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Review

The Application of Anti-Corrosion Coating for Preserving the Value of Equipment Asset in Chloride-Laden Environments: A Review

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Anti-Corrosion coatings are extensively applied in maintenance and vehicles used by transportation agencies, which have been used to protect a substrate by providing a barrier between the metal and its environment outside, especially in a chloride-laden environments. In order to provide adequate corrosion protection, the coatings must be uniform, well adhered, pore free and self-healing for applications where physical damage to the coating may occur. The aim of this review is to examine the state of the corrosion coatings for the protection of various metals/alloys commonly used in maintenance equipment and vehicles, and to identify cost effective, high-performance corrosion inhibitors that may contribute to the preservation of equipment assets. The focus is placed on the metallic corrosion induced or aggravated by chlorides at ambient temperature and pressure, and near neutral pH (6-8).

Keywords: anti-corrosion coating, metals, chloride, maintenance equipment, review

1. INTRODUCTION

Some metals and alloys, such as steel, aluminum and magnesium, are widely used in maintenance and vehicles by transportation agencies, which are often at the risk of corrosion associated economic loss [1, 2]. Many methods have been established to prevent or protect metals from corrosion, such as barrier protection [3-19], galvanization [20-23], and cathodic protection [24-32].

The corrosion resistant coatings have attracted many attentions for many years due to its simplicity and efficiency [33-35]. The Numerous corrosion coatings have been developed and tested in an attempt to combat the harmful effects of corrosion on metal. Due to the variations in the physical and chemical properties of the different types of metals and alloys, the protection provided by each coating is dependent on the type of metal it is applied to and the environment in which it is exposed. This review will focus on environments consisting of common outside temperature, near neutral pH conditions, and in the presence of chlorides. With advancements in materials science, new corrosion coating systems are being developed. The development of these coatings is focused on enhanced functionality comprising corrosion protection and adhesion, environmentally friendly materials, corrosion and mechanical damage detection, improved fatigue resistance, and water resistant [36].

The widespread use of metals in corrosion prone environments has lead to extensive research projects focused on developing coatings that protect against corrosion. These coatings must meet many requirements including: long-lasting, easy application, environmentally friendly, cost-effective, and high performance. Coatings based on metals, polymers, and various epoxies have been developed in addition to already produced commercial products. A review of the performance tests performed and their respective results are discussed.

1.1. Use of Coatings and Their Anti-corrosion Mechanism

Corrosion protection coatings are generally based upon barrier protection, inhibitive coatings, or anodically active metal coatings. Barrier protection coatings cause oxygen deprivation or resistance inhibition. Inhibitive coatings alter the chemistry at the surface of the metal substrate. Anodically active metal coatings are usually made of zinc and due to their anodic activity level they are able to prevent electrical current from discharging from the substrate and causing galvanic corrosion. The zinc sacrificially corrodes, forming a corrosion product that provides protection similar to a barrier coating [37].

It is a common method to use certain coating systems for protecting the metallic surfaces of vehicles from corrosion. Some common coating systems include conversion, electrocoating, metallic, organic, wax, autodeposition, and powder. Conversion coatings such as phosphate conversion coatings improve the ability of paint to adhere to the metal surface. Electrocoating method is based on the use of electrically charged particles, which are dissolved within a tank. A conductive piece of metal is submerged in the tank in order to deposit the charged particles on its surface. Metallic coating is the application of a metal, often zinc or aluminum, via hot-dipping, electroplating, or mechanical plating. Recently, research in the area of organic coatings has provided alternative coating systems to potentially replace some of the traditional coatings that don’t meet environmental standards. Organic coatings inhibit the transfer of charge from the metal to the corrosion inducing solution. Waxes are generally applied by melting the wax and subsequent dipping of the metal object into it. Autodeposition is based on a chemical reaction that causes deposition to take place. Powder coating is applied by spreading a dry powder on the metal to be coated, and then the dry powder is heated causing the powder to create a film [38]. These coatings all prevent direct interaction between the metal and the corrosive environment, therefore impeding corrosion.

Sitaram et al. [39] have found that a general approach to coating systems often involves the application of three types of layers. Most commonly, the first layer consists of a metal oxide that inhibits corrosion. The next layer is a primer that contains inhibitors in order to provide cathodic protection for the metal. The top layer is generally a barrier that separates and protects the underlying coatings from the surroundings.

A study focused on the corrosion of automobiles found that the main factor influencing perforation corrosion was coating weight; this finding was independent of the type of coating [40]. A different study found that the thickness of the coating does not determine the amount of coating protection it will provide. It was found that an aluminum coating, a couple micrometers thick, protected steel better than cadmium and chromate-coatings that were tens of micrometers thick on steel samples [41]. It has been concluded that increasing the thickness of a certain coating will generally increase its corrosion protection, but the corrosion protection provided by two different types of coatings cannot be related solely based on thickness.

In addition, surface preparation is a key component in the success of corrosion protection coatings. The ability of the coating to adhere to the metal surface is directly related to the corrosion protection performance. The coating performance is significantly enhanced over a surface containing little or no contaminants [42].

When replacing a coating that is no longer environmentally acceptable, it is important that special attention is given to the corrosion behavior differences of the coatings to ensure that the new coating is an acceptable alternative. For example, many zinc-nickel alloys have been used to replace cadmium layers but issues arise due to the differences in their corrosion behavior. Zinc-nickel alloys exhibit localized corrosion and cracking, while cadmium layers are susceptible to uniform corrosion [43]. The differences in corrosion behavior will play a crucial role when providing the necessary corrosion protection system.

Many coatings methods have been used in the passivation of steel surfaces. It was found that most of the effective corrosion protection systems for metals were chromates-based metallic coatings [44-46]. The mechanism of chromates-based coatings for corrosion protection is the hexavalent chromium compounds, which loosely bonded in the chromate coating, slowly leached on exposure to aqueous media, healing scratches and other defects. Meanwhile, the chromate ions released from coating layer can interact with the metal surface forming a $Cr_2O_3{\cdot}nH_2O$ solid hydrated conversion coatings. Organic coating has been recognized as the most cost-effective method for metals and alloys protection against corrosion. The mechanism of organic coatings for the protection of metal substrates may be attributed to a barrier and an electrochemical process. It is well-known that organic coatings have a high resistance to ionic conductivity, which can offer good barrier properties and retard the diffusion of chemical species to and from the metal surface [47-49]. Recent years it was found that the protective coating properties essentially were determined by the rate of water and oxygen diffusion through the insulating layer, promoted by the osmotic pressure in the pores and capillaries of the coating. For example, ceramics-based coatings for metals protection such as sol-gel coatings have emerged as versatile methods for substitution of the chromate pretreatments [50-55]. Based on the advantages of excellent chemical stability, oxidation control and enhanced corrosion resistance for metal substrates, sol-gel technology can offer various ways to prepare functional coatings with different properties. Moreover, the sol-gel method is an environmentally friendly technique for surface protection, which may be potentially used for the replacement of toxic pretreatments and coatings which have traditionally been used for increasing corrosion resistance of metals in the near future.

Due to their advanced mechanical and physical properties, nanostructure materials have been the focus of many researchers attempting to create advanced corrosion resistant coatings [56-59]. Work has focused on the types, production, and applications of various nanostructure coatings. Saji and Thomas [60] have demonstrated that a polymer nanocomposite coating can effectively combine the benefits of organic polymers (e.g., elasticity and water resistance) and advanced inorganic materials (e.g., hardness and permeability). In addition to these advantages, nanomaterials also remove the need to use components that may have negative effects on the environment.

2. COATINGS FOR STEEL

2.1. Metallic Coatings

Metallic coatings have been widely used to protect against the corrosion of metals. Metallic coatings have two functions. The coating first acts as a barrier and also provides cathodic protection by galvanically corroding. Metallic coatings often consist of zinc or zinc containing alloys that have been applied by hot-dipping or electrodeposition. Surface cleaning is essential to ensure electrical contact between zinc particles and the coated surface. Results of studies focusing on these coatings and their corrosion protection relative to some of the other anticorrosion coatings are presented.

Stainless steel, hot-dip galvanized, zinc-rich primer with epoxy topcoat, and phenolic epoxy-coated steel were exposed to chlorides from the ocean air. Galvanized steel exhibited complete corrosion protection during the test period. The zinc-rich primer with epoxy topcoat and the phenolic epoxy-coated steel both provided good protection but suffered from corrosion at the scribes. Stainless steel exhibited localized corrosion and rust staining [61].

Galvanized zinc coatings have been very common within the automotive industry for many years. However, new zinc coatings with better performance are desired. Recent research shows promising results of magnesium-zinc coatings as an alternative. Corrosion protection of a Zn-Al-Mg alloy coating was compared to that of hot dip galvanized zinc coating. These were tested in an array of conditions including the following environments: chloride, chloride free, neutral pH, acidic pH, constant humidity, and cyclic humidity levels. The Zn-Al-Mg alloy provided better protection due to the formation of a zinc aluminum carbonate hydroxide layer [62]. Zinc-Aluminum-Magnesium coated steel was found to provide much more corrosion protection than zinc coated steel in chloride containing environments due to the formation of a long lasting aluminum rich oxide layer [62].

Another study found that zinc magnesium coated steel protected about three times better than electro-galvanized and hot dip galvanized steel. The improvement is attributed to the formation of magnesium hydroxide on the surface, which slows oxygen reduction reactions and enables the formation of a protective simonkolleite Corrosion resistance of zinc-magnesium coated steel [63, 64]. Testing at the Kennedy Space Center (KSC) found that inorganic zinc rich primers performed better than organic zinc rich primers in the corrosive coastal environment [65].

To find the most effective coating system, corrosion resistance of certain coatings must be compared. Coating systems are comprised of a sacrificial metallic layer, then a sealer or conversion layer, followed by a primer and lastly a topcoat. Schmidt et al. tested 16 different coating systems by immersion testing in artificial seawater. Steel exposed to marine conditions exhibited good barrier protection when coated with ZnPhos + E-coat + solvent-based primer/topcoat. Thermal zinc spray coatings provided the best sacrificial protection, performing significantly better at the scribe than those without a sacrificial layer [66]. Steel sheets coated with either 55% Zn-Al alloy or traditional galvanized zinc, were exposed to atmospheric corrosion testing in Bandar Abbas. The testing found that galvanized steel corroded at a rate of 1.7-2.3 times greater than the Zn-Al coating. Both coatings experienced uniform general corrosion. However, the Zn-Al coating experienced denser corrosion within its interdendritic regions composed of Zn than within its dendritic Al regions. The aluminum-zinc sulfate corrosion product associated with the Zn-Al coating adheres better than the galvanized zinc corrosion product, leading to better corrosion protection [67].

Material selection of aircraft components is focused on fatigue and corrosion properties because fatigue and corrosion are the primary failure modes of structural components. Coating systems are crucial on aircraft thus research plays an important role in determining the most effective corrosion protection systems. Steel samples with varying types and thicknesses of coatings were exposed to acetate and formate-based deicers commonly used on aircraft. It was determined that the aluminum coated steel performed the best. Cadmium-coated chromate-treated steel was found to undergo general corrosion. Difficulty producing a consistent and defect free chromate coating exposed the cadmium, which undergoes anodic dissolution that developed into general corrosion and consequent substrate exposure. An alternate aluminum coating for steel was also tested. Results showed the formation of a protective coating on the surface, likely due to inhibitors included in the deicers, along with periodic localized corrosion [41].

Due to the environmental concerns associated with the use of cadmium and chromium coatings, new developments are crucial, and new zinc-nickel alloy coatings have been developed. These alloys are composed of 85-95% by weight zinc and 5-15% by weight nickel. In addition to replacing cadmium, zinc-nickel alloys having 6-15% by weight nickel have also been used to replace hexavalent-chromium (chromate phase) for toxicity reasons. The hexavalent-chromium replacing coatings consist of three layers: the first is a zinc-nickel alloy layer, on top of that is a trivalent chromate layer, and finally a resin layer. Lastly a binder containing phosphate is used to prevent the chromate phase production [68].

2.2. Organic coatings

Recently, significant research, focused on polymer coatings, has shown many potential applications for polymer coatings as corrosion protection systems[69-72]. It has been observed that effective passivation of iron occurred with the use of conductive polymers. For selected polymers, the coating thickness, thermal treatment, methods of preparation and application have been analyzed and reported.

Herrasti and Ocon [73] investigated the corrosion protection of polypyrrole and polypyrrole/carboximethylcellulose (Ppy/CMC) coatings on stainless steel. The interface between the metal and coating remained stable for long periods of time in the presence of 3% NaCl solution. The Ppy/CMC's compact framework was found to attribute to stability. When exposed to low current density, uniform films and significant corrosion protection were observed; however, when exposed to high current density, corrosion protection was minimal. Additionally, thermal treatment up to 150^{o}C increased corrosion protection whereas; higher temperatures caused damage to the structure of the film. Consistent with other literature, successful corrosion protection using conductive polymers was observed.

Electropolymerization of poly(o-phenylenediamine) (PoPD) onto stainless steel using cyclic voltammetry from an acidic solution containing the monomer was performed to create 100 layers, each layer was about 1 micrometer thick. After testing the coating, the surface was almost free from pitting corrosion [74]. The corrosion protection is associated with the passive film that forms beneath the PoPD. This passive film contains iron (Fe), chromium (Cr), and nickel (Ni) hydroxides, which make up the majority of the stainless steel surface composition. The PoPD creates a barrier between the solution and the passive film on the surface of the stainless steel, resulting in significant pitting resistance in the presence of 3% NaCl [75].

Advancements in sol-gel technology have enabled potential corrosion protection applications with numerous advantages. Sol-gel-derived films provide good adhesion to metallic surfaces, low cost, low environmental impact, and simple application procedures. However, more research is needed to determine the best formulation for high performance corrosion resistance. Current approaches involve the incorporation of controlled release corrosion inhibitors. A sol-gel coating combined with an encapsulated corrosion inhibitor on mild steel was examined. The corrosion inhibitor cerium nitrate was encapsulated within a hydrophobic sol-gel coating enabling a long-term, controlled release. Cerium nitrate was selected due to its low price, environmental safety, and effectiveness. It was found that the encapsulation of cerium nitrate in the sol-gel improved corrosion protection through the controlled release and formation of cerium hydroxide, which interrupted the reaction at the cathodic sites. It was also found that using multiple layers increased the corrosion resistance and that when cured at 250^{o}C an optimal coating thickness of 3-4 micrometers was obtained [76].

Hydrophobic treatment, a recent corrosion protection method, applied to steels provides an effective barrier against moisture on the metal surface and electrically insulates the underlying metal. Thus a hydrophobic fluoropolymer film, deposited on carbon steel by use of inductively coupled radio frequency plasma and the carrier gas octafluorocyclobutane, is proposed as a corrosion protection system. Fluoropolymer films offer low surface energy, good thermal stability, and chemical resistance. The resulting films adhered well to the steel surface and were hydrophobic. The optimal thickness of 90 nm resulted in a cost-effective and successful approach of corrosion protection.

It is clear that many different polymers have been developed with successful results. Advances have found that combining the polymer coatings with inhibitors leads to additional corrosion protection; in some cases these coatings are self-healing. Further testing focused on the comparison of the polymer coatings with one another and on the length of time corrosion protection is provided, specifically in the form of on-vehicle or field-testing should be performed.

Epoxy coatings offer a wide variety of benefits and are often effective when used as corrosion protective systems, which can be attributed to their excellent chemical resistance, strong adhesion, and good electrical insulating properties. Epoxy coatings protect against corrosion by forming a physical barrier and when integrated with corrosion inhibitors, resist attack of aggressive species. It has been determined when nanoparticles are incorporated into epoxy resins, corrosion rate is significantly reduced. Shi et al. have proposed that the nanoparticles occupy small defects and can increase the cross-linking density causing improved durability of the coating. Shi et al. investigated the effects of corrosion of steel when integrating Zn, SiO_2, Fe_2O_3 and clay nanoparticles with epoxy coating. After a 28 day immersion test in 0.03% and 3% NaCl solution, epoxy with clay and Fe_2O_3 were determined to be the most effective corrosion protection coatings which is consistent with the results **[17]**.

Additional corrosion prevention coating systems combined organic compounds and metals with epoxies and acrylics have been developed. These types of coatings are generally applied while wet and adhere to the surface after drying. The less demanding application makes them more suitable to be produced and sold commercially rather than requiring manufacturer application. Epoxies offer great versatility and good performance.

In the past several years, great advancement has been developed for epoxy corrosion coating systems. Along with accelerated tests and atmospheric exposure, electrochemical data for the corrosion resistance of eight acrylic and epoxy coatings was collected. The following coating systems: epoxy-polyamide, homogeneous acrylic paint, epoxy-amine homogenous, and epoxy-acrylic heterogeneous in the presence of a zinc pigmented primer were tested for their corrosion protection of steel. It was found that the epoxy-polyamide systems provided the best protection. Intermediate protection was provided by the epoxy-amine homogeneous and epoxy-acrylic heterogeneous coatings. The homogeneous acrylic paint provided the worst corrosion protection, exhibiting blister formation and filiform corrosion. Correlations between atmospheric exposure and accelerated salt spray test were found [77].

Paint is a method through mixing pigments and resins in a solvent, which will cause a hardening effect after a surface evaporates applied. Resins are mostly made of polymers while pigments can be ceramic, metallic or composed of polymers. A study focused on the effects of manipulating concentrations of dispersant, anticorrosion pigment, and wollastonite in styrene-acrylic resin paints on the corrosion protection of carbon steel has been done. The paints were composed of 31% pigment by volume. Constant amounts of ethylene glycol, titanium oxide, water, rheological agent, inhibitor, and defoamer were used. The paint tested with 25% pigment volume concentration, 0.4% wollastonite, 0.40% zinc, and 0.41% dispersant by weight was found to provide the best corrosion protection. A paint consisting of 31% pigment volume concentration, 2.5% zinc, 2.5% wollastonite, and 0.42% dispersant provided decent protection[78].

Research was focused on creating alternative anticorrosive paint pigments that can be used to replace toxic zinc chromate. Phosphates have been the most successful nontoxic corrosion inhibitive pigments. Recent research has found advantages including low cost, nontoxic, and easy application of zinc phosphates as pigments in corrosion prevention systems. Three different types of alkyd paints were exposed to 3% NaCl solution. The paints were composed of the pigments calcium acid phosphate, micronized zinc phosphate, and zinc chromate. It was found that zinc phosphate provided the best protection followed by calcium acid phosphate, and zinc chromate respectively. The results show that divalent cation phosphate pigments are potential effective replacements for chromate coatings [79]. Similarly, the corrosion protection provided by zinc ethyl silicate was determined to display excellent barrier performance [80]

In less corrosive environments, single coat zinc-rich primers offer effective corrosion protection. However, an additional barrier layer is needed in more aggressive environments. Micaceous iron oxide and titanium dioxide are the most effective barrier pigments available. Micaceous iron oxide, titanium dioxide and chlorinated rubber, known for its high impermeability to water and corrosion causing ions, have been combined to create the topcoat. Application of a barrier finish coating on top of zinc-rich primer has been found to hinder corrosion of mild steel in the presence of 3% NaCl solution. The micaceous iron oxide and titanium dioxide pigments are used due to their excellent performance in barriers. The chlorinated rubber finish coats were produced by adding the two pigments independently and were implemented on a butyl titanate zinc rich primer, cashew nut shell liquid zinc rich primer, and an epoxy polyamide zinc rich primer. It was found that the organic zinc rich primer behaved differently than the inorganic primer, which was caused by the cathodic protection of the inorganic primer. Use of both micaceous iron oxide and titanium dioxide with zinc rich primer systems was found to be very effective, yet smaller pigment volume concentrations of micaceous iron oxide was found to be equally effective as larger pigment volume concentrations of titanium dioxide [81].

Specific issues involving the use of organic coatings are: non-uniform film distribution on the surface of the metal substrate, uneven crosslink density throughout the film, varying pigment concentration in the coating, and expansion/damage when exposed to gases/liquids. In order to combat these issues the use of multiple layers has been employed. Using multiple layers prevents areas with defects from overlapping, therefore ensuring that the entirety of the surface is coated. Another approach for mitigating the concerns with organic coating is the use of a primer and middle layer with wet adhesion and dense crosslinking along with a topcoat that is UV resistant and hydrophobic. Enhanced corrosion protection and chipping resistance was found to result from a coating system made up of an initial cation electrodeposition coating, followed by a liquid coating, next a powder coating, another liquid coating, and lastly a topcoat. One additional method to prevent pinholes and damage of organic coatings is the use of a resin that cures when exposed to UV light [82].

The effectiveness of organic coatings greatly depends on permeability, thickness, electrical properties, and adhesion to the substrate. These coatings prevent corrosion by acting as a physical barrier, inhibiting the corrosion process, or by increasing the electrical resistance. Four paint systems were used on galvanized steel to test their protection in 3.5% NaCl and in weathering tests. Two of the systems were composed of a primer (wash primer and high built primer) and special acrylic resins (containing micaceous iron oxide, zinc chrome pigments, and titanium dioxide pigments depending on the layer), while the other two systems were made up of an epoxy primer (wash primer and two-component primer) and a finishing coat of epoxy paint including zinc chromate and iron oxides. Systems 2 and 4 were composed of two layers, not having the additional wash primer layer that Systems 1 and 3 had. All of the systems performed better than galvanized steel alone. The three layer system composed of the wash primer, two-component epoxy primer (with zinc chromate and iron oxide), and two-component epoxy paint supplied the best corrosion protection. The two layer epoxy primer and epoxy paint system without the wash primer layer performed well but suffered from a lack of coating adhesion. The acrylic resin system with the wash primer performed close to as well as the two layer epoxy coating mentioned previously and the acrylic resin system without the wash primer performed the worst [83].

The corrosion protection provided to steel by anticorrosion pigments containing aluminum polyphosphate was examined. It has been found that aluminum triphosphate can reduce the amount of corrosion and is strongly impacted by the pigment used. A downfall to the use of aluminum triphosphate is the need to bring its pH to a neutral value from its original acidic pH, finding a component to fill this task is difficult as many with high pH values cause issues with adhesion. The incorporation of aluminum triphosphate pigment at 10% vol was found to be optimal. Lastly, using pigments with barrier properties may be beneficial by adding additional barrier protection to the paint [84].

A study was performed that tested a treatment for corrosion protection of electrogalvanized steel consisted in the immersion of the samples in a complex solution composed of a mixture of 2-butyne-1.4-diol propoxylate with cerium nitrate, sodium sulfate and sodium nitrate, which resulted in the formation of a mixed polymeric/inorganic film on the surface. It has been found that the treatment time is important for the anti-corrosion performance, and the electrochemical test results proved that a 10 minute treatment time showed the best corrosion performance[85].

3. COATINGS FOR ALUMINUM

Thus far the focus has been various coating systems used on steel, which have included metallic, polymer, and ceramic coatings. However, aluminum, which contains a high strength to weight ratio, is commonly used within the airline industry and becoming more popular in many other industries. Since corrosion affects various metals through different mechanisms, the design of corrosion coating systems is changed. Using a coating system on aluminum, which is susceptible to pitting corrosion, will prevent loss of structural integrity due to corrosion. Here the focus shifts from steel corrosion protection to aluminum protection.

An investigation of organic-inorganic composite materials for use in corrosion protection permits a better understanding of both organic and inorganic properties and how these properties can be utilized. These composite materials are able to combine diffusion barrier and the required flexibility gained from the inorganic network. These composite systems can contain SiOH or SiOR components, which creates stable complexes with the aluminum metal surface. In the reference 86, figure 3 displays a schematic of a nanocomposite coating on aluminum. Evidence suggests that the formation of Si-O-Al is thermodynamically favored. A thin coat of 5-10 μm thick is applied and displays good corrosion protection after 240 hours of salt spray test [86].

Another variety of organic-inorganic composite material used as a corrosion protection system consists of organically modified silicates. These are formed by the hydrolysis and condensation of modified silanes with alkoxide precursors. Metroke et al. studied the corrosion protection characteristics of 3-Glycidoxypropyltrimethoxysilane (GLYMO) modified Ormosils used as a coating on aluminum. Electrochemical analysis was used to determine the corrosion potentials of abraded and deoxidized aluminum alloys exposed to 1 M sodium chloride solution. E_{cor}, corrosion potential, for abraded aluminum was -0.669 mV and -0.719 mV for deoxidized aluminum. It was determined that corrosion protection was related to organic content concentration and hydrolysis water content (W). Highest corrosion protection performance was observed with films with high organic content and low water content [86].

Surface treatment and coating deposition play crucial roles in the overall effectiveness of a coating system. Adhesion properties have been known to be directly related to coating performance. A synergistic approach is believed to be appropriate in order to obtain similar surface protection as conventional chromate coatings. Research on pseudoboehmite(PB)-silane hybrid coatings has shown the formation of a M-O-Si bond forms between the silanes and the metal surface. The PB coating increases the surface area and the porosity, leading to greater stability due to increased Al-O-Si bond density. The corrosion protection due to the coating was synergistic and was increased when the AA2024 was prepared by exposing it to boiling water. The corrosion protection from the PB coating was found to be better than a chromate coating on aluminum or alkali pretreatment [87]. Similarly, the study of AA2024-T3 coated with bis-sulfur silane found the interfacial layer contributed largely to the corrosion protection of the aluminum alloy due to the extremely cross-linked arrangement of the layer, high level of adhesion to the aluminum alloy, and lack of porosity in the layer. These characteristics block pitting by decreasing the transfer through the layer. Furthermore, the Al-O-Si bonds that form at the interface of the film stop the development of cathodic sites [88].

Nanoporous silica is one of many materials being explored for use in encapsulating and controlled-release of corrosion inhibitors. Nanoporous silica is a ceramic whose pore size can be controlled and has other desirable traits such as small pore size distribution, stability both mechanically and thermally, environmentally friendly, and cost-effective. In particular, nanostructure silica particles with a core of cerium corrosion inhibitor have been successfully used to prevent the corrosion of AA2024-T3 in the presence of 0.05 M NaCl [89].

During the last few years, sol-gel films have been extensively studied for potential applications in corrosion prevention. Both active and passive corrosion protection offer important components to a corrosion protection system. Passive protection occurs with a barrier film preventing contact with corrosive species and active protection begins when a coating is damaged. The addition of corrosion inhibitors to hybrid sol-gels enables self-healing in addition to the barrier protection provided by the sol-gel. Cerium salts and 8-hydroxyquinoline were tested and found to provide active protection in while the sol-gel barrier provided passive protection. The addition of metal oxides to the siloxane strengthens the close-packed –Si-O-Si- bonds [90]. Another self-healing coating is based on pre-formed hybrid organo-silicate nano-particles with epoxy functional groups that are applied to the metal surface where they cross-link, a type of self-assembled nanophase particle (SNAP) coating process. These SNAP coatings exhibit good barrier protection and adhesion to aluminum alloys but perform poorly if damaged [91]. These hybrid organo-silicate coatings contain an inhibitor that is released at damaged locations of the coating, therefore providing self-healing protection. Several inhibitors, including mercaptobenzothiazole (MBT), mercaptobenzimidazole (MBI), mercaptobenzimidazole-sulfonate (MBISA), and thiosalicylic acid (TSA), have been tested. Two different methods for inhibitor storage and delivery, cyclodextrin-assisted molecular encapsulation and ion-exchange anchoring of the inhibitor, were also examined. Results showed that MBT and MBI, the non-ionizable inhibitors, encapsulated in their molecular forms, or as inclusion complexes with β-cyclodextrin provided better protection than ionizable inhibitors, such as TSA and MBISA. At the equilibrium of the complex, the β-cyclodextrin encapsulation has a slow release and continues inhibitor transfer to corrosion locations [92]. These additions of inhibitors and encapsulation of inhibitors displays encouraging results in terms of adding inhibitors to barrier corrosion protection systems.

Sol-gel coatings provide good barrier protection but do not participate in active corrosion protection. It has been found that the integration of nanoparticles into sol-gel films can increase corrosion protection. A self-repairing coating for aluminum alloys based on cage like oil core/silica gel shell particles was created. The repairing agent, methylmethacrylate, and catalysts, potassium persulfate and sodium thiosulfate, were encapsulated in the cage like microspheres as the microspheres were constructed. The microspheres were self-assembled on AA2024 and then coated in a sol-gel film. Analysis showed that the film worked as a primer with self-repairing capability [16].

The sol-gel method also can potentially offer a promising approach in the development of a corrosion protection system. The sol-gel preparation methods influence the properties of the coating and subsequently the corrosion protection. The increase in TPOZ hydrolysis time and temperature increased the amount of ZrO_2 nanoparticles within the sol-gel film. The ZrO_2 nanoparticles enhance corrosion protection and were also found to cause pore blocking of the film [93]. Similarly, Voevodin et al. evaluated the performance of a Zr-epoxy sol-gel coating which reinforced the many possible advantages of sol-gel coatings. The effectiveness of the sol-gel coatings is attributed to their ability for form inorganic-organic and hybrid networks [94].

Nano-engineering, engineering at the nano scale, may offer some valuable applications in corrosion prevention. It is proposed that nano-engineered coatings can use energy produced during the corrosion process to produce and distribute an inhibitor. A recently developed smart coating system utilizes corrosion energy to cause the release of corrosion inhibitor only when needed. Aluminum alloy 2024-T3 was protected using conducting polyaniline films and anionic inhibitors including Ce^{3+} and Cr(VI) and a couple types of polyaniline films. The Cr(VI) provided much better corrosion inhibition than the Ce^{3+}, it was also observed that the less porous polyaniline films provided better protection. Corrosion at the scribe causes the aluminum substrate to polarize the polyaniline film, resulting in inhibitor discharge and scribe protection [95].

The application method was also found to have a significant impact on the ability to coat surfaces; electrochemical deposition enables the coating of structures with intricate geometries much more effectively than dip and spin coating methods. The greater the hydrophobicity of the monomer the better the corrosion protection, displayed by phenyl trimethoxysilane performing much better than tetraethyoxysilane [96].

Synergistic effects have been known to play an important role in the protection of metals against corrosion. More detail of this synergistic mechanism was revealed during the work of Kachurina et al. Corrosion of aluminum exposed to 0.35 wt % $(NH_4)_2SO_4$ and 0.05 wt % NaCl protected by a synergistic layer by layer organically-modified silicate coating was investigated. Individually both layer by layer (LBL) and organically-modified silicate (Ormosil) coatings cause passivation of the aluminum but neither individually provided much protection. By including cobalt (III) into the LBL as an active inhibitor and matching the LBL with the Ormosil topcoat, corrosion protection obtained was much better than that of either alone. This increased corrosion protection is due to the densely cross linked layer of clay composite that is produced at the juncture of the LBL and Ormosil layers. The Ormosil layer also keeps corrosion inhibitors from escaping the LBL [97].

The search for protective coating alternatives has lead to the possibility of using zeolites, microporous crystalline aluminosilicates. It has been revealed that coatings on aluminum alloy containing high-silica-zeolite contain exceptional corrosion resistance. More results show that the best corrosion resistance is obtained with a dense polycrystalline zeolite coating with no intercrystal porosity and no intracrystal porosity, which is usually achieved with the use of bulky organic molecules during synthesis. The corrosion protection provided by zeolite coatings to aluminum alloy 2024-T3 exposed to NaCl in salt fog testing was observed. It has been found that the bare zeolite coating provides good corrosion protection where the coating is been damaged, corrosion will concentrated in that area. Additionally, AA 2024-T3 samples coated with a complete zeolite coating of MFI (mordenite framework inverted) structure, a primer (Mil-PRF-23377 Type I Class C), and both in the presence and absence of a topcoat (Mil-PRF-85285) were found to perform great, passing 3100 hours of salt-fog exposure without any issues with adhesion or corrosion at the scribe [98].

Experimentation on the effect of the type of thermal spray coating process to the corrosion protection of AA2024-T3 was conducted. Using powder flame spray, atmospheric plasma spray, and high velocity oxy fuel (HVOF) thermal spray coating processes a 99-99.8% Al coatings were applied to the aluminum substrate. Analysis of the mechanical properties, pre-corroded properties, microstructures, etc. show HVOF to be the most advantageous thermal spray process to use [89]. The HVOF can also be used to deposit a coating that contains corrosion inhibitors, further improving the corrosion resistance provided.

4. COATINGS FOR MAGNESIUM ALLOYS:

Magnesium alloys are becoming more popular in various applications [99-102]. Magnesium alloys are extremely lightweight, which makes it very useful within the aircraft and automotive industries. For maximum corrosion resistance, magnesium alloys must not contain any heavy-metal impurities. In addition, protective coating systems are recommended to improve corrosion resistance. A discussion of various techniques found to protect magnesium alloys against corrosion is presented.

Electrochemical plating is an economical and simple way to apply a metal coating to magnesium, which is much more complex than most metals due to its high reactivity. Magnesium quickly forms an oxide layer on its surface in the presence of oxygen, making a pretreatment that prevents this formation necessary. Zinc and nickel pretreatments have been used successfully. Electrochemical plating of magnesium alloys has proven difficult because of the intermetallics at grain boundaries result in inconsistent surface potential of the metal surface. The two methods of electrochemical plating, electroplating and electroless plating each have their disadvantages. Electroplating can suffer from uneven current density resulting in inconsistent plating thicknesses. Electroless plating faces issues with its short bath life and environmental concerns over disposal of the baths. The application of a Cu-Ni-Cr plating provides corrosion protection in mildly corrosive environments. However, a coating that can withstand corrosive high salt and marine conditions that would be necessary for adequate protection in the automotive industry has not yet been established [82].

Conversion coatings can also be used to protect magnesium from corrosion and provide an adhesive surface for an additional paint layer. Conversion coatings are applied using a chemical or electrochemical treatment process that chemically bonds a layer of oxides, phosphates, or chromates to the surface of magnesium. Conversion coatings add protection by providing a barrier that prevents transfer of electrons between the metal and the surrounding environment. In addition, corrosion inhibitors are also added to conversion coatings to increase corrosion resistance. Conversion coatings are extremely dependent on the cleaning and pretreatment of the surface they are applied to. The more detailed the cleaning processes the better the corrosion resistance. Chromate, fluorozirconate, and phosphate/permanganate have successfully been used to create quality conversion coatings. The downfall of many corrosion coatings is the use of toxic materials in the treatment solutions and finding coatings that will evenly coat the wide array of elements found in alloys [82]. Magnesium alloy AZ91D treated with a cerium conversion coating had improved resistance to localized corrosion. Cleaning and surface treatment of the metal substrate with potassium hydroxide inhibits active sites on the surface and prevents chloride ions from contacting the surface and forming an oxide layer. The presence of cerium shifts the pitting potential although the amount of inhibition in NaCl is very dependent on the cerium concentration [103].

Hydride coatings are yet another system of corrosion protection. Hydride coatings are applied by immersing the magnesium alloy in an alkaline solution. The magnesium acts as a cathode and after polishing, degreasing, and acid etching, the magnesium undergoes cathodic treatment creating the hydride coating. It has been found that the hydride coating can reduce the corrosion rate of AZ91D magnesium alloy by 33%, providing corrosion protection similar to that of a dichromate coating [82].

Anodizing can be used to create a stable oxide film on a metal surface using an electrolytic method. Benefits of anodizing include better paint adhesion and results in passivation of the surface. The resulting anodized coating consists of two layers and an outer sealing layer. The layer at the interface of the metal and the coating is thin and acts as a barrier; on top of this layer is an additional layer with a cellular structure. These cellular structures contain pores, the size and density of these pores determines the magnitude of protection provided. The oxide layer must then be sealed either by treatment such as boiling or steam, or using a lacquer. Hard anodizing is performed by reducing the temperature of the electrolyte and by intensifying the current density. Hard anodizing may also be performed when additional hardness and wear resistance is required. The addition of solid film lubricants increases the benefits of hard anodizing. As with all coatings, anodizing has its disadvantages such as flaws, inclusions, pores, and difficulty obtaining uniform current density, which can lead to uneven coatings. Furthermore, the coatings produced are ceramic material that often becomes brittle [82].

Laser surface alloying can be used to melt a metallic coating and metallic substrate using a powerful laser. Use of the laser surface alloying is favorable because it is very accurate, not limited by the geometry of the surface, and relatively inexpensive, and only affects the surface a few millimeters deep. The laser causes the coating and metal beneath to melt, blend, and re-solidify very fast. Research has found that the use of aluminum, copper, and chromate coatings when laser surface alloying results in increased corrosion prevention [82].

Organic/polymer coatings are generally applied as a topcoat of a coating system. The main purpose is to create a barrier between the protected metal and the surroundings, preventing the transfer of water, oxygen, charge, and ions. Many coatings are used in locations where damage is likely to occur. In order to create a long-lasting coating, self-repairing coatings have been developed. Self-repairing coatings often incorporate additives to the coating, such as inhibitors, or sacrificial compounds. For example, the corrosion protection of magnesium is enhanced using a coating based on a phenolic resin primer and zinc chromate. Another study found that adding an inhibiting leachable pigment and an ion reactive pigment could reduce corrosion. In this case chromate acted as the inhibiting leachable pigment and small spherical aluminum particles acted as the ion reactive pigment. The protection is attributed to the fact that the spherical particles interact with ions that cause corrosion, controlling the pH and the chromate is released at damaged areas filling gaps in the coating [82].

The corrosion protection of AZ31B magnesium alloy, which was exposed to 0.005M NaCl, was heightened via the application of a sol-gel coating. More specifically, the sol-gel coating was created through copolymerization of epoxy-siloxane and zirconium alkoxides. The addition of tris(trimethylsilyl) phosphate provides supplemental corrosion protection through a chemical interaction with the magnesium, which leads to the formation of a stable film. The corrosion protection of the coating system is also attributed to the Mg-O-P bonds that are formed; these bonds are hydrolytically stable and show excellent adhesion of the coating to the magnesium alloy [104].

Magnesium and its alloys offer high strength to weight ratios and high thermal conductivity, which make it a valuable option in various applications. Conversely, magnesium alloys are highly vulnerable to galvanic corrosion, which has greatly restricted its extensive use. Plating, anodizing, conversion coating and polymer coating are a few techniques commonly used to protect against corrosion. However, recent research has investigated the use of poly(ether imides) as a corrosion protection polymer coating system. This research has yielded some promising results and demonstrated the effectiveness of poly(ether imides) to reduce corrosion rates [105].

5. COATINGS FOR OTHER METALS

5.1. Metallic Coatings

Hexavalent-chromium coatings have been found to be extremely effective for corrosion protection [106]. However, recent environmental concerns about the use of hexavalent-chromium have led to the banning of its use and the development of alternative coatings. However, research to improve other phases of chromium for use in coatings is being conducted. One approach is to focus on improving the electroplating bath, which includes a water soluble trivalent chromium salt, a complexant, hydrogen ion source to maintain a pH 2.8-4.2, pH buffering compound, and a sulfur-containing organic compound [107]. A military study approves the use of trivalent chromium pretreatment (TCP) as a hexavalent-chromium replacement as long as a chromated primer is used. It is important to note that compared to other hexavalent-chromium alternatives, TCP requires very tight control during the application process and specific surface preparation [108]. Focusing on the bath and pretreatment of the metal greatly improves coating effectiveness. Another alternative to hexavalent-chromium is a conversion coating that uses ferrate as the oxidizing agent. The coating consists of 0.0166-1.66% by weight ferrate ion and another transition metal oxyanion. The use of vanadate as the transition metal oxyanion/corrosion resistant material shows promising results and has been the issue of recent conversion coating related patents [68].

Another alternative to hexavalent chromium coatings is the aluminum pigmented ceramic coating. The coating is composed of atomized aluminum pigments and an acidic phosphate and dichromate binder. In addition to taking on the normal role of a binder, the dichromate passivates the aluminum particles and ferrous substrate, reducing the likelihood of a reaction with phosphate. The coating can be turned galvanically active and used as a sacrificial coating by bombarding with an abrasive. Finally, this coating can be sealed with an inorganic topcoat. This coating has nearly equal attributes to those of chromium containing aluminum ceramic coatings, making it an excellent replacement [109].

Similar to hexavalent-chromium, the environmental concerns associated with cadmium coatings have led to the development of alternatives. The Joint Cadmium Alternatives Team has been working on developing alternatives for the military. Their discoveries have shown that AlumiPlate, an electroplated aluminum, provides the greatest protection. The use of low hydrogen embrittlement ZnNi alloy plating (LHE ZnNI) currently performs equally to Cd nevertheless a new process for depositing nanostructured ZnNi via pulse electroplating is being examined [108]. Another area of research is focused on cold spray coatings. These cold spray coatings are Al and Al alloys that are applied to corroded and damaged areas to supply a sacrificial coating [108].

In attempt to reduce pitting corrosion of aluminum in NaCl, micro-crystallization and magnetron sputtering has been used to deposit aluminum film. Pure aluminum microcrystals about 400 nm in diameter were used to form the microcrystalline aluminum film. The film undergoes passivation and displays better corrosion resistance than cast aluminum. It is common for the pit initiation rate to increase and metastable pits to form. The resulting metastable pits are likely to form stable pits, preventing further pit growth. Therefore, the use of a microcrystalline aluminum film improves the repassivation and pitting resistance of aluminum [110].

Thermal spray coatings consisting of Zn, Al, or Zn-Al alloys are often used for corrosion protection. Most often these metals are applied via arc or flame spraying. It has been found that the preparation of the substrate surface and the application process play a large role in the uniformity and adhesion of the coating. Each of the following factors, which includes alloy composition, preparation of the surface, application, sealer, the conditions the object is to be employed, and any environmental issues that may arise must be examined in order to create the ideal coating system. Due to the porous nature of thermal sprayed coatings, it is very necessary to apply a sealant or paint. Optimally, a wash primer such as zinc-chromate is applied on the thermal spray coating, a sealer such as phenolic resins, polyester resins, or polyvinyl chloride is applied over the wash primer and a polyurethane or epoxy topcoat is often applied last. In all, a properly applied thermal spray coating can provide corrosion protection for approximately 10-20 years when supplemented with infrequent servicing [111].

5.2. Polymers Coatings

In many corrosion-coating systems, the preservation of an oxide layer on the metal surface is crucial to ensure corrosion protection. Frequently, these oxide layers were maintained through the use of chromates and other environmentally harmful substances. Intrinsically conducting polymers have been found to passivate and protect metals via the formation of an oxide layer on the metal surface. Any uncovered area of the metal is passivized by the coating due to the conductive property of the intrinsically conducting polymers (ICP). Testing on polyaniline/ICP systems has shown great potential [39].

Recent examination is being directed toward new corrosion coating technology concerning an interesting material called electroactive conducting polymers (ECP). Since ECPs offer similar properties as harmful chromate coating systems, they may offer a potential alternative in corrosion coating protection. Similar to chromate, ECPs have positive equilibrium potentials relative to iron and aluminum. Tests have shown successful corrosion protection of aluminum alloy by polyaniline and polypyrrole when exposed to sodium chloride solution. However, more exploration is needed to fully understand ECPs and if they offer advantages in corrosion protection [112].

Inorganic sol-gel coatings exhibit desirable barrier properties but cannot be used in conjunction with aluminum alloys or magnesium alloys due to necessary high curing temperatures. Inorganic-organic hybrid sol-gel coatings appear to offer encouraging results in terms of corrosion protection, flexibility, thickness, and curing temperature [113]. The ability of the hybrid sol-gel coating to prevent corrosion is directly related to its barrier properties. Any location where the electrolyte is able to reach the surface of the metal through defects in the coating is likely to result in localized corrosion. The development of coatings able to self-repair these defects is desirable. Self-repairing coatings made up of nanocontainers with the capability of controlled release of encapsulated inhibitor may develop into a new category of self-healing coatings. Unlike many other systems which constantly release small amounts of inhibitor independent of whether damage is present or not, the self-repairing system works by eliciting the release of corrosion inhibitors upon corrosion or damage to the coating, only in this manner is the corrosion inhibitor released. This improved release control, cuts down on inhibitor waste, and improves the durability of the coating. Research has focused on the use of triazole and thiazole derivatives as inhibitors [113]. Improvement in the encapsulation process and control of the inhibitor release is dependent on advancement in nanoreservoir production. As this technology advances, the incorporation of multiple active functions within each coating may be achievable [114]. An example of a self-healing hybrid sol-gel coating combines nanocontainers containing benzotriazole that are impregnated in a sol-gel film. Combining nanocontainers within the hybrid sol-gel film results in prolonged corrosion protection due to the self-healing ability. Furthermore, since the inhibitor is being contained within the nanocontainer, there is no negative reaction between the inhibitor and the hybrid sol-gel coating that would cause a negative impact on the barrier properties or inhibitor effectiveness [115]. Another organic-inorganic hybrid coating uses a SiO_2-methacrylate matrix and TiO_2–CeO_2 nanoparticles. It is presumed that the employment of a binary powder would improve corrosion resistance in two ways, first the even distribution of these nanoparticles throughout the coating should result in desirable barrier properties and secondly the cerium oxide will act as a corrosion inhibitor [113]. The organic-inorganic hybrid coating is only one part of the corrosion protection system; it is necessary to cover it with an additional paint layer. The resulting system has been found to provide good corrosion protection.

New advancements in nanotechnology offer new ideas for developing sophisticated corrosion prevention coating systems. Lvov et al. proposed some new designs of self-healing anti-corrosion coating systems with the addition of nanocontainers equipped with corrosion inhibitors. Upon mechanical damage or initiation of the corrosion process, these nanocontainers release the encapsulated inhibitor directly into the damaged area. This system was tested by loading halloysite nanotubes with the inhibitor benzotriazole and incorporated it into a ZrO_2-SiO_2 sol-gel coating then deposited it onto aluminum alloy. It was demonstrated after exposure to sodium chloride solution, the anti-corrosion efficiency increased and a self-healing effect was obtained. More investigation is needed to determine the fine details of the applicability of this nanotechnology [116].

A recent patent uses similar principles to those of the self-healing coatings, which consists of a coating with evenly distributed microcapsules that contain inhibitors, a film forming compound, and an indicator. Upon breakdown of the microcapsule shell due to the presence of acidic or basic conditions, the contained components are released. There are two types of indicators that could be applied. The first type, exhibits a color change based on pH such as phenolphthalein and the second type, fluoresces in the presence of metal oxidation or formation of a metal ion complex such as 7-hydroxycoumarin or coumarin [117]. Including an indicator would make checking for corrosion much easier. It would aid workers in finding corrosion early and quickly, preventing further damage and decreasing the amount of time needed to inspect vehicles.

Another patent focuses on a coating system that incorporates the corrosion inhibitor molybdenum oxide (MoO_3). The system is comprised of a particulate metal, organic solvent, silane binder with epoxy functional groups, thickener, MoO_3, water, and potentially a silicate. With all percentages by weight, optimal composition of the system includes particulate metal content of 10 – 40 % with zinc use particularly advantageous, 1 – 30 % organic solvent, 3 – 20 % binder, 0.005 – 2 %

thickening agent, 0.5 - 0.7 % or 2 % by weight MoO_3, water content of 30 – 60 %, 10 % epoxy functional silane, and 0.05 – 5 % silicate. The addition of molybdenum oxide was found to significantly increase corrosion protection when exposed to salt spray [118].

Polysiloxanes have shown promising results in terms of corrosion protection. In testing the acrylated urethane modified polysiloxane, exhibited great durability, film toughness, edge protection, and flexibility. Additionally, the epoxy modified polysiloxane displayed quick adoption of film properties especially in terms of hardness. As a whole, the organically altered polysiloxanes applied for corrosion protection in combination with a zinc rich primer coating show long-term corrosion protection, which is drastically improved compared to the conventional three coat system [119].

A thermoplastic polymeric composition has been developed for corrosion protection and noise dampening of vehicle underbodies and boxed components. This underbody coating and box filler is based on agents that expand upon exposure to heat. Improvements such as decreased weight, greater corrosion protection, boosted mechanical performance, and more significant noise dampening make this a very desirable material with many applications. This material withstands exposure to abrasives such as dust, gravel, or sand as well as those that cause corrosion such as salt, humidity, acidic rain, water, or pollutants at significantly reduced thicknesses than traditional polyvinyl coatings [120].

5.3. Pigment and Binder Focused Coatings

Some commonly used binders are polyurethane binders, epoxy resin-based binders, and alkyd resin-based binders. Polyurethane binders are polymers produced via a reaction between isocyanates and polyols. The type of isocyanate, the addition of hydroxyl, and the ratio of these materials used all play a function in determining the properties of the final polyurethane product. The hydroxyl groups are often polyester or acrylate based and the isocyanates are aromatic or aliphatic. There are also one component polyurethanes based on a polyurethane-isocyanate body that is attached to isocyanate groups. These one-component polyurethanes react with the moisture in the environment, which causes them to cross link and harden. Epoxy resin-based inhibitors are often used for corrosion protection because they provide good chemical stability, adhesion, hardness, flexibility, and toughness. Generally, epoxides are formed by reacting diane with epichlorhydrin that produce glycidyl ethers, which are the main component of the resin. The glycidyl ether based resins are often hardened by reacting them with polyamines or aminoamides. Alkyd resin-based binders are polyesters adapted with carboxylic acids, which are usually used in mild corrosion conditions due to damage to the ester bonds that are relatively common when exposed to atmospheric conditions. They have the greatest chemical stability but are also susceptible to hydrolysis. Testing showed that a two-component epoxy resin hardened with polyamine provided the best corrosion protection followed by a single component polyurethane, and the worst protection was obtained when the alkyd resin was used. The resins were pigmented with iron mica, muscovite, and graphite. Findings showed that iron mica outperformed muscovite and graphite in terms of corrosion prevention. Both synthetic and natural forms of iron mica were used, neither provided corrosion prevention. The use of graphite is also concerning because contact with the surface of the metal substrate could accelerate corrosion. The critical lamellar pigment volume concentration, or concentration of the pigments at which the coating is the most advantageous, were 20% vol for iron mica, 24% vol for muscovite, and 35% vol for graphite [121].

Electrodeposited coatings are commonly used to protect the metal surfaces of vehicles from corrosion. Nearly all vehicles are composed of pieces with sharp, box-like edges, fasteners, or hinges, which are areas vulnerable to corrosion. In order to prevent corrosion within these areas, coating thicknesses have been increased and the pigment content to binder ratio of the coating has been increased. The greater pigment content causes the flow to be restricted while curing but also leads to an undesirable textured film. The textured areas cause greater corrosion due to resultant micropinholes and voids. Microgels, high molecular weight resins, have been developed that provide similar flow restriction obtained by high pigment content, yet also achieve a smooth surface free of micropinholes and voids. A microgel that achieves this is a cationic microgel, which is created through the interactions between an amine and an epoxy oligomer, that when added to water containing an acid, causes emulsioning, lastly epoxy monomers are added to create the polymer [122].

Another study was performed that focused on the use of pigments and fillers in corrosion resistance paints. The coatings used an epoxy resin binder and were cured using a polyamine hardener. The fillers/pigments were tested and rated based on anticorrosion efficiency, adhesion of the barrier, and inhibition of corrosion at a film thickness of 150 μm. Overall performance showed wollastonite (filler) performed best followed by zinc phosphate (anticorrosion pigment), talc (filler), mixed filler, in order of decreasing effectiveness. Based solely on the physical-mechanical properties, talc (filler) performed the best followed by wollastonite (filler) and hematite (filler). The anticorrosion agent, zinc phosphate, was used as a standard to assess the corrosion protection of the fillers [123]. This study showed that a filler, which provides a balance of both corrosion protection and desirable physical-mechanical properties, must be found for each given application.

The dispersion binder used in a given water-borne coating plays a large role in determining the corrosion protection provided by the coating. The appropriateness of the binder depends upon the size of the polymer particle, more specifically, smaller polymer particles have been found to be more effective than larger particles. However, the mechanical and physical properties of a binder are also very dependent on its size. Research has found that binders consisting of styrene-acrylate or pure acrylate perform much better than vinyl acetate containing binders [124].

The use of pigments composed of a kaolin core and titanium dioxide shell has been found to improve corrosion protection over traditional pigments. Kaolin can be used to provide bulk to the paint product and reduce the amount of higher-priced pigments needed. Testing of the pigments found that optimal corrosion protection and optimal mechanical properties were observed when low concentrations of titanium dioxide were present on the kaolin surface. When using this pigment, the following pigment to binder ratios based on performance from best to worst were 3 > 1.74 > 2.175 due to alignment of the particle shapes creating a homogeneous film. Unlike regular pigments, the titanium oxide shelled kaolin pigments are anticorrosive and can be used in varying materials at most pH values [125].

An additional pigment with both barrier and anticorrosion properties is spinel MZF pigment. It is prepared by heating the oxidized solid molten phase of micaceous iron oxide to 600^{o}C, washing it with water, firing the oxidized molten phase at 1100^{o}C, and then undergoing calcination causing crystallization of the chloride components and the formation of spinel MZF pigment. The spinel MZF pigment provides barrier protection as well as chemical passivation. Characteristics that lead to the anticorrosive properties of spinel MZF pigment are its lamellar particle shapes and alkalinity [126].

5.4. Water-Rejection/Self-Cleaning

Self-cleaning coatings that reject water have been developed. These coatings consist of a sol-gel coating that self assembles. The coating is fractal and has a super-hydrophobic surface that prevents water saturation. It is also self-cleaning and does so by collecting and washing any materials that have been deposited on the surface of the coating [89].

5.5. Commercial Products

In terms of commercially produced products, the company NOF Metal Coatings Group has developed and commercially produces, GEOBLACK, GEOMET, and GEOKOTE coatings. When the combination of basecoat and topcoat is used in conjunction with one another, high corrosion resistance is provided; matching that expected for chassis components in the automotive industry. Furthermore, they are working on developing a lifetime coating for chassis components. To meet this goal a new product has been produced that is able to obtain thicker coatings. Testing of the new coating has resulted in promising results [127].

6. CONCLUSIONS

Corrosion of metals is becoming increasingly prominent as deicers such as sodium chloride and other highly corrosive chemicals are used on roadways. Developing a high performance, nontoxic, and cost effective corrosion prevention system is very important within the automotive and transportation industries. Numerous research efforts are investigating corrosion mechanisms in order to gain more knowledge to determine effective preventative strategies. Advancements in materials science and nanotechnology have greatly contributed to new and improved highly effective corrosion prevention systems. Along with metallic coatings, polymer and sol-gel coatings show great potential as effective nontoxic alternative low cost coating systems. New innovations such as self-repairing coating systems, capable of successfully protecting metals against corrosion both actively and passively, will become more common when further improvements are made.

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