour Bio Corrosion Inhibitor needs to be ascertained. utilizing a consolidation of equations of mathematical physics derived from Gas Law, Coefficient of Diffusion [1] and comprehending the principle of adsorption of VBCI ions on metals is of paramount importance for the development of all Vappro VBCI Products.

This journal focuses on the equations of mathematical physics used in the development of Vappro VBCI Products revolving around gas law and coefficient of diffusion.

Transport theory using concentration gradient can be described by boundary value problems for differential equations. A very wide class of models is reducible to such boundary value problems.

A complete description of the evolution of physical processes requires, first, the specification of the state of the process at some fixed moment of time (the initial conditions) and, secondly, the specification of the state on the boundary of the medium in which the process considered occurs (the boundary conditions). The initial and boundary conditions form the boundary value conditions, and the differential equations together with corresponding boundary value conditions define a boundary value problem of mathematical physics.

The principle used for the development Vappro VBCI Products using a consolidation of equations of mathematical physics derived from gas law and coefficient of diffusion [1], is herein described.

II. Vapour Pressure

Vapor pressure or equilibrium vapor pressure is defined as the pressure exerted by a vapor in thermodynamic

1

Article

Characterization of *Farfantepenaeus californiensis derived chitosan* for Smart-Active Food Packing Applications

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Abstract: The objective of this study was to carry out the extraction and characterization of chitin and chitosan from the exoskeletons of the *Farfantepenaeus californiensis* species of shrimp, as well as its application in the formulation of polymeric films plasticized with glycerol used in the process of food packaging. The characterization of the extracted polymer was made by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), and physicochemical analysis of chitin and chitosan, resulting in a theoretical performance of 29.33% and 16.46%, respectively. In terms of quality, it was determined that the extracted chitosan had a molecular weight of 1.10 x10^5 g/mol and a deacetylation degree of 80.23%, which classifies it as a low-molecular weight chitosan, suitable for food packaging. It was shown that the extracted chitosan is fit for the production of the films by using the casting method, presenting a tension resistance of 1 MPa. The Antibacterial analysis was carried out using *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*), bacterial models commonly found in food. The results showed an effective inhibition capability of the polymeric materials. Overall, the results for both chitosan and the films indicate a high potential for application in the food packaging sector.

Keywords: chitin; chitosan; packaging; biopolymers; biomaterials

1. Introduction

The incorporation of bioplastics of plant and animal origin has attracted enormous attention in the materials industry of the food packaging sector [1–3]. The advantages of biopolymers against traditional counterparts can be appreciated due to their biocompatibility, biodegradability, and occurring abundance [4]. Several examples of biopolymers that have been frequently used in the food industry are cellulose, hyaluronic acid, collagen, chitosan, and chitin, this last one standing out the most due to its availability (the most abundant after cellulose) and its intrinsic physicochemical properties [5].

Chitin is a natural polysaccharide characterized by its structural function. Its polymer is N-acetylglucosamine repeating units, which is abundant in the exoskeletons of crustaceans, insects, and some kind of fungi [6]. The chitin percentage found in exoskeletons of crustaceans and insects is around 30-40%, while in fungi, it ranges from 13-37% approximately [7]. Despite the potential of chitin and chitosan, the source of these biopolymers is still being wasted nowadays; this is because around 6 to 8 tons of crustacean waste are discarded, which causes contamination to both soil and water as a consequence [8]. In Mexico, about 60 species of shrimp [9] of which only 8 have cultivation

Inhibition of Seawater Steel Corrosion Via Colloid Formation

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***Abstract*— The main purpose of this research was to establish the effectiveness of the V844* corrosion inhibitor for seawater on various metallic materials: carbon steel, aluminum and copper alloy at different concentrations via colloid formation. The changes in both physical and chemical properties of seawater, including pH, total hardness, alkalinity, total dissolved solids (TDS) and conductivity at different concentrations of V844 were assessed, too. The test procedure involves dissolving the V844 corrosion inhibitor (CI) powder provided by Magna International Private Limited in seawater to obtain a stock solution of 4% V844 in seawater, which was further diluted to obtain the remaining concentrations. The analysis of parameters begun when various metal species, polished beforehand, were placed into the solutions. The analysis was observed over a period of 26 days and a total of 9 sets of readings were obtained. From our observation and ear power stations burning fossil-fuels generating acidic rains, the pH can diminish to 6.**

Key words- Colloidal Corrosion Inhibitor, Corrosion Inhibition Efficiency, Vappro 844 and Volatile Corrosion Inhibitors,

I. INTRODUCTION

Corrosion is a worldwide problem that strongly affects natural and industrial environments, in particular the oil and gas industry. All its numerous and diverse facilities, equipment and installations require products, methods and techniques to protect, mitigate and prevent the corrosion damage (Hummel, 2014; Raichev et al., 2009). Corrosion inhibitors (CI) are one of the modern technologies applied for the management of corrosion, for the benefit of the global economy (Garcia, 2013).

II The world and Mexico in particular are undergoing an intense reformation process in the energy sector that is involving its oil, natural gas, and electricity industries. The abundant resources, such as deep-sea oil and shale gas, will be utilized; and additional refineries and pipelines will be built with the active participation of heavy foreign investments. The reform was recently approved by the Mexican parliament and is setting Petroleos Mexicanos (PEMEX), the national oil company, on the way to becoming a world oil enterprise (Layoza, 2014).

II SEAWATER CORROSION

The sea is a dynamic system in permanent motion, with complex surface currents and winds blowing over its surface generating waves that reach the coast and its facilities and installations.

Seawater consists of a solution of many salts and numerous organic and inorganic particles in suspension. Its main characteristics are salinity and chlorinity and, from the corrosion point of view, dissolved oxygen (DO) content which ranges from 4 to 8 mg/L, depending on temperature and depth. Its minor components include dissolved gases – CO_2, NH_3 and H_2S – found in seawater contaminated by urban sewage. The oceans house algae, bacteria and phytoplankton that generate about half of the oxygen in the atmosphere.

Ocean surface salinity is determined by the balance between water lost by evaporation and water gained by precipitation. The salt concentration, particularly NaCl, varies from 2.0% to 3.5%, according to the sea location and the massive addition of fresh river water. For instance, in the Red Sea, an enclosed basin, salinity at high summer temperatures is 4.1%, but in the Baltic Sea it is about 2.0% since many rivers feed into it.

Seawater is slightly alkaline, with a pH about 8.0 but when it is contaminated by acids, such as in coastal regions near power stations burning fossil-fuels generating acidic rains, the pH can diminish to 6.

II. CORROSION INHIBITORS

In the last years the use of CI is rapidly expanding worldwide, for numerous technological and industrial applications; as cooling water systems (Schorr et al., 2012), steel reinforced

Optimization and characterisation of commercial water-based volatile corrosion inhibitor

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Abstract

Volatile corrosion inhibitor (VCI) provides protection for metal surfaces. VCI coating and molecules attach themselves to metal surfaces to form both a physical film when contacted and an invisible thin film for indirect contact through Vapour (only a few molecules thick), thus inhibiting metals atmospheric corrosion. Optimization and characterisation of commercial water-based volatile corrosion inhibitor VCI (Vapour-Phase-Protection, VAPPRO 837C diluted commercial solution from CORPPRO) was prepared to determine their characteristics and effectiveness against corrosion of carbon steel. The main scope of this work is to characterise the rheological and corrosion inhibition properties of the VAPPRO 837C with varying formulations and processing parameters (coating and drying times). Different tests were performed to determine the corrosion behavior of inhibitor. The application of VCI on the metal surface was done by dip-coating process. An Electrochemical Workstation from HCH Instruments has been used to evaluate the corrosion inhibition efficiency of the VCI and to determine the corrosion rate of the uncoated and coated samples. In addition, viscosity tests were carried out in order to determine the rheological properties of the formulation, as well as Freeze–Thaw resistance of water-borne coatings and pH tests were done. A FTIR spectrometer has been used to determine the functional groups present at a specific concentration. Results reveal that the most effective VCI film was obtained from a 0.25 CORPPRO (Concentrated VCI) (vol%) formulation using a coating time of 10 min and a drying time of 24 h. Therefore, 0.25 CORPPRO would be the optimum concentration to be used because it is able to achieve the highest corrosion inhibition efficiency with the optimum coating drying time.

Key words: *corrosion inhibitor, vapour phase protection, dip-coating.*

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Introduction

Metallic corrosion is a world-wide problem caused by the interacition of the metal surface with the surrounding environment. It has always been problematic to metal constructs and tools as degradation or rusting of metals due to the tendency to return to their natural state

Volatile Corrosion Inhibitor (VAPPRO 872)

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Abstract

The main objective of this collaborative project was to obtain an optimum formulation from the base formulation of VAPPRO 872, a commercial volatile corrosion inhibitor (VCI) product from Magna International Pte Ltd. Percentages of the corrosion inhibitor (CI) and calcium sulphonate (CS), type of kerosene and type of calcium sulphonate were varied, and the various formulated products were tested for its flammability and viscosity. The different formulations were each coated onto a metal test piece to further test for its corrosion rate using the Electrochemical Impedance Spectroscopy. The results showed that the optimum formulation with the best efficiency was 0.5% CI, 3% "old" CS, 19% mineral oil and 77.5% pure kerosene, with an efficiency of 89.14%. This was chosen because of its relatively high efficiency and reduced costs.

1. Introduction

Corrosion occurs when a material, usually metal, starts to weaken and its properties become less desirable. This is due to irreversible chemical reactions with the surroundings. Corrosion is a very common problem in many industries, where metals are used in their daily operations and when these machines fail, it costs a large sum of money to replace them. Hence, we are working on Vappro 872 (VCI) with the assistance from Magna International Pte Ltd.

Magna International specializes in corrosion preventive technology and cleaning surfactants, and they have developed an advanced and environmentally safe VCI known as Vappro, which stands for Vapor – Phase – Protection. This range is commonly used in the electronics and automotive industry, as well as in the military.