INTRODUCTION

Zinc silicates are widely specified as the primer for much of the steel utilised by the petrochemical and offshore industries. They may be used without topcoats as tank linings, but organic topcoats are normally specified for atmospheric exposure. In acidic and alkaline environments zinc corrodes rapidly and topcoats improve durability as well as appearance. Two main types of zinc silicate are now available. Water based alkyl silicates are mainly used as tank linings, although there is increasing interest in their use on structural steel. Solvent based ethyl zinc silicates are most commonly used on steel structures.

The following aspects are covered in this note:

1. Porosity
   - topcoat bubbling
   - removal of contamination
2. Excessive thickness
   - mud cracking
   - low cohesive strength
3. Formation of zinc salts
   - effect of salts on performance
   - removal of salts
4. Spot repair of old zinc silicate/organic systems

1. POROSITY OF ZINC SILICATES

Zinc silicates are by nature porous. The porous silicate matrix of a freshly applied zinc silicate does not fill all the available space between the zinc particles. This leads to a number of practical disadvantages. An understanding of these can help to avoid possible problems:

a. organic topcoat bubbling
b. contamination difficult to remove

a. Topcoat bubbling

Also known as popping or application blistering, this is a problem which causes more irritation than any other. As already mentioned zinc silicates are porous by nature. After several months of curing outdoors, the porosity gradually fills to form a close, dense film due to formation of zinc salts by reaction with moisture and carbon dioxide in the atmosphere.

Most construction schedules do not allow one or two months before topcoating and the primer must be topcoated while it is under cover and still porous. This often causes bubbling of the subsequent topcoat. There is always a risk of popping when overcoating zinc silicates, but the longer they have been weathered the less the likelihood of problems.
The mechanism

Popping is caused by the release of air and gas, in bubble form, from a porous surface through freshly applied wet paint films. This causes blisters which either break, leaving a pinhole, or remain in the film.

When a solvent containing organic topcoat is spray applied to a porous surface, some of the solvent penetrates into the pores. At the same time there is a drop in the surface temperature due to decompression and sudden solvent evaporation. The temperature rapidly increases again, expanding the air and gas in the pores. Additionally there is a tendency for the solvent trapped in the pores to try to release itself. These combined actions cause the formation of bubbles.

Popping

The higher the ambient temperature the greater the problem and if the surface temperature is steadily rising due to exposure to the sun the problem will be worse. Topcoat bubbling is also more likely with fast overcoating times or by drying of the zinc silicate in conditions of very low humidity.

The likelihood of topcoat pinholing or blistering over inorganic zinc primers depends on both the choice of primer and the choice of topcoat. Application of a glossy (high binder content/low PVC) finish directly to a zinc silicate primer is likely to cause problems.

Intact blisters or pinholes easily visible to the naked eye will usually not be accepted and will normally require repair. Very small hardly visible pinholes are usually acceptable and in practice, even if the zinc appears to be exposed at small holes, these are generally impregnated with coating.

Arguments sometimes arise over whether pinholes are or are not closed. The worry being that if the zinc silicate is exposed to the atmosphere, corrosion may take place. This can easily be checked using a low voltage wet sponge tester. Usually when this test is applied to a typical zinc silicate/epoxy/polyurethane system still showing some pinholes after application of the final coat, no holidays (holes) are indicated. Response is often negative even after the first coat of epoxy, but positive on the conductive zinc primer.
Minimising popping from the start

The quality of the application of the zinc silicate plays a crucial role. It should be spray applied as an even wet film to the correct wet film thickness. In hot conditions some extra thinner may be needed. Excessive film thickness should be carefully avoided. Dry spray/overspray should also be avoided as far as possible and must be removed before topcoating. It is a loose powder which can be rubbed off by light abrasion or by rubbing with aluminium wire mesh. (This may have to be done quite quickly in hot conditions where heavy overnight condensation is usual).

Conventional spray (air spray) gives the best results because it gives an extra degree of application control, but to obtain the highest productivity airless application is usually preferred.

Watch out particularly for the inexperienced applicator who applies zinc primers for maximum productivity using a powerful airless unit at high pressure with a large, worn tip. The effect will be rather like using a garden hose, with clouds of dry spray settling on the surface, making the subsequent topcoat application a nightmare. The topcoat usually gets the blame for the bubbling, but the problem has been caused by poor primer application.

Less problems are usually encountered if the applicator is experienced in the use of inorganic zinc primers.

What if the primer has already been applied?
There are a few well tried techniques which help avoid pinholing when organic topcoats are applied to a freshly applied zinc silicate. None of these can be guaranteed to be 100% effective if the primer application has been of poor quality:

I Sealer coat
The zinc primer is sealed by a sealer coat (also known as a tie coat) specially designed for porous surfaces eg. SigmaCover 522 (7420). Thin as described in the data sheet and apply 50µm (2 mils) dry film thickness. This is generally the most effective solution and it also works for sealing zinc metal sprayed substrates.

II High build micaceous iron oxide pigmented topcoats
Use a topcoat which is less sensitive for application bubbling. SigmaCover 435 (7427) is an example which works if the quality of the primer application is reasonable and application is done by mist coat as described below.

Some additional hints
If the primer is porous and popping occurs, a mist coat/full coat application can be helpful. The primer is first sealed by a very thin (hardly closed) film of the first topcoat. Shortly afterwards (usually within 15 minutes) the mist coat is recoated to reach the specified dry film thickness. This technique may have to be repeated with subsequent coats. It works quite well at low temperatures, but often will not help if the surface temperature is high.

Try to avoid application of the first topcoat if the surface temperature is expected to rise. If application to surfaces which have been in direct sunlight can be scheduled to take place as the surface temperature is reducing, pinholing will be almost completely avoided. (This also works for application of organic coatings to exposed concrete surfaces). Where application over a warm/hot zinc silicate cannot be avoided then the use of SigmaCover 522 (7420), thinned as described in the data sheet is a good solution.
Shop application

Zinc silicates require contact with moisture to enable full cure and a reduction in porosity. If it is practical to store steelwork outside for a while between zinc silicate and topcoat application then the risk of bubbling will be reduced. The surface may be sprayed with clean water. It is often not realised that steel coated with a solvent based zinc silicate can be moved outside very soon after application, even when it is raining.

None of the above is a perfect solution for all situations. When application bubbling becomes a problem it is usually because of a complex mixture of technical and commercial reasons. If you need help, write down all information which is relevant and contact your Sigma representative. Information needed includes the coating system, thinners being used and amounts per coat, ambient temperature and surface temperature during day and night, humidity during the day and night, application equipment with tip sizes, time and exposure conditions between zinc silicate and topcoat application, thickness of primer and topcoats, presence of dry spray etc..

General considerations

Topcoat bubbling occurs to some extent on all zinc silicate/organic systems. If the topcoat is a glossy yellow it will be more obvious than if it is a dull grey. Some plant owners are used to it and accept it as a fact of life, others find it unacceptable. As with most similar situations a compromise is usually necessary. It is impossible to reach an automobile finish with this type of high build system, which is primarily designed for corrosion protection in severe conditions. It is however unreasonable to expect the final customer to accept a surface that looks like the moon.

If you are faced with topcoat bubbling and a well tried and tested system is being used, remember that the application of the primer is frequently the cause. Try to get this improved. Also in hot conditions try to re-schedule the application or shade the area concerned.

b. Removal of contamination

The porous nature of zinc silicates can make certain types of contamination difficult to remove. Oils and greases can be particularly awkward with high pressure water washing with detergent, followed by clean water, being the best option for cleaning the cured primer.

Solvent cleaning is sometimes used for small areas. Apart from the health and safety aspects, this often only spreads oily contamination over a wider area.
2. EXCESSIVE THICKNESS OF ZINC SILICATES

If zinc silicates are applied at too high a dry film thickness, problems can arise eg. mud cracking or low cohesive strength. An understanding of what is happening can help avoid trouble:

a. Mud Cracking

In some situations after the application of a zinc silicate, the film cracks. This is due to shrinkage during drying and is known as "mud cracking" because it resembles the cracks which form in sun dried mud. There are a number of possible causes:

I Spraying to a too high dry film thickness.

II Application over areas of too low blast profile. This can happen particularly at welds where there are areas of very hard material. After blasting, the profile remains low and application of too much material can cause cracking.

III If relative humidity is high during the application and ventilation is poor this can also be a cause of cracking due to a too fast curing of the top layer.

IV A product beyond its shelf life will often have a higher mud cracking tendency than when fresh.

The thickness at which cracking takes place depends on the formulation of the zinc silicate. Some are very critical in this respect and others rather tolerant. The mud cracking limit can be as low as 75 microns (3 mils) up to as high as 200 microns (8 mils) dry film thickness. Sigma Coatings' products perform well in this respect with the limit generally being in excess of 150 µm (6 mils).

For most products mud cracking only becomes a problem when internal corners of small beams and angles etc are being coated. While trying to reach the minimum dry film thickness all over, the sprayer tends to make several overlapping passes in the corners. This often leads to excessive dry film thickness and mud cracking.
When this is occasionally a problem, brushing out the corners while the primer is still wet will help. If it becomes a serious problem during airless spray application, check the angle of the tip being used. A narrow tip may have been chosen for more economical spraying of small components. This requires more passes and can cause a high build-up of wet coating in corners, making the problem worse. Switching to a wider angle will usually solve the problem and is more economical in the end, even though more material may seem to be lost due to overspray.

b. Low Cohesive Strength

During and just after application, conditions must be dry to let the solvent evaporate. After this the curing phase starts. The film reacts with moisture to form an insoluble inorganic silicate matrix. After the initial drying the fastest cure is provided in conditions of high humidity. Overnight condensation and warm weather are ideal.

A zinc silicate which is not properly cured will remain weak and will not reach the high hardness levels expected from inorganic zinc primers. In very dry conditions a zinc silicate may take a long time to reach full hardness. (Regular spraying of the surface with clean water can be helpful in this situation). Also, if applied too thickly, through-hardening takes a long time or may even never take place. If topcoating is done on not adequately cured zinc silicate, the primer may never attain full hardness.

When epoxy topcoats are applied to a not fully cured zinc silicate problems arise from the low cohesive strength of the primer. The epoxy shrinks on drying and forms a relatively brittle film. Quite minor impact damage can result in delamination by splitting in the silicate primer.

The specification of a zinc silicate to be applied in conditions known to be very dry with continuous low humidity is best avoided eg. in some shop circumstances. Zinc epoxies are a better choice in this situation, although it should be noted that they generally have a lower heat resistance.

3. FORMATION OF ZINC SALTS

Occasionally on site there is a problem with zinc salt formation. Zinc primers protect steel from corrosion by sacrificial protection. The zinc corrodes instead of the steel. During this corrosion process zinc reacts with oxygen, carbon dioxide and water to form a zinc salt.

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\frac{O_2}{H_2O/CO_2} \rightarrow ZnCO_3.Zn(OH)_2
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The exposed zinc at the surface of a zinc silicate surface can also react directly with the atmosphere causing zinc salt formation. In both cases the zinc salts are visible as a white/grey surface colouring.

The composition of the zinc salts depends on the circumstances in which they were formed. In unpolluted atmospheric conditions (oxygen, carbon dioxide and water) they will be a mixture of basic zinc carbonate, zinc hydroxide and zinc oxide. These zinc salts, known as zinc patina, close-up the surface pores and thus help to protect the steel substrate.

When zinc comes into contact with pure (condensed) water and there is little or no air available, large quantities of zinc hydroxide are formed. This is called “white rust" and often occurs when a water layer is trapped between two zinc coated plates. It is also often seen in situations when a surface is almost continuously in contact with condensed water. This type of zinc salt is partially soluble in water.
Under the influence of air pollutants such as sulphur dioxide (industry) or chlorides (coastal) basic zinc sulphate or basic zinc chloride are formed. These are only slightly soluble in water and do not form a closed film and thus have no protective function.

The formation of zinc salts is influenced by various factors, including the time that water remains in continuous contact with the surface. Puddles which form on steel stacked outside often result in the formation of white rust. Acid rain or chloride containing rain water cause the formation of zinc salts. In coastal regions the higher concentrations of salt in the atmosphere lead to higher quantities of zinc salts to be formed.

**The effect of salts on system performance**

Zinc salts can have a negative effect on coating performance. Loose zinc salts (e.g. white rust) must be removed from the surface before topcoating or they will affect adhesion. Water soluble components in zinc salts may reduce adhesion of subsequent coatings. If these remain on a primer surface, then in damp conditions water is attracted through the organic topcoat (osmosis) and the zinc salts swell, damaging the intercoat adhesion.

Even if no visible zinc salts are present on a zinc primer surface, adhesion problems can occur if insufficient thickness of topcoat is applied. Water migrates through thin areas of coating and forms zinc salts under the topcoat, causing delamination. For this reason, in damp conditions or immersion, an adequate thickness of organic topcoat should cover the zinc primer.

**Removal of zinc salts**

Experience and testing have shown that small quantities of zinc salts on zinc silicate primers have a minimal influence on later anti-corrosive performance. Obviously any loose zinc salts on the surface should be removed before overcoating. Particularly for critical applications, such as immersion or service in damp conditions, it makes sense to make sure that all soluble zinc salts have been removed. Various cleaning techniques can be used:

- **a. Washing with clean water.**
  Ideally this is done by high pressure water washing, but washing with water and a nylon bristle brush is also a good way to make sure most soluble material is removed. Heavy deposits of white rust may have to be removed by mechanical means.

- **b. Sweep blasting.**
  This is frequently not possible due to excessive dust formation. It has the advantage that it roughens the surface improving the adhesion of the complete coating system. At the same time welds can be fully blasted, further improving the anti-corrosive performance of the system.

- **c. Mechanical cleaning.**
  This can achieve an acceptable anti-corrosive performance from the coating system. Cleaning the intact primer surface until visually clean is adequate. Complete removal of all traces of zinc salts is practically impossible and also not necessary.

The most effective mechanical cleaning technique is by synthetic disk (Scotch Brite). These disks enable a controlled cleaning of the surface with very limited removal of the primer.
Specifications

Sometimes specifications require that all zinc salts must be removed before topcoating. In practice the removal of all traces is difficult and reference to the Shipbuilding Research Association of Japan Standard (SPSS) for surface cleaning may be helpful. It shows photographs of zinc salt formation on zinc epoxy and zinc silicate shop primers. It can be seen that even after sweep blasting slight traces of zinc salts remain on the surface.

4. SPOT REPAIR OF OLD ZINC SILICATE/ORGANIC SYSTEMS

When zinc silicate primed systems, which are in reasonable condition, are to be repaired by spot blasting of rusty areas and touch-up of the primer, followed by an organic topcoat, it is best to avoid the use of a zinc silicate for repair. This is because when sprayed on the blasted areas there will always be an overlap onto the surrounding organic coating. This inevitably results in areas of poor adhesion. The solution is to patch prime using a zinc epoxy.

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