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Influence of volume concentration of active inhibitor on microstructure and leaching behaviour of a model primer

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ABSTRACT

Model primers with different volume concentrations of active inhibitor were prepared. Strontium aluminium polyphosphate hydrate was incorporated as the active inhibitor in the polymeric matrix. Leaching measurements were performed in 0.86 M NaCl solution while the concentrations of strontium (Sr) and phosphorus (P) were monitored over 21 days. Analytical electron microscopy was employed to characterise the primers with different volume concentrations of active inhibitor. Different release behaviours were established for Sr and P in the aforementioned environment. P had an approximately linear release trend over the 21 days of immersion, whereas Sr exhibited an initially high release rate which reduced with immersion time. The different release behaviours are attributed to the higher dissolution/release rates of strontium-rich particles and a cationic exchange mechanism influencing the release of Sr. Furthermore, whilst higher volume concentrations of the active inhibitor incorporated in the primer layer resulted in the release of higher concentrations of Sr and P, it was not the only factor that led to high leaching rates of Sr and P from the primer. Variations in the coating microstructure occur as a result of the increased pigment volume concentration of the active inhibitor, which leads to the formation of heterogeneities through the thickness of the primer layers, and appears to play an important role that influences the transport paths for the inhibitive species within the primer layers.

1. Introduction

Different types of inorganic additives are added to organic coatings, not only to provide the desired colour and viscosity, but also to enhance the corrosion protection performance [1,2]. The main inorganic pigments which improve the protective performance of organic coatings include: 1-active inhibitor pigments such as different salts of chromates and phosphates, which provide active inhibition and form a passive layer on metallic substrate [1,3]. 2-Barrier pigments such as talc, aluminium flakes and micaceous iron oxide. This group of pigments increases the length and complexity of diffusion pathways for aggressive species (e.g. water, oxygen and Cl^-). Therefore, the barrier pigments increase the time to failure of the organic coatings [4–7]. 3-Sacrificial pigments such as zinc powders and magnesium powders which can provide cathodic protection for steel and aluminium substrates respectively [5,8,9].

Active inhibitor pigments are employed in many industries such as coil coatings and aerospace. Chromate salts are the most effective and well known active inhibitors for a wide variety of application. However, chromate is known for its toxic and carcinogenic properties, and its use is limited by health and safety regulations [9–14]. Therefore, significant research is in progress to understand the protection mechanism of chromate pigments and non-chromate pigments incorporated into organic coatings, in order to develop non-hazardous active inhibitor pigments with comparable protective properties to chromate ones [5,12,15]. Nonetheless, for all active inhibitor pigments, certain processes need to take place prior to the protection of the substrate. A "trigger" is required for the release of the active inhibitive species. In many cases the presence of water/electrolyte in the organic coating acts as the external stimulus ("trigger") [15–18]. Therefore, water needs to permeate into the organic coating matrix which then results in the dissolution/release of the inhibitive species. After that, the inhibitive species need to diffuse/migrate through the medium and leach out of the primer layer where they react with the metallic substrate to form a protective film on the exposed corroding areas. Therefore, the water uptake properties of the system, the release/dissolution properties of the active inhibitor pigments, the transport

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mechanism and the transport paths for the released/dissolved inhibitive species all play critical roles in the corrosion protection performance of organic coated systems pigmented with active inhibitors [5,19–21]. Thus, a clear and comprehensive understanding of various chemical, physical and structural parameters and their influence on the mentioned phenomena is vital to design and formulate a system with enhanced corrosion protection performance. In addition, understanding the influence of the microstructure of the primer, and the evolution of this microstructure as a result of exposure to the environment, on the transport paths is essential for the design of a well-functioning anticorrosion primer [12,18,22–24].

The local concentration of inhibitive species at the defective area significantly affects the resulting inhibition and therefore protection. The concentration of the inhibitive species should be at or higher than a critical concentration to provide sufficient protection for a metallic substrate at the defective area [5,16,25]. Also, in order to maintain the protection over the service lifetime of the components, the release of inhibitive species should not lead to complete and fast depletion of the inhibitive species from the primer layer [5,16,19]. Therefore, the release and leaching processes should deliver the minimum concentration of inhibitive species at the initial stages (which should be above the critical concentration) to form the protective layer on the defective areas [12] and, then, in order to maintain the protective layer, a continuous supply of the inhibitive species during the service life of the system is required, probably at lower rates and concentrations compared with initial stages [26,27].

The variation of pigment volume concentration (PVC) within the primer layer alters the protective properties of the applied coating. It can change the permeability and diffusion of various species, including the aggressive species or the inhibiting ones which, consequently, can influence the formation and maintenance of the protective/passive film (i.e. the change in PVC can result in either increased or decreased transport phenomena of different species depending on the type, size and nature of pigments and the binder). An increase in the PVC of active inhibitors can lead to an increase in the released concentration of active inhibitor [2,15,18,28]. However, exceeding the critical pigment volume concentration (CPVC) of the system significantly deteriorates the protective properties of the organic coating and leads to the formation of microscopic and isolated voids. Therefore, the PVC of primers incorporated with active inhibitor pigments should be kept below the CPVC [2,15,18,26,29], but to achieve the optimum performance and better systematic design, the influence of active inhibitor volume concentration (while PVC < CPVC) on transport paths, leaching and depletion behaviour of organic coatings need to be understood, and critical factors should be identified. A comprehensive understanding of these mechanisms will facilitate easier calculation of the depletion rate and better prediction of the service life.

The leaching properties of active inhibitor pigments are important factors to consider in formulation [19]. It has been shown that the protection of the cut edges and defects is controlled by the leaching rate of the active inhibitor while the solubility of the active inhibitor plays a minor role [30]. Howard et al. [30] showed that when active inhibitor pigments are incorporated into an organic coating layer "sufficient solubility of inhibitor in a corrosive environment is a necessary but not sufficient condition for providing effective corrosion control" [30]. Therefore, leaching measurements have frequently been performed to investigate the influence of different parameters on the leaching behaviour. It has been found that the leaching process is influenced by several parameters including the chemical composition of the polymeric binder [14,19], pigment distribution and concentration [31], temperature, composition [19,32] and pH of environment [12,14,19,31,33], the diffusion rate of water within the polymeric binder, and ageing and history of the polymeric binder [19]. Further, leaching measurements can be used to model transport mechanisms within the primer layer (models have been proposed to fit and simulate the leaching measurement data) [12,19]. It has been claimed that the release of strontium chromate from a polyester based model primer and several commercial epoxy and acrylic based primers followed a logarithmic trend with time, whilst one of the acrylic based primers exhibited a release behaviour that is best fitted with a power function [19]. Furman et al. [12] studied the leaching behaviour of strontium chromate from an epoxy polyamide based primer which appeared to be a function of $t^{0.25}$ (non-Fickian).

The aim of this work is to study the influence of the pigment volume concentration of the active inhibitor on the morphology and leaching behaviour, in order to correlate the microstructure of the primer to its corrosion protection performance, and to provide mechanistic insights for primer formulators to identify the critical factors that should be considered during formulation, which can lead to a reduction of trial and error (guesswork) for anticorrosion primer development. Therefore, a series of primers (without a topcoat) with different volume concentration of active inhibitor were formulated and applied on a flat substrate (Galfan, Zn + 5% Al, coated steel). Scanning electron microscopy (SEM) was then used to observe the influence of PVC on the morphology of the intact primer layers. Exposure and leaching measurements were performed in 0.86 M NaCl (equivalent to a 5 wt% salt-spray solution, commonly used to test organic coatings) at 30 °C. The exposed samples were also characterized with SEM and energy-dispersive X-ray spectroscopy (EDS). Finally, aliquots were removed for analysis of the elemental concentration of inhibitive species within the leachate by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2. Experimental

2.1. Materials and samples preparation

A series of model primers with different volume concentrations of active inhibitor were formulated. Inorganic particles, including SiO_2 and TiO_2, were added to all the systems at constant volume concentrations, nominally equal to 0.40% and 4.52% respectively. The inhibitor used here was strontium aluminium polyphosphate hydrate (SAPH), provided by AkzoNobel with density 2.9 g cm^{-3}, nominal particle size in the range 2.0–3.5 μm and oil adsorption of 40 g/100 g. The active components of the model polymeric matrix were a polyester resin (Dynapol LH820-16) with median molecular weight (5000 g/mol) and polyisocyanate (Tolonate D2) as the crosslinking agent. First, specific weights of SAPH, SiO_2 and TiO_2 pigments were added to the first part of the polymeric matrix, which contained Dynapol LH820-16. Then, a dual axes centrifuge (Speedmixer DAC150) was used for 5 min at 2400 rpm to assist in mixing and comminution of the particles. After milling, the second part of the polymeric matrix, containing Tolonate D2, was added to each system. The non-volatile volume fraction of the primers in the liquid state was adjusted to ~0.4 by the addition of an appropriate amount of dibasic ester solvent in an attempt to keep the thickness of all primers in the same range, when using a draw bar paint applicator. Finally the mixture was agitated for 3 more minutes at 1600 rpm and the particle sizes in the mixture checked with a Hegman gauge; if the fineness exceeded 5 μm further milling was undertaken. The PVC of each system and the nomenclature referred to each system in this paper are shown in Table 1.

The primers were manually applied onto a flat substrate (Galfan, Zn-5%Al, coated steel) using a wire wound K-bar applicator resulting in 24 μm wet film thickness. The thickness of the zinc layer on the steel was approximately 9 ± 3 μm while the substrate