Abstract: The right coatings system correctly applied on structural steel and tankage in process plants can confidently be expected to give good corrosion protection for periods between 10 and 20 years. However, on hot areas both atmospheric, with temperatures up to 500°C, and protection under insulation for high temperature pipes and vessels, this is often not the case. Many coatings used in these areas are too intolerant for site application and general use in this industry, leading to expensive premature failure.

This paper describes development of new products in these areas and also the difficulties encountered in the development of a non-zinc high-temperature coating for use up to 400°C. An alternative approach to thermal insulation with in-built corrosion and damage resistance is also covered. The development of internal test methods necessary to undertake this work is also described.

BACKGROUND

Use of the correct high performance coating specification with the required standards of surface preparation and application currently gives systems which will last in excess of 10 years, and even over 20 years, before significant maintenance is required, depending upon the corrosivity of the atmospheric environment. This is the situation for ambient atmospheric exposed steel.

Unfortunately, it is not the case for hot process areas such as vessels, piping and stacks, where failure and breakdown are all too common.

It is worth considering what factors lead to eventual coating breakdown under the two situations described above. Firstly, considering the atmospheric coatings, this has been the main area of coatings study over the past years, and there is now general agreement that breakdown is due to the synergistic effect of a number of climatic conditions. Coatings degrade by an accumulation of the effects of wetting and drying, some diurnal temperature cycling and U.V. degradation of the polymer. This is well recognised in that the use of ASTM B117 Salt Fog as a method of selecting coating systems is now treated with severe scepticism, and it is being replaced by a variety of wet and dry cyclic tests combined with U.V. exposure, primarily ASTM D5894.

What happens when a typical organic coating is subjected to high temperatures? Eventually as the temperature rises “charring” or “browning” of the coating occurs as the organic polymer degrades, eventually leaving a mixture of ash and pigments on the surface with no film integrity and no protective value. However, even before these stages are reached, significant changes are likely to have occurred in the coating. In crosslinked coatings, the effect of high temperatures is generally to further drive the crosslinking reaction, increasing the crosslink density, generally improving most aspects of performance of the film but potentially causing increased brittleness at ambient temperatures. With the old chlorine-based polymers, widely used in chlorinated rubber and vinyl coatings, as the temperature approached 100°C the thermally unstable polymer would “unzip” and hydrogen chloride gas formed. The other immediate effect of heat on a coating film is to drive out any low molecular weight or volatile components, often included as diluents, flexibilisers or plasticisers, or extending resins. Typical materials here can be plasticisers such as di-iso-decyl phthalate, diluents such as benzyl alcohol, low molecular weight unreacted resin or curing agent, and liquid hydrocarbons used as extending resins. Cycling between elevated temperature and ambient temperature places further stress on the coating, especially when considering the differences in coefficients of thermal
expansion. It also needs to be realised that with many coatings taking them above their Tg will cause an increase in permeability with the possible consequence of increased corrosion.

Historically, the approach adopted for high temperature areas has been to move to inorganic coatings, typically based on silica where the –Si–O– type bonds are very thermally stable. Unfortunately, coatings based on these types of polymer tend to be inferior to organic coatings in many other aspects, such as adhesion, flexibility toughness etc. Up to around 250°C it is possible to modify the organic resins (as is normal in high durability polysiloxanes) to impart improved film properties to the glass-like silicone or siloxane coating.

Often these inorganic films have only been suitable for application in thin films of 0.5–1.0 mil, thus giving limited corrosion resistance (especially on blasted steel) and relatively poor mechanical properties.

Silicone coatings which fall into this category do not crosslink until around 200°C, part of the reaction is to produce water vapour which must leave the film. When the film is too thick blistering and flaking occurs because of the inability of this reaction product to escape.

When considering coatings on high temperature uninsulated surfaces it is worth listing the various stresses on the coating, which include those mentioned earlier plus others:

- U.V.
- Wetness:
  - at shutdown or low temperature part of cycle;
  - thermal shock from rain at high temperatures.
- Thermal cycling, expansion/contraction.

**HIGH TEMPERATURE EXPOSURE SURFACES**

As well as the silicones mentioned earlier, there have been other approaches to corrosion resistance in these circumstances (i.e. exposed uninsulated high temperature steel), e.g.

- **Zinc Dust/Graphite/ Bodied Oil**  
  | Heat |
- **Inorganic Coating**  
  (corrosion resistance but no film integrity)

- **Zinc Silicate**  
  | Ambient |
- **Corrosion Resistance**  
  to 400°C

There has been concern with zinc silicate, with the belief that the zinc would melt at 400°C, and this was thus the maximum temperature of use (as with galvanising). In fact, this does not happen, the zinc particles remain intact because of being embedded in the silicate matrix, and more rapid oxidation occurs.

Electron micrograph zinc silicate panel before heating  
Electron micrograph zinc silicate panel after heating (3 hours 600°C)

(Note, zinc dust subjected to same conditions melted.)

The zinc silicate can be overcoated by silicone aluminium, but over-application of this type of material frequently leads to loss of adhesion from the zinc silicate and flaking as the temperature is increased.

In this case, unlike atmospheric coatings, there are no sensible test methods, those mentioned in ASTM (e.g. D2485) are more or less inadequate and so it has been necessary to develop in-house methods involving thermal cycling, thermal shock and corrosion resistance.

One beneficial circumstance for high temperature uninsulated atmospheric coatings is that they do not stay wet. When operating at high temperatures they are only wet for very limited periods of time during part of the cycle or shut down. In these circumstances zinc silicate by itself can give good protection for long periods of time.
INSULATED SURFACES

With insulated surfaces, cycling and thermal shock situations are ‘damped’ and are less drastic than those previously described. However, this benefit to the coating is far outweighed by the fact that extremely corrosive environments can be achieved with wet insulation and maintained for long periods of time, to give either a hot wet or hot humid environment. The presence of chloride can make the environment even more aggressive, as can any soluble materials in the insulation, taking the pH of the hot water to slightly acid or alkaline condition, extremely aggressive for any zinc which may be present due to its amphoteric nature.

Initially, zinc silicates appeared to be the solution for piping and vessels to be insulated, it allowed them to be prepared and coated off site and had ample robustness and corrosion resistance to allow coated objects to remain uninsulated during erection, without being damaged. However, the amphoteric properties of zinc meant that in the conditions described earlier the coating had an extremely limited life. There has also been a suggestion with zinc silicate in these hot, wet conditions that there can be a reversal in polarity so that the steel protects the zinc and pitting corrosion occurs. This is based on a well documented phenomena regarding zinc metal and steel in chloride solution. It is difficult to find any literature references to this being the situation with zinc silicate and being proven experimentally. Certainly, attempts made to do this at International have not been successful.

In practice, this area of 60-80ºC under insulation has been found to be the most aggressive because of both the longer period of wetness and the acceleration of zinc, and other, corrosion due to temperature. This has led to considerable reluctance of many engineers to use zinc silicate under insulation and the current NACE recommendation is not to do so. Some individuals, however, find that the flexibility and workability of zinc silicate coated objects outweighs these potential problems, and by adopting various methods of sealing off the zinc they attempt to harness the anti-corrosive properties without suffering from the in-use problems mentioned. It should be stressed that thin film silicone coatings do not have sufficient corrosion resistance on blasted steel for use in these circumstances, and it is best to use thicker barrier coats over zinc silicates, such as zinc free inorganic silicate.

CURRENT POSITION

There are a number of drivers for the current product types used in this area, mainly performance and a desire to simplify the process by using a ‘universal’ system.

In many instances the bulk of hot steel does not operate above 200ºC, and often not above 150ºC. These type of temperatures allow the possibility of coating all steel, insulated and uninsulated, with an organic coating, typically this is a specially formulated epoxy phenolic which will resist dry heat up to 230ºC (450ºF), when applied in 2 coats to give 200-250 microns d.f.t. Corrosion resistance is achieved from both ambient cure films and from coatings which have been heated. This type of densely crosslinked coating will resist the hot, wet conditions which can be found under insulation.
Often areas down as low as 60ºC are insulated for personal protection, greatly increasing the potential for the problem of corrosion under insulation, and although most high performance epoxy systems will work okay in hot, wet conditions at 60ºC, this tends to be a maximum.

Where a universal primer is needed for a wider temperature range, zinc silicates are often still used, the practicalities of paint application and construction outweighing any concerns regarding the performance of zinc primers under insulation. The topcoat is selected depending on the area of use, the topcoat being based on silicone or siloxane resins, silicate or a silicone/acrylic blend for lower temperatures. With the exception of the zinc free silicate type, these are often too thin to give good long term protection, and the conventional silicones also suffer from sensitivity to over-application.

In the absence of any well recognised or meaningful methods of coatings evaluation under these conditions, it has been necessary to consider the development of new test methods to evaluate the performance of both existing systems and developmental materials. These have needed to consider both uninsulated and insulated situations. The basis of these tests is as follows:

**Coating evaluation tests**

**Cyclic heating/anti-corrosive tests.** Panels of applied system are heated in a furnace to target temperature at a ramp rate of 20ºC/minute. This target temperature is maintained for 8 hours and then allowed to cool naturally to ambient (~16 hours).

Two heat/cool cycles are performed before exposure to various anti-corrosive tests (accelerated and natural weathering).

**Thermal cycling based on ASTM D2485.** Coated panel is exposed to thermal cycling/ quench, each cycle is incrementally higher up to the target temperature (400ºC). The cycled panel is then subjected to anti-corrosive testing (prohesion/water immersion 40ºC).

**Cyclic heating/wet dry cycling (pipe test).** A coated pipe is insulated and placed on a hot plate where a measurable thermal gradient (typically 450ºC → 60ºC) is created. The pipe is heated for 8 hours with 16 hours natural cooling, the calcium silicate insulation is soaked before and after the heating cycle – 30 cycles are performed.

**Atlas Cell Evaluation – Modified SMT 52H.** Immersion in hot water (500 hours at 95ºC) is carried out on coating system. Systems are evaluated for breakdown and also any changes in adhesion.

**Thermal cycling cold/hot.** Panel is cycled from –200ºC to 200ºC, depending upon type of coating to be tested.

Intention here is to evaluate coating performance under insulation on refrigerated pipework with occasional steam purge.
CURRENT DEVELOPMENT

Work is now directed at developing an inorganic coating which will extend the temperature range where corrosion resistance can be achieved by non-zinc coatings, in both insulated and non-insulated environments, above that which is currently achievable with the epoxy phenolics. The main technological barrier to cross here is to achieve good anti-corrosion properties before any high temperature cycles are present.

Examples of the type of performance which has been achieved to date are shown in the photographs below. In all instances the coating is an aluminium pigmented inorganic system applied at 1 x 125 microns d.f.t., direct to grit blasted steel.

After cyclic testing under wet insulation up to temperatures of up to 450°C

9 months exposure aggressive marine/industrial site

2 years exposure aggressive marine/industrial site after temperature cycling
5000 hours hot salt spray
Single coat systems 100-125 microns d.f.t. 
(after temperature cycling)

1 x 125 microns d.f.t.
after cycling to 300°C

1 x 125 microns d.f.t.
after cycling to 400°C

ANTI-CORROSIVE THERMAL
INSULATION SYSTEMS

An alternative approach to corrosion protection under thermal insulation has been considered, i.e. to produce an insulating epoxy based syntactic foam which will act as both a thick anti-corrosive coating and a thermal insulator. A further benefit of this type of approach is that the system is much more mechanically robust than conventional insulation systems, resisting impact damage, e.g. operators stepping on insulated pipes.

Graph showing thickness – determination by calculation and by actual temperature measurement against thickness on a coated vessel containing hot oil.

Although the thermal efficiency may not be as high as for conventional systems, such as foam glass, the benefits of off site or spray application, resistance to mechanical damage and corrosive environments and potential lifetime use without replacement outweigh the greater thickness.

The maximum steel temperature for this system is 150°C, which allows most of the hot areas on a typical site to be insulated. This temperature has been determined by coating a steel pipe and running hot oil through it then examining adhesion etc., (see picture). Further tests on adhesion at 150°C, 180°C, 200°C, have shown no significant adhesion drop until 180°C.

Apparatus for circulating hot oil up to 160°C around test pipe
Epoxy syntactic foam 1 week at 110ºC
No detrimental effect

Epoxy syntactic foam
1 week at 110ºC - decrease in physical properties as indicated by drop in adhesion

Properties for this insulation coating are shown in Appendix and help to demonstrate the robust, water resistant nature of the material.

SUMMARY

A number of typical product types used to protect high temperature steel have been reviewed, along with assessments of them by a range of test methods. The performance of a new experimental material has been described, showing significant advantages over current approaches.

Finally, an alternative approach to protection at the corrosively aggressive bottom end of the high temperature range has been presented, utilising an epoxy syntactic foam which functions as both an anti-corrosive and thermal insulation.
REFERENCES


(3) NACE Publication 6H189 (Latest Revision), “A State of the Art Report on Protective Coatings for Carbon Steel and Austenitic Stainless Steel Surfaces under Thermal Insulation and Cementitious Fireproofing”, (Houston TX, NACE)
## APPENDIX

### EPOXY SYNTACTIC FOAM

#### Physical Properties

Density = 0.6g/cc

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>VALUE</th>
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<th>TEST METHOD</th>
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<tbody>
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<td>Specific Heat</td>
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<td>International Coatings</td>
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<td>At 100ºC</td>
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<td>At 20ºC after Exposure to Water at 3000 p.s.i. and 93ºC</td>
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<td>FMC</td>
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