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PROTECTING BOTH AIR AND STEEL

Water-borne silane creates heat-resistant low VOC zinc dust primers. By Philipp Albert, Evonik.

A water-borne inorganic binder for two-pack zinc dust paints is almost VOC-free and can replace both organic and inorganic solvent-borne binders. Both fast drying shop primers and heavy-duty anticorrosive paints can be formulated. Good corrosion resistance was obtained in salt spray tests.

Damage caused by corrosion leads to costly and time-consuming repairs and its estimated cost to all the world's economies is US$ 2.2 trillion annually [1]. Steel is by far the most widely used metal, since there are many different applications ranging from steel bridges to buildings. Further applications are pipelines, offshore plants and automotive constructions and parts.

World steel production is huge, as can be seen in the production of 1,621 million tons in 2015 [2]. However, steel needs good corrosion protection, especially for exterior applications in corrosive environments such as offshore plants.

The ability of zinc to protect steel from corrosion was first demonstrated in 1742 by a French chemist named P.J. Malouin [3]. The first zinc dust paints were formulated in 1840 [4].

The hot-dip galvanising process is one of the most widely used forms of protecting steel from corrosion. When interior and exterior items cannot be hot-dip galvanised due to size limitations, an on-site coating application is required. The maintenance or repair of large steel parts cannot be done by the hot-dip process, and they have to be coated with zinc dust paint.

WHY ZINC DUST PAINTS ARE HIGHLY EFFECTIVE

Different zinc dust paints are available based on organic or inorganic binders. The organic binder, e.g. an epoxy resin/polyamine or inorganic binder, e.g. silicic acid esters, act as glue, hold the zinc dust particles together and promote adhesion to the steel substrate. The concentration of the zinc dust particles has to be high enough to provide conductivity in the dry film.

This conductivity is necessary for cathodic corrosion protection. No corrosion will take place at a surface scratch of steel coated with zinc dust paint as it will be protected by the sacrificial loss of zinc in the vicinity of the exposed steel.

The undamaged zinc dust paint forms a dense barrier against moisture and corrosive environments containing chloride or other elements. The zinc slowly corrodes and forms white rust. The barrier property of such a zinc dust paint depends on the coating thickness. There are excellent articles available which describe the corrosion protection mechanism of zinc dust paints in greater detail [5].

TWO DISTINCT APPLICATIONS FOR ZINC DUST PAINTS

Zinc dust paints can be applied in the paint shop or in the field. Those applied in the shop are called shop primers and the requirements of such a zinc dust paint are usually different from zinc dust paints applied for heavy duty corrosion protection.

RESULTS AT A GLANCE

➞ Zinc dust primers can provide highly effective corrosion protection when galvanising is impracticable (large items, maintenance operations etc.). Both shop primers and heavy duty corrosion protection paints are formulated on this basis.

➞ Inorganic silicic acid esters offer better resistance to heat, UV and chemicals than organic binders but until now they have contained significant levels of VOC.

➞ A water-borne inorganic binder for two-pack zinc-rich paints has been introduced. It is almost VOC-free and can replace organic or inorganic solvent-borne binders in both shop primers and high build heavy-duty anticorrosive paints.

➞ Zinc dust paints based on this binder can be used where high heat resistance is necessary - for shop primers or exhaust pipes etc.

➞ Formulations cure at room temperature. Salt spray tests confirmed that good corrosion protection can be achieved.

Figure 1: Reduction of VOC emissions when a standard silicic acid ester binder is replaced by the water-borne binder. Coated area: 20,000 m²; dry film thickness: ~ 70 µm; VOC-reduction: > 90% (w/w).

A shop primer is applied as a thin film with a dry film thickness in the range of 20 µm on blasted steel. It should protect the steel against corrosion during storage, transport and during construction work. This requires a paint which dries fast, is cuttable and heat resistant so that welding can be done.
The requirements for heavy duty corrosion protection are different. A dry film thickness of 70 µm and more is used to achieve long term corrosion protection. Heat stability can be an issue when welding is done at construction sites. The zinc dust paint is usually overcoated after one day with an epoxy coating and a PU top coat.

ENVIRONMENTAL AND PERFORMANCE ISSUES

In contrast to their counterparts based on organic binders, zinc dust paints based on silicic acid esters are heat resistant. They are available as one-pack and two-pack systems. The one-pack system sold as "Dynasylan MKS" is stable for at least half a year when formulated and cures with the aid of moisture at room temperature.
Zinc-rich paints based on inorganic binders have good chemical resistance, heat resistance and UV stability. The advantages of these binders are obvious, but formulations based on inorganic binders still contain organic solvents.
Coatings containing organic solvents are receiving more and more pressure because of environmental issues. New legislation and regulations are emerging and are different from country to country. China in particular, with serious environmental problems, is forcing the use of water-borne coatings.
Water-borne zinc-rich paints based on organic binders are already entering the market; however these new systems based on organic binders do not have good heat resistance. The company therefore developed "Dynasylan SIVO 140", a novel water-borne organic-inorganic binder for two-pack zinc dust paints with a higher heat resistance compared to water-borne organic binders.

APPLICATION PROPERTIES OF THE NEW BINDER

Zinc-rich paints based on this novel binder are nearly VOC-free, heat resistant and cure at room temperature. This new binder is an environmental improvement as it is based on silanes that are fully hydrolysed and is almost VOC-free.
It can be thinned with water or polar organic solvents such as ethanol. The active silanol groups are stabilised and the system can be formulated with fillers and pigments. The pot life of such a formulation depends on the filler type and concentration, but typical pot life times are over seven hours or even more.
Such a formulation has to be applied on a clean iron or steel surface. Alkaline cleaning can be done on production lines; but outdoors, abrasive blasting of the iron/steel surface is necessary. Depending on the formulation, these new systems can be sprayed or brushed. The drying time is approximately five minutes for a 90 µm wet film thickness at 20 °C and 50 % relative humidity.
The silanol groups are activated when the zinc is added and when the water evaporates during the application process. Full curing takes more time. The dry film can be overcoated after some hours, since the reactive silanol groups can react and crosslink further even when overcoated.
This binder can be flexibly formulated for both shop primer and for heavy duty corrosion protection applications. Overcoating is possible with different coating systems and typical epoxy coatings show a very good adhesion.
Figure 1 shows a comparison of the VOC emissions of a standard solvent-borne silicic acid ester based zinc dust paint with one formu-

lated on the inorganic water-borne binder. A steel construction of 20,000 m^2 was coated with the solvent- and the water-borne system and the dry film thickness of both zinc dust paints was 70 µm. The VOC emissions could be reduced by more than 90%.

HOW SUBSTRATE QUALITY AFFECTS CORROSION PERFORMANCE

As already discussed, a clean steel surface is necessary. It does not matter whether it is a new steel structure or if it is applied on an already existing structure as part of a maintenance procedure.
Zinc dust paints are usually applied outside in the field to constructions such as steel bridges. The steel will be blasted to be free of dirt and rust. The blasting process results in a rough surface and the surface roughness also has an influence on the performance of the paint.
Three different test panels having different surface roughnesses were cleaned in an alkaline solution and coated with a basic water-borne zinc dust paint based on the new inorganic binder. The first panel is cold rolled steel (1). The second (2) has a surface roughness of 0.12 to 0.25 mm and the third panel (3) one of 0.8 to 1.2 mm. All three panels were cured for 24 hours at 20 °C.
Figure 2 displays the test results after 250 hours in the salt spray test. The cold rolled steel panel (1) shows red rust at the scribe and in the coating area. The second panel (2) with a surface roughness of 0.12 to 0.25 shows red rust at the scribe but no red rust in the coating area. Best results are observed for the third panel (3) with a surface roughness of 0.8 to 1.2 mm. No red rust is visible either at the scribe or in the coating area.

MAIN FACTORS AFFECTING FORMULATION

Solvent-borne zinc dust paints based on silicic acid esters have been known for a long time. There are one-component and also two-component systems available. The performance of such zinc dust paints depends very much on the formulation. Different formulations are necessary depending on the type of application, as stated earlier.
For a shop primer application, thin films are applied and a fast drying with some crosslinking is necessary because the parts have be stored outside after a short time even when it is raining. Formulations for heavy duty corrosion protection are usually applied as a thick film and sometimes dry film thickness of 100 µm or even more are required. A fast drying time for these systems can be a disadvantage, since cracks can be formed in the film during the drying process.
With solvent-borne systems one approach to avoiding this cracking is to apply formulations with higher boiling solvents. There is also the option to apply two layers to get a thick dry film of 100 µm and more.
Water-borne binders have to be formulated with fillers, pigments and additives in a similar way to solvent-borne systems. Some fillers or pigments have a strong influence on the pot life and curing time. Zinc oxide and other zinc-based pigments in particular reduce the pot life depending on the concentration in the formulation. (Zinc oxide works as a catalyst for the crosslinking of the silanol groups during the curing process.)
Other fillers or pigments do not influence the pot life and therefore it is also possible to formulate these fillers with the water-borne binder for long term storage. However, additives that are commonly used in coating systems for defoaming or viscosity adjustment can reduce the crosslinking density at low-curing temperatures.

RAPID OVERCOATING MAY BE POSSIBLE

Table 1 shows two formulations for different applications. A formulation for a thin film application of ca. 20 µm as used for shop primers can be seen alongside a formulation for a heavy duty corrosion protection application with high zinc content.
The pot life of such a two-component system should be at least seven hours (a working day) or more. If the pot life has to be extended, an addition of water in the range of 1 to 6% (w/w) is possible.
Water-borne formulations based on the inorganic binder can be applied in the same way as solvent-borne systems. A typical application of water-borne zinc dust paint on a clean steel substrate is done via spraying. A shop primer with a wet film thickness of 40 µm will be dry at 20 °C within 1 – 3 minutes. Overcoating with a water-borne or solvent-borne epoxy resin can be done after a curing time of one day. There are promising results which indicate that the zinc dust paint

Figure 2: Cold rolled steel panels with different surface roughness tested according to EN 9227 for 250 hours.

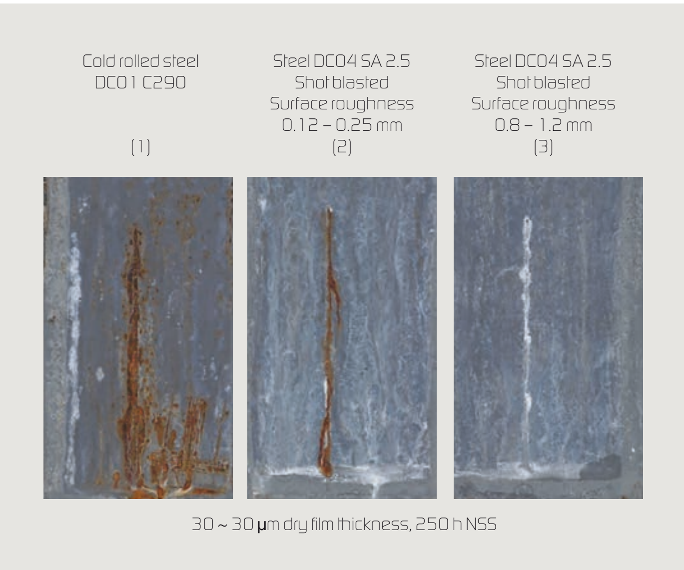

Figure 3: A high zinc content formulation (*Table 1*) was applied on shot blasted steel and overcoated after only one day with a solvent-borne or water-borne epoxy coating. Samples were exposed to neutral salt spray fog for 1550 hours (EN 9227).

can be overcoated even after two hours. Test panels were coated with a water-borne formulation, cured for two hours at 20 °C and overcoated with an epoxy coating. No adverse effects have so far been found in the performance of these test panels.

SALT SPRAY TESTS AFTER OVERCOATING SHOW GOOD RESULTS

Solvent-borne and water-borne epoxy coatings can be used for overcoating. In some cases the epoxy coatings have to be optimised for such applications but there are water-borne and solvent-borne epoxy coatings available which give excellent performance in combination with zinc dust paint formulated on the new inorganic binder. The corrosion protection performance of such a zinc dust paint in combination with a water-borne or solvent-borne epoxy coating can be seen in *Figure 3*. This shows the corrosion protection performance of a high zinc content formulation with a dry film thickness of about 30 µm on steel together with a solvent (grey) and a water-borne epoxy coating (white).
For the panel with the solvent-borne epoxy coating, some corrosion is visible at the top and bottom of the scribe after 1,550 hours in the salt spray test. Also some red rust has formed at the scribe. No blistering or corrosion is visible in the coating area.
The sample with the water-borne epoxy coating also shows a good performance after 1,550 hours. Some rust is visible at the bottom of the scribe but no rust can be found at the top part of the scribe. No blistering or corrosion can be observed in the coating area.

MAIN APPLICATIONS AND BENEFITS IN SUMMARY

A novel water-borne silane binder system has been developed for the formulation of two-pack zinc dust paints. The binder is almost

Table 1: Shop primer and heavy duty primer formulations. The fillers and pigments have to be added to the dissolver at a speed of 10 – 20 m/s. The formulation should be homogenised for 15 minutes.

Raw materials	**Parts by weight**		**Supplier**
Component I	**Shop primer**	**Heavy duty primer**	
"Dynasylan SIVO 140" binder	23.0	15.0	Evonik Resource Efficiency, Germany
Deionised water		4.0	
	Add under stirring		
"Aerosil 200"	0.6	0.6	Evonik Resource Efficiency, Germany
Component II (fillers)			
Zinc dust (4P/16)	30.0	64.0	EverZinc, Belgium
Zinc oxide (Red Seal)	12.0	8.5	EverZinc, Belgium
"Miox Micro 30"	34.4		Kärntner Mwontanindustrie, Austria
"Mica MKT"		7.9	Imerys Ceramics, France
Total	**100.0**	**100.0**	

"The temperature resistance is important for shop primers."

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3 questions to Philipp Albert

Recoatability seems to be an essential improvement. How do you quantify "after some hours" – in relation to layer thickness, processing temperature or humidity? *I do not want to quantify this since we are still testing formulations and applications with different film thickness, humidity and processing temperatures. For the tests we have done so far (~30 µm and 90 µm dry film thickness, humidity 70% and 25 °C curing temperature) we could not find a difference in the performance if overcoated with an epoxy coating after 1 hour or 3 days.*

How can the improved temperature resistance of the novel systems compared to conventional ones be quantified? *The temperature resistance is important for shop primers since the steel parts are usually welded. The formation of gas and bubbles at the welding seam and the back burning of the shop primer at the back side of the welded part are investigated. If there are too many bubbles in the welding seam, the stability of the welding seam and the construction is less. A back burning can reduce the corrosion protection performance.*

Looking at the recoatability, what is meant by "promising results" and how have they been determined? *This questions is related to question one. Our water-borne zinc dust paint was overcoated with an epoxy resin after different times starting from 1 hour to 3 days curing time at room temperature. We could not find a difference in mechanical properties or corrosion protection performance between the different curing times.*

VOC-free and can replace solvent-borne binders based on organic resins/polymers or silicic acid esters.

Zinc dust paints based on this binder have better heat stability compared to systems based on organic binders. Therefore applications with higher heat resistance, as may be necessary for shop primers or exhaust pipes, are possible.

The binder offers many formulation options for high and low zinc content formulations. Zinc dust paints based on this product can also be used in the field of heavy duty corrosion protection where a dry film thickness of 70 µm and more is necessary.

No temperature activation is necessary for the curing since the formulations can cure at room temperature.

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