

Thin film Pretreatment Coating for Multi-Metal Application

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Summary

Multi-metal structures like car bodies must be pretreated to ensure strong adhesion between the metallic substrate and the electrophoretic coating as well as provide excellent corrosion protection. Trication zinc phosphate layers have been state of the art for some decades since it possesses excellent adhesion as well as corrosion performance and self-healing properties. Driven by environmental concerns and the need to reduce process costs an alternative thin film pretreatment has been developed. This technology is represented e.g. by Oxsilan[®], which is based on zirconium oxide and organosilanes. The start of the conversion process on the surface is the same with thin film technology as it is with zinc phosphates. But due to its different chemistry thin film technology offers significant advantages: the pretreatment products are free of heavy metals, the treatment bath runs at room temperature and produces significantly less sludge than the zinc phosphate process. Moreover, the chemistry of thin film technology works on all substrates used in lightweight multi-metal assemblies without limitations including aluminum."

1 Introduction

1.1 Need for pretreatment

The demands of automotive assemblies require the use of pretreatments layers, which are applied prior to the electrophoretic coatings. Since automotive bodies are constructed of different metallic alloys, the pretreatment layers have firstly the function to homogenize the multi-metal surfaces. With this not only are the physical states and the morphology homogenized, but also heterogeneities deriving from the different intermetallic phases. The pretreatment layer is fundamental for a uniform deposition of the electrophoretic coating, including edge protection and throwing power.

Moreover, the pretreatment layer functions as an adhesion promoter between the metallic substrate and the subsequent organic coating. Strong adhesion is not only necessary for the resistance of the coated assemblies under mechanical loads but also for the corrosion inhibition. This is based on the fact that the delamination processes occurs mainly along the metal/pretreatment/ED-coating interface. This process is not only triggered by an electric conductivity between the local anode and cathode but also by ionic conductivity, which is necessary for the charge compensation. While the electrochemical process occurs within the metallic matrix of the substrate, the ionic process takes place at the interface between the metal and the ED coating. The ion transport is impeded by the formation of the pretreatment barrier layer that slows the overall kinetics of the corrosion

processes and therefore reduces delamination of the organic coating from the metal surface.

1.2 Principle of conversion formation

Commercial pretreatment systems are aqueous solutions based on inorganic and/or organic compounds. The principle of layer formation on metallic substrates is a conversion process, which proceeds in different stages that will be summarized.

Conversion baths are formulated to initially pickle the metallic surfaces. This takes place due to an acidic pH and the addition of different additives, like oxidizing or complexing agents, which promote the etching attack. When an automotive body is immersed into the conversion solution this etching process leads directly to anodic dissolution of the metal or metal oxides on the surface. Cathodic proton reduction also occurs as a counter reaction. The pH increases at the metal surface in the Nernst Diffusion Layer as protons are consumed in the pickling reaction. This happens because the transport of matter in Nernst Diffusion layer is based on diffusion and not on convection.

Moreover, the solubility products of the compounds of the conversion bath are pH-dependent. Due to the pH increase of the interfacial area the pretreatment bath is destabilized. This causes the aggregation and subsequent precipitation of the bath compounds on the metal surfaces, which is the initial step of conversion layer formation. The precipitated layer can be crystalline, semi-crystalline or even amorphous and has electrical insulating properties. The longer the metal surface is immersed in the conversion bath the more the conductivity of the metal surface is reduced and more of the surface area is covered by the conversion layer.

Since the electric conductivity is mandatory for the charge transfer process, the layer formation occurs only on those surface areas, which are not already coated by the conversion layer. This process of intrinsic limitation of film formation guarantees an overall homogeneous layer thickness and a wide surface coverage. Finally the conversion formation process slows down or stops when the uncoated metal surface decreases and therefore the electric conductivity becomes too low to sustain the etching process between the conversion bath and the metal surface. In this case the pH gradient breaks down and the entire conversion process comes more or less to an end.

2 Zinc phosphate coating

2.1 Composition and Properties

A traditional conversion treatment in the automotive industry is based on zinc phosphate coatings, which provide very good adhesion promotion and anti-corrosion properties on several metallic substrates such as steels, galvanized steels, magnesium or aluminum alloys [1]. The pretreatment process is conducted in acidic zinc phosphate solutions, which also contain manganese and nickel. This composition is known as trication zinc phosphating.

The film formation process proceeds according to the previously described mechanism. Starting with pickling of the metal surface, formation of a pH gradient near the metal surface and finally formation of the conversion layer, which has a thickness of a few micrometers and consists of zinc phosphate crystals as shown in Fig. 1. The size of the crystal differs slightly depending on the substrate but in all cases show a homogeneous surface coverage.

The chemical composition of these crystals is mainly Hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ or on iron containing alloys Phosphophyllite, $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ [2]. In case of a trication zinc phosphate layer, manganese- and nickel-containing Hopeite crystals of the type $\text{Zn}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zn}_{3-x}\text{Ni}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ also grow during the film formation [3].

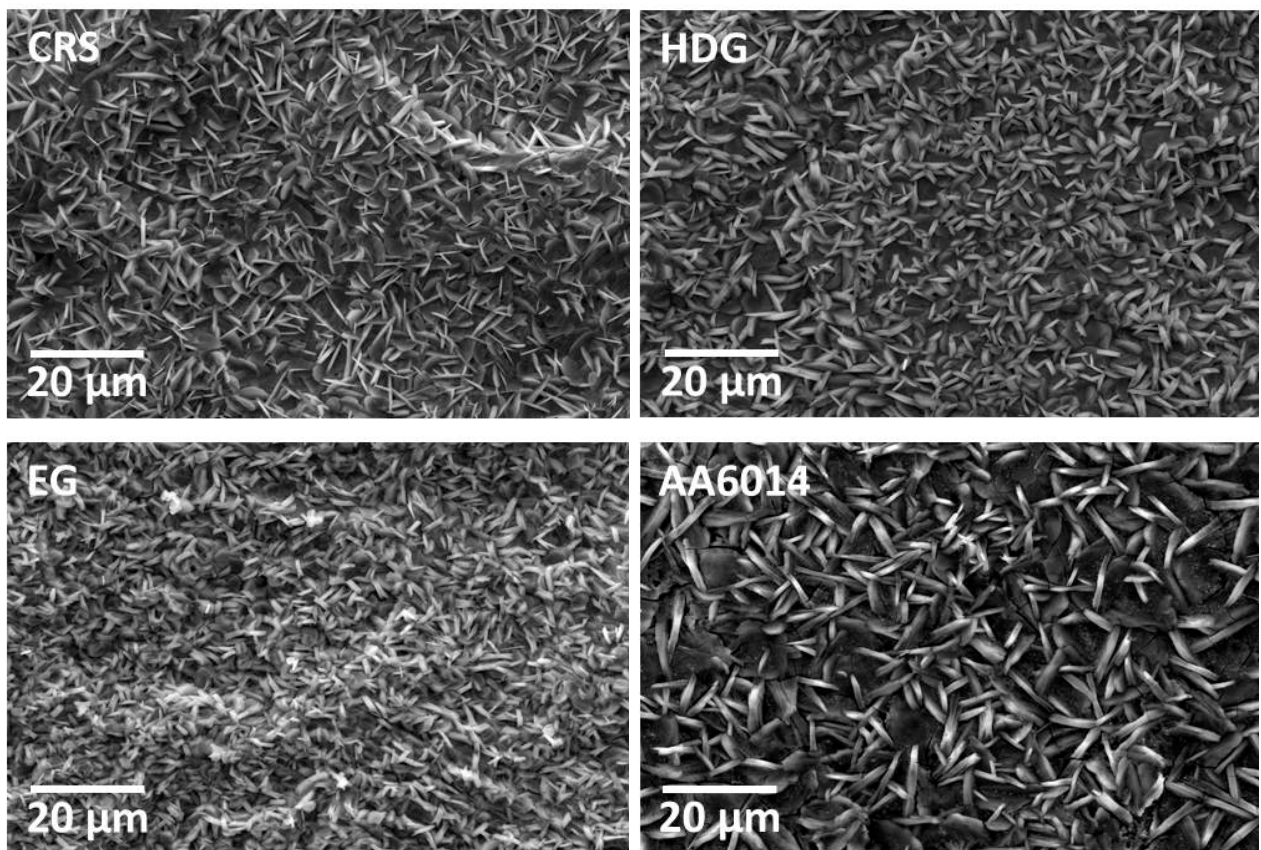


Fig. 1 Scanning Electron Microscopy images of zinc phosphate layers on CRS (top left), HDG (top right) EG (bottom left), AA6014 (bottom right).

Manganese and nickel are added to the conversion solution because they promote a growth of smaller crystals and hence improve the adhesion to the top coating [4]. Additionally they improve the alkaline and thermal stability of the zinc phosphate layer and reduce its porosity [5,6]. The latter effect is derived by the electrochemical deposition of elemental nickel in pores between the zinc phosphate crystals which results in a nearly complete surface coverage.

The conversion process is additionally accelerated by oxidizing additives, like nitrates, chlorates, peroxides or organic nitro-functional compounds in order to achieve high-performance layers already after a few minutes of pretreatment [7]. A highly refined crystal

shape and size, which is necessary for excellent adhesion is achieved by a surface activation bath prior to the zinc phosphate treatment. This activation bath contains either titanium phosphate colloids [8] of the type $\text{Na}_4\text{TiO}(\text{PO}_4)_2 \cdot 0-7\text{H}_2\text{O}$ or in recent times nanocolloids of zinc phosphate. These colloids have a similar stoichiometry as the zinc phosphate crystals and can therefore function as seeds for epitaxial growth of the conversion layer [9,10].

Zinc phosphate layers promote good corrosion protection, during oxygen corrosion. In case of automotive assemblies, the anodic metal corrosion starts usually in a defect area. The cathodic oxygen reduction takes place underneath the intact E-coating. This causes firstly a strong alkalization of metal/E-coat interface and secondly the formation of oxygen radicals. Both weaken the physical and chemical bonding between metal, conversion layer, and E-coating and finally result in cathodic delamination along these interfaces [11-13].

In case of zinc phosphate pretreated substrates, the $\text{Zn}_3(\text{PO}_4)_2$ is alkaline dissolved and partly transformed to $\text{Zn}(\text{OH})_2$. This effect buffers the pH and thereby the alkaline attack. Moreover the dissolved $\text{Zn}_3(\text{PO}_4)_2$ and $\text{Zn}(\text{OH})_2$ diffuse from the local cathodic area to the local anodic area, where they are re-precipitated initiated by the lower pH. Hence zinc phosphate layers have two beneficial effects on the corrosion stability. The first is impeding the degradation along the local cathode by buffering the pH and secondly the inhibition of the anodic metal dissolution by re-passivation of the defect area.

2.2 Need for replacement

Despite the benefits of pretreatments based on zinc phosphate other concerns resulted in the development of alternative conversion treatments.

One of these considerations was based on the implementation of environmentally-friendly technologies, since the nickel containing zinc phosphate baths are environmentally hazardous for aquatic species. This issue especially became a focus of research and development since by 31 May of 2018 all chemicals produced or imported to Europe with a volume of more than 1 ton a year need to be registered by the European Chemical Agency (ECHA). In the course of this REACH registration (**R**egistration **E**valuation **A**uthorization and **R**estriction of **C**hemicals) more and more hazardous chemicals will be restricted in use in Europe.

A further downside of zinc phosphating is the production of sludge during the conversion process, which must be separated from the baths and deposited in a hazardous waste site. Furthermore traditional zinc phosphate baths need to be heated up to approximately 55°C to ensure an optimal conversion process. Both, the deposition of sludge and energy-consuming heating of the baths causes additional costs and promoted the development of new conversion systems, which solve these challenges.

3 Thin Film Technology

3.1 Composition

One of the most promising developments which were brought to market in this context was the Oxsilan[®] technology. It is able to avoid the disadvantages of the zinc phosphate systems without suffering performance losses in terms of adhesion promotion and corrosion inhibition. Oxsilan[®] baths can be run at room temperature and have even shorter application times than in zinc phosphating lines. Moreover, nearly no sludge is produced during the conversion process since the etching is much milder. The bath forms amorphous thin films with a thickness range in nanometer scale, as shown in Fig. 2.

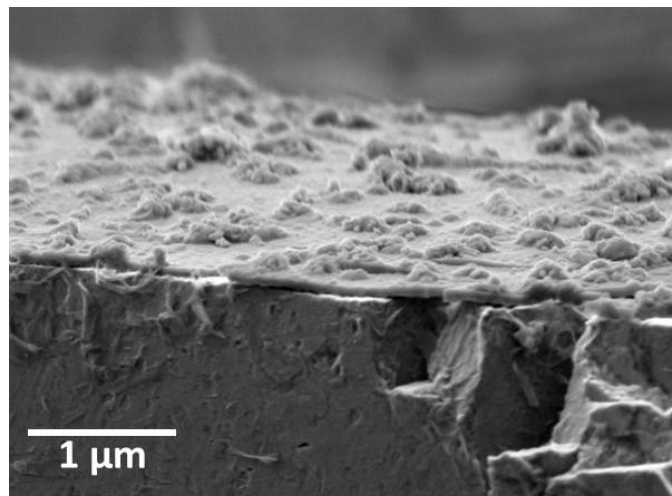


Fig. 2 FE-SEM image of Oxsilan[®] layer on HDG substrate at cut edge

The composition of the thin-film layer is based on two main ingredients, which are zirconium oxides and organosilanes. Zirconium is used, since its oxide possesses high hardness as well as high mechanical and chemical stability. Since zirconium oxide is already highly oxidized it is chemically inert even in highly corrosive environments. That is the reason why ultra-thin Oxsilan[®] layers illustrate the same corrosion stability as the much thicker zinc phosphate layers.

In addition to good anti-corrosion properties of the zirconium-based conversion layers, another key factor for the performance of the Oxsilan[®] technology is the addition of organosilanes. These are generally composed of an alkoxysilane head, which is connected with an organo-functional tail by an aliphatic or aromatic chain.

In contact with aqueous solutions the alkoxysilane head becomes hydrolyzed, where the alkoxy-group is substituted by a hydroxyl group. This leads to the release of silanol-functions. In case of the Oxsilan[®] film formation these silanol groups are able to condense on the hydroxyl-terminated metal surfaces. Furthermore they are capable for crosslinking the film by formation of a siloxane network [14-17].

While the surface condensation greatly improves the adhesion between the metal substrate and the pretreatment layer, the in-layer-condensation leads to a highly dense film matrix, which is characterized by a -Si-O-Zr- network.

The task of the organo-functional tail is to promote adhesion to the E- coating. Therefore the tail is modified according to the specific demand of the top coating, using different functional groups. In principle, groups like pyridine ($-\text{NC}_5\text{H}_5$), mercaptan ($-\text{SH}$), phenyl ($-\text{C}_6\text{H}_5$), methyl ($-\text{CH}_3$), cyano ($-\text{CN}$), or vinyl ($-\text{CH}=\text{CH}_2$) could be used [18-19]. Of these, amino ($-\text{NH}_2$) functional organosilanes have especially demonstrated superior corrosion resistances as well as excellent adhesion promotion [20-22]

Fig. 3 illustrates the key factors for the success of the Oxasilan[®] technology, which are the combination of the excellent corrosion stability provided by zirconium oxide and the strong adhesion to the substrate and the E-coating deriving from the organosilanes.

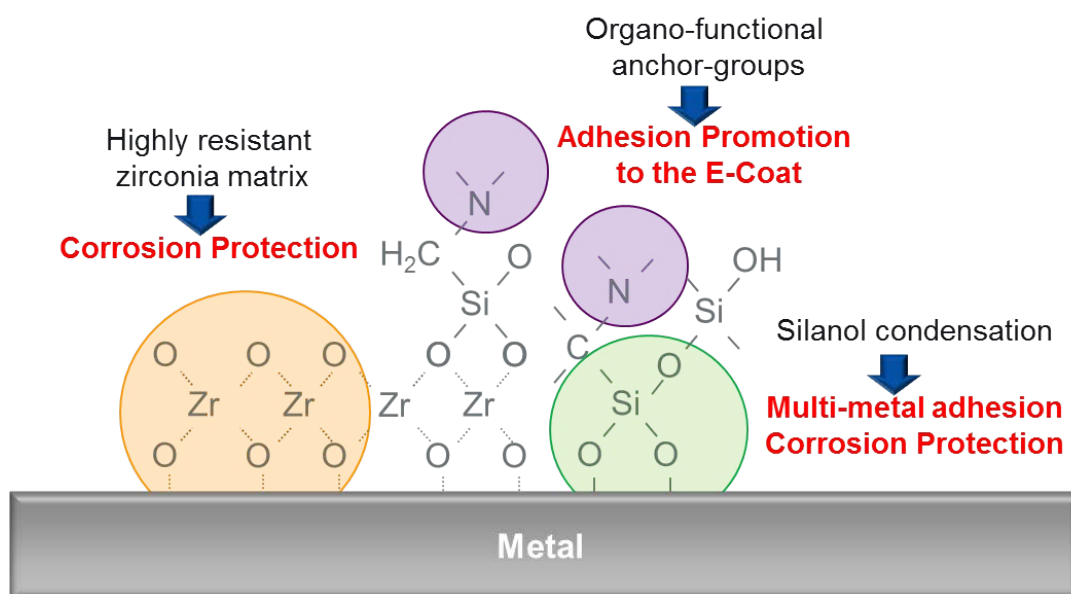


Fig. 3. Scheme of the compounds in Oxasilan[®] layer and their functions.

3.2 Film formation and properties

The mechanism of thin-film formation is based on the same three stages as described earlier for the zinc phosphating process. After immersion of the automotive body in the Oxasilan[®] solution, the conversion process starts with an acidic attack to the metal substrate. Thereby cations are anodically released and protons are reduced, which causes a pH increase near the surface from approx. pH 4 – 5 up to pH 8 – 9. The alkalization within the Nernst Diffusion Layer leads firstly to the formation of hydroxide-rich zirconates which subsequently precipitate on the substrate after exceeding its solubility product. Moreover, the alkaline pH leads to the agglomeration of the zirconates and the organosilanes near the surface, which causes their co-deposition on the metallic body.

The film formation, layer morphology and chemical composition of Oxasilan[®] layers were investigated by several techniques. Fig. 4 illustrates FE-SEM images on galvanized and non-galvanized steel. All images show a complete surface coverage with a homogeneous Oxasilan[®] layer. Very important for excellent anti-corrosion properties is the complete coverage of grain boundaries, since their intermetallic phases often initiate corrosive processes.

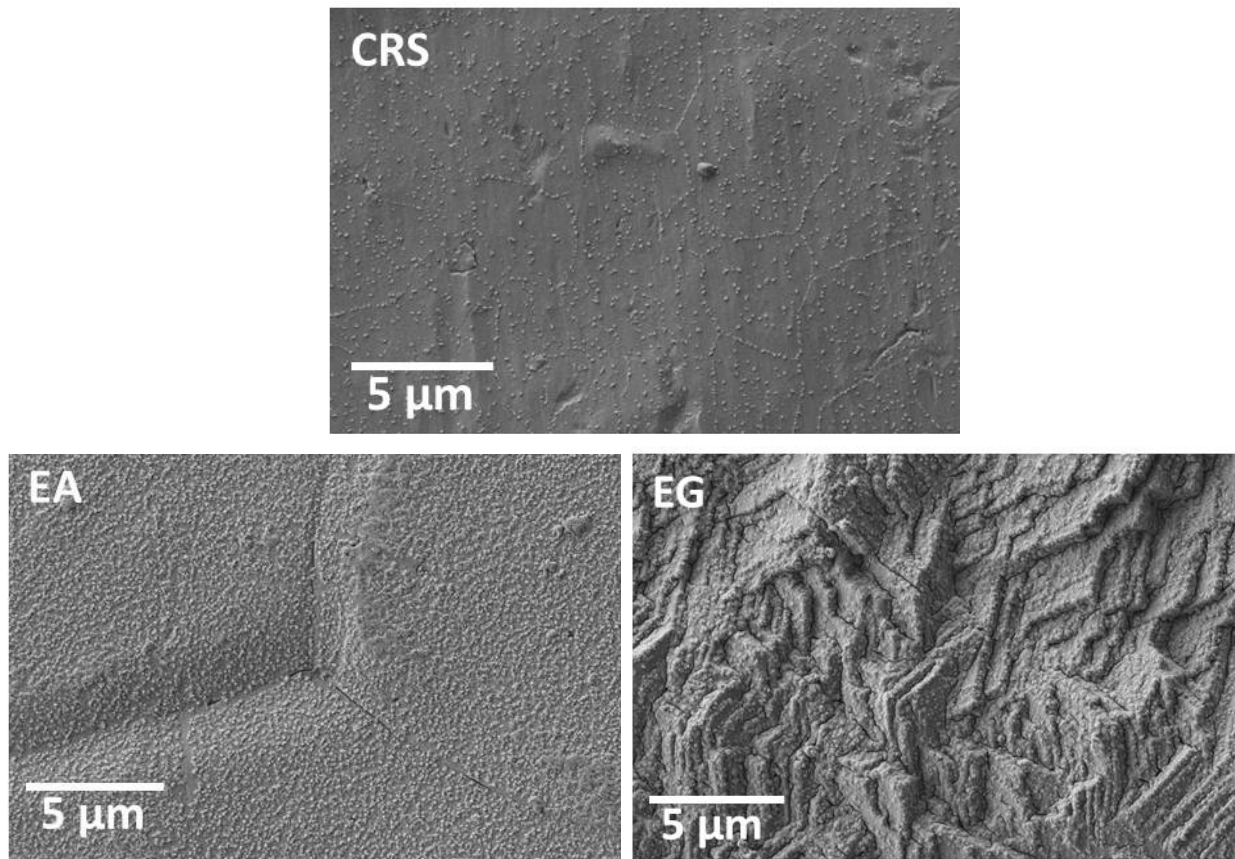


Fig. 4 FE-SEM images of Oxsilan[®] layers on non-galvanized and galvanized. Top Cold rolled steel (CRS); left: Hot dip galvanized steel (HDG), right: electrogalvanized steel (EG)

The element distribution in Oxsilan[®] layers were studied by means of μ -WDX. Images of mapping of an HDG surface are shown in Fig. 5. Thereby the ZrL α -signal illustrates the distribution of zirconium and the SiK α -signal the distribution of the organosilane. The results confirmed the homogeneous surface coverage, where the overall amount of zirconium is higher than the amount of the organosilane.

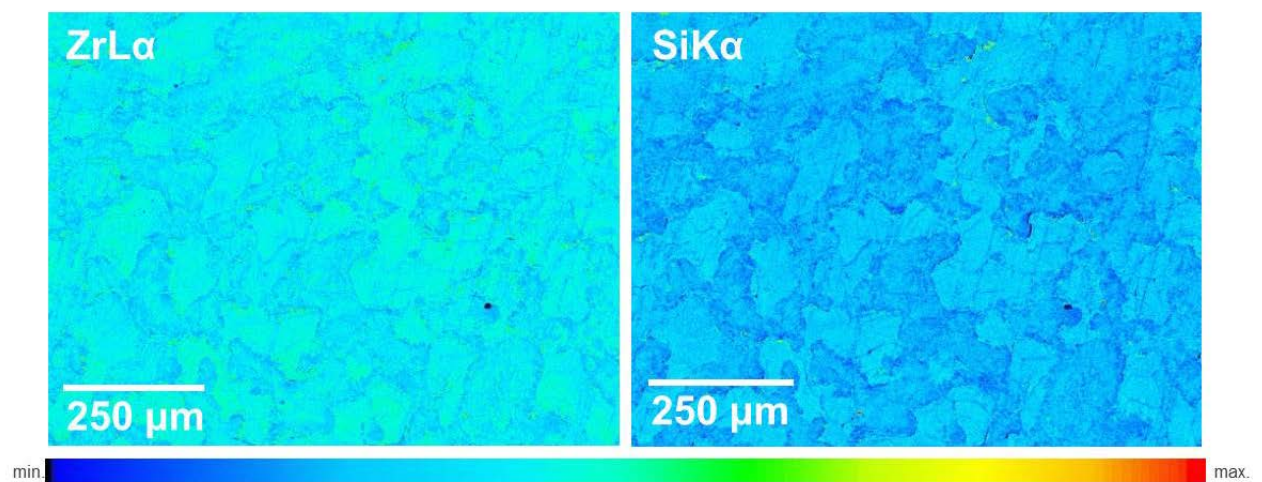


Fig. 5 μ -WDX images of Zr and Si distribution on Oxsilan[®] coated HDG.

4 Pretreatment Process

When comparing the principle sequence of a traditional zinc phosphate process e.g. for car-bodies with a modern thin film process it becomes obvious that the latter process is much shorter. The main reasons are that activation and an (optional) passivating rinse stage are not necessary. For a green field application this decreases the investment significantly.

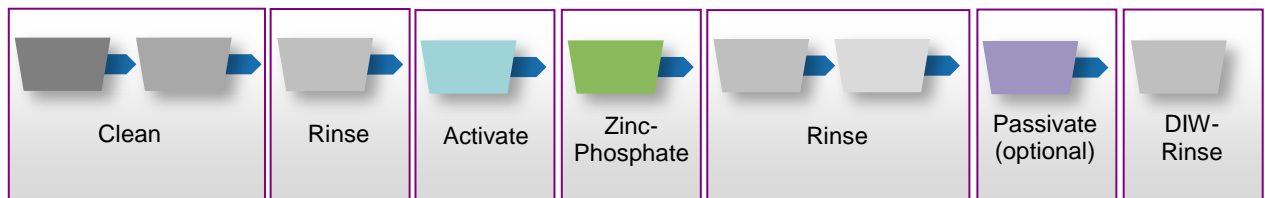


Fig. 6 Traditional zinc phosphate pretreatment sequence (principle)

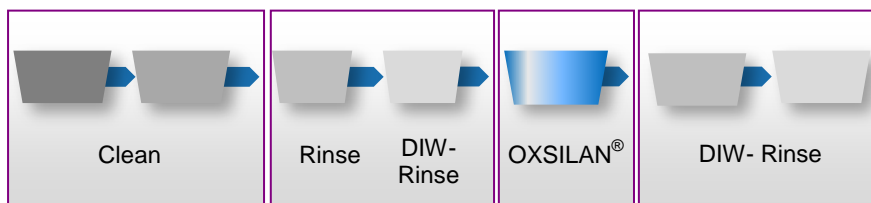


Fig. 7 Thin film pretreatment sequence (principle)

For the thin film technology an alkaline cleaning is performed in dip or spray stages (or a combination of both) at temperatures usually between 55 and 60°C for about 1 minute per stage. This step is a very critical one for the performance of the whole pretreatment process. It not only removes contaminations like organic or inorganic substances and particles from the surface but also pickles metals, especially aluminum or zinc, to prepare them for the conversion coating in the Oxsilan® stage. As the bath itself is less aggressive to metals this etching step in the cleaner bath is even important compared to ZnPh and needs to be carefully adjusted for the material mix and the line conditions.

By rinsing the surface with tap or DI-water between the active stages (at ambient temperature for about 30 seconds per stage) the excess of chemicals is removed. This avoids the drag over between the stages. To prevent major oxidation of the metal surface or to condition the surface in the rinse stages additives may be added. To save water the rinse stages are run by cascading the water flow.

In the Oxsilan® bath the thin film layer is formed at room temperature which may vary from 25 to 40°C with a usual treatment time of about 2 minutes. The pH of the bath is slightly acidic (about 4-5). This leads to less metal removal and consequently to significantly less sludge which needs to be filtered out and disposed of. The overall concentration of the ingredients in the Oxsilan® bath is much lower than in a zinc phosphate bath. This further reduces the overall water consumption. Many years of experience show that the conversion bath itself is highly robust. Controlling pH, free fluoride, and the concentration of the accelerator are normally sufficient. Defects which have impact on the appearance of the final painting can be resolved in a similar way as with zinc phosphates by adjusting physical and chemical parameters.

There are three critical advantages of the thin film technology over the traditional conversion coating zinc phosphate:

- (a) Its ability to pretreat all different kinds of materials which are or will be used in the lightweight multi-metal car body: not only steel, galvanized steel (different alloys) or high strength steel but also aluminum (without limitation as with zinc phosphate) or even magnesium.
- (b) It is free of heavy metals and by this far more environmentally-friendly than zinc phosphate.
- (c) It offers significant cost advantages mainly by consuming less water and energy and by producing less sludge and waste water.

5 Performance Data

The corrosion inhibition properties of Oxsilan[®] layers were statistically studied in comparison with a commercial trication zinc phosphate which is standard in automotive lines. In Fig. 8, different tests on aluminum, steel and hot dip galvanized as well as electro galvanized steel are presented.

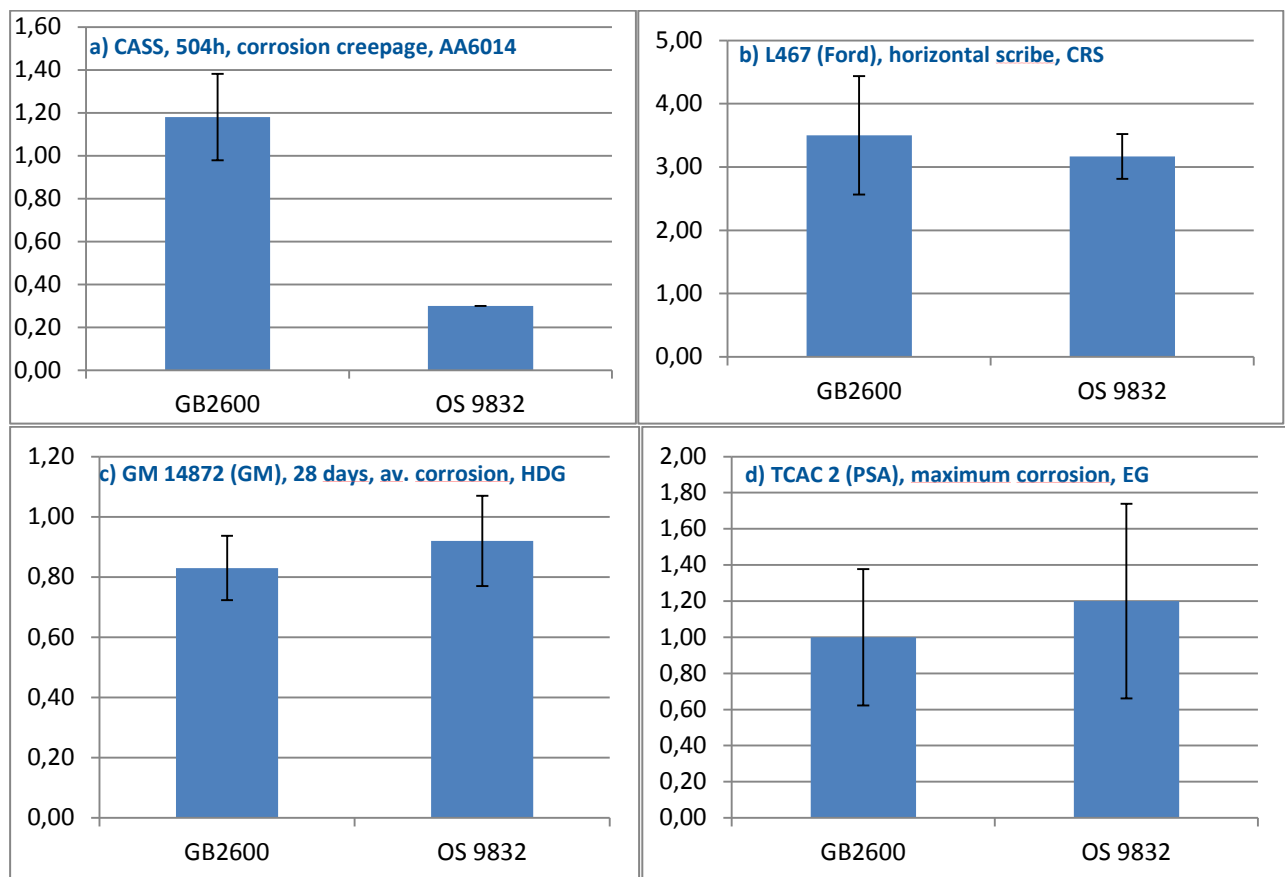


Fig. 8 Average results of corrosion test of Oxsilan[®] (OS 9832) vs. the trication zinc phosphate system, Gardobond[®] 2600 (GB 2600) a) CASS 504h $n_{OS9832} = 10$, $n_{GB\ 2600} = 10$ b) L467 (Ford) CRS $n_{OS9832} = 30$, $n_{GB\ 2600} = 30$ c) GM 14872 28 days $n_{OS9832} = 10$, $n_{GB\ 2600} = 10$ d) TCAC 2 (PSA) $n_{OS9832} = 10$, $n_{GB\ 2600} = 10$.

All test results reveal that Oxsilan® layers perform as well as commercial zinc phosphate layers independent of the substrate. This evidences that it is possible to achieve excellent anti-corrosion properties by using an environmentally-friendly thin film technology.

6 References

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