WHITE PAPER

PERFECT TEAM FOR ECO-FRIENDLY CORROSION PROTECTION SYSTEMS

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Leading Beyond Chemistry

INTRODUCTION

Experts estimate that one-third of all iron and steel products manufactured worldwide per year are used to replace corroded structural components. The economic damage, therefore, is enormous. The term "resource efficiency" is used widely in the paints and coatings market. The aim is to offer customers the products they need to produce resource-efficient paints and coatings. In this market, "resource efficiency" characterizes the bundling of the environmental and economic pillars of sustainability.[1]

More than any other sector, the corrosion protection market illustrates the impact the use of perfectly tailored pigments and binder systems can have on the function of the coating as a whole and furthermore on the protection/durability of valuable objects.

CAUSES AND MECHANISMS OF CORROSION

The metallic state is defined as a property of solid materials in which the atoms are localized, closely packed, on the lattice sites of a crystal structure while the bonding electrons are free and distributed over the entire crystal.[2] Because of the free availability of electrons, even on the external surfaces of the crystal, all metals are fundamentally subject to corrosion processes.

The driving force for corrosion is determined by how easily the electrons are liberated and how easily the metal is oxidized. This depends on the type of metal and is characterized by its electrochemical potential. The chemical reactions that occur during the atmospheric corrosion of iron can be described by the following redox reactions (equations 1-4).

Corrosion requires an anode where iron is oxidized to Fe^{2+}. Oxygen is reduced to hydroxide ions at the cathode that is located elsewhere. Between the anode and cathode, a potential difference exists (see equations 1 and 2).

Equation 1: Anodic partial reaction

$$Fe \longrightarrow Fe^{2+} + 2\,e^- \qquad E^0 = -0.44\ V$$

Equation 2: Cathodic partial reaction

$$H_2O + 1/2\,O_2 + 2\,e^- \longrightarrow 2\,OH^- \qquad E^0 = 0.87\ V$$

Equation 3: Sum of the reactions

$$Fe + H_2O + 1/2\,O_2 \longrightarrow Fe(OH)_2$$

Equation 4: Subsequent oxidation with formation of rust

$$2\,Fe(OH)_2 + 1/2\,O_2 \longrightarrow 2\,FeO(OH) + H_2O$$

In addition, an electrolytic connection allowing transport of ions between anode and cathode and an electric connection for the flow of electrons is required. The latter is usually provided by the corroding piece. A thin liquid film, a water droplet, or even human sweat may serve as an electrolyte. Dissolved ions such as chlorides and sulfates accelerate the corrosion process.[3] Fe^{2+} ions are further oxidized to the more stable Fe^{3+} ions and form insoluble Fe(III)-oxide hydroxide, better known as rust, on the surface.

In this case, the anode and cathode are of the same metal, but when the oxygen concentration differs, a potential difference is established.[3] Usually the oxygen-deprived location becomes anodic. Another reason for a potential difference on one and the same metal is the inhomogeneity of its surface. Edges, steps, kink sites, or voids in the crystal lattice and contaminants all lead to local potential differences, sufficient to initiate corrosion.[4]

In some cases, like aluminium, corrosion results in a passivating layer of the corresponding oxide. In case of iron however, the oxide does not adhere to the metal surface as its specific volume is much larger. The rust platelets that form flake off constantly, so air, oxygen, and water will continue to reach the metal surface, until the metal has rusted through.

Corrosion proceeds more slowly in the absence of:
- water
- oxygen
- ions

This is usually achieved by the application of an organic coating.[5,6] However, coatings inevitably have weak points, allowing water, oxygen, or ions to diffuse to the metal surface. Therefore, protective coatings usually consist of at least three different layers, each with a specific function: a zinc-rich primer, a thick epoxide base-coat, and a polyurethane top coat providing weathering resistance. However, to save costs it is desirable to reduce the number of layers. In addition, increasing environmental awareness and legislative restrictions, which require low-VOC systems, are also a factor. In this work we present a two-layer system that is exceptionally low-VOC and provides full protection against corrosion.

PRIMER BASED ON A WATERBORNE SILANE – TOP COAT BASED ON A SILICONE HYBRID RESIN, A 100 % LIQUID RESIN

The novel waterborne silane system was specially developed for use in two-pack zinc dust paints, which are the coating of choice for long-term corrosion protection. Zinc is usually added as the second component to the aqueous binder. Upon addition, formulations based on the waterborne silane binder cure at ambient temperatures. Such formulations can be applied with a different film thickness on the substrate. The curing time depends on the formulation (type and amount of fillers and additives used) and the applied wet film thickness. As water has to evaporate, the curing time of zinc dust paints containing the water-based silane binder is impacted by the wet film thickness. Additional factors impacting the curing time are temperature and humidity.

The waterborne silane binder is exceptionally safe for the environment yet easy to process and was designed for a better compatibility with additives and fillers. The system contains special organofunctional groups which can interact with the filler and stabilize the formulation.

The advantages of the waterborne silane binder can be summarized as follows:
- almost zero-VOC
- low-temperature curing
- low or higher film thicknesses are possible
- improved heat resistance compared to organic binders.

Reducing VOCs is a main requirement from the coatings industry and in many countries there are legislations restricting the use of VOCs in coatings. Formulations based on the waterborne silane binder can be used to formulate nearly VOC-free zinc dust paints (Table 1).

SILICONE HYBRID RESIN FOR CORROSION PROTECTION APPLICATIONS

Silicone hybrid resins can be used for corrosion protection applications.[7] In these applications, the coating must meet different requirements to fulfill the needed corrosion resistance. It has to protect the underlying layer by adhering well, while simultaneously preventing harmful substances from migrating to the substrate. It must also be weather resistant. This means not only resistant to rain, snow, and ice but also to the high-energy UV component of sunlight. However, active protection of the steel, with for example a zinc primer, is additionally gained by this second layer, working as a barrier.[8]

Table 1. Guiding formulation based on waterborne silane-based binder

FORMULATION	
COMPONENT	**PARTS BY WEIGHT**
Dynasylan® SIVO 140	15.0
Deionized water	4.0
TEGO® Wet 270	1.0
TEGO® Twin 4100	0.5
AEROSIL® 200	0.6
Zinc oxide (Red Seal, Ever Zinc)	8.0
Mica MKT	7.9
Zinc dust powder (4P16, Ever Zinc)	63.0
Total	**100.0**
COATING PROPERTIES	
theoretical solids content	~ 88 %
density coating	2,8 g/cm³
cup efflux time (DIN 4)	20-30 s
VOC (calculated)	~1 g/l
PVC	~ 81 %
DRYING CONDITIONS	
recommended drying temperature	20-30 °C
recommended rel. Humidity	40-80 %
drying time – touch dry – 60 µm	10 min
drying time – overcoatable – 60 µm	1 hour

Conventional coating systems for heavy corrosion protection are based on a three-layer application system, built to reach the aforementioned requirements, specified in ISO 12944 (C5, high). The market standard is based on a zinc-rich primer, an epoxy intermediate layer, and a PU top coat.[9]

Silicone hybrid resins can be used as solvent-free, ultra-high solids binders for resource-conserving in many different industrial top coat applications. This technology allows formulation of coating systems with significantly less than 250 g/L VOC (sometimes even less than 100 g/L) and moreover permits isocyanate-free crosslinking.[9]

The silicone hybrid resin technology combines the positive effects of an aliphatic epoxy resin, like corrosion protection and chemical resistance, with the UV resistance and low yellowing characteristics of an alkoxy silicone resin.

Figure 1. Advantages of silicone hybrid resins

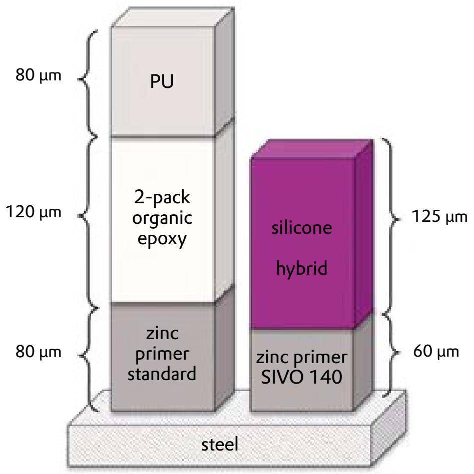


Table 2. Guiding formulation based on the silicone hybrid resin

FORMULATION	
COMPONENT	**PARTS BY WEIGHT**
SILIKOPON® EF	55.0
TEGO® Foamex 840	0.7
TEGO® Wet 260	0.6
AEROSIL® R 972	1.0
BENTONE® SD-2	0.5
FINNTALC® M40	8.0
Blanc Fixe ZB	20.0
Black FW 200	1.5
butyl acetate	10.7
butyl glycol acetate	2.0
Total	**100.0**
COATING PROPERTIES	
theoretical solids content	~ 87 %
density coating	1.27 g/cm^3
cup efflux time (DIN 6)	15-18 s
VOC (calculated)	~ 170 g/l
MIXING RATIO	
hardener	Dynasylan® AMEO
coating: hardener = 100 : 12.8	

Together with an amino alkoxy silane hardener, the abilities of the intermediate epoxy layer and the PU top coat can be combined (Fig. 1).[8] This allows to reduce three to two coating layers, using a combination of water-borne zinc dust primer based on special low-VOC silane binder and a top coat based on a silicone hybrid resin.

This two-layer system spares costs and time in many ways:

- material cost
- labour cost
- production time.

Thus, new two-layer corrosion protection systems with lower total film thicknesses and better corrosion protection abilities can be achieved. By reducing the film thickness, fewer coating materials are needed.[8] Labour costs are reduced significantly by skipping the second primer coating layer. Moreover, the working time is considerably reduced due to lowering the total drying time for the coating,[10] which leads to a faster throughput in the production.

ECO-FRIENDLINESS (VOC-REGULATIONS)

Zinc dust paints that are formulated with this innovative binder and ultra-high solid top coat based on the silicone hybrid resin enable the formulator to develop low-VOC coatings systems without compromising properties (versus traditional systems with a higher VOC content).[10] The VOC emission can be reduced from 120 g/m^2 to 20 g/m^2 compared to a common solvent-borne coating system.

This reduction not only protects the substrate, it also protects the environment. The eco-friendliness is obvious, because of the reduced coating thickness and hence less material using fewer solvents. The silicone hybrid resin based top coat is produced according to the guiding formulation shown in table 2.

The recommended additive and filler package, used in the guiding formulation, ensures a good performance in the corrosion tests.

TEST RESULTS

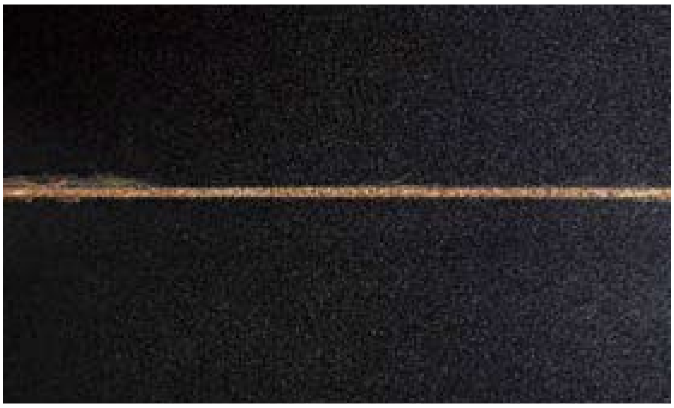
The corrosion protection performance was investigated with coatings on blasted steel (surface preparation degree Sa 2.5), according to DIN EN ISO 12944-6 (C5 high, test program 1). A standard three-layer coating, a commercial 2-pack zinc dust epoxy-primer, a 2-pack epoxy-intermediate layer, and a 2-pack polyurethane top coat (in total: 280 µm dry film thickness) were compared to the two-layer combination of the waterborne silane-primer with the 2-pack silicone hybrid top coat (in total: 185 µm dry film thickness).

The results after 1440 hours of neutral salt spray test, according to ISO 9227 have shown in figures 2 and 3.

In the humidity chamber test, carried out according to ISO 6270-1, no difference could be detected. Both coating systems showed no blistering after 720 hours exposure. However the adhesion on the two-layer system was better (GT 0-1 versus GT 2). Another advantage, which is achieved by using top coats based on silicone hybrids, is the higher chemical resistance, because of their higher crosslinking density. The coating was exposed at room temperature to 10 % solutions of sodium hydroxide and of sulfuric acid; no damage was evident on the paint surface. Surfaces based on silicone hybrids also show a good performance in terms of easy-to-clean-properties and good abrasion resistance.

Figure 2. Three-layer standard coating system: 2-pack zinc dust epoxy-primer, DFT: 80 µm + 2-pack epoxy-intermediate layer, DFT: 120 µm + 2-pack polyurethane top coat, DFT: 80 µm

Figure 3. Two-layer combination of zinc dust primer based on waterborne silane, DFT: 60 µm + 2-pack silicone hybrid top coat, DFT: 125 µm



SUMMARY

The high crosslinking of coatings based on a silicone hybrid resin qualifies this binder-technology for highly durable coatings – extraordinary gloss, colour retention and weather resistance. Compared with a conventional three-layer system, this two-layer system has better corrosion protection, even though the dry film thickness is 95 µm less. In combination with the waterborne zinc dust primer, formulated with the innovative silane-based product, we can achieve an eco-friendly coatings system, which offers a brilliant solution for the reduction of solvents and material and thus the reduction of costs and additionally provides a long-lasting protection against the formation of micro-channels.

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