INORGANIC
ZINC COATINGS

History, Chemistry, Properties, Applications and Alternatives

A Compilation of Papers published in Australia and New Zealand

2nd Edition

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In memory of Victor Nightingall (1881 - 1947) of Heidelberg, who in 1937 patented a unique protective coating now known as inorganic zine silicate. This coating protects millions of square metres of steelwork around the world from the ravages of corrosion.

Erected by the members of the Australasian Corrosion Association November 1997

Memorial plaque placed on Nightingall’s grave.
The formation in 1997 of the Protective Coatings Technical Group (PCTG) of the Australasian Corrosion Association (ACA) coincided with two landmark dates in the history of the development of inorganic zinc coatings. It was exactly 60 years since the patent for the first inorganic zinc coating was taken out by its inventor, Victor Nightingall of Melbourne. Furthermore, it was exactly 50 years since his passing in 1947. The coinciding of these events made the celebration of this important Australian contribution to corrosion prevention an ideal inaugural activity of the PCTG. A number of events and other activities were carried out, of which this publication is the culmination.

A series of seminars on inorganic zinc coatings were run in Australia and New Zealand. The first was in Auckland on 18th September 1997. Later seminars were held in Sydney, Melbourne, Adelaide and Launceston. The majority of the papers presented at these seminars are included in this publication.

The PCTG also agreed to make an annual award known as the ‘Victor Nightingall Award’ to honour a coatings specialist who has made an outstanding contribution to the protective coatings industry in Australia and New Zealand. The inaugural award was made at the 1997 ACA Conference in Brisbane to John Biddle and the second award to David Donald at the 1998 Conference in Hobart. Both these recipients have papers in this publication.

The PCTG also ensured that Nightingall’s final resting place would have some record of his contribution. A memorial plaque was cast and placed on his grave at Warringal cemetery in the Melbourne suburb of Heidelberg. The Victorian Branch of the ACA kindly sponsored this memorial.
TECHNICAL PAPERS

The papers in this publication come from two sources. The first eight papers were presented at the seminars run in 1997 and 1998 in Australia and New Zealand.

The second group of papers are papers from local authors presented at various conferences or locally published over the years. The first paper is a copy of Nightingall’s original Australian patent. While the papers concentrate on inorganic zinc silicate (IZS) coatings, some branch into related subjects such as galvanizing and epoxy zincs and issues such as performance of top coats over zinc coatings.

A number of papers have been expanded or edited for this publication, and most of the historical papers have been reformatted, although an attempt has been made to keep the format as close to original as possible. For this edition, multi-column papers (other than the original patent) have been formatted to single column for ease of reading in electronic format. The following gives a brief description of the papers in this publication.

The first paper by Rob Francis is in two parts and describes the early development of IZS coatings. The first part describes the work of Victor Nightingall and some early applications. The best known early example is the coating on the Morgan-Whyalla pipeline in South Australia, described in Part II.

The paper by Greg Wiggins describes the manufacture and chemistry of inorganic zinc silicates, including the differences between the main types and some of their properties.

In the next paper, Kerry Dalzell provides an overview of the critical properties of IZS coatings, both during application and after curing. He shows they require a high degree of surface preparation, proper mixing, straining and agitation during application, along with well-maintained application equipment and skilled applicators.

Willie Mandeno and Tony Sutherland compare IZS coatings to metal spray coatings. Both methods produce hard, durable coatings which can provide long-term protection, either alone or as part of a paint system. New developments in metal spray will see it becoming more cost effective, providing an increasingly economic alternative to inorganic zinc.

Ted Riding of Jotun describes the chemistry of IZS coatings, including the properties of the different types, curing and protective mechanisms and recoating properties.

Gerry Eccleston of the Scientific Services Laboratory covers his research into the cure of solvent-borne inorganic zinc coatings (SB IZS). Gerry shows the effects of temperature and humidity on cure, through gas chromatography and abrasion resistance. His conclusion was that the cure reaction in the film used the water formed from the initial condensation reaction, and high humidity was necessary to prevent this evaporating. There is no absorption of moisture for cure, as commonly believed.

Michael Mitchell, in a paper presented by Ern Hemmings, compares inorganic zinc primers and zinc-rich epoxy primers. The results from work carried out in the UK showed that, while inorganic zinc is clearly superior as a single coat system, in a multi-coat paint system an epoxy zinc works just as well.
Alex Szokolik covers the use of IZS as a single-coat system. His work, both laboratory and in the field, clearly showed that IZS gives a much longer life when used as a single coat system, rather than as part of a multi-coat system. These findings are supported by examples from around the world.

The historical papers commence with Nightingall’s original Australian patent taken out in 1937. The formulation and application method described are mainly of historical interest, although there are a number of features not that far removed from today’s product and uses.

There was a 20 year delay until the next paper. The ACA formed in the mid 1950s, and a few years later produced a Journal (Australian Corrosion Engineering, later Corrosion Australasia and now Corrosion and Materials) and commenced running annual conferences. Most of the following papers are from these sources.

The short paper by O’Neil from 1959 is what now would be termed an ‘advertorial’, and describes various features, properties and applications of the patented ‘Galvanite’ inorganic zinc coating. At that stage, the self-curing coatings were not available, but it is interesting that most of the description of the heat-cured and post-cured products could be justifiably applied to today’s products.

A short report by Russell in 1963 presents the results of exposure trials of three coating systems on test panels exposed at a number of Victorian bridges. Although limited in coating types and exposures, the inorganic zinc coating system was superior to alternatives.

The first of the truly technical papers in this section is by Thomas, Cox and Richardson published in 1964. These authors look initially at the mechanism of protection given by zinc-rich primers but concentrate on the importance of the size of the zinc particles, comparing protection given by the inorganic zinc coating to a number of organic zinc materials. They showed that the protection mechanism was considerably different from protection afforded by galvanising and other massive zinc coatings.

The 1967 paper by Marson compares the performance of the different types of zinc rich coatings, showing the superiority of the zinc silicate coatings. He summarises the advantages and disadvantages of the organic and inorganic types.

1971 started a golden decade of original research into inorganic zincs by David Donald of Dimet Coatings, Hans Jaeger of CSIRO and their co-workers. The first of these by Donald and Worsnop looks at the three types of inorganic zinc silicates then in use and compares their abrasion resistance. The heat cured showed the greatest resistance, the solvent borne the least resistance and the self-cured water-borne had a wear resistance between the two. They also found wear resistance decreased as humidity increased.

The structure of an inorganic zinc coating as determined by electron microscope work is described in two papers presented to the International Corrosion Conference held in Sydney in 1975. Jaeger and Sherwood looked at coating changes during weathering, showing such coatings provide protection mainly by barrier effect with cathodic protection only in damaged areas. In undamaged areas, the metallic zinc particles at the surface corrode away initially forming corrosion products in pores and voids. The corrosion product layer advances further into the coating with continued exposure, but this layer continues to provide protection even when much of the zinc has corroded away. The second paper by these authors, along with
Donald and Yuan, metallographically compared coatings that had weathered naturally with those that were exposed to accelerated testing. They showed that the mechanism of breakdown was different in both cases, confirming the difficulty in comparing accelerated tests with natural exposure for these coatings.

Jaeger, Donald and Yuan continue their work on the breakdown of inorganic zinc coatings in a paper presented to the First Asian Pacific Corrosion Control Conference, held in Singapore in 1979. In this case they investigate the changes using x-ray diffraction. By investigating changes as layers of the coating were removed, changes in the distribution of zinc dust and zinc corrosion products were noted, with different behaviour in marine and industrial atmospheres. Further x-ray diffraction work by these authors was published in *Corrosion Australasia*, Vol. 4, No. 2, pp 9 - 13, June 1979.

In his final paper on inorganic zins in this publication, Donald presents his work improving the curing of water-borne inorganic silicates at the 1980 ACA Conference. This paper, which also contains a good summary of the advantages of water-borne inorganic zinc coatings, shows the importance of temperature and humidity in influencing the time for water insolubility of these coatings.

Ivan Baxter presented a paper at the 1992 ACA Conference outlining the features of inorganic zins. An extract published in *Corrosion Australasia* compares the coating with galvanizing and also gives some useful practical advice for avoiding curing problems of IZS.

John Biddle, in a paper presented at the 1993 ACA Conference, describes the chemistry of zinc and silicate, and describes the compositions of the different types of zinc silicate coatings, and the various chemical reactions occurring during cure.

In a 1998 paper, Francis compares the nature, properties, applications and other features of inorganic zinc coatings to hot dip galvanizing, concluding that both provide excellent protection in the correct environment, but are complimentary rather than competitive.

At the 2000 ACA Conference, Francis and Szokolik presented a paper describing work looking at the performance of inorganic zinc coated bridges; comparing their performance to those coated with more conventional coatings such as aluminium alkyds. The inorganic zinc coated bridges show around three times the life of the alternative systems. IZS also had the benefit that when it did break down, there was no undercutting of the coating making condition assessment and subsequent maintenance much easier.

Hemmings, in a paper presented to the 2001 ACA Conference, draws attention to the problems observed during curing of WB-IZS coatings, looking at the required ambient conditions and effect of coating thickness.

At the next ACA Conference, Salome continued the theme of curing conditions for IZS coatings showing how humidity and temperature influence the curing of the WB and SB coating types, comparing them to organic zinc primers. He notes that specifiers need to be aware of these curing condition requirements when selecting coatings.

Szokolik broadened the discussion at the same conference by looking at zinc-based primers and galvanizing as part of a multi-coat system. Accelerated tests and case studies indicate that
the long-term intercoat adhesion between inorganic or organic zinc primer systems and their
topcoats was far superior to adhesion of top coats over galvanizing.

At the 2006 ACA conference, Szokolik, along with Lofhelm and Hemmings, continued the
work presented in 2002 with the results of similar systems exposed this time to Prohesion
testing, and the earlier results were confirmed. These exposure tests further confirmed the
excellent performance of the single coat IZS, whether SB or WB.

At the 2007 ACA conference, Francis, Ellis and Walker looked at the important issue of
maintenance of degrade IZS coatings. The paper covers the breakdown of IZS coatings and
how it differs from other types. Contrary to popular belief, overcoating with itself is possible,
and maintenance of IZS coatings is relatively straight forward.

The paper by Thomas presented at the Surface Coatings Association conference in 2008 looks
at the sadly-neglected ‘S’ in the IZS. The chemistry of silicates is a fascinating if complex
subject even without the zinc, and this paper provides a thorough review of silicate properties,
formulations and uses of the many types of silicate coatings.

The paper by Zhang and Walker presented at the 2011 Austroads conference looks further
into the matter of IZS repair. These authors carried out a field trial varying surface preparation
and repair coating types, and evaluated the effect of these on performance and coating
adhesion.

The final document is a field method developed by Riding for evaluating the degree of cure of
IZS coatings. While methods for testing cure of SB-IZS are well established, this provides a
method for testing of WB products.

These papers cover virtually all aspects of inorganic zinc and related coatings and should
provide useful and detailed information for anyone concerned with the protecting structural
steelwork from corrosion.

Rob Francis
March 2013
Note on Inorganic Zinc Coatings in Australian Standards

There are a number of Australian and New Zealand standards that refer to inorganic zinc that have been produced over the years and these are mentioned in many of the papers. There have been numerous changes to the content and numbering and there may be confusion because of some of the statements made. A brief review of these standards follows.

Inorganic Zinc performance
The code for selection of protective coatings for steelwork, AS/NZS 2312 gives durability figures for a number of inorganic zinc silicate systems. The systems and such figures have changed with the various versions of this standard, as discussed in a number of papers in this book. The following table gives these durability figures for 1994 and 2002 versions of this code using the current ISO environmental designations for environment (see AS4312), although environments were defined differently in 1994. The table also gives figures for the standard hot dip galvanizing system for comparison.

Table 2: Life to first maintenance in years of inorganic zinc and hot dip galvanizing coatings from AS/NZS 2312 1994 and 2002 versions.

<table>
<thead>
<tr>
<th>System</th>
<th>Designation</th>
<th>ISO Environment</th>
<th>Tropical</th>
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<tr>
<td>Sa 2½/ 75µm IZS-SB</td>
<td>1994 MP1A</td>
<td>5-10</td>
<td>NR</td>
</tr>
<tr>
<td></td>
<td>2002 IZS1</td>
<td>10-15</td>
<td>5-10</td>
</tr>
<tr>
<td>(not in 1994 version)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sa 2½/ 125µm IZS-WB</td>
<td>1994 LP3</td>
<td>10-20</td>
<td>10-20</td>
</tr>
<tr>
<td></td>
<td>2002 IZS3</td>
<td>25+</td>
<td>25+</td>
</tr>
<tr>
<td>Hot Dip Galvanize</td>
<td>1994 GZ</td>
<td>10-20</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>2002 HDG 600</td>
<td>25+</td>
<td>15-25</td>
</tr>
</tbody>
</table>

NR: Not recommended.

Inorganic Zinc Formulation
The standard which specifies performance and formulation requirements for inorganic zinc silicate coatings is AS/NZS 3750 Part 15 (Paints for steel structures – Inorganic zinc silicate paint). This standard describes six types of which Type 3 (WB), Type 4 (SB) and Type 6 (WB High Ratio) are currently used as single coat systems and primers. This standard was originally designated as AS 2105

Inorganic Zinc Specification
AS 4848.1 (Application specifications for coating systems – Single coat inorganic (ethyl) zinc silicate – Solvent-borne) describes surface preparation, application and QC requirements for the application of such coatings to fabricated steel.
INORGANIC ZINC SILICATE COATINGS – THE EARLY DAYS

Part I: Invention and Early Applications

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Inorganic zinc silicate coatings would generally be unknown to the person on the street, but probably protect more square metres of structural steelwork in Australia and the USA at least, alone or as part of a paint system, from the ravages of corrosion than any other single type of coating, apart from galvanising. When we consider that a not insignificant proportion of the economy is devoted to corrosion protection, and that rusting steel is a waste of valuable resources, such a protective system is an important part of our lives, whether it is generally realised or not. These coatings were not developed, like common oil-based paints, over the ages from artistic or decorative usages, nor were they produced as a result of concerted research by a team of chemists in a large chemical company. Rather, they were invented and developed by one man working away in a shed at the back of his house in a Melbourne suburb. This paper describes the work of Victor Nightingall, the product he invented and some of the early applications. The coating of the famous Morgan-Whyalla pipeline in South Australia is discussed in Part II. But first a little background information.

It is not the intention of this paper to provide complete details of the uses or protective mechanism of inorganic zinc silicate coatings. These are described in various degrees of detail elsewhere (see for example 1, 2, 3, 4, 5). Nor indeed does it give a full history of the development of inorganic zins. But for the reader not familiar with the material, it is worth quickly drawing attention to some of the remarkable properties of inorganic zinc coatings and how they differ from normal paints for corrosion prevention. Being inorganic, they are unaffected by sunlight, ultra-violet radiation, rain, dew, bacteria, fungi or temperatures up to about 400 °C. If they are damaged or worn away, the zinc continues to provide galvanic protection and holes are filled with corrosion products. As the zinc is further eaten away, rust may start forming, but will not grow under the intact zinc coating, unlike normal paints. They resist most organic solvents and have excellent friction characteristics. In fact, they are usually the only coating allowed when structures contain friction-grip joints. Most importantly, a properly applied single coat of inorganic zinc will give excellent protection to steel for years or indeed decades, even in some quite aggressive environments. They are truly unique and it is little wonder that they have revolutionised the means of protecting structures from corrosion.

Inorganic zinc coatings are, in other ways as well, totally different from any other paints. The liquid part or binder consists of a silicate, sodium silicate in early formulation but potassium, lithium and ethyl silicate in more recent developments. A large amount of zinc is added to this, usually just before it is applied, the mixture is thoroughly stirred, and the coating applied to a clean, abrasively blasted steel surface. The coating dries and hardens fairly quickly, but does not resist rain until some time has passed, which may be some days. Moreover, it continues to harden over next six to twelve months. There are clearly a number of chemical reactions of different rates taking place which are covered in some of the references cited earlier. Even so, it is clear that a complete understanding of the curing mechanism of inorganic zins, explaining all its unusual properties, has not yet been made.

Other Zinc Coatings

Inorganic zinc coatings are not, course, the only way of protecting steel from corrosion using a zinc-based coating. The simplest way to apply a protective coating of zinc on steel is to dip the steel item in a bath of molten zinc. This procedure, known as galvanising, has been around since the mid 1800s, and continues to be an important means of protecting steel from corrosion. Hot dip galvanising has a number of important limitations. It can only be used for coating objects that are of a size that can be immersed in the galvanising bath. Furthermore, steelwork can be distorted by the temperatures of 450 deg C needed to maintain the molten zinc. Zinc can also be applied by metal spraying where a wire of zinc is fed into a very hot flame and a stream of compressed air sprays it out a nozzle similar to a spray gun. The tiny molten zinc particles travel through the air and impact on the steel surface building up a protective zinc coating. This has the advantage over galvanising that it can be used on items of any size, but it tends to be very expensive and can be difficult to apply in cavities and other similar
areas. Zinc metal spraying has been used since the early 1900s. The disadvantages of both these processes led to the search for a zinc coating that could be applied with the same ease as a coat of paint.

Organic zinc coatings were developed slightly earlier than the inorganic coatings covered in this paper. The idea to put zinc dust in paints had been around since the mid 1800s, but early products had limited use. Even though the zinc initially provided some galvanic protection, the alkaline zinc corrosion products caused the oil-based binders that were the only ones available, to break down. It was not until synthetic binders, such as polystyrene, chlorinated rubber, vinyl and other products became available, that zinc-rich paints became successful. The most successful of these were those based on chlorinated rubbers, and in fact such coatings are still available today, albeit with a fairly limited market. In the 1940s, epoxy resins became available and these were found to be a suitable vehicle for zinc pigments, and today are the most widely used of the organic zinc coatings. The resin resists the alkalinity of the zinc corrosion products and is, in itself, very resistant to many corrosive environments. Organic zinc primers can be used on slightly less well prepared surfaces and are easier to repair and overcoat than inorganic zinc primers (in fact, a major use is repair of damaged inorganic zinc or galvanised coatings) but they do not provide anywhere near the protection of a properly applied inorganic zinc coating.

Victor Nightingall

Victor Charles John Nightingall (Figure 1) was born in the Melbourne suburb of Windsor on 27 May 1881, the son of a sea captain, Charles Nightingall. He was educated at O’Hara’s College in South Melbourne, closed many years ago, where he obtained a diploma in electrical engineering. He was a foundation member of the Victorian Institute of Electrical Engineers (now absorbed by Institute of Engineers Australia), which was established in 1905. He carried out further studies in chemistry and chemical engineering, including research at Melbourne University and Birmingham University. However, he appears to have gained no formal academic qualification, and only ever quoted as his qualifications his associate membership of the Institute of Engineers Australia.

His early career covered a wide range of subjects. His first research work was into radioactive ores as fertilisers for stimulation of plant growth (6) and for wireless telegraphy. Figure 2 shows Nightingall during his early work, carrying out microscopic investigations on plants. He later carried out research into x-rays, thermostatic controls for heating apparatus (7) and electrical instruments for locating underground oil, metal and ores. A number of firsts were built by Nightingall. He built the first Australian wireless set for communicating from ship to ship, made the first electromagnet for removal of steel from eyes, built the first Australian x-ray apparatus and made and patented Australia’s first electric stove. He lectured to the Society of Chemical Engineers and to the Royal Society of Victoria. During the First World War, he did research for the Department of Defence. For the next twenty years, he worked as a consulting chemical and electrical engineer, specialising in industrial chemistry, from a shed at the back of his home in the Melbourne suburb of Heidelberg. It was during this period that he worked on the inorganic zincons and their development, as described below. He suffered heart problems in the mid 1940’s, probably exacerbated by his almost complete devotion to his work. He died on the 1st August, 1947 and is buried at Warringal Cemetery, not far from his home. He was survived by his wife Ruth, son Richard (Tom) and daughter Peg.
On his death, one newspaper obituary referred to him as ‘Australia’s Edison’ (Figure 2). This is clearly over generous, but like Edison he was a practical rather than academic man. He worked from experimentation towards theory, the opposite of the scientific method. He was dedicated to his work in keeping with Edison’s dictum that ‘Genius is one per cent inspiration and ninety-nine per cent perspiration’. Also like Edison, he realised that he not only needed to invent something, but it had to sell and spent a great deal of effort perfecting his invention of the inorganic zinc coating so that it was marketable. Like Edison he took out numerous patents in his lifetime, although, unlike Edison, only the one described in this work made any significant impact. However, unlike Edison, he lacked skill in self promotion and his important work is virtually unknown. Furthermore, Edison lived well into his eighties, Nightingall only reached his sixties.

There is little information on how he commenced his work on zinc coatings, although with such a wide range of interests, discoveries in any field would not be surprising. We do know he patented a plaster board material in the late 1920s (8), perhaps leading to an interest in construction materials and at about the same time became interested in electrochemistry. He patented a new type of battery in the early 1930s (9) although this was not successful. It is unlikely that he commenced work without some commercial goal, and it has been suggested that he was approached by the Electrolytic Zinc company, who operated a zinc refinery in Hobart. Zinc dust was produced as a by-product of the refining process and they were looking for markets for this product. It was probably this interest in electrochemistry that led to corrosion studies along with the commercial demand from the zinc company that led to the zinc silicate coatings.

However, this is just speculation. We do know he started work on the silicate coatings in the early 1930’s and finally patented the invention in 1937 (10), although the patent was not finally accepted until the following year. It is believed that commercial use of the product commenced in 1936, although no examples of its use until 1938 are known.

It may be thought that the invention was the result of work on sodium or other silicate solutions. The title of the patent – ‘Improvements in and connected with silicated compositions’ – suggests this. Sodium silicate had been an important chemical for many years and had a wide variety of uses, including as a coating for steel (11). It was, and is still used as an inhibitor for corrosion protection. (Incidentally, its inhibitive action is the reason a water-based coating can be used as a primer on clean steel. Normally a water-based coating would not be used on steel, but the alkaline silicate acts as an inhibitor while the coating is wet and prevents the steel rusting). At that time, a common application for sodium silicate was as a preservative for eggs. Before widespread refrigeration, eggs were dipped in a sodium silicate solution which gave them a glassy seal coat and preserved them. It may be thought that perhaps the combination of the hard coat which silicate gave, and its inhibitive properties, led Nightingall to its invention. There is, however, no evidence of this. The rather prosaic title of the patent is a common occurrence in patenting. To minimise any
risk of litigation, inventions were claimed as a ‘development’ or ‘improvement’ rather than an out-and-out new invention. For example, the Wright Brothers were credited simply with ‘certain new and useful improvements in flying machines’ for their invention of the aeroplane, perhaps the most important invention of the century. In the case of inorganic zinc, there is no evidence that Nightingall was investigating silicates and came upon their use as a protective coating this way.

Nightingall did not publish any papers or articles while he was experimenting but did describe his work in an internal Di-net report he produced in 1940 (12). However, it is quite likely that by that time, he may have forgotten or overlooked some of the details of his research. In that report, he said he developed his coating as a result of investigations into corrosion. According to his son ‘…he saw a need for an improvement in anti-corrosion techniques.’ This may have been a follow on from his electrochemical work developing batteries, although this is not mentioned. His battery work undoubtedly led him to the literature on electrochemistry where, at that time, basic electrochemical mechanisms of corrosion were being debated (separate technical journals on corrosion did not appear until some years later). After investigating the scientific theories of corrosion and the use of zinc for corrosion protection he concluded:

‘…we have every scientific and technical reason to expect satisfactory results. It was on this basis that the technical work was undertaken for the development of a process based on the above principle. The difficulties were by no means small. First the process had got to be fundamentally correct as set out, secondly it had to be commercial, that is easy of application, keeping properties in stock, and reasonable in cost.’

So according to this report, it was an investigation of the fundamentals of corrosion that led Nightingall to his search for a new way of using zinc to prevent corrosion. However, the search was not easy. As he said in his report:

‘…Many formulas were tried in the development of the process now put before you, and I may say that after a year of failures it looked a difficult task to find a coating that could be applied to iron to provide a hard zinc surface that would not electrolytically short circuit to the iron, because if we were to have ionised hydrogen protection, then obviously the zinc must develop a potential between itself and the iron.’

What he wanted was zinc in some form so that it would develop a potential between itself and the iron, but, unlike galvanising, it would have a resistance between the two poles so that the potential remained high. (In later part of his report, however, he described that an important quality of his coating, and where it differs from zinc dust in oil paints, was that the vehicle was conducting, both in the liquid and final cured state, rather than highly resistant. No explanation for this apparent contradiction is given.)

Success in this was finally achieved by looking at natural ores, an area of research he had been involved in early in his career. He claimed:

‘Success in this direction was ultimately obtained after a very long research by observing that many of the ores of zinc as they occur in nature contain very large percentages of iron, and if nature had been able to preserve her zinc and her iron over the periods of geological development of these ore bodies, it seems obvious that there was the secret of the preservation of combined iron and zinc and it was when attention was turned in this direction that success was ultimately achieved.’

We can now see a fundamental error in his thinking, because zinc and iron in nature are not in their metallic form, but rather as ions, effectively in their corroded form. Iron in its natural form is iron in its corroded form. Despite this misunderstanding, he eventually achieved his aim by studying iron-zinc minerals, and that is the fact of ultimate importance.

Figure 4 shows a list of zinc ores from Nightingall’s work, giving the chemical composition and some physical properties. He noted that many elements naturally combined with zinc, and that zinc compounds have naturally been preserved for geological periods of time. He was most interested in ores containing zinc and iron, especially Frankinite which contains a high percentage of iron and zinc. Artificial production of this ore was his aim, recognising that nature has temperature, pressure and time to produce her compounds, but these are not generally available commercially, especially pressure and time.

He first tried to achieve this in one step but found that very high temperatures and long times were required. Moreover, the resulting product was not insoluble and broke down under weathering tests. Clearly, direct production of Frankinite was not possible so he tried to do it in two stages. The first stage was to produce Willemite, or silicate of zinc, and to react this with the iron. It appears he managed to mix zinc dust successfully with a silicate vehicle and apply this to a steel surface. He wanted significant reaction between the zinc, the iron and the silicate and this proved difficult to achieve. Application of heat helped, and this became an essential part of the process. While not happy with this coating because of the apparent small degree of chemical reaction with the iron, the coating was tested in a salt spray cabinet and did not break down over reasonable periods of time,
three or four months. He believed he had achieved a coating that, while not the same as the natural ore bodies he was searching for, did ‘possess some of the characteristics as regards permanency that nature has aptly developed’ to preserve zinc in combination with iron and other elements. This original coat did need a long period of time, four months or so, to develop acceptable hardness. It dried within a short period of time, but the coating would dissolve if wetted with water. Interestingly, inorganic zinc coatings that dry but do not cure properly are still a problem with applicators over sixty years later. Nightingall claimed that some of the panels with his original formulation showed no deterioration after exposure to the weather for five or six years. However, while the coating appeared to meet the corrosion protection requirements, it did not meet the commercial requirements. Nightingall knew from his long career that commercial success did not only depend on technical success. After another year or so, probably from trial and error, Nightingall found two chemicals that would speed up the reaction to a level acceptable for commercial use. He believed these compounds accelerated the reaction between the zinc silicate and the iron surface to form his desired iron-zinc silicate.

### Figure 4: Table of zinc ores in nature and their properties from Nightingall’s report (12)

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula of Composition</th>
<th>Colour</th>
<th>SG</th>
<th>pH</th>
<th>CS</th>
<th>Products &amp; Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adamite</td>
<td>MnCO3 (MnO2)</td>
<td>Yellow to violet</td>
<td>4.5</td>
<td>3.6</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Arthabasite</td>
<td>MnCO3 (MnO2)</td>
<td>Greenish blue</td>
<td>5.0</td>
<td>5.0</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Yellow to green</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>White</td>
<td>5.0</td>
<td>5.0</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Greyish green</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Silvery grey</td>
<td>2.5</td>
<td>2.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>White</td>
<td>5.0</td>
<td>5.0</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Orange yellow</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Yellow</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Red</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Blue</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Green</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Pink</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Brown</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Purple</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Black</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>White</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Grey</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Red</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Blue</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Green</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Pink</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Brown</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
<tr>
<td>Binghamite</td>
<td>MnCO3 (MnO2)</td>
<td>Purple</td>
<td>4.5</td>
<td>4.5</td>
<td>IV</td>
<td>Tannin (8% solution)</td>
</tr>
</tbody>
</table>

**Note:** Table 4: Zinc ores in nature and their properties from Nightingall’s report (12).

However, while the coating appeared to meet the corrosion protection requirements, it did not meet the commercial requirements. Nightingall knew from his long career that commercial success did not only depend on technical success. After another year or so, probably from trial and error, Nightingall found two chemicals that would speed up the reaction to a level acceptable for commercial use. He believed these compounds accelerated the reaction between the zinc silicate and the iron surface to form his desired iron-zinc silicate. The most important compound for accelerating the reaction was carbon dioxide. This caused a release of silicic acid which then resulted in, so Nightingall believed, ‘rapid silication of the silica zinc iron’. At first he tried heating in a carbon dioxide atmosphere, but this was not successful as the gas took far too long to penetrate through the coating. A better method was to include a carbonate or bicarbonate compound in the formulation which would give off carbon dioxide as it was heated. The second chemical which helped speed up the reaction was a borate, although this was not included in commercial formulations. He believed this actually inhibited some of the reactions to allow the zinc and iron to combine with one another in a controlled manner. No further detail is provided. With these additions, Nightingall reached his final formula. He had produced a coating which provided good corrosion resistance, and just as importantly, could be applied commercially. He called the process di-
metallisation because of the two metals, zinc and iron, which were involved in the process. The product was called Artificial Franklinitate at one stage, although the trade name ‘Galvanite’ was soon adopted. An Australian trade mark was taken out for the term in October 1940. Figure 5 shows a drum of a later formulation of Galvanite liquid. Zinc powder was packaged in a separate container. Exactly when and how this name was arrived at is not described, but it would appear to be a combination of galvanising and the suffix ‘ite’ commonly used with the names of minerals. The term ‘galvaniting’ was adopted at the same time to describe the process of protecting steel using Galvanite. The better known term ‘Dimetcote’ was not to appear until some years later, as described further on.

Nightingall spent a great deal of time trying to make the process work on steel covered with mill scale or rust. He believed that the zinc dust should reduce the oxide to iron and that the resulting iron would be taken up in the silication reactions. He claimed he was successful in this, and that the product could be used on less well prepared surfaces, but always concluded that it behaved better on a pickled or sand blasted surface. We know now that such products are only suitable for very clean surfaces.

Work over the past fifty years or so has studied the curing mechanism of the zinc silicate coatings and we have a much better understanding of the processes than Nightingall had. The original product basically consisted of zinc dust dispersed in a solution of sodium silicate, with a small amount of sodium carbonate and, for some formulations, lead pigments. After application to the steel surface, the water evaporates from the film and the alkaline silicate becomes quite reactive towards the zinc particles. The silicate ions cross-link and polymerise forming polysilic acid and the silicate matrix reacts with zinc at the surface of the zinc particles forming a silica-zinc polymer which holds the zinc particles together. There would also be some reaction with the steel surface to form ferrous ions and these probably take part in the polymerisation reactions, at least at the steel surface. So a reaction occurs between the steel, the zinc particles and the silicate binder causing a complex chemical structure which forms part of the steel surface. The silicate binder forms a conducting lattice structure which allows good electrical contact from zinc particle to zinc particle and from zinc particle to steel substrate. The zinc particles can sacrifice themselves without destroying the continuity of the coating. Moisture and carbon dioxide from the atmosphere further react with the polymer over the following days, weeks or months, ionising the zinc so that it can react with further silicate. The acidic combination of water and carbon dioxide assist in neutralising any residual alkaline silicate. This reaction proceeds slowly, resulting in a dense metal-like coating. Zinc corrosion products also form and assist in filling the pores. Unlike organic coatings, inorganic zinc coatings can improve in durability with age so, as mentioned earlier, an inorganic zinc film has little in common with a normal paint film.

The Original Patent

Nightingall took out Australian Patent Number 104,231 for his invention in 1937. It is worth looking into the original patent in some detail. The commonly used term today – inorganic zinc silicate or similar - was not used until the mid 1960’s and the product was referred to at the time as a ‘silicated composition containing finely divided zinc’. Nightingall called the process ‘di-metallisation’ although the trade name ‘Galvanite’ was used for the early applications and this term will be used in this work.

The patent claims in its introduction that:

‘This invention relates to improvements in and connected with silicated compositions and refers especially, but is not limited, to the formation of protective coatings from materials containing soluble silicates and finely divided metals (particularly zinc) such coatings being applicable to the surfaces of metal, glass, concrete and other materials.’

The patent acknowledges that mixtures containing soluble silicates and finely-divided metals had already been proposed, although no reference was given. The claimed aim was to improve such coatings by converting them to a substantially insoluble condition by heating in an atmosphere of carbon dioxide, which arises when bicarbonate in the mixture is heated. While a number of different compositions were given, the important one was ‘a coating material containing zinc dust, sodium silicate and sodium bicarbonate’. The ingredients are mixed together and applied by spraying, brushing or dipping and the coating ‘is then heated to a temperature of 200 deg. F for a sufficient time to convert the coating to a substantially insoluble condition’. Higher temperatures were required for the commercial product. The patent claimed that if the mixture contained basic oxides or hydroxides, it was not essential to heat it to convert it to the insoluble condition. Both the faster drying heat cured product and the slower curing air-dried product were produced commercially. The patent continued ‘Coatings produced as above described are suitable for a variety of uses including the protection of iron and steel sheets, ship’s bottoms and iron and steel structures which are subject to corrosive influences’.
While the basic description of the material and its application are similar to inorganic zinc products used since Nightingall’s patent, the patent contains a number of statements we would find rather strange today. The invention allows the use of metal powders other than zinc, and suggests the material can be used on glass, wood and concrete. On steel, it suggests that it is advantageous for the surface to be lightly oxidised or rusted for a more adherent coating. One variation suggested the addition of powdered graphite to impart anti-friction properties. We now know that it can only be used for clean steel surfaces and that zinc is an essential component for corrosion protection and other metals cannot be used. The friction properties are now seen to be one of its advantages.

The only technical paper published on the product by Nightingall was a paper he presented to a meeting of the Adelaide division of the Institution of Engineers on February 20th, 1942 (13). An edited version of the paper was published in the UK (14). Much of the presentation was taken up with a description of his interpretation of the principles of corrosion. No mention was made of his study of zinc ores and how that led to development of the silication reactions. He believed that his invention consisted of zinc embedded in zinc silicate of high resistance which prevented the zinc short circuiting with the steel surface. He had accepted by this stage that a perfectly clean surface was required and that all mill scale must be removed. His conclusion made it clear that he correctly believed he had made a considerable advance in corrosion protection:

“...if progress is to be made with this important problem (corrosion), new fields of investigation must be sought, in an effort to prevent iron and steel proceeding in that vicious cycle of coming out of the earth and, ultimately, returning to the place whence it came.”

Nightingall appears to have narrowed his formulation over time. In the original patent, he claims magnesium could replace zinc, and that the product could be used on concrete, wood and glass as well as steel. By the time he produced his internal Di-met paper in 1940, no mention was made of magnesium, and concrete was the only other surface suggested as one on which the product could be used. In his paper to the Institute of Engineers in 1942, only its application to steel is covered. This seems to suggest that, despite his claims that the product was based on theoretical principles of corrosion control, there was a significant degree of empirical work involved.

Nightingall did not rest on his laurels with Galvanite, but continued to invent further protective coatings, working at his home in Heidelberg. He patented one product based on zinc dust, red lead and linseed oil in 1940 (15). The most successful was an oil-based product given the name ‘Zinceron’, which consisted of the zinc dust with Tung oil for more rapid drying and was for applications where the product could not be blast cleaned, pickled, heated or protected from moisture for a long period of time, areas where the heat curing or cold curing Galvanite could not be used. It was conceded that the product would not give the same life as Galvanite, and under more aggressive conditions would need reapplication every year or two. Galvanite was claimed, when correctly applied, to stop all corrosion, while Zinceron would keep corrosion losses low. A number of other Australian patents were taken out on various formulations of zinc-rich coatings in the early 1940s (16).

During his experiments, Nightingall had clearly been trying to develop a product which did not require stoving. At the end, he obviously decided that this was going to prove very difficult. The stoving, or hot curing material, was an excellent product and applicable to many situations, so this was to be widely marketed. However, he did produce a cold setting Galvanite which contained a lead chromate paste (17). This did not require stoving, but did need at least seven days protection from the rain and weather for it to harden sufficiently to provide protection. There were also other developments of the basic Galvanite. The term Leadex Galvanite appeared in the early 1940’s for a product containing up to 16 per cent red lead which dried and cured much faster, so was less susceptible to moisture during the crucial initial curing.

The Di-met Company

Once the material had been perfected to Nightingall’s requirements, he set up a company to market it, naming it after the process he had invented. Nightingall founded the Di-met company in Melbourne in partnership with Sir Gerald Mussen on 25 January 1939. Sir Gerald Mussen (1872-1960) was a journalist who founded the Adelaide News, but was best known as a negotiator and industrial relations expert whose sympathies and liberal views were able to assist in solving industrial relations and community problems in Port Pirie and Broken Hill during and soon after the First World War. Di-met had its registered office at 360 Collins St, Melbourne, but a manufacturing plant was set up at the corner of Adderley and Stanley Streets, West Melbourne. A laboratory was built at the plant later, but Nightingall continued his development work at home, calling it the ‘Technical Department of Di-met’. The office and technical department were moved to West Melbourne in the late 1940’s, where they remained until the 1960’s when a larger plant was built at the outer western suburb of Brooklyn. The Di-met company continued for many years, becoming simply Dimet in the late 1940s. The firm was bought out by the Norwegian coating company Jotun in the early 1990s, and the name has now disappeared in Australia.
Early Examples

Nightingall worked on developing his zinc silicate product from the early 1930s although there are no records of any items coated with his experimental materials. It is likely that the early materials were not greatly successful and only those developed at around the time of the patent in the late 1930s had anything like the protective properties of the commercial product. According to Nightingall’s son, he remembers a flag pole in Melbourne being used as a test panel, but we have no record of its location or fate. The following are examples from the South Australian Parliamentary Committee report (18) described in Part II.

The first recorded example of the use of Galvanite in a large scale industrial structure is for part of a petrol tank at the Vacuum Oil Company’s depot at Yarraville, at the mouth of the Yarra River in Melbourne, in 1938. At the top of the tanks was a water seal and dip ring which required protection as a differential aeration cell is created in the water seal between the roof and the tank shell (see Figure 6) and it was difficult to maintain. According to the Chief Construction Engineer (Mr. Aubrey Old), Mr Nightingall approached the company and after laboratory tests, they felt it was worth trialling Galvanite. About 1250 square metres was pickled with hydrochloric acid and a single coat of Galvanite applied. Old admitted that preparation was not totally effective and rust spots appeared about six months later. These were repaired with Zinceron. After three and a half years, the galvanited areas showed no corrosion. As a result of its experience, Vacuum Oil decided to extend its use to pipelines and oil tank interiors and exteriors. Other oil companies also saw the benefits of Galvanite. In a paper presented in 1955 to the first major corrosion conference in Australia (19), N Boas of the Commonwealth Oil Refineries Ltd, described the corrosion problems in petrol storage tanks and reported that zinc silicate paints ‘have stood up remarkably well under these (i.e. corrosive) conditions’. Another oil company, H. C Sleigh started using the product about a year later and due to its success, decided to use it on its ships in Sydney.

Another early application was treatment of 230 gallon army water tanks during the early part of the Second World War. The army were troubled with internal rust and had been considering a porcelain treatment as used in the USA, but decided this was not only too expensive but no-one was capable of carrying it out in Australia. They searched for a suitable material and gave Galvanite a try when it was drawn to their attention. It was tested and there were no problems with the acidic water in Darwin (a result of the filtration process used there) and after further testing there decided to use Galvanite for water tanks sent to the Middle East.

The Rapid Machinery Company of Brighton in south east Melbourne used the product in an application which seems unusual today. They marketed industrial washing machines made in England and found that the galvanising used for hydro-extractor cages was satisfactory for some years, but they could not be re-galvanised as they would have warped. Zinc metal spray was used for repair but only lasted 12 months or less. They moved to Galvanite and had no trouble for 20 months and decided it was ‘a good protector against rust’, according to the Managing Director. As an additional advantage, Galvanite did not suffer from any abrasive action due to buttons and metal clips.

The final early example of the use of Galvanite was in construction of the Russell Street Police Headquarters in Melbourne in 1940 (see Figure 7). Angle steel supports for the external brickwork were galvanited to prevent them from corrosion which otherwise could have fractured the external brick walls. The Chief Architect of the Victorian Public Works considered Galvanite to be the nearest approach he could get to permanent protection for steel work. He had also wanted to use Galvanite for coating the steel window frames but this was an application which showed one of its weaknesses. In this case, Galvanite was abandoned in favour of red lead paint because the frames would have had to be dismantled and there would have been losses of small parts and delays. Moreover, the drilling process resulted in a greasy substance on the surface which prevented the Galvanite from adhering. Even today, inorganic zinc is rarely used for smaller, intricate items.

However, not all potential customers were convinced. The State Electricity Commission had carried out experimental tests and believed the product ‘had something’, but felt more tests were required. In the meantime, they would continue to use three coats of red lead and a top coat of conventional paint as their standard method.
of corrosion protection. The Bridge Engineer for the Country Roads Board had also carried out tests on the product in 1939 and had problems with adhesion so did not use the product in the early days. Some years later however, both the Roads Board and Electricity Commission became major users of Galvanite and its developments.

One other early application reported in the literature should be mentioned. According to Munger (2), the first well-documented field test was on a section of the Woronora pipeline in Sydney in 1942. However, as already pointed out, there were applications well before this. None of the literature from the early days of Di-met mentions any applications outside of Victoria and South Australia during the war years. Furthermore, the Committee looking into the coatings for the Morgan-Whyalla pipeline does not mention this at all. It would seem strange that a committee looking into pipeline coatings would not inspect and report on an example where the material was used as a pipeline coating. It seems likely that this coating was applied after its successful use in South Australia as described in Part II of this paper.

**Other Major Projects and Overseas Acceptance**

With its acceptance for the Morgan-Whyalla pipeline and success in this application, along with engineering developments which sprang up across Australia with the end of the war, Galvanite was widely specified for numerous projects across the country. In August 1947, the Vacuum Oil Company, with nine years successful use of the product, decided to use Galvanite on all bulk tanks and other steelwork on the new refinery it was constructing in the Melbourne suburb of Altona. Aubrey Old, Chief engineer for Vacuum, said in a letter to Di-met that “…where metallic coatings have been required during this period, we have exclusively used Leaded Galvanite…and have achieved such satisfactory results that we have standardised on the use of this coating wherever possible”.

Other early examples of the use of Galvanite in Australia in the late 1940s included:

- 32 kilometres of 61 cm diameter pipe for the Broken Hill - Menindee pipeline in 1947.
- 2,600 metres of 2.7 metre diameter pipe, 25 kilometres of 2.2 metre diameter and 9,800 metres of 2.1 metre diameter pipe for the Warrangamba Pipeline for the NSW Metropolitan Water Supply and Drainage Board in 1947.
- The Bellarine pipeline for the State Rivers and Water Supply Commission in Victoria.
- The Uly-Wanilla pipeline and Mannum-Adelaide pipeline for E&WS, South Australia.
- Structural steelwork for the electricity authorities in Victoria, Western Australia and South Australia
- Petrol storage tanks for Commonwealth Oil Refineries in Victoria and New South Wales.
- Water pipelines in Brisbane, Townsville and Tasmania and from Port Augusta to Woomera in South Australia.
- Treatment of upper side of the steel decking for three Battle class destroyers for the Royal Australian Navy built at naval dockyards in Sydney and Melbourne.

It was some time before interest outside Australia was obtained. Nightingall patented the product in the UK (20) almost immediately after taking out his Australian patent. Interestingly, the first mention of the product in a scientific journal was also in a British publication (21), although it was some years later. However, interest in the UK and Europe was limited, probably because organic zinc-rich coatings were developed in Europe just before the development of the inorganic product in Australia. The need for the inorganic product was not apparent in Europe, and even today their use in that part of the world is less than in Australia and the USA.

It was their acceptance in the USA that really brought inorganic zinc silicate coatings to world notice. Patents were not even taken out in other countries until after Nightingall’s death (22). By this time, the Di-met company had become a major coating supplier in Australia and started looking overseas for new markets. Managing
Director Max McKenzie, armed with numerous case studies and testimonials visited the United States in 1948 to try to get interest in his product. An impression was made on the chemist for the big American paint company, the Ameron Company of California, Charles ‘Chuck’ Munger.

Chuck Munger visited Australia in 1949 to inspect first-hand applications, including the Morgan-Whyalla pipeline. He was impressed, and his company licensed the dimetallisation process in the United States. The name ‘Galvanite’ was not available for use, and the product was termed ‘Dimetcote 2’ (there was no product marketed as Dimetcote 1, although years later the original product was sometimes referred to using this name). The trade marks for the term ‘Dimetcote’ were taken out in Canada and the UK in 1945, Australia in 1946 and the USA in 1948, although the term ‘Galvanite’ was still used in Australia until the early 1960s. Dimetcote is probably still the best known brand name for inorganic zinc silicate coatings, and still used around the world (although no longer in Australia). The term ‘dimetting’ is sometimes used to describe application of such products, an indication of its acceptance in the market. The stoving process was, of course, a severe limitation and work by Ameron and in Australia developed a post-cured product where an amine phosphate was washed onto the material at ambient temperatures. This product greatly expanded the applications, and large structures could be much more easily protected. By the 1960’s self curing water-borne products were available, soon followed by solvent-borne products, simplifying application even further. These are the products in use today and are generally treated by applicators and specifiers alike as normal ‘paints’ although, as shown in this paper, in many ways they are really a unique material.

Nightingall’s Legacy

There is no doubt that the invention of the inorganic zinc silicate coating made a remarkable contribution to both the coating industry and to the corrosion control industry in general. With this product, structures too large to be hot dipped galvanised could be given a single coat of paint that would totally protect the structure, often for its life in many environments. Before inorganic zins, regular maintenance was accepted as an expensive and difficult, but essential, chore. With inorganic zins, the corrosion problem, while not beaten, was certainly diminished in many applications.

However, its importance goes beyond the coating and corrosion industry. Chuck Munger’s view, while perhaps a little over the top, is worth quoting as a final tribute to Victor Nightingall, and the product he invented:

“Inorganic zinc coatings have been one of the true technological developments of our time which has made a real and positive impact on modern society. While this impact is not as dramatic as that of television or space travel, inorganic zinc coatings have nevertheless made a solid contribution towards the preservation of scarce materials, thus eliminating the need for replacement of existing structures, reducing the cost of steel structures, saving manpower, reducing the energy required for metal replacement, and providing new structures with a substantial increase in life expectancy.”

Acknowledgments

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INORGANIC ZINC SILICATE COATINGS – THE EARLY DAYS

Part II: The Morgan Whyalla Pipeline

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The Morgan Whyalla pipeline in South Australia is the best known structure to be coated with the first inorganic zinc material, the development of which was covered in Part I of this paper. This pipeline is widely quoted in literature from all over the world, often incorrectly referred to as the first major structure to be so coated. As we have just described, this was not the case. However, there is no doubt that it was this project that brought the product attention, not only in Australia, but throughout the world.

Background

South Australia is not well supplied with water and the Murray River is used to provide water to many parts of the state. The town of Whyalla on the northern Spencer Gulf had been the port for shipping of iron ore from the mines inland since 1915, but the decision was taken to expand facilities and build a blast furnace and shipyard. However, a major supply of water was required and the decision was taken in 1940 to build a 360 kilometre pipeline from Morgan on the Murray River to Whyalla at an estimated cost then of just over $6 million. Because of experience with external corrosion on earlier underground pipelines, the decision was made to lay it above ground. The main was constructed from steel pipe welded together and supported on concrete piers above the ground. It commenced with a rising main of 30 inch (76 cm) diameter pipes with four pumping stations providing the required lift. Most of the route consisted of gravity main varying from 26 to 21 inches (66 to 53 cm) in diameter. Figure 1 shows the route taken. The pipes were delivered from factories in Adelaide and Port Pirie and were lined with a spun cement mortar lining of 13mm thickness. The pipe laying operations were completed in 1943 and the pipeline was officially opened on March 31st 1944. Demand developed rapidly and exceeded design capacity within ten years. Pumps on the rising main were replaced, but demand was not met until a duplicate line was built in 1961. This followed the same route as the original, apart from a submarine crossing of Spencers Gulf. However, it is the coating of the original pipe which is of interest.

The Di-met company introduced Galvamite to the SA Engineering and Water Supply Department (E&WS) in February 1940 as a possible coating for its steel pipes. In a letter to the E&WS from Dimet’s agent in Adelaide, they introduced what they referred to as ‘the latest development in the scientific treatment of iron and steel surfaces to prevent corrosion.’ In the letter, a detailed description of Nightingall’s theory on dimetalisation was given, along with an economic justification. The pipe manufacturers, Mephan Ferguson, also lobbied the department, considering dimetalisation to be ‘a revolutionary and wonderful proposition. We have carried out a great deal of work here with the process and consider the results are extremely good.’ In September 1940, Nightingall visited the E&WS and explained the materials, how they would be applied and plant necessary for application. He also submitted various samples of iron which had been treated with the various products. Di-met were so confident of Galvamite that they offered to inspect the pipeline every six months for twenty years, and supply material to repair any damaged areas at their own expense. The

![Figure 1: Route of the Morgan-Whyalla Water pipeline.](image-url)
E&WS, as was its practice, investigated the claims with practical tests, beginning in November 1940. By this time, tenders had already been accepted for coating the pipeline with red lead primer and aluminium paint, but the Department believed that Galvanite should be investigated further. Experiments were carried out where steel samples were pickled and coated with Galvanite according to Di-met’s recommendations and subjected to partial immersion in salt water solution. Uncoated samples were also tested. The uncoated samples showed rust after 24 hours, but the galvanited samples showed no signs of rust after six weeks. As a result of these tests, the Engineer-in-Chief (Mr. H.T.M. Angwin) was convinced the product would be successful as a protective coating and might result in considerable savings. The Engineer for Water Supply wrote to him in an internal memo: ‘I have a very strong conviction that the use of Galvanite as an effective preventative to the rusting of iron and steel offers very great possibilities, and I consider that it will be extensively used for these purposes as its merits become more widely known and experience is gained in its use. I realise that it is a big step to recommend the use of this material for the project, but nevertheless I feel convinced that it will be a success, and I am prepared to make such a recommendation. In doing so attention is drawn to the fact that, from a financial point of view, the Department does not stand to lose to any great extent, but on the other hand the use of the material may mean a considerable saving on the Morgan-Whyalla main quite apart from the savings that can be made in the future if the coating is a pronounced success’. Angwin recommended it be used on the portions of the pipeline which still had to be coated. Di-met made arrangements with the companies providing the pipework (Hume Steel and Mephan Ferguson) and guaranteed a life of twenty years. This was a major departure from a contract already underway and, in October 1941, a parliamentary Committee was charged to look into the matter (1).

Parliamentary Commission

The Committee, consisting of seven members of parliament with The Hon. George Jenkins as its Chairman, not only looked into the question of whether the existing method of protection should be substituted by Galvanite, but also reviewed the whole question of determining the most effective method of protection for the pipeline. The Committee co-opted a technical expert and they took evidence from representatives of the E&WS, users of Galvanite in Melbourne and representatives of paint manufacturers. The Committee did recognise early on that a protective coating may not be economically worthwhile as most of the route was through regions whose climate was relatively benign, and corrosion rates were expected to be low. However, E&WS felt that protection was essential because of the risk of attack from grass fires, sand and dust as well as wind, rain and sun. The Committee agreed.

Only two methods of protection were considered: a priming coat or coats of red lead or similar material covered by a metallic paint or a single coat of Galvanite. One major supplier of the red lead system believed he could guarantee five years for a four coat system, while a second supplier believed two coats of metallic paint over red lead would give four years. Di-met claimed twenty years for its product and was willing to provide a substantial financial guarantee that it would not be less than that. However, the Committee needed evidence as Galvanite had only been on the market a few years and had not stood the ‘test of time’. The Committee observed the results of the E&WS tests which consisted of Galvanited plates exposed to tidal zone, damp ground, fresh water and exposed to full weather and sunshine. The tests had only been under way for six months to a year, but all panels were in good to excellent condition. None of the paint products emerged as satisfactorily as Galvanite and the Engineer for Water Supply expressed his belief that ‘nothing could hold a candle to Galvanite’. The Committee also had welding tests carried out which determined that Galvanite would not be adversely affected by welding except where the actual weld was made.

The Committee travelled to Melbourne and inspected a number of the applications outlined in Part I and took evidence from a number of witnesses. From the evidence, the Committee was convinced that ‘Galvanite, applied under suitable conditions, acts as an effective anti-corrosive. In the opinion of the Committee, it is most significant that reputable engineers and firms who have used it are extending its use’.

On return from Melbourne, the Committee asked Professor A. Killin Macbeth, Professor of Chemistry at the University of Adelaide, to review its evidence collected so far. Professor Macbeth was not convinced by Nightingall’s claim that a major part of the coating was converted to zinc silicate, nor that there was a reaction between the iron and the silicate to form an iron silicate compound. Macbeth discussed the performance of zinc-coated steel in the UK, and concluded that Galvanite should be best considered ‘a protective zinc coating, with a life probably of the same order of other zinc coatings, but with the advantage over galvanised coatings of easier application and greater adhesion to the surface of the steel’. He also considered that it had definite advantages over paint. It had better adhesion, it would not be damaged by fires and it appeared to have better penetrating
power into cavities than paint. Macbeth believed it would give a longer life than paint but would not give an opinion on the actual period of life.

Finally, the Committee looked at the economics of the alternative methods of protection. Galvanite was more expensive, at a quoted cost of £124,000 ($248,000), but estimated to last twenty years. The paint system was estimated to cost £72,000 ($144,000), with £21,000 ($42,000) of maintenance every four years. On a simple estimate, Galvanite would show a saving of around £50,000 ($100,000). The committee concluded that Galvanite would be the most economical coating for the pipeline, as well as the most effective coating and recommended this to the Government. The Committee released its report in December 1941 and Di-met was immediately awarded the contract to coat the pipe.

**Coating the Pipeline**

Di-met had insisted that that the heat cured or stoved product and the cold cured or air-drying product would give equivalent performance in the long run, with the air drying product requiring protection from the rain while it cured. The Committee was not entirely convinced and recommended that stoved Galvanite be used as far as possible and the air drying product only used where necessary, such as at weld joints and for repairs. This was an important decision, as unseasonal rain hampered much of the construction of the line and field coating work.

The contract required Di-met to coat up to 4,000 linear metres of pipeline a week at the two pipe manufacturer’s works at Outer Harbour and at Port Pirie in South Australia. The coating was to contain an average of one ounce per square foot of zinc (300 grams per square metre), with a minimum of three-quarters of an ounce per square foot of zinc (230 grams per square metre). A lead hardener was also to be added and pipes were to be stoved at 200 to 280 degrees F for at least 20 minutes. Field welds and damaged areas were to be coated with cold process Galvanite, with such regions protected from moisture and weather for three weeks. Di-met were to be paid between two shillings and two shillings ten and a half pence per linear foot (about $0.60 to $0.90 per metre). Di-met agreed to guarantee the coating for twenty years, with the E&WS withholding 17 per cent of the total value of the contract, but repaying this in small amounts over the following twenty years. Di-met was responsible for repairing any areas of the coating which failed over this period of time, other than those damaged by ‘flood, fire or acts of the King’s enemies’.

The Morgan-Whyalla contract was not the only one which occupied both Di-met and the E&WS. In September 1942, soon after construction commenced on the pipeline, the E&WS awarded Di-met another pipeline coating contract. This was for the LeFevre Peninsula main in suburban Adelaide. Unlike the Morgan-Whyalla line, this was largely underground. A number of new conditions were included in the contract, including the requirement that the coated pipeline be not covered with earth until the Galvanite had set or that, if it was necessary to do so, Sisalkraft paper be placed around such areas. As with the earlier contract, the E&WS kept an amount of the payment aside as a guarantee, to be paid in five years’ time if inspection showed the coating condition was satisfactory.

Application of the coating at the pipe manufacturing plants required a number of stages. The pipe was pickled in sulphuric acid to free it from mill scale (Figure 2), scrubbed with fibre brushes to remove pickling deposit and washed with dilute sodium hydroxide to neutralise the remaining sulphuric acid. Finally, it was rinsed in dilute phosphoric acid to prevent rusting before the coating could be applied. The coating was mixed by adding twenty pounds (9 kg) of zinc and one to three pounds (0.45 to 1.3 kg) of red lead to 10 pounds (9 kg) of sodium silicate to which a small amount of sodium bicarbonate had been added. The mixture was stirred vigorously and applied to the pipes with a six inch (15 cm) brush. The coating was worked well into the surface to eliminate holidays and a surprisingly even coating thickness was obtained. The coating was stoved using a flame blown in one end and out the other. This heated it to around 150 °C (300 °F) for about half an hour.
per pipe. The concrete lining was applied by spinning the pipes on rubber belts which polished, but did not damage, the zinc in these regions.

Figure 3: Pipes curing in Hume pipe works at Port Pirie, March 1943

Figure 4: Transporting coated and cured pipes to site.

A great deal of effort was taken to ensure that the coating was not damaged between application and installation. The pipes were covered with hessian during curing of the inner concrete lining which also prevented damage to the Galvanite (see Figure 3). When cured, they were delivered by rail, barge and truck to the laying site on racks, with the coating protected by rope cordage (Figure 4). They were laid on the ground using a special clamp lifting device protected with hessian wrapped around the steel jaws.

Problems

The coating application for the Morgan-Whyalla pipeline took place from 1942 to 1944. It was not without problems. There were difficulties getting the pipes descaled, washed and phosphated at the Hume pipe plant at Port Pirie. Nightingall believed too much acid was being used in the descaling, and a new washing system had to be developed at that plant. Furthermore, phosphoric acid was in short supply due to wartime conditions. However, these problems were all fixed and galvaniting proceeded without further problems. A number of the early pipes for the Morgan-Robertstown section of the line were coated with the air-dry formula, as the heaters for heat treatment had not been installed at the Outer Harbour pipe works. Continuous rain or showers (Figure 5) caused great difficulty in getting the material to cure, although the trouble was finally overcome by using Sisalkraft paper covers. Rust patches, misses and areas of peeling Galvanite were noted at Morgan on delivery of pipes in May 1942. Some of these were due to mishandling during transport but some were due to poor application, and had to be fixed in the field. The field coating of the welds proved to be a very slow process and Di-met fell well behind schedule in this part of the contract. Shortages of zinc powder on November 1942 due to wartime conditions required a reduction in the zinc content below the specified minimum. Nightingall considered this not to be serious and believed protection would not suffer, but supplies were soon resumed and the normal content was restored.

But the biggest problems arose when the galvanited product was buried underground. Di-met and Nightingall had always claimed that the product was suitable for underground work and must have had examples where this was the case, although these are not recorded. Nightingall had insisted from his first contacts with the E&WS that Galvanite would be entirely suitable for steel pipes laid underground, although in later comments he recommended that Galvanite with a higher percentage of lead be used in soils containing a high percentage of chlorides. However, the buried
portions of the Morgan-Whyalla line showed failures soon after installation. Pipes to be buried underground were given a second coat of Galvanite in the field in an attempt to provide sufficient protection. However, rain, dampness and humidity interfered with the application, and it was difficult to obtain curing of the second coat. Nightingall himself spent a great deal of time investigating the problem, looking at the nature of the soils and the mechanism of breakdown. While he could not find definite relationships between the degree of breakdown and soil chemistry, he was convinced that chlorides and sulphates were the major problem. However, ill health prevented him from carrying out thorough investigations. In December, 1945, he did furnish the E&WS with a 15 page report on the nature of the coating failures and his suggested solutions. In the same month, the E&WS insisted that they would not pay for the second coat of Galvanite applied to underground sections. The second coat needed to be applied to 23 kilometres of the pipeline at a cost of some £10,000 ($20,000). The then Chairman of Di-met, Mr. J. H. Roxborough, felt that repayment of this amount would bankrupt the company. Mr Roxborough suggested the cost be recovered from the amount retained on account of the guarantee period. As a result of these problems, underground sections were in future to be coated with cement mortar, and later on, coal tar enamel.

The first formal inspection of the pipeline under the terms of the agreement was made in February 1946. There were some problems on the above ground portions covered with the stoved Galvanite but these were fairly minor. The air-drying lead chromate Galvanite was generally inferior to the stoved product, although these were patched satisfactorily with the newer Leaded Galvanite. However as noted above, in some of the underground regions corrosion back to the metal was evident. At a later inspection in August that year, the original Galvanite on the above ground sections was also in very good condition apart from a few small spots, but further areas underground were found to be in poor condition or expected to quickly deteriorate. Under the terms of the agreement these were fixed by Di-met. In the region near Morgan where the pipeline was often inspected, an extra coating was given to the entire pipeline to improve the appearance of the patch-repaired coating.

The underground regions continued to be a problem, and neither the extra coating nor improved formulations worked. These problems were also noted on the LeFevre main in the metropolitan area of Adelaide, where it was thought that stray current electrolysis may have been the cause, but investigations quickly ruled this out. The Government Chemist was asked by the E&WS to look at the problem in June 1948 and concluded that, while Galvanite would give good service in normal atmospheres and some soils, in acidic and swampy soils the layer of moisture on the surface would cause rapid dissolution of the zinc. Di-met had ceased treating work which would be placed underground in 1946, but did believe it was only certain such environments where they would not perform satisfactorily. In 1949, Dimet accepted that its coatings would never meet the required guarantees and settled with the E&WS to repay them the costs, as agreed in the original contract. By this time, other contracts had been let which included underground sections and similar agreement was reached. The then Managing Director of Dimet, Mr Max McKenzie was philosophical and wrote in a letter to the E&WS:

“The very poor performance given by Galvanite in underground sections is most unfortunate and, although obviously not envisaged by your Department nor the late Mr. Nightingall, certainly justifies discontinuance of the practice. In fact, there is some consolation in the fact that its lack of protective capacity underground was discovered sufficiently early to prevent the subsequent contracts being treated in a similar manner”.

But the above ground sections were performing admirably. These constituted by far the bulk of the pipeline and, as noted, few problems were found. Weather conditions had been bad during laying, wartime conditions had created shortages and there was difficulty in training workers to apply the material correctly in the pipe plants and in the field. Most importantly, Di-met were applying a new product in vastly greater amounts than they had ever applied and under unfavourable conditions. It was truly a remarkable feat, and its success in providing a unique degree of corrosion protection made the task even more impressive. As Mr McKenzie wrote to the E&WS:

“…observations on the above-ground pipelines fully justify the optimism which we and yourselves maintain, that the coating will continue to afford protection for a very long period, probably in excess of the twenty years originally envisaged.”

In 1965 the guarantee passed with no major maintenance required. In the early 1970s, after nearly 30 years of service, a complete survey was made to ascertain its condition (2) to determine future maintenance requirements. Isolated rust points were found covering approximately one per cent of the total length. In most cases these were ascribed to regions of low thickness, not surprising when it was brush applied and film thickness gauges were not available. Demand for water in Whyalla and surrounding regions resulted in the line being duplicated in the early 1960s, and again stoving Galvanite was used, albeit a more refined formulation (Figure 6). By the 1990s, repairs were required to some areas of both coatings, but generally it was still in sound condition (Figure 7).
Conclusion

The coating of the Morgan Whyalla pipeline in South Australia was perhaps the most critical part of the history of the development of inorganic zinc coatings. It was the first large scale application of Nightingall’s invention, it drew the coating’s attention to the rest of the world and, most importantly, showed what excellent corrosion protection inorganic zinc coatings could give to steel. That fact that it remains largely intact after fifty years of service is testimony to the value of Victor Nightingall’s remarkable invention.

References


Inorganic Zinc Coatings have been the foundation of corrosion protective coatings for many years. A discussion regarding inorganic zinc coatings would not be complete without a mention of the famous Morgan Whyalla pipeline in Australia coated with a post-cured inorganic zinc. Although the concept is basically the same today, formulations have been upgraded over the years to become more user and environmentally friendly.

The manufacture and chemistry of inorganic zinc in essence is reasonably simple although the chemistry can appear to be quite complex. Before we discuss the hows and whys of inorganic zinc, let's discuss what characteristics an inorganic zinc should have to give effective cathodic protection and long service life.

1. The coating should have the ability to carry a high volume of zinc and maintain good film integrity.

2. The coating should permit electrical contact between the zinc particles and between the zinc particles and the metal substrate. The binder or vehicle must not surround and insulate individual particles of zinc, nor insulate the zinc particles from the steel at the surface interface.

3. The zinc must be allowed to sacrifice freely without destroying the integrity of the film.

4. The binder must have fairly good overall alkali resistance as the zinc salts that are formed are alkaline.

5. The film should be porous. This point is somewhat controversial since it goes against the conventional way of thinking for protecting metallic substrates. However if you will remember the mechanisms of cathodic protection, three items are necessary to set up a galvanic cell – anode, a cathode and an electrolyte. The porous nature of a film will allow the easy penetration of electrolyte to set up a good galvanic cell. The porosity also allows for the internal formation of salt without the destruction of the integrity of the film due to the additional solid volume.

There are many types of inorganic zinc coatings. There are advantages and disadvantages of each type. As one type is predominantly used today, we will limit this discussion primarily to alkyl silicates or more specifically, ethyl silicate.
The structure of condensed ethyl silicate is shown below.

\[
\begin{align*}
OC_2H_5 \\
H_4C_2O - S_1 - OC_2H_5 \\
OC_2H_5
\end{align*}
\]

In manufacture, the ethyl silicate is blended with alcohol and partially hydrolysed with water.

The ethyl silica will undergo a hydrolysis reaction and a condensation reaction – hydrolysis simply means a reaction with water. Condensation simply means a reaction that produces and gives off water.

The basic chemistry used in solvent based inorganic zinc primer is as follows:

Many variations to these reactions exist but serve no purpose here for discussion. The example will start with the Hydrolysis reaction of condensed ethyl silicate (Tetra ethyl ortho silicate - TEOS).

Either an alkaline or acid catalyst may be used. Also, note the formulation of silicic acid. This product is unstable but participates in the second step of the reaction called condensation. These reactions may appear not to be chemically balanced. However the intention is only to give a basic understanding on what is going on. Below is a simplified explanation of the condensation reaction that now occurs.

\[
\begin{align*}
\text{TEOS} & \quad \text{WATER} & \quad \text{SILICIC ACID} & \quad \text{ETHANOL} \\
\quad & \quad \text{OH} & \quad \text{HO} & \quad \text{OH} \\
\quad & \quad \text{EA} & \quad \text{OH} & \quad \text{Eho}
\end{align*}
\]
This partially hydrolysed silicate solution is mixed with zinc and spray applied to a blast cleaned steel surface. With moisture from the atmosphere, the reaction continues with polysilicic acids formed reacting with zinc ions from the pigment (zinc dust) and ferrous ions from the substrate to form a zinc silicate polymer which gives the coating its excellent chemical bond to the steel surface.

Note that it is the functional (OH) groups that react from the silicic acid to provide condensation. If enough water is used to completely polymerise the TEOS the end product will be a gel. Therefore when manufacturing inorganic zincons based on ethyl silicate only a partial amount of water is used. The coating itself after being applied, becomes water insoluble within a matter of minutes. Adhesion to commercial blast cleaned surfaces is excellent. Because the major solvents are alcohols, it can be applied at low temperatures and high humidity conditions. Unlike water based alkali silicates, the solvent based silicates cure best under high humidity. The reaction process may continue for many months and the reaction products – zinc carbonate and zinc hydroxide – fill the pores of the coating creating, over time, a very hard abrasion resistant film. The most important characteristic of inorganic zinc coatings is the electrical conductivity of the matrix. This enables the coating to provide cathodic protection to any steel area that may be exposed. There are significant differences in the solvent-based inorganic zinc coating depending whether an alkali catalyst or acid catalyst is used. The alkaline catalysed materials are more sensitive to moisture contamination during mixing. Also the alkaline catalyst tends to remain in the film after curing and unless removed it can cause topcoat blistering in wet environments.

The performance of solvent based ethyl silicates are excellent and have greater field tolerance than other inorganic zinc primers.
As previously mentioned, this chemistry is a simplification. Other additives can be included such as antisettling agents and inorganic extenders such as clay, mica, silica etc to help minimise mudcracking.

Some examples of the conductivity of various zinc rich coatings can be seen in fig.1 (not supplied). The examples are of panels coated with various zinc rich coatings and various zinc loadings.

Known as the "bullet hole test", a small circular area on the panel is left uncoated and the panels are immersed in a solution of seawater containing 3% hydrogen peroxide which initiates a rapid reaction of the zinc to galvanically protect the bare steel area.

You will note that the panel coated with ethyl silicate and 86% zinc shows that the zinc over the entire panel is working to protect the bare steel, as opposed to the epoxy polyamide panel with 67% zinc in the dry film which shows only the zinc immediately surrounding the bare steel is working. This demonstrates the excellent conductivity of the ethyl silicate binder as opposed to the organic epoxy polyamide binder.

This also can be seen in fig 2 (not supplied) showing SEM. pictures of zinc-rich coatings with bright spots showing areas of electrical isolation. Other observations can be made from these photographs, such as particle size and distribution, tightness of pigment packing and any cracking.

**Zinc Dust**

Zinc dust used with ethyl silicate should ideally be of a mixed particle size between 4 and 10 microns. Microfine zinc dusts are sometimes favoured as they result in a smoother applied coating which is less likely to give topcoat bubbling problems. This is because there is less void space in the cured film. However this is less than ideal for the coating to give its best cathodic protection. Fine zinc dusts or zinc dust of a constant particle size can lead to poor wetting of the steel surface and are more likely to result in mudcracking at higher film thicknesses.

This can be likened to making concrete with a mixture of cement and fine; like-sized aggregate. It will be OK in thin film but at high thickness it will crack. It just does not have enough integral strength to hold it together.

The metallic zinc content required to meet AS/NZ 2105 (as determined by gas evolution method) is 77% minimum (Type 4 Alkyl Silicates).

**Coating Types**

SSPC – Paint 20 classifies inorganic zinc rich coatings into three categories.

- Type 1-A post curing, water borne
- Type 1-B self curing water borne
- Type 1-C self curing solvent borne

Type 1-A post cured water borne is used very little today. This type was used on the previously-mentioned Morgan Whyalla pipeline. The procedure was to mix sodium silicate and a small amount bicarbonate with zinc dust. The mixture was applied generally with large brushes and then heat cured in a large oven or by large burners at a temperature of around 95 to 150°C.
Later formulations of post cured inorganic zinc involved the application to the zinc silicate solution of an acid curing compound. This innovation enabled a more general field use of this type of coating. The principle use of post cured IOZ was as a single coat corrosion protection in atmospheric and tank lining situations. The cured coating is extremely hard, abrasion resistant and offers excellent protection.

**Type 1-B** Self curing water borne types may be based on potassium silicate, lithium silicate, ammonium silicate etc. or a combination of these. They have all the attributes of the post-cured material with the benefit of being self curing.

Like the post-cured material, adhesion to other than white metal abrasive blasted steel is inadequate. When applied under high humidity conditions, drying and curing will be prolonged and time to water insensitivity will be increased. In low humidity conditions, water borne alkali silicates have fast dry and cure characteristics. Because of the alkali nature of the binder, topcoated systems using this type of self curing inorganic zinc may exhibit topcoat blistering in wet environments. The performance of properly applied self curing alkali silicates will be excellent.

**Type 1-C** Self curing solvent borne is probably the most used inorganic zinc currently and as previously discussed is predominantly based on ethyl silicate.

Other innovations include: single pack alkyl zinc silicate, inorganic weld through primers (SSPC Paint 30) and more recently high-ratio inorganic zinc.

The main advantage of a single package silicate is of course convenience. Instead of blending a zinc filler with a silicate base, one simply remixes the paint as supplied, thins as necessary and applies the material.

One limitation of single package zinc silicates is the incompatibility of certain topcoats that would normally be compatible with two package solvent based zinics. The problem exhibits itself through non adhesion and blistering of topcoats in certain wet environments and is due to the residual alkaline material present in the dry inorganic zinc film.

Performance untopcoated, over commercial blast, has been found to be similar to a standard two package system at the same zinc loading. Stability is a problem, careful control over manufacturing is required for excluding excessive moisture to prevent gassing upon storage, careful formulation can provide materials with a minimum of settling and caking of the zinc even after long storage.

Weldable inorganic zinc coatings are generally based on solvent borne silicates and are specifically formulated to be applied in thin film – approximately 25 microns. They are used when it is advantageous to shop blast and coat steel prior to fabrication. They can be gas cut and welded through without any apparent loss of speed or weld strength. The formulation generally contains an iron phosphide additive which improves the weldability without any apparent lessening of the corrosion resistant characteristics.

High ratio inorganic zinzcs are a more recent development. "High ratio" means higher silica and rapid cure. The formula was developed by NASA and uses a potassium silicate solution with a 4.8 – 5.3 to 1 SiO$_2$ to: K$_2$O ratio. The benefits of this type are –the relatively fast cure, exceptional hardness, can be applied to 200 microns without mudcracking, excellent single coat performance, water borne reducing health and safety hazards and has the ability to recoat without time limit.

High ratio inorganic zinzcs show a lot of potential and innovation for future corrosion protection. However, trials witnessed by the writer to date have shown mixed results.
particularly in relation to application characteristics. Their use will become more popular when development improves the ease of application.

**Slip Resistance**

Inorganic zinc silicates up until recently were the only paints approved and suitable for coating friction grip joints, i.e. application to surfaces used in high strength bolted joints.

Static load tests (reported as coefficient of friction) by an independent steel company give the following figures. The higher the value, the better the resistance to slip.

- Proprietary Inorganic Zinc SSPC Type 1C: 0.47
- Bare mill scale: 0.27
- Hot dip galvanised: 0.16
- Zinc metallised: 0.64

The application of IOZ to bolted joints prevents previously seen unsightly rust bleeding from these areas.

**High Temperature Resistance**

Wide use of inorganic zinc is made in high temperature applications up to 400°C such as stacks, incinerators, kilns, piping duct work etc. To extend their life, they are generally topcoated with high temperature resistant silicone coatings.

**Coverage of inorganic Zincs**

For conventional coatings, a product that has 50% volume solids will get a coverage of 10 square metres per litre at 50 microns. However this calculation is valid only for coatings that form a continuous film with no porosity present. The calculation for coverage of inorganic zins is somewhat more complicated. The porosity or air space in the coating will obviously extend the coverage.

Most manufacturers of IOZ do not quote a volume by solids figure in their data sheets as a direct calculation of coverage from this would be misleading. A calculated theoretical coverage allowing for void content is generally given. To calculate coverage you could use an equation as follows:-

\[
\text{Theoretical Coverage: } \frac{\text{Theoretical Volume Solids} \times 10}{1 - (\text{Void Content})}
\]

(10 equates 10 m² per litre at 100 microns)

**Example:** Suppose the theoretical volume solids of an inorganic zinc primer is 50%. Further assume that the void content in the film is measured to be 20%. The coverage is then calculated as follows:-

\[
\frac{0.5 \times 10}{1 - 0.2} = 6.25 \text{ m}^2 \text{ per litre.}
\]

**CONCLUSIONS**

Inorganic zins in various formulations will continue to be the foundation of corrosion protection of steel structures, etc.
When used as a primer and topcoated with suitable topcoats, inorganic zinscs have a proven record of long term atmospheric protection of 10 to 20 years. Future developments could well see improvements in water born technology particularly high ratio types as Volatile Organic Content (VOC) emission controls come into force.

This paper has been an attempt by a non chemist to put into reasonably not too technical form the chemistry and other attributes of inorganic zinc.

References- for this paper were made to:

Clive Hare- "Silicate Resins" Protective Coatings: Fundamentals of Chemistry and Composition.
John Montle (Carboline): Silicate Complexes Solvent Based.
"Zinc Filled Coatings" John Ladage (Carboline).
"Zinc Rich Primers" Charles G Munger.
ABSTRACT

An overview is presented of the critical properties of inorganic zinc silicate primers during both wet application and at full cure. The performance attributes of these primers, untopcoated and topcoated, is established by their longstanding use as a premium corrosion protection option. Comment is made that continued widespread use would be determined by their cost effectiveness, and use by applicators who perceive productivity gains achievable with innovative and proven formulations.

INTRODUCTION

It is a truism that the coatings industry can deliver to the client almost anything he wants, not necessarily what he needs. In reacting to the constraints of financial budgets, coating suppliers and applicators have developed a staggering array of responses, both technical and commercial. Provided the client’s objectives are realistic, but sometimes a challenge, the various industry groups respond with competitive spirit.

- **Consultants** – with generic specifications; documenting in detail what system to use, and how the project should be managed and inspected.

- **Suppliers** – with propriety coating systems; hopefully with the necessary case history evidence to support their selection and pitched at a realistic price/m².

- **Applicators** – with the particular skills they have; to apply such systems successfully, (whether under shop or field conditions) on time and within budget.

For the painting of structural steel there is a wealth of experience available to meet the demands of clients. This is particularly relevant in the case of inorganic zinc silicate primers (IOZ primers hereafter) which, whether topcoated or not, has consistently fulfilled client expectations for many years now.

IOZ primers, since their development in the early 1940’s, have claimed that part of the marketplace where there exists a requirement for long term asset protection from the ravages of corrosion. For industrial applications they have been regarded as “Rolls-Royce” primers for structural steelwork, especially where surface area to weight ratio of steel fabrications makes their use preferable to that of hot-dipped galvanising. Standards abound world wide detailing IOZ primer based coating systems for various service environments. among which our own joint Australian New Zealand Standard AS/NZS 2312 (1) has obtained acceptance.

This paper will address those factors that have ensured the sustained use of IOZ primer based coating systems. As with all coatings there are advantages and disadvantages associated with their selection. A knowledge of these is an important element in selecting the best corrosion protection option for a given service environment.
IOZ PRIMERS - ADVANTAGES AND DISADVANTAGES

In a recent publication by Gordon H. Brevoort (2) there appears a summary table of such advantages and disadvantages of IOZ primers, and is reproduced in this paper with acknowledgement. The information serves as a useful platform with which to discuss IOZ primer attributes in commercial applications.

SURFACE PREPARATION

It is a fact, undiminished by repetition, that IOZ primers require a very high quality surface preparation.

Pretreatment for steel, either ex fabricator or ex site will require some, if not all, of the following steps summarised below.

- Degreasing either by solvent washing or with emulsion cleaners.
- High-pressure water jetting to remove other contamination, including loose rust scale and, in particular, soluble salts down to an acceptable level (generally less than 10 µg/cm²).
- Power or hand tools to remove burrs, laminations, shelling, weld spatter; and to smooth weld margins and radius sharp edges and corners.

Primary treatment involves mandatory abrasive blast cleaning, usually with angular abrasives, to at least the quality defined by the Swedish Standard (3) as Sa2½ for various grades of steel. The abrasive blasted surface must have an optimum surface profile of about 40 to 70µm and be measured.

The ordering of these activities is important. For example, dry abrasive blasting, given that it is a mechanical process, will not of itself remove surface oily residues nor will it remove soluble salts. So, while special consideration of surface preparation could be seen as a disadvantage, such exacting requirements predispose the primer to a successful application, albeit at a cost. Let us also recall that abrasive blasted surfaces are highly reactive and especially so to the degrading influence of moisture; therefore priming without delay (usually within 2 to 4 hours) is a primary concern for the applicator.

WET APPLICATION CHARACTERISTICS

The developments in formulation technologies have been such that most IOZ primers (at least the self-curing types), can be easily applied. The essential rules are well known and some of the important ones are summarised below.

- Gradual addition of the zinc dust component to the vehicle component with adequate mixing.
- Straining of mixed components to remove coarse aggregate material.
- Use of minimal thinners restricted to adverse application conditions.
- Constant mechanical agitation of mixed primer within the pressure pot reservoir to prevent stratification of pigment.
- The use of well maintained conventional spray or airless spray equipment, and application of even overlapping passes to obtain an optimum film build.
For one-pack products, save for the fact that components are packaged premixed, all other rules apply.

**CURING AND CHEMICAL ADSHESION**

IOZ primers are a complex combination of zinc dust and reactive silicate solution, formulated at a high zinc to silica ratio by weight. A good description of the curing mechanism has been given by Charles C. Munger (4). In essence, with loss of solvent (alcohol or water), the concentration of reactive components causes some ionisation of zinc, and hydrolysis of silicate releases silicic acid. These products form a complex zinc silicate matrix that binds the metallic particles together. In addition, silicic acid reacts with ferrous ions on the steel substrate thereby achieving an intimate chemical bonding with the surface, additional to mechanical adhesion due to wetting of the surface profile. The insoluble silicate matrix gives both cohesive and adhesive strength to the cured primer film.

The outcomes of this curing mechanism are the rapid development of "shower resistance", the development of initial film hardness to enable handling within hours, and to allow topcoat application within 8 to 24 hours depending on suppliers recommendations. From the applicators perspective these are critical elements enabling him to plan for and achieve productivity.

During application and post application stages, it is important that the applicator not only to have a knowledge of ambient environmental conditions, but to select the type of primer best suited to achieve a result. By way of example some considerations are summarised below.

- In the case of ethyl silicate type products, application is best carried out in conditions where relative humidity is within the range 50 to 85% (with some latitude allowable to 95%) to achieve film cure.

- In the case of alkali silicate type products (these being water borne), application is best carried out when relative humidity is less than 50%.

- With both types of product the ambient temperature is less critical; normal application being achievable within the range 5 to 35°C, provided steel temperature is 3°C above the dew point.

**OVERCOATING WITH ORGANIC TOPCOATS**

The two determinants are; has the primer achieved its initial state of cure, and what steps (if any) need to be taken to prevent topcoat bubbling or blistering when applied over a porous primer?

**Initial Cure**

In an interesting study by Thomas L. Starr (5), the progress film cure of unmodified ethyl silicate primers was followed using Diffuse Reflectance Infrared Spectroscopy. The loss of organic material from the film was monitored as a function of time, at different combinations of temperature and relative humidity.

The results obtained were compared with more simple methods entrenched within the industry; such as, the "coin rub" test, MEK solvent rub, pencil hardness, cross-hatch adhesion, and topcoat adhesion (using the Elcometer ‘pull off’ adhesion test). He concluded that the only reliable test to assess cure was the MEK rub test, and it correlated well with the infrared method in following the hydrolysis reaction to completion. Among other factors, he
also affirmed the importance of ambient temperature and relative humidity, during both wet application and post application cure of the primers studied.

The importance attaching to monitoring of environmental conditions throughout and confirmation of film cure is emphasised to all coating inspectors.

**Overcoating**

Evenness of primer application to achieve an acceptable target dry film thickness (nominally 75µm) is an important factor. However, even more crucial is the recognition that cured films of all IOZ primers are porous, with porosity up to 40% in some proprietary brands. There are some well established techniques to overcome topcoat bubbling and/or blistering. Among these are:

- Applying a thin coat of vinyl butyral etch primer.
- Applying a thinned mist coat of the topcoat prior to a full unthinned coat.
- Applying an intermediate coat formulated near to the critical pigment volume concentration.

For applicators such measures represent extra materials and labour to be on-charged to the client or product supplier. Suffice it to say that when such difficulties occur remedial measures must be carried out.

At the time overcoating is carried out the primer film has not necessarily reached full cure hardness. Applicators therefore need to exercise care, depending on the system to be applied, that "cure time to overcoat" has been observed in accordance with the supplier’s recommendations.

In a rather elegant set of experiments reported by Gelfer and Vandorsten (6), semi-cured "fast dry" primers were overcoated with a series of common topcoats;

- chlorinated rubber,
- coal tar epoxy,
- high build polyamide epoxy,
- high build ‘fast drying’ epoxy,
- epoxy tie coat/urethane topcoat,
- high build vinyl,
- vinyl tie coat/vinyl topcoat,
- vinyl-acrylic.

Topcoats were applied at time intervals ranging from ½ hour to 24 hours and, after an initial curing period, were placed in a salt fog chamber (ASTM B117) for 4000 hours exposure. At the conclusion of salt fog exposure coating systems were examined for adhesion, blistering and scribe corrosion. The results indicated that topcoats with low permeance, such as chlorinated rubber and epoxy/urethane, required a minimum 4 hour period of initial primer cure to achieve overall good coating system adhesion to steel. Coal tar epoxy topcoat required a 24 hour primer dry time interval which correlated with its very low permeance. Other topcoat generic types did not adversely affect the ability of the primer to achieve full cure hardness despite its encapsulation.
CORROSION PROTECTION

There is no doubt that zinc rich primers, and in particular IOZ primers, have been used to advantage in corrosion protection of steelwork. It is well known that zinc rich films, due to their high zinc dust content offer a high degree of protection both cathodically and by barrier action. Prime advantages of the zinc rich film are to protect bare steel at damages by "throwing power" of the zinc, and to resist undercutting corrosion of adjacent intact paintwork. Topcoating systems add the element of synergy in overall corrosion protection.

It is noted that much literature has been devoted to optimising the level of zinc dust in IOZ primers. Classical formulations established levels of measurable metallic zinc at 77% minimum for ethyl silicate types and 85% minimum for alkali silicate types by weight. Such levels have been enshrined in many Standards worldwide. In recent years however there has been renewed interest in lowering the zinc dust loading whilst maintaining performance attributes.

Standards authorities have shown a reluctance to reduce zinc loadings, and compromise the safety factor hitherto offered. It is apparent that simple substitution of zinc with other conductive pigments (such as di-iron phosphide or micaceous iron oxide) cannot be done without regard to other formulation parameters. Options that have been used in recent times include the following.

- Use of IOZ primers with lowered zinc levels but with mandatory topcoat system application.
- Use of a single coat of IOZ primer, especially those incorporating high ratio silica binders. On certain structures where corrosion protection is the primary concern, there is evidence of successful long term corrosion protection in the literature (7,8)

CURED FILM PROPERTIES OF IOZ PRIMERS

The cured film properties of IOZ primers are indicative of the diverse service environments in which they find applications, either untopcoated or topcoated. Set out below are the important attributes in summary form.

**Cathodic Protection** – The primary protection mechanism.

**Adhesion/Cohesion** – Strong chemical/mechanical adhesion to steel surfaces giving resistance to undercutting corrosion.
- Strong cohesion within the film giving abrasion resistance.

**Weathering Resistance** – Inorganic composition gives generally excellent weathering properties.
- Not generally recommended for aqueous immersion without topcoats at least.

**Minimal Shrinkage** – Lack of tensile pull on curing is an advantage in protecting pitted steel surfaces.

**Temperature Resistance** – Recommended for high temperature applications up to 400°C untopcoated, or topcoated with selected generic topcoats.

**Chemical Resistance** – Resistance limited to environments not strongly acidic or alkaline, and topcoating recommended where use is appropriate.
Solvent Resistance – Unaffected by aliphatic solvents, aromatic solvents, ketones and alcohols. Reference to comprehensive supplier data is recommended.

Radiation Resistance – Use history is well established for containment vessels of nuclear reactors.

Welding – No significant loss of weld margin strength.
– Speed of welding and minimal porosity is reported for ship’s pre-construction primers with reduced zinc dust content.

One-Coat IOZ Protection – Typically used for internal tank linings (neutral conditions), in refineries and in off-shore applications.

IOZ Primer plus Selected – Use is well established in power generation facilities, Topcoat Systems pulp and paper mills, tank exteriors, bridges and marine structures.

Within our own local New Zealand environment many examples of the applications shown above can be observed. IOZ primers have developed a substantial track record of successful performance in mitigating corrosion. Their continued use will hinge on maintaining performance through innovative formulation developments, and through cost effectiveness in relation to other protection options. Suppliers will need to demonstrate, to clients and applicators alike, that productivity improvements are possible with its use, otherwise such primers may, by default, become an expensive option.
Inorganic Zinc-Rich Coatings

Advantages
1. Easily and readily applied to large or existing structures.
2. Unaffected by weather, sunlight, or wide variations in temperature. Will not chalk, peel, or lose thickness over long periods of time.
3. High adhesion to clean steel and offers a primary chemical bond in addition to mechanical adhesion.
4. The inorganic binder partially insulates the zinc particles and meters out the sacrificial use of the zinc for longer life.
5. Fire resistant.
6. Heat resistance somewhat above the melting point of zinc.
7. Unaffected by most organic solvents.
8. Surface formed is metallic, strongly adherent, and abrasion resistant.
9. Excellent undercutting resistance and galvanic protection of scratches, scrapes and damages up to $\frac{1}{4}$ in. (6mm).
10. Can be used on faying surfaces (friction joints) without roughening.
11. More easily topcoated than galvanizing.
12. Application in place to completed structures enhances protection since all flat surfaces, edges, and joints are protected with a continuous film.

Disadvantages
1. Must be applied over bare, abrasive-blasted clean steel.
2. Will not tolerate organic contamination of steel surface.
3. Will not adhere to all metals or alloys – performs best over steel or zinc.
4. Many types require medium range of application temperature and humidity to properly cure and attain optimum properties.
5. Not satisfactory for continuous immersion in electrolytes.
6. Sensitive to strong acid or alkali environments. Zinc is reactive in pH range of less than 6 (acidic) or greater than 10.5 (alkaline).
7. Solvent-borne, inorganic zinc-rich coatings may exceed limits on volatile organic compound content.
9. Excessive film build frequently results in mudcracking.

Extract from the paper by Gordon H. Brevoort reference 2.

REFERENCES:
1 AS/NZS 2312:1994. "Guide to the protection of iron and steel against exterior atmospheric corrosion".
3 Swedish Standard SIS 055900 (ISO 8501-1 :1988)
4 Charles C. Munger, "Zinc Silicate Coatings - 40 Years Experience" JPCL Vol. 2 (No. 3), March 1985, pp 34-44
5 Thomas L. Starr, "Improving The Reliability of Zinc Rich Paint Systems" JPCL Vol 3 (No. 3), March 1986, pp 22-31
INORGANIC ZINC SILICATES vs METAL SPRAY IN INDUSTRIAL APPLICATIONS

by W L Mandeno* & TA Sutherland**

Presentation to the NZ Inorganic Zinc Seminar
One of a series arranged by the Protective Coatings Technical Group
of the Australasian Corrosion Association Inc.
to celebrate 60 years of Inorganic Zinc Silicate.

Summary
There are many similarities between the inorganic zinc silicate and metal spray coatings that have been used for over fifty years to protect steel from corrosion. Both are spray processes that produce a hard, slightly porous and very durable coating, which is applied to the substrate after abrasive blasting to a near white metal surface. These coatings can have a service life which may be greater than that provided by pure metal applied by electroplating or hot dipping. This superior life is thought to be due to the embedment of the active metal in an inorganic or oxide matrix, that then provides a less reactive barrier coat while still giving galvanic protection to steel exposed at small breaks in the coating. Also both coatings have been used for many years as a primer overcoated with an organic paint system, but in recent times have been found to give excellent, and in some cases superior, performance as a ‘stand alone’ system.

This paper reviews the various metal spray processes, the alloys used, their performance history, and available standards for thermal spray coating systems. Also discussed are the advantages and disadvantages of thermal metal spray when compared to inorganic zinc silicate, the other premier long life coating system for steel.

Keywords
Aluminium, Corrosion Prevention, Inorganic Zinc, Steel Structures, Thermal Metal Spray, Zinc

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INTRODUCTION

There are many similarities between the inorganic zinc silicate and metal spray coatings that have been widely used for over fifty years to protect iron and steel from corrosion. Both are spray processes that produce a hard, slightly porous and very durable coating, and both require application to an abrasive blasted near white metal substrate. These coatings have a service life which may be greater than that provided by pure metal applied as relatively thin coatings by electroplating or hot dipping. Thermal metal spray can be applied as a thicker coating which in some instances also includes a thin sealing coat of paint.

This paper reviews the various metal spray processes, the alloys used, their performance history, and available standards for thermal spray coating (TSC) systems. Also discussed are the advantages and disadvantages of metal spray when compared to the premier ‘wet paint’ coating system of inorganic zinc silicate (IOZ).

HISTORY

The process of spraying molten metal onto steel was first patented in Switzerland by Dr Schoop and introduced to the UK in 1912, but did not become a commercial reality until the early 1920's. Metal spraying of bridge components (eg the Menai Straits bridge) was carried out in Britain before World War II. Because of the significant reduction in maintenance, flame sprayed zinc supplemented by paint became widely specified by British engineers for many major structures around the world, including New Zealand’s Auckland Harbour Bridge (1958), the Forth Road Bridge (1964), and the Pierre-Laport suspension bridge across the St Lawrence at Quebec (where from 1978-84 some 165,000 sqm was coated after failure of the original paint system). Use of flame sprayed zinc as a primer declined with the introduction of the self curing types of inorganic zincsilicates in the 1970's and has since mainly been used to coat steel components that could not be “galvanized”, ie by dipping into a bath of molten zinc. Typical deposition or melt rates of zinc wire when flame spraying were 10-20 kg/hr.

The arrival of arc spray technology in the mid 1960's greatly increased coating adhesion and gave typical application rates of 10-35 kg/hr using a 2.5 mm maximum sized wire, but the finish of the sprayed metal was quite rough and spray efficiencies of 50% were typical. In 1990 high deposition low energy systems became available which were also much lighter and portable. These give deposition rates of 20-88 kg/hr with deposition efficiencies of over 70% when arc spraying 4.8 mm wire. However there is an inherent problem of arc shorting when spraying large diameter wire at low amperages (250 – 400 A) which has been overcome by one manufacturer with a patented control system that can adjust the arc gap while spraying in less than 0.02 of a second. This and other recent developments in atomisation control giving smoother finishes, have reduced application costs and made thermal metal spray a very competitive long life coating system.

Spraying of street lighting columns with a coating of aluminium was introduced in the UK in the 1950's, and this was also used to protect roof beams in steelworks as well as many chimney stacks. More recently Thermal Sprayed Aluminium (TSA) has been widely used in the offshore oil and gas industry with over 400,000 sq metres of TSA applied to oil platforms in the North Sea.
PROCESSES

Thermal Metal Spray essentially involves the spraying of molten or semi-molten materials onto an abrasive blast cleaned surface. Pure or alloyed metal, as a wire or powder, is melted in a gas flame or electric arc, and then blown as molten droplets onto the prepared substrate with compressed air. The four main processes now used are as follows;

**Flame Spray**
Also known as “Metallising”, the original term for flame spray derived from the Metallising Gun designed by Metco in 1935. It uses gases as a heat source, generally oxygen/acetylene or propane/oxygen and in some cases natural gas. Wire of up to 4.8 mm diameter is driven through the flame gun where it is melted in the nozzle, then atomised by compressed air, and blasted onto the substrate in a plastic state at velocities of 100 to 200 m/s.

**Arc Spray**
A similar process to flame spray, but where the heat source is provided by an electric arc. This gives an increase in temperature (from 3000°C with gas, to between 4000 and 6000°C) which results in hotter particles giving superior adhesion and production rates. Two wires are fed into the gun with different polarities and by controlling voltage and amperage, an arc is formed at their point of contact. Power supply is similar to that required for arc welding and is typically 20 - 40 VDC at 100 to 800 A, with particle velocities of around 250 m/s. This system gives high interparticle and interface bond strengths which can vary from 500 to 2500 psi coupled with a lower porosity. It is also known as the twin wire electric arc (TWEA) process.

**Powder-combustion**
This is a flame spray process where the metal and fluxes are supplied in a powder form which is fed into the gas stream and sprayed at lower velocities of 50 m/s, often without the use of compressed air. This system is often used for hard facing work and is capable of spraying almost any material including ceramic powders. A variant of this, where high pressure gas is added with stream velocities of 1500 m/s, is also known as the high velocity oxygen fuel (HVOF) process.

**Plasma Spray**
This is a sophisticated metal spray system developed for the aircraft industry for high temperature service, eg coating turbine blades with tungsten or chromium carbide. A plasma forming gas such as argon is ionised with an electric arc, and powder is then introduced into the plasma stream. Temperatures of between 8,000 and 30,000 °C are used with particle velocities of up to 600 m/s.

For applying corrosion protection to industrial structures, the arc spray is now the most commonly used process because of its higher production rate. However for small items and field repairs the traditional flame spray or metallising process is still being used.

**SPRAYABLE METALS AND ALLOYS**

Virtually any metal, can be applied by the metal spray process. However for the protection of steel from corrosion, either pure zinc, aluminium, or their alloys are used as these are more anodic materials, ie provide galvanic protection. Research into duplex systems (eg aluminium on top of zinc), pseudo alloys (ie arc spraying with mixture of metals), and prealloyed wire
has lead to the development of alloys with optimised properties. Various studies have confirmed that 85/15 zinc/aluminium alloy is superior to pure zinc in marine atmospheric environments. However aluminium is recognised as being the most durable spray coating for severe marine and/or high temperature conditions, but is more difficult to apply due to its higher melting point and lower ductility. Most of these difficulties can be overcome by the use of the AlMg5 alloy (ASTM B285 ER5356) wire which is the material preferred by STATOIL and the Norwegian offshore industry. In a recently reported test series of Zn, Zn85Al15, AlMg & AlSi; AlMg5 was the best performing alloy for salt water immersion.

PERFORMANCE

Zinc metal spray coatings have a service life which can be greater than that provided by the relatively thin coating of pure metal applied by electroplating or hot dipping. This superior life is mainly due to their generally greater thickness and also, especially when the pores are sealed, the coating provides a less active barrier coat while still giving galvanic protection to steel exposed at small breaks in the coating. The durability of thermal metal sprayed coatings was confirmed in a series of test exposures undertaken by the American Welding Society (AWS) in 1953-54. Steel panels were prepared with various abrasive media, coated with flame sprayed zinc and aluminium, and then sealed with four different paints. Panels were exposed at American Society of Testing and Materials (ASTM) test sites which included sea water immersion, industrial and “Severe marine” environments. The latter was at Kure Beach, North Carolina with racks 24 m from the sea. Inspection results were reported by the AWS after 6, 12 and 19 years exposure. The current condition of these panels after 44 years, and of aluminium arc sprayed steel wharf beams after 29 years exposure, can be seen in a recent report by the LaQue Centre for Corrosion Technology.

The expected performance of coating systems can be found in codes of practice such as ANSI/AWS 2.18, BS 5493, and AS/NZS 2312 (see full reference under Standards listed at the end of this paper). Extracts of Table 6.3 from AS/NZS 2312 are given in the following table. (Subscript ‘S’ denotes a sealed coating with the TSC thickness given in microns).

<table>
<thead>
<tr>
<th>Atmospheric Classification</th>
<th>Years to first major maintenance</th>
<th>&gt;2 to 5</th>
<th>&gt;5 to 10</th>
<th>&gt;10 to 20</th>
<th>&gt;20 to 25</th>
<th>&gt;25 to 40</th>
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<td>Moderate</td>
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<tr>
<td>Marine</td>
<td></td>
<td>-</td>
<td>-</td>
<td>ZN100</td>
<td>ZN150</td>
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<td>ZN300</td>
</tr>
<tr>
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<td></td>
<td>ZN100</td>
<td>ZN150S</td>
<td>ZN150S</td>
<td>AL150</td>
<td>AL275</td>
<td>AL275S</td>
</tr>
</tbody>
</table>

Metal spray systems were ranked the best in a recently reported exposure test of “environmentally acceptable coatings” (which included uncoated and topcoated “high-ratio” and other IOZ’s) for bridge painting carried out for the US Federal Highway Administration, with no undercutting at scribe marks after 6.5 years exposure, and had the lowest Life Cycle Cost.

SEALING AND PAINTING OF METAL SPRAY

Thermal sprayed coatings, and zinc in particular, can have their performance in marine
environments enhanced by sealing the pores and surface with a low viscosity material with good wetting properties such as vinyl, polysiloxane, or thinned epoxy or urethane. Silicone aluminium paint is used for high temperature applications. This seal coat is applied soon after spraying and until absorption is complete. Use of aluminium or coloured pigments improves the appearance of the coating, while the binder decreases exposure of the metal to the environment. High build paint coatings are unnecessary, and in fact may reduce the system life by trapping salts and moisture against the metal at coating defects. The increased life due to sealing is shown in the table above, where sealing zinc is approximately equivalent to adding a third more metal thickness.

**ADVANTAGES OF METAL SPRAY**

**Over zinc-rich paint**
- No mixing or clean up as with wet sprayed coatings, so higher productivity from applicator.
- No pot life restrictions and fewer weather constraints for application
- Easier quality control
- No handling delays due to waiting for cure or dry time
- No sags or runs
- Better high and cyclic temperature resistance
- Superior abrasion and impact resistance (reducing corrosion and repair costs from transport and erection damage)
- Easy to increase thickness when underbuilt or to suit microclimate
- No overspray with outdoor application
- Zero volatile organic compounds (VOC)

**Over galvanizing**
- No limit to size of item
- Reduced surface temperature so no distortion or annealing
- Better control over thickness, also no runs, spikes or dross inclusions
- No problems with some alloys, eg silicon killed steel
- No risk of hydrogen or strain age embrittlement
- Better surface for paint adhesion (degreasing, etch priming not required)
- Heavier coating thickness possible
- Better high temperature performance (with TSA)
- Better corrosion protection in marine atmospheres (with TSA and sealed TSZ)
- Field application possible
- Cost competitive on sections >7 mm thick (galvanizing priced per kg dipped)

**Disadvantages**
- Requires a clean surface with adequate profile
- Operator requires eye & hearing protection and air fed masks with some units
- Generation of noise, dust and smoke
- Operator fatigue with some units
- Higher capital outlay than a paint spray unit
- Rougher surface finish with some units
- Cannot coat into recesses like brush applied paint or galvanizing
CASE HISTORIES

Local early examples of metal spraying in New Zealand are on the Auckland Harbour Bridge and at the Ellerslie Race Course. In 1956 the Harbour Bridge specification was amended to the “best protective treatment known at the time” ie flame sprayed with zinc at 50 microns and top coated with 3 coats of phenolic paint. The old grandstand at Ellerslie had the main roof trusses and seat supports sprayed with zinc on site prior to painting about 1960, and the owners have advised that these have been free of maintenance for 37 years. The following is a listing of some recent applications of TSC in the Auckland area.

- Pipe spooling at Freemans Bay and Wiri Oil Terminals
- Steel piles to Onehunga wharf
- Chimney bases at Otahuhu Power Station
- Ballast tanks on the HMS Charles Upham
- Lighting columns for Southern motorway and the International Airport
- Overarch apexes on the Auckland Harbour Bridge
- Dock gate bridge at Calliope Wharf
- Entrance canopy to the City Council Administration Building

Another recent and different use of arc spray has been to apply zinc to concrete wharf piles to provide a sacrificial anode for the cathodic protection of reinforcing steel.

METAL SPRAY vs INORGANIC ZINC SILICATE

General
Unsealed TSC provides a relatively rougher substrate to provide good adhesion for a cosmetic overcoat, and both are porous (TSC 8-15% cf. IOZ 30-40%), which can lead to problems with solvent entrapment. However in recent times, both TSC and IOZ have been found to give excellent, and in some cases, superior performance as a “stand alone” system. Caution is required when spraying both IOZ and TSC in the vicinity of stressed stainless steel to prevent its embrittlement at elevated temperatures.

Coating Thickness
The thickness and hence the life of Type 3 & 4 IOZ coatings are limited by their tendency to “mud-crack” when applied with DFT’s above 125 microns. “High ratio” IOZ (Type 6 to AS/NZS 3750.15) is required to be free of mudcracking at up to 200 microns although it is normally applied at 125-150 microns. This high performance water borne type has not yet gained acceptance in NZ due to application problems in our lower temperatures and higher humidities (and also its high price relative to Type 4 ethyl silicate). On the other hand, zinc metal spray can be applied at up to 400 microns in one application and is less affected by weather conditions. Top coated zinc metal spray is less prone to shear failure and so maintains protection under impact during installation with less site repairs necessary. It also performs better on pipe flanges and splice plates during bolting.

Faying Surfaces
Both provide good friction factors for HSFG bolted joint faying surfaces. Inorganic zinc has been found to have an average slip coefficient of 0.50 compared with 0.35 for organic zinc rich primers. TSC are significantly better, testing at 0.62 for flame sprayed zinc and 0.71 for...
flame sprayed aluminium. AS/NZS 3750.15 requires a minimum slip coefficient of 0.35 for Types 1 to 4, and 0.5 for Type 6 for use in design with AS 4100 or NZS 3404.1. With TSC, optimum results have been obtained when the coating thickness was between 50 to 100 microns, and faying surfaces should not be sealed. For design purposes, a coefficient of 0.5 is recommended for arc sprayed zinc, and 0.6 for arc sprayed aluminium.

**Marine Exposure**

Both provide sacrificial cathodic protection to steel at defects in the coating, especially when not overcoated. However 100 microns of TSZ provides 700 gm/sqm of Zn vs. 200-250 gm/sqm for the usual 75 microns DFT of IOZ. Aluminium is less anodic than zinc but provides better barrier protection due to the formation of less soluble oxides. When alloyed as AlMg5 it will give good galvanic protection and prevent the initial “bleed through” staining that can occur with pure aluminium. As previously mentioned, TSA has been widely used in severe marine environments ranging from valve protection, buoys and non skid decks for the US Navy, to coating tension legs (eg Hutton TLP 1984), risers, flare booms, and pipelines (60 to 450°C) on offshore oil platforms.

**Chemical Resistance**

Aluminium has better acid resistance so is more suitable for use in geothermal and most industrial environments involving acid fallout. Recommended pH range for aluminium in buried or immersed environments is 4.5 to 8.5, whereas for zinc it is 6 to 12.5. In atmospheric environments, aluminium forms a stable inert protective oxide layer whereas zinc oxides are converted to soluble zinc hydroxide and zinc carbonate which are removed at a linear and predictable rate.

**Heat Resistance**

According to AS/NZS 2312 which gives maximum heat resistance in Table 7.8, IOZ is rated at 400°C. Unsealed TSA and IOZ sealed with butyl titanate or silicone aluminium are both rated at 480°C, zinc metal spray at 260°C, and galvanizing at 200°C. However NACE suggests a maximum service temperature for IOZ as 315°C, but notes that sealed IOZ has been reported as withstanding intermittent service up to 593°C. (NB melting point for Zn is 419°C and Al is 661°C). The high temperature performance of TSC is similarly improved by the use of an appropriate sealer coat.

**Adhesion**

The adhesion strength of IOZ to freshly blasted steel is of the order of 200-300 psi. (It is also vulnerable to cohesive failure, especially when overcoated too soon). Table C2 of AWS C2.18 gives typical bond values in psi for laboratory sprayed samples 375-500 microns thick and tested to ASTM C633. These are reproduced in the following table, together with typical NZ test results (in brackets) measured using an Elcometer 106 to ASTM D4541.

<table>
<thead>
<tr>
<th>Material</th>
<th>Flame Spray</th>
<th>Arc Spray</th>
<th>Minimum*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>1000 (700-900)</td>
<td>2500 (1400-1800)</td>
<td>800</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2800 (1100-1400)</td>
<td>5000 (1900-2600)</td>
<td>1500</td>
</tr>
</tbody>
</table>

* Minimum tensile test result for AWS Operator Certification

Adhesion of TSC depends on the ductility of the metal, the quality of surface preparation, the coating thickness, the application method and spray set up parameters. The adequacy of these and the competence of the operator, can be easily confirmed by spraying 200-250 microns onto a prepared 1.25 mm thick steel test coupon and bending it around a 13 mm mandrel. This
is the AWS C2.18 Bend Test and a failure is recorded when the coating cracks and can be “picked off” with a knife blade.

**Application Costs**

Typical rates, (supplied by the NZ Abrasive Blasting Association, PO Box 51 942, Pakuranga, Auckland) for the shop preparation and application of coating systems to AS/NZS 2312, with life to first major maintenance in various defined environments, are given in the following table.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Material</th>
<th>System</th>
<th>Life</th>
<th>$/sqm</th>
<th>$/sqm/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate</td>
<td>75IOZ/Type 4</td>
<td>MP1</td>
<td>5-10</td>
<td>16.00</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>100Zn</td>
<td>ZN100</td>
<td>10-20</td>
<td>30.00</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>175Zn</td>
<td>ZN175</td>
<td>25-40</td>
<td>37.50</td>
<td>1.17</td>
</tr>
<tr>
<td>Marine</td>
<td>150IOZ/Type 6</td>
<td>LP3</td>
<td>10-20</td>
<td>29.00</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>100ZnS</td>
<td>ZN100S</td>
<td>10-20</td>
<td>35.00</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td>150ZnS</td>
<td>ZN150S</td>
<td>20-25</td>
<td>42.00</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>375ZnS</td>
<td>ZN375S</td>
<td>&gt;40</td>
<td>70.00</td>
<td>1.56</td>
</tr>
<tr>
<td>Severe</td>
<td>150IOZ/Type 6</td>
<td>LP3</td>
<td>10-20</td>
<td>29.00</td>
<td>2.42</td>
</tr>
<tr>
<td>Marine</td>
<td>100Zn/75HBE</td>
<td>ZN100+E75</td>
<td>10-20</td>
<td>38.00</td>
<td>2.53</td>
</tr>
<tr>
<td></td>
<td>275Al</td>
<td>AL275</td>
<td>20-25</td>
<td>63.00</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>325Al</td>
<td>AL325</td>
<td>25-40</td>
<td>70.00</td>
<td>2.18</td>
</tr>
</tbody>
</table>

**Repairs**

Some types of IOZ are self recoatable but generally only before they become fully cured. Repairs are usually made using an organic zinc rich primer before overcoating. When used as a stand alone system, eg as a tank lining or on a chimney stack, repairs to damaged IOZ require reblasting and reapplication. Repairs to TSC are similarly treated by patch painting, or sweep blasting to provide a clean profiled surface and reapplying. However TSC can be applied to itself which simplifies shop repairs where underbuilt areas are found.

**CONCLUSION**

Inorganic zinc, which was initially developed 60 years ago by Victor Nightingall as a long life field applied protective coating for steel with similar sacrificial properties to galvanizing, has now been fully developed by paint chemists. It has been widely used over the last 20 years in many forms, eg as a weld through shop primer, fuel tank lining and a high build offshore coating, but mainly as a base for high performance multicoat systems to protect many millions of square metres of steel.

Similarly, thermal sprayed coatings of zinc, aluminium and their alloys have been used for many years to give long life to steel components and structures. However recent developments in high deposition rate arc spray units, mean that specifiers now have an increasingly economic alternative to inorganic zinc silicate. When total life cycle costing is used for steel structures in aggressive environments and/or which are difficult to maintain, thermal metal spray is now likely to be the most cost-effective choice where a long life protective coating system is required.
ACKNOWLEDGMENT

The authors acknowledge the support and approval of Opus International Consultants Limited and Metalspray & Gritblast New Zealand Limited to present this paper. Also acknowledged is the support of Thermion Metalizing Systems Ltd of the USA.

FURTHER READING


National Thermal Spray Conference Proceedings published each year by ASM International.

T Cunningham, “Quality Control of Thermal Spray Coatings for Effective Long-term Performance”, JPCL Vol 13 No 1, January 1996.


National Thermal Spray Conference Proceedings published each year by ASM International.

(See also the International Metalizing Corporation Home Page at http://www.intmetl.com)

REFERENCES


2  R Snook, “Corrosion Control by Zinc Thermal Spraying”, Third World Congress on Coatings Systems for Bridges and Steel Structures, 1983.

3  F. Rogers & W. Gajecak “Cost and Effectiveness of Thermal Sprayed Coating with Zinc, Zinc-Aluminium, and Aluminium using a High Deposit Rate Machine”, SSPC Conference, San Diego, USA, November 1997.


GUIDES AND STANDARDS

The following is a list of the various guides and standards that are, or have been, used on metal spray projects:


BS 5493:1977, “Code of practice for protective coating of iron and steel structures against corrosion” (Section 11.2)

AS/NZS 2312:1994, “Guide to the protection of iron and steel against atmospheric corrosion” (currently under revision)
ANSI/AWS C2.18-93, “Guide for the Protection of Steel with Thermal Sprayed Coatings of Aluminium and Zinc and their Alloys and Composites” (currently under revision)


ASTM D4541-93 “Pull-off strength of Coatings using Portable Adhesion Testers”
INORGANIC ZINC SILICATE COATINGS
Chemistry and Protective Properties

E. Riding
JOTUN Australia Pty Ltd

1. Background.
Inorganic Zinc Silicate coatings were invented in Australia in 1930’s. This was a significant step in the use of liquid applied coatings that utilised silicon based chemistry rather than carbon based (organic) chemistry. Fundamental to the success of these coatings in the highly stable and strong silicon-oxygen bond which provides the very durable binder to form the coating film.

The use of zinc as a protective material for steel and iron was already well established and had been used for almost 100 years and in this development was being used as a finely divided pigment – typically 0.5 to 7 µm in diameter. Zinc provides corrosion protection in general corrosive atmospheres but is limited to environments with a pH range of approximately 6 – 10.

Alkali metal silicate solutions also had wider industrial applications for a similar period being used in adhesives, detergents, cleaners etc and were colloquially referred to as “water glass”.

In this development though long term Corrosion Protection became possible from a paint coating.

The film consists of finely divided zinc dust particles cemented together by a silica matrix. The silica is produced by precipitation of polysilicate from the silica solution.

The first development required post curing with heat but as the product type was refined ambient “curing” materials became available.

Typically the coating is applied in one coat at a dry film thickness of 75 µm.

The coating is applied over clean steel – usually abrasive blast cleaning in accordance with AS1627:4 class 2½ – although acid “pickling” was used for the original applications.

The formulation may have small amounts of reinforcing extender pigment eg mica, and organic binders to assist early film formation.

The progress of development of the system has resulted in two broad categories – water borne products and solvent borne products which were a later development and give greater tolerance of high humidity during application and curing. The solvent borne types require atmospheric moisture to react with in order achieve a “cured” state.

The two classes are very similar as a cured film and provide galvanic protection during initial service periods and also provide protection to exposed substrate when film is damaged during service.

2. Types of Coatings
The coatings are described by AS2105 – 1992 and are classified according to silicate type (and thus the curing mechanism).

Alkali metal silicate solutions are aqueous solutions of an alkali metal oxide (M₂O) and silica (SiO₂). The ratio of these two species expressed as the molar ratio of SiO₂ to M₂O determines the properties of the solution and thus the curing characteristics of coatings made from this solution. These solutions are highly alkaline and thus will react adversely with the zinc pigment and are therefore packaged in separate packs. The solvent borne materials are
typically acidic and are also packaged separately although they may be produced in a neutral phase and single package options have been developed.

*Classification by Silicate Type*

**Type 1**  Alkali metal silicate requiring elevated temperature for curing, typically 180 - 230 °C. 
Low ratio of silica:alkali metal oxide – approximately 2.5 - 3.0.

**Type 2**  Alkali metal silicate cured by application of an acidic solution. 
Intermediate ratio of silica:alkali metal oxide – approximately 3.0 - 3.5.

**Type 3**  Alkali metal silicate capable of curing at ambient conditions. 
High ratio of silica:alkali metal oxide – above 3.9.

**Type 4**  Solvent based alkyl silicate (usually ethyl) which cure by reaction with atmospheric moisture.

**Type 5**  Similar to Type 3 & 4 but applied at lower thickness (30 µm) and with lower zinc content and are used for temporary protection to preserve surface preparation (usually up to 12 months).

This standard is due to be re-issued as AS3750.15 and will also propose the inclusion of **Type 6** which is for Alkali metal silicate coatings with a higher ratio of silica:alkali metal oxide of 4.7. The principal intent is to describe products which achieve the water insoluble state in shorter times and have quicker curing schedules.

The original formulations for Type 1&2 products contained red lead which stabilised the mixture and minimised the undesirable side-reaction between the alkaline solution and zinc metal. This is not necessary in the higher ratio and solvent borne products but is often added for traditional reasons.

### 3. Important Physical Properties

The relevant physical properties are prescribed in AS2105 and are summarised in the table below.

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>Metallic Zinc Content (%$\text{w/w}$)</th>
<th>Abrasion Resistance (g/5000 cycles)</th>
<th>Possible Dry Film Thickness (µm)</th>
<th>Dry to Handle Time</th>
<th>Time to Water Insolubility (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>80</td>
<td>0.07</td>
<td>100</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Type 2</td>
<td>85</td>
<td>0.2</td>
<td>125</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Type 3</td>
<td>85</td>
<td>0.4</td>
<td>200</td>
<td>3 hours</td>
<td>3</td>
</tr>
<tr>
<td>Type 4</td>
<td>77</td>
<td>0.4</td>
<td>150</td>
<td>24 hours</td>
<td>1</td>
</tr>
<tr>
<td>Type 5</td>
<td>60</td>
<td>N/A</td>
<td>30</td>
<td>10 mins</td>
<td>N/A</td>
</tr>
</tbody>
</table>

In addition to these there are a number of properties which are important in the use of Inorganic Zinc Coatings.

Suitable for application to mating surfaces of friction-grip bolted connections; minimum friction coefficient requirement of AS4100 (Appendix J) is 0.35 - inorganic zinc
coatings are typically 0.45 - 0.60.

Suitable for use in environments with a pH range of 6 - 10 approximately.

Resistant to temperatures up to 400°C - tolerant of temporary excursions up to 540°C. Melting point of Zinc is 419 °C and Boiling point is 906 °C.

Virtually unaffected by UV radiation with excellent resistance to the most extreme weathering conditions.

Insoluble in a large range of organic solvents – caution is required for esters and halogenated solvents as these will produce acidic species with even low levels of moisture contamination.

Compatible with a wide variety of top-coats except alkyd/oleoresinous coatings which can be adversely affected by the alkaline nature of the film.

**Composition of Zinc Pigment**
In addition the quality of the Zinc Pigment is specified to meet the following requirements;

- Total zinc (as Zn).................98.0 % min.
- Metallic zinc (as Zn)............94.0 % min.
- Total lead (as Pb).................0.2 % max.
- Total cadmium (as Cd)..........0.1 % max.
- Total iron (as Fe)...............0.05 % max.
- Arsenic (As).....................0.0005 % max.

**4. Typical Coating Compositions (as formulated)**

<table>
<thead>
<tr>
<th>Water borne Coating</th>
<th>Item</th>
<th>% w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic Zinc (as Zn)</td>
<td>90.4</td>
<td>Note : 85 % in dry film &amp; 50 % v/v in dry film.</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Silicate</td>
<td>5.8</td>
<td></td>
</tr>
</tbody>
</table>
## 5. Protective Mechanism

The presence of the metallic zinc pigment provides galvanic protection initially and in the event of mechanical damage to the film. The oxidation potential for zinc is suitable for allowing zinc to corrode in preference to steel when suitably coupled together; viz

Standard Oxidation potentials are 0.763 V for Zinc and 0.440V for Iron ie. Zinc has a greater potential to react (Standard Oxidation Potentials measured at 25°C relative to Hydrogen Electrode).

This is brought about by the direct contact between the zinc particles themselves and also the steel substrate. Zinc coatings are able to provide protection even where the substrate is exposed due to mechanical damage. The surrounding film is still capable of providing sufficient galvanic action to prevent corrosion of the exposed steel – in most cases the damage is “sealed” with zinc reaction products and the substrate is further protected.

As the film is progressively exposed the outer surface is saturated with the by-products of the zinc reaction and a protective film is produced which retards the ongoing consumption of the zinc pigment. This zinc corrosion product layer is a complex mixture of oxides/hydroxides/carbonates that is highly stable and water insoluble and this allows the original film to remain substantially intact. The corrosion product is also sufficiently conductive to allow the metal to metal contact to remain effective even though less efficient than the original direct particle contact.

It is possible to observe in the cross section view of the film this corrosion product layer developing.

Another important property is the reversal of the protective mechanism by zinc at temperatures in the region of 60 – 70°C and this has given rise to premature failure under the appropriate conditions – typically this has been observed in hot dip galvanising situations.

There have been some attempts to improve the efficiency of the zinc pigment by utilising zinc in different forms,

1. Zinc / Aluminium alloys to improve anodic effect – this has been established in cathodic protection systems. However, the cathodic effect is not so critical and this option does not realise any benefits.

2. Flake zinc - improved particle contact. This option uses the dual advantage a high specific surface and large diameter flakes to improve the particle to particle contact. The possible reduction in zinc levels are significant with this approach but the cost penalty does not make this a viable option.

3. Atomised zinc dust – improved particle contact in larger particle size region. This uses particles with elongated egg-like shapes to improve contact but is also penalised by the
high cost of producing the particles.

4. Zinc coated microspheres – this approach uses hollow ceramic or polymeric spheres which have been impregnated with zinc particles. This allows the substitution in the film of large voids which still have good electrical contact to the rest of the film. There is a high cost penalty for the production of these particles but there is not yet sufficient data to determine the possible level of reduction and thus the viability.


Inorganic Zinc Coatings are capable of service for very long periods of time and this presents a difficulty in assessing the effect of changes to the formulation of a coating on the long term performance. The ability to correlate accelerated laboratory data with real service exposures remains a significant challenge.

1. Neutral Salt Spray as per ASTM B-117. This is a routinely used test to expose coatings to highly aggressive marine exposures. This has found some application in organic coatings but the results with inorganic zinc coatings have been highly unreliable and do not produce consumption patterns in the zinc particles which are consistent with normal exposures.

2. Aerated Tap Water. This test is difficult to standardise and this has made the larger application difficult – however, the pattern of zinc consumption can be readily correlated with real exposure with a common apparatus.

3. Cyclic Testing (Salt Spray/Weatherometer) -as per Lee Bone III: Materials Performance, November 1989. (Alternating one week cycles of Salt Spray and Atlas Weatherometer – operating on one hour on/one hour off cycle). This is gaining wider acceptance as a reliable method although the routine is complicated by the need to rotate the panels between the two test apparatus.

4. Prohesion Chamber ASTM G-85. (Alternating one hour cycles of Salt Spray/Drying). This method uses a modified application of standardised testing methods which give patterns of zinc consumption and film depletion consistent with natural exposures.

In summary Methods 2, 3 and 4 produce results more consistent with natural exposures with regard to the consumption of zinc and accumulation of zinc corrosion product. Method 2 is difficult to “standardise”. Method 3 requires 2 exposure chambers and regular rotation of panels. Method 4 provides a very straight-forward test method with very good correlation with real exposures.

7. Recoating Properties

A further important consideration in the overall usefulness of Inorganic Zinc Silicate coatings is the maintenance of film performance after extended service periods. Some recent study into the requirements for surface preparation have been carried out. In this testing panels of a Type 3 product (water borne Inorganic Zinc Silicate) which had received an initial exposure of 16 and 29 months were recoated with the same product after varying levels of preparation. The panels were then assessed for adhesion after 6 months exposure and thenafter a further 6 months exposure. The results of the intercoat adhesion testing is summarised in the following table.
Recoating After Extended Atmospheric Marine Exposure

<table>
<thead>
<tr>
<th>Period of Natural Exposure (months)</th>
<th>Method of Surface Preparation</th>
<th>Adhesion Rating * after further 6 months Exposure</th>
<th>Adhesion Rating * after further 12 months Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FRONT</td>
<td>BACK</td>
<td>FRONT</td>
</tr>
<tr>
<td>16</td>
<td>Brush</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>Wash</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>Wash &amp; Brush</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>Wash &amp; Sweep Blast</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>29</td>
<td>Brush</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>29</td>
<td>Wash</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>29</td>
<td>Wash &amp; Brush</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>29</td>
<td>Wash &amp; Sweep Blast</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

*Assessed in accordance with AS1580: Method 408.2

The results of this test programme indicate that the ultimate adhesion is virtually identical for all situations and provided the film is not subject to mechanical stress the adhesion will fully recover even where the initial adhesion is only fair. A significant feature of the results is the significantly more rapid stabilisation of the system on the back of the panels. This is most likely due to the greater accumulation of “salts” on this face and the more prolonged periods of condensation.

8. Conclusion

Although these materials have been available for over 50 years the full scope of their use is still not fully realised. The protective mechanisms and the difference to other sacrificial zinc coatings is becoming more fully recognised. The possibility of very extensive service lives is now a real possibility.
The Effect of Cure Temperature and Humidity on the Long Term Properties of Solvent-borne Zinc Silicate Coatings

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1.0 Introduction

Fifty years after their invention by Nightingall (1) an Australian engineer, inorganic zinc silicate coatings are widely used as primers to protect structural steelwork. Whilst the early products were water based alkali silicate products, the 1960’s saw the introduction of the self curing solvent borne ethyl silicate coatings. Today these coatings are the workhorse of the industry. One of their important virtues is that they typically develop resistance to rain within 30 minutes of application in contrast to the alkali silicate coatings which remain sensitive to water for up to twenty four hours and thus run the risk of being washed away.

Despite their many advantages, there is ample qualitative and anecdotal information indicating that alkyl silicates can form soft, friable coatings when applied and cured under conditions of low humidity (2). If they are then overcoated they are prone to delamination, commonly termed zinc splitting. This is particularly prevalent in the drier states such as SA and WA and seasonally in other states. The time to topcoating is also an issue to applicators.

Manufacturers unfortunately give little guidance on the subject. The data sheets provide statements such as:

"Premature topcoating may result in zinc splitting due to insufficient cure".

and

"If applied on hot surfaces or in conditions below 60% RH, hardness can be accelerated by hosing".

Given the importance of these coatings and their vulnerability in hot, windy conditions often encountered in Australia, there is surprisingly little information on the subject.

This paper summarises the results of some applied research carried out at SSL to determine the effects of climate during application and initial cure on the long term physical properties of the coating and consequently whether curing is significantly retarded or impaired at low humidities.

To achieve this, it was necessary to develop a method to monitor the curing of the ethyl silicate based coating chemically and relate the degree of cure to the physical properties of the coating.
In overview, the reaction is one where the partially hydrolysed ethyl polysilicate is converted to a silicate matrix. It is possible to follow the reaction by measuring the rate of change in the number of organic or ethoxy groups attached to the silicon atom \( (3,4) \). In this case we developed a gas chromatographic method to follow the reaction and the physical properties were determined by Taber Abrasion resistance.

2.0 Materials and Methods

2.1 Formulation

The ethyl silicate binder was produced by prehydrolysing commercially available Silbond 40 to 80%. The formulation is that based on that originally patented by McLeod \( (5) \) in 1968 and is the basis for most of the commercially available products. The formulation differs from commercial products in that thixotropic agents were omitted. Otherwise the binder represents a typical 80% prehydrolysed binder used by commercial manufacturers.

The binder was prepared by taking 45.0 g Silbond 40 and 49.8 g ethoxy-ethanol together with 5 ml of distilled water and 0.22 ml of 0.05 M HCl, 8.2 g zinc dust (Lysaght’s Standard Grade) was added to 5.08 g of 80% prehydrolysed alky silicate solution to obtain a zinc silicate paint similar to that produced by commercial manufacturers.

2.2 Following the Chemical Reaction

In theory the curing of ethyl silicate takes place in two distinct steps \( (6) \):

i) Hydrolysis

In an acidic solution water reacts with the alkoxy groups to produce silanol groups and ethanol \( (7) \). The reaction is rapid in such conditions and is the predominant reaction during the prehydrolysis step that occurs during the preparation of the binder.

\[
-\text{Si–O–Et + H}_2\text{O} = -\text{SiOH} + \text{EtOH}
\]

ii) Condensation

This involves the reaction of two silanol groups or an ethoxy group and a silanol group crosslinking with the production of either water or ethanol respectively \( (8) \)

\[
-\text{Si–OH + HO–Si} = -\text{Si–O–Si} + \text{H}_2\text{O}
\]

\[
-\text{Si–O–Et + HO–Si} = -\text{Si–O–Si} + \text{EtOH}
\]
This reaction will continue until all the silanol groups have condensed to form the silica matrix. The reaction is very slow in acidic solutions and only occurs at a realistic rate when the zinc is mixed with the binder. The zinc reacts with the residual acid to speed the reaction which occurs much more rapidly at an elevated pH.

Overall as the reaction proceeds, the ethyl silicate is converted to an inorganic silicate matrix. It was therefore possible determine the degree of cure by measuring the unreacted alkoxy groups using gas chromatography, whilst the silicon content was measured using a gravimetric method. Thus the ethoxy to silicon ratio and hence the degree of cure can be determined.

2.3 Physical Properties

To determine the physical properties of the film, the formulation was also applied by conventional spray to steel panels blast-cleaned to an AS 1627.4 class 3 finish (9). To ensure that the zinc dust remained in suspension the solution was constantly agitated in the spray gun during application.

Periodically panels were removed and the Taber abrasion resistance was determined in accordance with AS 2105-1980 ‘Inorganic Zinc Silicate Paints’ (10).

e) Curing Conditions

Immediately after application the zinc silicate coated panels were placed in the humidity cabinet under a range of cure conditions, and removed periodically to determine the alkoxy/silicon ratio and Taber abrasion resistance.

3.0. RESULTS AND DISCUSSION

3. 1 The Effect of Relative Humidity on Cure Rate

Once the coating had been applied it was cured for various periods, at either 80% RH, 60% RH or 40% RH at a constant temperature of 25°C. By keeping the temperature constant and varying the humidity it was possible to assess the effect of atmospheric moisture on the cure rate. Air flow was maintained at constant velocity across the curing film to preclude convection effects.

The results for the cure rate at different humidities (Fig. 1) show that the coating cures much more rapidly at 80% RH than at 60% RH and 40% RH. At 60% and 80% RH both coatings approach the same steady state cure conditions although at 60% RH the time taken is nearly three times as long. However, at 40% RH the degree of cure does not approach the steady state achieved at 60% RH and above even after a much longer period.

The physical properties as measured by Taber abrasion (Fig. 2) results show a strong correlation with those obtained for the alkoxy/silicon results at the same humidity. At 80% RH and 25°C the coating reaches its steady state maximum abrasion resistance after 30 hours whilst at 60% RH and 25°C the maximum abrasion resistance, which is slightly less than that cured at 80% RH and 25°C, is reached after 50 hours. A coating cured at 40% RH and 25°C, however, does not
approach the abrasion resistance achieved at the higher humidities even after 170 hours.

The results show that the extent and rate of cure are directly related to the relative humidity of the atmosphere to which the coating is exposed. More importantly they show that a coating cured at 40% RH (or less) and 25°C is unlikely to achieve a satisfactory cure and will remain soft and friable even after prolonged cure.

### 3.2 The Effect of Temperature on Cure Rate

The above results show that the relative humidity during application of ethyl silicate coating is critically important. Relative humidity by itself is not an absolute measure the amount of atmospheric moisture unless the temperature is known. (Relative humidity is defined as the ratio of the actual vapour pressure to the saturation vapour pressure at the same temperature.)

In order to gauge the effect of temperature on cure rate of these coatings, the absolute humidity was kept constant at 0.0115 g moisture/g of dry air whilst the temperature, and therefore the relative humidity, varied as follows:

- 20°C at 0.0115 g moisture/g dry air (80% RH)
- 25°C at 0.0115 g moisture/g dry air (60% RH)
- 32°C at 0.0115 g moisture/g dry air (40% RH)

A graph of alkoxy/silicon ratio versus time for the coatings cured under these conditions is given in Fig. 3. The rate of decrease of alkoxy groups is most rapid at 20°C and reaches a steady state maximum after 30 hours, whilst at 25°C the rate of decrease is slower but after 75 hours the alkoxy/silicon is similar to that at 20°C. At 32°C the rate of decrease is very slow and the alkoxy/silicon ratio does not drop below 0.4 even after 100 hours, indicating that at this temperature the coating is unlikely to achieve satisfactory cure.

The Taber abrasion resistance of the coating (Fig. 4) show a similar trend to that of the alkoxy/silicon ratio. As the Taber abrasion resistance increases (i.e. the coating becomes harder) the alkoxy/silicon ratio decreases. The results indicate that at constant moisture content, as the temperature increases the rate or extent of cure and the Taber abrasion resistance decreases.

These trials were carried out in the light of contemporary literature which suggests that interaction of atmospheric moisture with the film was the driving force for the curing of the coating. It was expected that an increase in the temperature would lead to an increase in the rate of hydrolysis and condensation reactions and hence the loss of alkoxy groups should be greatest at the higher temperature. It now appears that it is the rate of evaporation of the moisture from the film is the critical factor.

### 3.3. The Effects of Water Addition on Zinc Silicate Coatings

In practice it is frequently recommended that a fine mist of water be applied to alkyl zinc silicate coatings that have been applied under conditions of low humidity. In order to quantify the effectiveness of this practice it was decided to monitor the
effects of water addition to the zinc silicate coating some time after the start of cure, in this case 5 hours after, at both 80% RH and 40% RH with the temperature kept constant at 25°C.

The coatings were immersed for a period of 10 minutes in water after 5 hours in order to determine if a coating cured initially under 'poor' conditions could be redeemed by water immersion to improve the degree of cure and hardness of the coating. The effect of water immersion on the coating cured at 80% RH and 40% RH were compared, in terms of alkoxy/silicon ratio and Taber Abrasion resistance of the coatings (Figs 5 & 6).

After the coatings had cured at 80% RH for five hours, immersing them in water results in a significant decrease in the early alkoxy/silicon ratio and a corresponding early increase in the Taber abrasion resistance. However, after the coatings were cured at 40% RH, immersion did not result in any appreciable loss in the alkoxy groups or any change in the Taber abrasion resistance. This suggests that the film cured at 40% RH is dry and unreactive after 5 hours and has dried out much faster than a similar film cured at 80% RH.

Immersion of a coating in water after it has dried out does not measurably reduce the number of alkoxy groups or increase either the hardness or abrasion resistance. The physical and chemical condition of the coating after solvent evaporation has occurred appears to be irreversible. Indeed, attempts to improve the properties of a coating that has been cured under low humidity conditions by the spray application of water will only succeed if carried out prior to the coating drying out.

4.0. DISCUSSION & CONCLUSION

This work has shown that the atmospheric conditions prevailing during the initial reactive period of film formation of ethyl silicates are critical to the long term properties and performance of the coating. During this time the film formation is influenced by the rate of solvent evaporation, temperature and humidity.

An explanation of the results would appear to lie in the fact that during the curing process the film changes from a liquid to a solid and the reactivity of the components within the film must therefore change. In the liquid phase, before evaporation of the solvent is complete, the mobility of the reacting species allows the condensation and hydrolysis reactions to occur at a much faster rate than in the drier film where the mobility of the reacting species is severely retarded and the reaction proceeds more slowly, if at all. Thus, as the temperature increases even though the hydrolysis and condensation reaction rates increase, the rate of evaporation of the solvent also increases, and hence the film will dry out more quickly and be reactive for a shorter period.

What is not generally realised is that the condensation which occurs when the zinc dust is mixed with the ethyl silicate binder produces further water within the coating. This allows the hydrolysis reaction to proceed on mixing and application. At high humidities the water produced is slow to evaporate off and the coating is reactive for much longer. Whereas at low humidities this water evaporates much quicker thus
drying out the coating much quicker and the amount of reaction is significantly reduced.

At a higher a temperature of cure at constant atmospheric moisture content, both the water and the organic solvent evaporation rate increase. The film therefore, has less time to react with either atmospheric moisture or the water released from the condensation of silanol groups before the cure reaction ceases.

5.0 RECOMMENDATIONS

It is vital to monitor or control the temperature and humidity during the initial application and curing of the ethyl silicate coating. Low humidities and/or high temperature will adversely affect the long term properties of the coating. The higher the temperature or lower the humidity the shorter the time available to rectify the situation.

In practical terms, hot, dry or windy conditions need to be avoided during application and drying if an inorganic alkyl zinc is to achieve its performance potential. If this is not possible the coating would need to be sprayed with water before the coating completely dries out. Friable zinc silicate coatings are intractable and cannot be reconstituted thus they must be removed.
FIGURE 1
Degree of Cure vs Time
at Constant Temperature

- 80% RH & 25 C
- 60% RH & 25 C
- 40% RH & 25 C

FIGURE 2
Taber Abrasion Resistance vs Time
at Constant Temperature

- 80% RH & 25 C
- 60% RH & 25 C
- 40% RH & 25 C
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8 R. Richardson, J.A. Waddam, Research 7, 542 (1954)
9 Australian Standard A.S 1627, 'Abrasive Blast Cleaning of Steel Surfaces' Part 4, Standards Association of Australia, Sydney, Australia, 1974
10 Australian Standard A.S 2105, 'Inorganic Zinc Silicate Paints', Standards Association of Australia, Sydney, Australia, 1974
SUMMARY: Zinc silicates and organic zinc rich primers are compared and a proposal made to achieve good anti-corrosive performance, together with controlled application.

INTRODUCTION

The important position of zinc dust based priming paints in structural steel protection is well documented and has been increasingly used over the past few decades, becoming more prevalent with the development of more user friendly silicate binders and surface preparation by blasting.

The basic precept behind using zinc primers is the belief that they will provide protection to the substrate by electrochemical means, i.e. they will act as sacrificial anodes to protect damaged areas of coating. This is very much the understood function of galvanising but with this, as with zinc based coatings, an electrolyte needs to be present to allow the following reaction to take place.

Also, the zinc coating of whatever type needs to be in contact with the steel and to be accessible to the electrolyte.

In the years of oil based film forming resins it was generally difficult to formulate zinc based coatings because of the propensity for the zinc to cause saponification of the polymer. Synthetic resin polymers such as vinyls and chlorinated rubbers did allow primers to be formulated, but again these had limited use.

ZINC SILICATES

In the structural steel protection industry, the advent of zinc silicates started to give the first major move to zinc primers because of a number of features:-

1. Extremely high zinc dust levels possible (and necessary)
2. Excellent adhesion to blasted steel.
3. Extremely good durability and corrosion resistance.

Zinc silicates can be pigmented above the CPVC (Critical Pigment Volume Concentration). At this level with most polymer systems a severe loss in properties occurs. The converse is true in zinc silicate.

Although the first major project with zinc silicate was undertaken in Australia, the bulk of the subsequent development to give the current high ratio water based alkali silicates and the solvent based ethyl silicates was undertaken in the U.S.A. Interestingly, in Europe the bulk of application of zinc primers was undertaken with zinc epoxy primers (raw material supplier influence - a wish to take a different approach or an unwillingness to learn how to handle a new technology?).

Without doubt all around the world I believe that zinc silicate, used as single coat systems at around 75 microns d.f.t., have outperformed similar thicknesses of zinc epoxy in both laboratory testing and in the field. This can be quite easily understood but does bring us to some loose talking, which goes on in many parts of the paint industry, i.e. zinc primers are almost always referred to as “zinc rich” coatings, although I am not too sure what this means and the definition does appear to vary from country to country, and standard to standard. Secondly, the zinc level in the film is always referred to as weight percentage, although this actually means little in terms of accessibility of the zinc, and is
actually much more relevant to galvanising where reference is often made to the weight of zinc per unit area.

Epoxies have become popular as binders for high zinc level paints in many areas because:

1. They can be pigmented with high levels of zinc dust and are chemically stable to the environment created by zinc, i.e. alkaline. However, it is not possible to achieve good films when pigmenting above the CPVC.
2. They show good adhesion to steel.
3. They are compatible with high performance paint systems.

The difference in single coat performances becomes obvious when two high zinc loaded coatings are studied, one organic, one inorganic. The key physical difference is in the S.G. of the respective binders, typically 2.5 for the cured silicate and around 1.1 for the cured epoxy. Table 1 illustrates the situation for dry films of commercially available products with 90% w/w zinc dust.

<table>
<thead>
<tr>
<th></th>
<th>Zinc Silicate “86% Zinc”</th>
<th>Zinc Epoxy “90% Zinc”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Dust</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>12.68</td>
<td>12.68</td>
</tr>
<tr>
<td>Additives</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>0.50</td>
</tr>
<tr>
<td>Binder</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>8.18</td>
</tr>
<tr>
<td>% Zinc by Volume</td>
<td>75.5%</td>
<td>60.6%</td>
</tr>
<tr>
<td>Pigment Volume Concentration</td>
<td>78.5%</td>
<td>64.7%</td>
</tr>
</tbody>
</table>

Clearly from the above the zinc silicate has a significantly higher level of zinc dust present by volume than the epoxy, and a simple consideration of pigment packing shows the zinc to be in particle/particle contact throughout the film and to the steel.

It is interesting to consider various compromises which may be required in formulating zinc silicates and zinc epoxies. As mentioned previously, zinc silicates (primarily ethyl silicates) must be formulated at very high pigment loadings, above the Critical Pigment Volume Concentration, and thus the film contains many voids. Pigmenting below this level makes through cure difficult and also leads to cracking (mudcracking) due to film stresses. The rate of cure (degree of polymerisation of the silicate binder) can affect the tendency to mudcrack with fast curing systems showing the greatest propensity. Similarly, the more binder present the easier to overcoat but the greater the likelihood of mudcracking. However, with a high zinc level, high humidity during curing and a prolonged time of weathering, the zinc particle - zinc particle contact virtually guarantees good anti-corrosive performance (especially as a single coat).

With a zinc epoxy the formulation is below the CPVC and the zinc level and actual PVC can have a massive influence on performance. Very high zinc loadings, in the order of 92% w/w zinc dust in the dry film, were used at one time in order to maximise the chance of zinc/zinc particle contact and hence obtain galvanic protection. Examples of this could be found in a number of major oil company specifications and in a number of national standards, e.g. British Standard BS.4652 which specified 62-66% PVC for a zinc paint of which a very high percentage was required to be zinc dust.

These high levels of zinc can in fact down-grade the overall performance of a system in terms of adhesion, overcoatability, mechanical strength, corrosion creep from damaged areas, and overall these factors can outweigh any short term benefits likely to be achieved from possible cathodic protection.

Although zinc silicate based systems have an excellent track record in all parts of the world, and have given service lives often well in excess of 10 years on offshore structures, features of the chemistry
involved can cause severe problems in some painting processes. For example, in offshore structure construction in many parts of the world the full coating system is applied at the end of the fabrication process. Curing times are paramount, and as the curing for the widely used solvent based zinc silicates is humidity dependent, this can be very difficult to control and thus production is difficult to plan. Further difficulties are caused by the correct use of ASTM D4652 as a curing check and adhesion pull-off testing to ASTM D4541 as a final quality check. Instances of poor curing of zinc silicate and consequent difficulties in touch-up at the “hook up” stage of new construction are well known. It is interesting to note that outside of North America because zinc silicates are generally overcoated when fresh rather than weathered, then a sealer coat is used, to “fill up” the porosity and prevent pinholing of topcoats.

It can be readily understood from the data previously presented why zinc silicates can perform so well, and as single coat systems so much better than organic zinc primers. A programme of work has been undertaken to compare the performance of both single and topcoated inorganic and organic zinc primers to attempt to confirm our general expectation of a single coat system and evaluate the effect of topcoating.

To this end a small number of zinc primers were evaluated, two long standing commercial products with long track record and good performance in the field, and the other an experimental single pack moisture cured polyurethane. Relevant data is shown in Table 2.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>% Zinc by Weight</th>
<th>% Zinc by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Ethyl Silicate</td>
<td>86.0%</td>
<td>68.3%</td>
</tr>
<tr>
<td>Zinc Epoxy</td>
<td>90.0%</td>
<td>60.6%</td>
</tr>
<tr>
<td>Zinc Polyurethane</td>
<td>88.0%</td>
<td>52.0%</td>
</tr>
</tbody>
</table>

**Testing as Single Coats**

Accelerated testing in ASTM B117 Salt Spray and ASTM G85 Prohesion testing was undertaken. Photographic records are shown in Appendix 1. Also, E.I.S. (Electric Impedance Spectroscopy) testing was performed (Method - Appendix 2). Results are shown in Appendices 1-1 and 1-2. Assessment has concentrated on the “scribe” or damaged area. As might be expected, in salt spray testing to ASTM B117 the zinc silicate showed best performance, however, when the wet/dry cycle Prohesion test is used then differences become much less apparent. Similarly, with E.I.S. it is clearly obvious that the zinc silicate gives a much longer electrochemical effect than the organic zinks. All of these results confirm the effectiveness of zinc silicate as a single coat system (Figure 1, Appendix 3).

**Topcoated Zinc Primers**

When even a thin topcoat is included (e.g. 60 microns of an aluminium pigmented polyurethane) then differences become much reduced. This can clearly be seen from the accelerated test results shown in Appendices 1-1 and 1-2. Again, concentrating mainly on the damaged area, differences in the amount of steel corrosion are much reduced and in some cases the zinc epoxy based system appears to show less corrosion than the zinc silicate. Again, in this case, the E.I.S. results confirm the accelerated test results with very little difference being observed and readings being difficult to obtain in most cases.

**High Build Anti-corrosive Systems**

A second stage of work was then started and is still underway. In this case high build epoxy topcoats were applied to both the zinc silicate and zinc epoxy. At the time of writing, testing has been underway for around 300 days and results are shown in Appendix 5 for accelerated testing and external exposure and Appendix 6 for electrochemical testing.

Basically, at this time, although there is clear evidence from the E.I.S. measurements of micropores in the coating, there is no evidence of any varying effects from the primers as insufficient electrolyte is
present. This result is repeated in both ASTM B117 Salt Spray and Prohesion testing, where there is no sign of any face breakdown on any test panels after testing for in excess of 7,000 hours. This is not an unusual feature for high performance coating systems and to attempt to show differences between systems normally careful and thorough examination of the “scribe” or damaged area is made. Here the criteria is the amount of underfilm creep or corrosion spreading back from the scribe, and a numerical assessment can easily be made. Typically, assessments in the case were made visually and then finally by removal of the coating and assessing the corroded area. No significant differences could be observed between the zinc epoxy and zinc silicate primers.

It is worth digressing here slightly in considering the mechanism of protection of zinc primers at damaged areas in practice. Generally here damage is caused by impact or gouging and not cutting with a sharp object. In this type of damage the relatively soft zinc metal can be left in the blast profile and give a degree of protection for a period, depending on the environmental conditions. In some instances, fully cured zinc silicates can give excellent protection in this situation, however, if curing is poor the barrier coating is very easily removed along with most of the zinc primer which, in this instance, has very low cohesive strength.

An attempt has been made to evaluate the amount of zinc left on steel surfaces following gouging impact, as this is where zinc coatings have traditionally been believed to give excellent performance.

The three zinc primers previously described with and without topcoats were all subjected to gouging impact. The areas of impact were then photographed by scanning electron microscopy and were also subjected to XRMA for elemental mapping. Photographs are shown in Appendix 8, and XRMA traces in Appendix 9.

The results can be summarised as follows. With untopcoated panels the zinc silicate leaves significantly more zinc present on the surface - the comment from the Analytical Department being that this looked like galvanising - whereas the other materials did leave some zinc on the surface but, in this instance, just a few discreet spheres and quantitatively much less. This result is very much in keeping with the traditional belief that single coats of zinc silicate are by far the most effective anti-corrosive system when moving structural steel around, giving better damage resistance than organic zinc primers.

However, when the zinc primers are topcoated and then subjected to gouging impact, little evidence of any difference is present, suggesting that:

1. The present of organic topcoat on the zinc silicate helps pull the whole from the surface. or

2. Most likely that the zinc silicate when topcoated relatively quickly may not gain the ultimate properties which can be achieved after time. Consequently it appears similar to the epoxy and polyurethane systems.

The second of these scenarios is the situation which happens with zinc silicates in many parts of the world outside of the U.S.A., i.e. all coats are applied together. Perhaps this is why the possible advantages of zinc silicates are not as clear in other regions.

CONCLUSION

This work has confirmed the well recognised performance of single coats of zinc silicate in a variety of tests, however, it has also illustrated and started to quantify what many Protective Coatings Technologists and coatings users have long suspected, i.e. that when high zinc containing primers are used as the basis of a barrier coating system little differences can be discerned between inorganic and organic polymer based materials. Forecastable film strength, adhesion, lack of mudcracking and pinholing act cumulatively to give consistently high performance, along with an economic painting process.
One further interesting feature to note, is that with current technology it does appear unlikely that viable solvent based zinc silicates with less than 250 g/l solvent can be formulated. It has been possible for many years to formulate zinc epoxies at less than 250 g/l solvent albeit these were often slow curing and somewhat impractical products. However, recent epoxy curing technology has allowed both fast curing and low temperature curing zinc rich epoxies to be formulated which meet the strictest environmental legislation currently enacted, without the possible complications of using water based systems.

ACKNOWLEDGEMENT

The efforts of Angela Walsh - Department of Chemistry, University of Newcastle upon Tyne, on undertaking the electrochemical investigations, and those of Peter Turnley of Courtaulds Coatings have been essential to this project.
APPENDIX 2

Impedance Spectroscopy Test Procedure
All impedance measurements were performed using a Solartron 1255 frequency response analyser coupled to a Solartron 1286 electrochemical interface and controlled by a Viglen 486 microcomputer. The frequency range employed was between 100 KHz - 10 mHz at an amplitude of ±5 mV. A three electrode cell design was used for all measurements, using a saturated calomel reference electrode, a stainless steel counter electrode and the steel substrate as the working electrode. All spectra were recorded at the open circuit potential in a 0.5 M CaCl₂ electrolyte under normal aerated conditions at a temperature of 23±2°C.

Impedance measurements upon the non-overcoated primers were performed after 1 hour immersion and then at intervals of approximately 7-10 days. For the overcoated (standard and high build) samples the impedance was recorded after 1 day’s immersion and then at intervals of approximately one month. Each time an impedance spectrum was recorded, the more simple one-point gain phase response was also measured using a custom built meter. The open circuit potential, using a high impedance digital voltmeter, was recorded every 3-5 days for the non-overcoated primers and every 7-10 days for the overcoated samples.
### APPENDIX 5

<table>
<thead>
<tr>
<th>Material</th>
<th>Coating</th>
<th>Environment</th>
<th>Test</th>
<th>Exposure</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild Steel</td>
<td>Zinc Plating with Top Coat</td>
<td>High Build</td>
<td>1,112 Hours</td>
<td>Cross Section</td>
<td>None</td>
</tr>
<tr>
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<tr>
<td>Mild Steel</td>
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<td>High Build</td>
<td>7,112 Hours</td>
<td>Cross Section</td>
<td>None</td>
</tr>
</tbody>
</table>
INORGANIC ZINC SILICATES AS  
SINGLE-COAT  
PROTECTIVE SYSTEMS FOR STEEL

INTRODUCTION

In 1937, Victor C. Nightingall, from his Melbourne laboratory, gave us an amazing protective coating that became the most important tool in corrosion mitigation since the invention of galvanising in the 1850s. Like galvanising, it is a single-coat process, that is elegantly simple yet versatile in its use, that provides effective, long term protection yet is cost efficient. Since its invention, its use spread to all corners of the world, attaining an unbeaten track record in protecting steel surfaces in environments ranging from mild rural to severe marine.

This extraordinary invention was the for-runner of what we now refer to as the:

Single-Coat Inorganic Zinc Silicate (IZS) Protective Systems

It is timely to discuss this topic now, because last year was the 50th anniversary of Victor Nightingall's death and the 60th anniversary of patenting his discovery. It is also very appropriate because it is an opportunity to increase awareness of this very important corrosion mitigation system amongst such an eminent group of facility owners, designers, specifiers, suppliers, contractors and corrosionists, all of whom are, or should be, endeavouring to reduce the cost of corrosion to their own advantage and the economic benefit of this great country of ours.

Evidence will be presented showing that the single-coat IZS systems not only yield a significant cost advantage; but they also deliver an unequalled long-term performance. I hope that it will give you absolute confidence about specifying, recommending and using these systems for the protection of steel surfaces exposed to a wider range of environments than you may have been prepared to consider in the past. Even though the title of this paper suggests a generic approach to the subject, I'll be using the protection of marine structures and steel bridges to illustrate the technically and economically beneficial attributes of the single coat IZS systems.

Most of the information presented is based on personal experience with the utilization, application and performance of IZS coating systems, as well as on the results of some recent work, commissioned by BHP Integrated Steel, which included an international literature survey and the assessment of coating performance on some 30 steel bridge structures in Victoria.

Before we go any further, I should make it clear that I am not promoting any specific product made by any particular paint manufacturer; but rather a generic group of protective coatings, namely the Inorganic Zinc Silicates.

I'll be mostly using this generic term to cover all the types of inorganic zins, including the waterborne (WB- IZS), the high ratio (HRZ) and the solvent borne zinc silicates (SB-IZS), because, field experience suggests that there is no significant difference in their performance when used as single-coat systems.

You may ask then, why do seemingly very different coatings perform in such a similar manner. The answer lies in their chemistry. Even though we start off with somewhat different base resin binders, once the binder is mixed with the zinc powder and the mixture is applied to a steel surface, and the intrinsic chemical reaction are allowed to take place to their completion, ie., full cure, the final composition and chemical structure is exactly the same in each case. This is well illustrated by the much simplified process of the chemical reactions that take place in the following two examples:
**DISCUSSION**

**Laboratory Testing.**

We will begin with discussing the laboratory testing program that compelled me to keep promoting single-coat IZS systems whenever and wherever I am presented with the opportunity.

The laboratory testing program was to provide comparative performance data on the then new high ratio inorganic zinc (HRZ) when used as a single-coat system, compared with the other types of IZS coatings, as well as a number of multi-coat systems based on IZS primers. In particular, we wanted to know whether the single-coat HRZ systems would be suitable for protecting oil and gas production facilities in marine environments. We selected a total of 23 systems (11 single coat zinc and 12 multi-coat) to be included in the laboratory test program. Each system was applied, by spray, to three abrasive blasted panels, two for testing and one for retention as control. After curing for at least one week, a 100mm long scribe, made on a milling machine, penetrating through the coating and 0.13mm into the steel substrate, was vertically centred on each test panel.

The panels were exposed in an Atlas Weatherometer and then in a salt fog cabinet for sequential, one week (168 hours) periods until the total of 2500 hours was reached, after which the lower half of the scribe area only, was abrasive blasted on a selected number of panels, then repaired with a system recommended by the manufacturer. All panels were then returned for another 2500 hours of the same cyclic testing.

**Evaluation Criteria**

For evaluation of the results we adopted a method that gave a numerical rating to each coating feature, such as hardness, adhesion, blistering, pitting and undercutting. The lower the total number of attained evaluation points, the better the performance.

**Discussion of Results**

Whilst the laboratory testing program has generated a large amount of information, I’ll highlight only the results related to the most important features of coating performance here:
Dry Film Thickness
Thicknesses were found unchanged after the test exposure.

Hardness
Whilst the pre-exposure hardness was found to range between 400 and 1000P, all hardnesses were >2000P after exposure.

Adhesion:
Pre and post-exposure adhesion values in the case of the single-coat zinscs remained practically the same. The multi-coat systems showed mixed results, but mostly adhesion seemed to have deteriorated.

Undercutting/Pitting:
Only panels coated with multi-coat systems were found to have tight to severe pitting and undercutting. The single coat HRZ systems, on the other hand, were completely free of all undercutting/pitting.

Summary of Final Rating

Once the assessment was completed, the results compiled and the evaluation points assigned, they were added up for each system as shown in the table below. The smaller the total number of points, the better the performance:

The results of that study are supported by work performed elsewhere as is indicated by:

1. **Letter in 1992 from Steve Pinney**, who worked for NASA in the early '70's and was involved in developing the first HRZ coating; here is part of what he says:
   "...we (NASA) have a rack of panels with one coat of Ioz directly on the ocean since 1970. They still rank 10's. Their top coated counterparts left to the ground after about seven years exposure, I anticipate at least another 10 years out of the single coat concept. "

2. **Conversation with David Ellis, Materials Officer, E. W & S.** Materials Sciences Group, who is responsible for the corrosion prevention maintenance on the famous Morgan-Whyalla pipeline. David said:
   "...I have noticed that panels coated with a single coat IZS only, showed no signs of any corrosion after years of exposure. On the other hand, panels coated with IZS based multi-coat systems have developed significant undercutting and general corrosion. I put this difference in performance, down to the fact that the single-coat IZS film was 40-50 microns thicker than the zinc film in the multi-coat system. .. "

3. **Technical paper from Norway**, "Selection and experience with different pipeline coatings" written by Dr, Svein Eliassen states;
   "...Testing in our laboratory indicated, however that systems with aluminium metal spray performed better than aluminium metal spray plus a heavy duty coating. The testing were primarily salt spray tests,... "

---

**Details of Coating Systems Tested**

<table>
<thead>
<tr>
<th>Generic Type</th>
<th>DFT, Microns</th>
<th>No. of Test Panels</th>
<th>Total Number of Evaluation Points(1)</th>
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<tbody>
<tr>
<td></td>
<td>Min.</td>
<td>Max.</td>
<td>Average</td>
</tr>
<tr>
<td>HRZ</td>
<td>150-200</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>HRZ</td>
<td>60-90</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>IZS-WB(2)</td>
<td>60-90</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>IZS-SB(3)</td>
<td>60-90</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>HRZ + Top Coats</td>
<td>200-490</td>
<td>10</td>
<td>65</td>
</tr>
<tr>
<td>IZS-WB + Top Coats</td>
<td>235-340</td>
<td>4</td>
<td>103</td>
</tr>
<tr>
<td>IZS-SB + Top Coats</td>
<td>235-490</td>
<td>10</td>
<td>93</td>
</tr>
</tbody>
</table>

(1) The smaller the total number of points, the better the performance.

---

30-03-98 A & A Szokolik Consulting Pty Ltd

    "The untopcoated inorganic zinc has performed well to date (8 years exposure). The
topcoated systems have not performed as well. This correlates accelerated corrosion tests
performed in the lab."

    "In a separate location after a near-white blast cleaning, the surface received only a 25-50
micron DFT (IZS) coating .... After the first year the area displayed freckle rust, ... in the five
years since there has been no further degradation. .. "

5. **Technical Paper, "Inorganic zinc-rich coatings and galvanizing: a comparison",** by Gordon
Brevoort, states:

    "...in an 11 year test fence evaluation of a variety of zinc-rich systems, untopcoated zinc-rich
primers gave overall superior rust and scribe undercutting resistance at a marine exposure
site..."

6. **Technical Paper, "Inorganic zinc-rich"** Nov. 1996, by Harlan Kline, states:

    "The mechanism of protection...is most effective for untopcoated inorganic zinc-rich primers...
One-coat untopcoated inorganic zinc is often used for tank lining, structural steel...and refinery
facilities in marine atmospheres..."

Clearly, the results produced by our study are not a once-off phenomenon, because people from
round the world are reporting that untopcoated IZS systems substantially outperform topcoated
systems in laboratory and field exposure tests. In a moment we will have a look whether this excellent
performance shown in tests and panel exposures does in fact translate into long term performance on
real life structures. But before we do that, perhaps we should ask:

**WHY IS IT SO?**

The evidence presented in relation to the superior performance of untopcoated IZS coating systems
leads naturally to the following questions:

1. **Why do IZS coatings perform so well?,** and

2. **Why do untopcoated IZS coating perform so much better than top coated zinzcs?**

Perhaps the most efficient way to answer the first question is by quoting the world-renown authority on
protective coatings, C. G. Munger;

    ...a review of the chemical characteristics of inorganic zincs, their general and chemical
resistance is extremely good compared with metallic zinc by itself. This characteristic simply
can not be overemphasized since galvanizing has been a standard of corrosion resistance
since the beginning of this century. .... One of the most significant properties of inorganic zinc
coatings is the cathodic protection they provide. . ....an added increment of protection to
damaged areas of coating. An inorganic zinc coating, being completely inorganic, is
unaffected by weathering, sunlight, ultraviolet radiation, rain, dew, bacteria, fungus, or
temperature. Zinc silicate coatings provide. . ....adhesion by the inorganic binder chemically
reacting with the underlying steel surface. . ... This is the property responsible for the
effectiveness and life of the coating in addition to the prevention of undercutting of the coating
by corrosion.

There has been no specific research (to the Authors' knowledge) carried out to produce a definitive
answer to the second question. An untested but reasonable hypotheses is offered as the most logical
answer.

As stated before, IZS coatings provide cathodic protection so that when the coating is damaged, any
exposed steel surface (depending on the size of the exposed area) will be protected as long as there
is available metallic zinc in the film to continue the cathodic reaction. In the case of untopcoated IZS
systems, that zinc is available from the entire external surface of the zinc film as indicated in Fig. 1. It
can be readily seen that the ratio of exposed steel area to the area of coating from which zinc is
available is almost infinitely large.
When such a breach in a top coated zinc system is examined, Fig. 2, it is evident that the exposed cross-section of the zinc film is relatively small. Consequently the small amount of zinc available for the cathodic reaction is rapidly consumed. The zinc corrosion products form an insulating barrier between the remaining zinc particles in the film and the exposed steel substrate, and render it ineffective in terms of cathodic protection. The steel corrosion products may add to the insulating effect.

This theory, which is based on results from all the comparative testing and data from much field experience then leads to the following conclusions:

first, that the cathodic protective ability of zinc in a topcoated state seems to be impaired when the coating system is breached by damage, and

second, that topcoating does not increase the life expectancy of the underlying zinc, on the contrary, it seems to significantly reduce it.

Review of Application and Performance in the Field

We have seen that IZS single-coat systems performed significantly better than most multi-coat systems. We should now review their behaviour in the field.

HRZ Performance

The HRZ coatings need to be singled out here because they are relatively new to the Australian market and because the original study was specifically undertaken to evaluate the HRZ coatings. Their application characteristics and performance in service were assessed at locations along the Southern and Eastern seaboard of Australia, both on new construction and in maintenance painting. Over 100,000 litres of HRZ coating have been applied during the past 6-7 years, on projects such as:

- Two new oil & gas production platforms for the Bass Strait, the steelwork was blasted and coated at Newcastle, Sydney and Wollongong.
- The repainting of the marine woodchip loading facility at Eden.
- Maintenance painting of several offshore platforms in the Bass Strait.

The performance in service of single-coat HRZ, observed during the past 8 years, closely reflects the excellent results obtained in the laboratory testing program. It is interesting to note that as a result of our original study, the Oregon DOT (USA) is now specifying HRZ single-coat systems for the protection of their steel bridges.

Application Characteristics

The application characteristics were assessed both in a shop/yard environment and in maintenance painting situations. Some HRZs suffered from recurring cure-related problems, consequently, three of the original five HRZ coatings tested, were dropped from use. Their manufacturers, at that time, were not able to make the necessary formulation changes that would have produced the desired characteristics needed for problem-free application. Since then, one manufacturer has made those changes and has released the product to the market place.
The field application assessment results clearly indicate that if a well formulated HRZ coating is accepted for what it is, namely a sophisticated, water borne, heavy duty inorganic zinc silicate, and if the appropriate care is taken to be aware of the changes in the conditions during application so that the necessary adjustments can be made to the application techniques, then the application will be as easy as the application of any other type of sophisticated, high-performance coating. Still, it is appropriate to provide some guide lines that will promote trouble-free application, for example:

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>Application Condition</th>
<th>Optimum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface Temp., °C</td>
<td>RH, %</td>
</tr>
<tr>
<td>HRZ</td>
<td>5 – 45</td>
<td>25 – 90</td>
</tr>
<tr>
<td>IZS-SB</td>
<td>5 – 45</td>
<td>40 – 90</td>
</tr>
</tbody>
</table>

(1) For optimum drying DFT should be <150µm and wind speed should be 1.5m/sec.

The prevailing ambient conditions (including the surface temperature) can affect the drying/curing process, during and immediately following the application of water-borne inorganic zinc silicate coatings. The influence of the prevailing ambient conditions can be eliminated or at least minimised to a point of irrelevance by following a few simple guidelines.

The drying/curing rate is a function of the relative humidity, the ambient and the surface temperatures. In other words, low temperatures and high humidity impede, whereas high temperatures and low humidity enhance water (removal) evaporation from the coating. Once this principle is understood, the conditions controlling the drying process can be exploited by lengthening shortening – or completely eliminating the “flash-off” time between coats* thus ensuring that the film dries and cures properly under almost any conditions.

* Note that “coats” in this instance, means two separate passes; the first one having a thickness of about 40 - 60µm.

Case histories

To further boost our confidence, we will have a quick look at some notable case histories of various types of IZS single-coat applications:

**Morgan-Whyalla Pipeline and Bridges** - Baked or air-cured, IZS-WB, 75 microns. Much of the coating is still in an excellent condition after some 50 to 55 years service.

**Drilling Mud Tanks** - Barry Beach Marine terminal, 75 microns of IZS-WB, in perfect condition after 20 years service in marine environment.

**Ballast Tank roofs** - Long Island Point, Fractionation Plant, 75 microns of IZS-SB, in perfect condition after 20 years service in marine environment.

**Okinawa Refinery** - 75 microns of IZS-WB, 15 years to first maintenance.

**Gas Plant 3, Longford** - 75 microns of IZS-SB, in perfect condition after 20 years service in marine environment.

**Power Generation Facilities, Latrobe Valley** - Structural steelwork. 20-25 years service in industrial environment.

**Bridges** - The results of a coating status survey on some 37 bridges in Victoria are summarized in the following Table:
Clearly, there is any amount of evidence for us to say that single-coat IZS systems are indeed able to provide truly long term protection to steel surfaces in a host of different environments, ranging from mild to severe.

Just as a matter of interest, galvanising has an admirable and longer track record, by virtue of having been around since the 1850’s; but it needs to be pointed out that IZS systems can significantly outperform galvanising in severe environments. For example, on an offshore platform below the cellar deck, galvanising is completely removed within 1.5 to 3 years; in contrast, the IZS keeps on keeping on. The reason for this is that the zinc particles in an IZS film are encased in an inert silica resin matrix, galvanising on the other hand is pure zinc metal which can go into solution very easily when exposed to more corrosive electrolytes.

**Cost**

We have thus far covered all the technical aspects of the single-coat IZS systems and the only remaining important factor to be considered is the cost. Whilst it is an important factor, it should not be the main factor upon which a coating system is selected. It is important that by the time the specifier arrives at the point of considering costs in the coating selection process, all technically unsuitable coating systems need to have been eliminated. In other words, there should be only a few systems with proven track records of long-term protection that are subjected to the required economic evaluation process. This process considers the following costs:

**Initial cost** - Include surface preparation, coating application, inspection and repairs at the time of construction, and

**Maintenance cost** - Include the total cost (in terms of Net Present Value) of all painting operations during the structure’s life. They take into account the number and frequency of maintenance inspections and applications.

However, only the **life-cycle cost**, which is the sum of the initial and the maintenance costs, should be used to compare the real worth of proposed coating systems for particular environments.

The quickest and easiest way to illustrate the cost advantages offered by the single-coat IZS system, is by way of examples. Following are details of comparative costing, both initial, maintenance and life-cycle, of an HRZ system and an HRZ/HB-Epoxy/2P-Acrylic system, on a structure, such as a bridge for example, with a ‘design life of 100 years:
1. **Initial Costs:**

<table>
<thead>
<tr>
<th>COST ITEMS/ACTIVITIES</th>
<th>1 x HRZ</th>
<th>3 x coats</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unloading &amp; setting up</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>Abrasive blasting</td>
<td>695</td>
<td>695</td>
</tr>
<tr>
<td>Primer application, top side</td>
<td>340</td>
<td>298</td>
</tr>
<tr>
<td>Primer application, reverse side</td>
<td>427</td>
<td>375</td>
</tr>
<tr>
<td>HRZ material</td>
<td>380</td>
<td>320</td>
</tr>
<tr>
<td>Touch-up handling marks (day 2)</td>
<td>63</td>
<td>---</td>
</tr>
<tr>
<td>Load-out (day 2)</td>
<td>94</td>
<td>---</td>
</tr>
<tr>
<td>Epoxy coat, top side (day 2)</td>
<td>---</td>
<td>152</td>
</tr>
<tr>
<td>Turn &amp; epoxy coat, reverse side (day 3)</td>
<td>---</td>
<td>214</td>
</tr>
<tr>
<td>Epoxy material</td>
<td>---</td>
<td>395</td>
</tr>
<tr>
<td>Sand &amp; top coat, top side (day 4)</td>
<td>---</td>
<td>152</td>
</tr>
<tr>
<td>Turn, top coat reverse side (day 4)</td>
<td>---</td>
<td>246</td>
</tr>
<tr>
<td>2-pack Acrylic material</td>
<td>---</td>
<td>385</td>
</tr>
<tr>
<td>Load-out (day 5 or 6)</td>
<td>---</td>
<td>141</td>
</tr>
<tr>
<td>Total:</td>
<td>2076</td>
<td>3450</td>
</tr>
</tbody>
</table>

$/m^2$: 25.95 43.12

Rounded off to ($/m^2): 26 43

**Notes:**
2. DFT: HRZ = 100-150um & 3 coats = 225-345um.
3. Costs based on blasting and coating 80m2 steel surface.

2. **Maintenance Costs (Including Access etc., Costs)**

![Single-coat IZS System in Marine Environment](image)

![Multi-coat (IZS/Epoxy-MIO) System in Marine Environment](image)

**Notes:**
1. The 'site difficulty' denotes the degree of difficulty associated with a particular site. The difficulty is categorised as: 'EASY', 'MODERATE' and 'HIGH'. The differences between the categories can be illustrated by the following example:
   - **EASY** = Simple scaffold only required. Plain, easy to get to surfaces, etc;
   - **MODERATE** = Special scaffold and/or cranes are needed. High traffic volume, etc;
   - **DIFFICULT** = Gantry and/or special cranes are required. Moderately intricate surfaces. Site is very remote.
   A check list of cost factors that influence site difficulty and should be considered when calculating maintenance costs for life-cycle costing, is provided in the table below.
2. Years after construction of structure. The '0' denotes the year of construction, it allows the inclusion of the initial cost ($/m²) of painting and its use as the basis for the maintenance painting costs.

3. Cost/m² of steelwork ($/m²). The first figure in the column is the initial cost of the particular coating system. The other figures in the column are the weighted cost/m² applicable to a particular site depending on its degree of difficulty. This cost is the sum of the initial cost and a specific cost/m² for that site, e.g., 'EASY' site = initial cost + $12; 'MODERATE' site = initial cost + $36; 'DIFFICULT' site = initial cost + $60.

4. Net Present Value (NPV) calculated as NPV = Cost/(1 +DR/100)^Years
   Recommended Discount Rate (DR) for Victoria is 8%. (Based on the Economic Planning and Advisory Committee (EPAC) report for Private infrastructure Task Force, 1995)

5. The life-cycle cost ($/m²/100 years) is the sum of the initial, and all maintenance costs during the 100 year design life of the structure.

### Cost Factor Checklist for Site work

<table>
<thead>
<tr>
<th>Access (to work face)</th>
<th>Site Allowance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accommodation</td>
<td>Site Cleanup</td>
</tr>
<tr>
<td>Containment</td>
<td>Site Establishment</td>
</tr>
<tr>
<td>Demobilization</td>
<td>Transport/travel</td>
</tr>
<tr>
<td>Design (ie., surface configuration etc)</td>
<td>Waste Disposal</td>
</tr>
<tr>
<td>Equipment Hire</td>
<td>Weather</td>
</tr>
<tr>
<td>Mobilization</td>
<td>Work Restrictions (Traffic etc)</td>
</tr>
<tr>
<td>Safety (Public Protection)</td>
<td></td>
</tr>
</tbody>
</table>

### 3. Inspection/Painting Requirements at Each Major Maintenance Intervention

<table>
<thead>
<tr>
<th>System No</th>
<th>INSPECTION: Type and Scope Details</th>
<th>MAINTENANCE PAINTING: Surface Preparation/Application Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single coat IZS</td>
<td>Thorough visual. Identification of isolated defects or areas of breakdown. Comprehensive DFT checks. Determination of remaining zinc in film. (2)</td>
<td>Thorough high pressure fresh water wash, spot blast corroding areas, touch up and apply a 100 - 125 µm IZS refresher coat.</td>
</tr>
<tr>
<td>Multi-Coat IZS/ Epoxy MIO</td>
<td>Thorough visual. Identification of defects or areas of breakdown. Comprehensive DFT checks. Encompassing adhesion tests (to cover the various structural segments and surface orientations).</td>
<td>Thorough high pressure fresh water wash, spot blast corroding areas, touch up with primer and intermediate coat and apply a100 - 125 µm E-MIO refresher coat to the entire surface.</td>
</tr>
</tbody>
</table>

### Notes:

1. Maintenance intervention intervals vary according to the environmental conditions applicable to the site and the type of coating system being applied. Since the intervals are an integral part of the cost calculation they are given in the life-cycle cost tables below.

2. In the case of inorganic zinc silicate coatings, DFT values are not a measure of the amount of zinc depleted from the film. Where long term protection is an essential requirement it is important to know the amount of available zinc remaining in the film, since it determines the length of effective protection that the film can provide. The amount of zinc remaining in the film can only be determined (with any degree of accuracy) in the laboratory. It is therefore recommended that a number of test coupons (made of the same material as the structure) are coated with the same system as the structure and attached to the structure (during construction) in the following orientations: vertical, horizontal-top and horizontal-underside. Sufficient sets of coupons are installed on the structure to allow the removal of one set of coupons, during each major maintenance program, for the determination of the amount of zinc remaining in the film.

### Summary of Benefits

- Long term performance (40-50 years), even in severe environments, provided corrosivity is not outside the pH6 - pH12 range.
- Low annual cost.
- Cost savings - from less labour/material requirements and reduced inventory.
- Fast cure and water resistance (HRZ & SB-IZS)
Early hardness (HRZ)
Handling - much reduced, is faster and easier.
Application procedures - much simpler.
More work per unit time.
Rapid turn-around of work in shop.
Scaffolding - stay per location reduced by one third.
Very high reduction in amount of handling, transport and erection damage and a consequent reduction in repair needs.
Recoatability & topcoatability
Amount of maintenance required much reduced.
Maintenance techniques - are simple and easy.

CONCLUSIONS

In conclusion, there are volumes of data and evidence to indicate that single-coat IZS’s are superior in performance to multi-coat systems and are cheaper both initially and over the life of the structure. Of course, I am not saying that the IZS coatings are the panacea for every corrosion mitigation problem that has ever confronted you. But in my view they are very much under utilised despite their technical effectiveness and cost efficiency. Less effective and costlier systems are often used simply because “that is how we done things for years” and besides it does not interfere with our “comfort zone”.

So I hope that your awareness and your confidence has been raised sufficiently for you to be comfortable with specifying and using single-coat inorganic zinc silicate systems for the protection of steel bridges and other structures. I am absolutely convinced that if you start specifying and using these systems, you will be well satisfied with the results.

REFERENCES

COMPLETE SPECIFICATION.

"Improvements in and connected with silicated compositions."

I, VICTOR CHARLES JOHN NIGHTINGALL, Consulting Engineer, of 79 Mount Street, Heidelberg, in the State of Victoria, Commonwealth of Australia, hereby declare this invention and the manner in which it is to be performed, to be fully described and ascertained in and by the following statement:

This invention relates to improvements in and connected with silicated compositions and refers especially, but is not limited, to the formation of protective coatings from materials containing soluble silicates and finely divided metals (particularly zinc) such coatings being applicable to the surfaces of metal, glass, concrete and other materials. The invention also comprehends the formation of articles of manufacture from materials of the same general character.

It has been previously proposed to employ mixtures containing soluble silicates and finely divided metals as cements, paints and the like.

It has also been proposed to form protective and like coatings on metals by applying thereto a mixture containing water glass and finely divided aluminium or magnesium or alloys thereof, such coatings being alloyed to the base metal by a subsequent heat treatment.

Now, the object of the present invention is to provide improvements in the formation of coatings and moulded bodies from mixtures containing silicates and finely divided metals and/or compounds thereof.

The invention broadly resides in forming a coating by applying an aqueous solution of silicate and a finely divided metal or metals and/or compounds thereof to a surface and converting the mixture to a substantially insoluble condition in the presence of carbon dioxide.

For this purpose the coated article may be heated in an atmosphere of CO₂ to facilitate the conversion of the coating to a substantially insoluble condition.
Alternatively, the coating material may contain a suitable bicarbonate (preferably alkaline bicarbonate) which is capable of releasing CO$_2$ upon the application of heat to the coating. A suitable carbonate having similar properties may be used in lieu of or in addition to the bicarbonate.

A salient form of the invention resides in the use of a coating material containing zinc dust, sodium silicate and sodium bicarbonate.

For some purposes the coating material may advantageously contain basic oxides or hydroxides (e.g. magnesium oxide and calcium hydroxide) in conjunction with or independently of a suitable carbonate or bicarbonate according to the nature of the surface to be treated.

Another feature of the invention, which is particularly applicable to the formation of firmly adherent coatings on metals and glass, resides in the use, in the coating mixture, of a borate, such as borax.

A modification of the invention resides in incorporating a finely divided reagent, such as graphite, in the coating to impart antifriction properties thereto.

The ingredients may be mixed together and then applied to a surface as by spraying, brushing or dipping, or alternatively the metallic powder and the liquid vehicle may be applied separately to the surface or may be admixed in a spray immediately prior to being applied to the surface.

The coating so applied is allowed to set and, except in the circumstances hereinafter described, is then heated to a temperature usually above 200°F., for a sufficient time to convert the coating to a substantially insoluble condition.

When the coating mixture contains basic oxides or hydroxides, in addition to zinc and sodium bicarbonate, it is not essential to heat the coating in order to convert it to the substantially insoluble condition.

Moulded bodies may be formed from the materials above referred to and subsequently rendered substantially insoluble as above indicated and hereinafter described.

Other features and objects of the invention are set forth in the ensuing detailed description of practical applications thereof.

**Example 1.**

A vehicle suitable for applying coatings to iron, steel and glass was prepared from the following ingredients:

- 100 parts by vol. of aqueous solution of sodium silicate (water glass) about 1.4 specific gravity.
- 12 parts by vol. of an aqueous solution of sodium bicarbonate which solution is substantially saturated at 60°F.
- 6 parts by vol. of an aqueous solution of borax, said solution being substantially saturated at 60°F.

These ingredients were intimately mixed at normal temperatures and in the order stated. Such mixtures have been found to be stable for prolonged periods.

This liquid vehicle was then intimately mixed with an equal part by weight of commercial zinc dust and the mixture was then immediately brushed, in a like manner to paint, onto a lightly oxidised steel sheet, a specimen of wood and a specimen of glass.

The surfaces of the test pieces were previously treated to remove any oil or grease therefrom as it had been found that same are detrimental to the formation of satisfactory coatings.

Plaster of paris had previously been rubbed into the surface of the wood specimen to fill the pores thereof and provide a foundation for the coating.

The coated specimens were then allowed to stand at normal temperature for a period of six hours during which time the coatings became set.

The coated specimens were then subjected to heat treatment in an oven. In the case of the sheet of steel, the temperature of the oven was 450°F. and the duration of the treatment was 2 hours.

The specimen of wood was subjected to a temperature of 80°F. for a period of 2 hrs, whilst the specimen of glass was subjected to a temperature of almost 700°F., for a period of 2 hrs.

At the conclusion of the respective heat treatments the specimens were allowed to cool and the coatings thereon were then washed with warm water to remove soluble alkali therefrom.

It was found that in each case the finished coating was insoluble or practically insoluble in both cold and boiling water and that the
The finished coatings, when produced as above described, are dull in appearance, but a metallic lustre may be imparted thereto by rubbing same as with a wire brush at the conclusion of the heat treatment and before the coatings are allowed to become cool.

In lieu of or in addition to zinc dust, I may employ finely divided alloys of zinc (particularly magnesium-zinc and aluminium-zinc) and/or any other metal powders.

Furthermore, potassium bicarbonate or other bicarbonate may be substituted for sodium bicarbonate or alternatively any suitable carbonate such as sodium, potassium or magnesium carbonate may be used. It is preferred, however, to employ sodium or potassium bicarbonate.

The above-mentioned composition and method may also be employed for coating concrete, plaster ceramic and other materials and compositions. However, in the formation of coatings on concrete, plaster and other like materials having a silica-lime base, the omission of borax from the coating mixture does not materially affect the satisfactory character of the coating.

Furthermore, even in the treatment of iron, steel and glass surfaces, it is not essential to include borax in the coating mixture, though its presence, under such circumstances, assist the formation of a more resistant and more tenacious coating.

If the bicarbonate is omitted in the above-described example, the coating may be converted to a substantially insoluble condition by carrying out the heat treatment in an atmosphere of CO₂. The coatings so produced, however, are less firmly adherent and less homogeneous than those containing the bicarbonate.

Coatings suitable for some purposes may also be formed by substituting finely divided metallic oxides and/or metallic carbonates for the bulk of the finely divided metal. In general, however, the coatings so formed do not present a metallic appearance and do not possess marked protective properties.
**EXAMPLE 2.**

A liquid vehicle was prepared from the ingredients and in the manner described in Example 1. The liquid vehicle was then sprayed onto the surface of a lightly oxidised steel sheet which was free of oil and grease. A coating of zinc dust was then sprayed onto the layer or film of the liquid vehicle whereby a mixture thereof was formed in situ and the coated sheet was allowed to stand for a period of several hours until the coating had set.

The coated sheet was then heated in an oven for a period of 3 hrs. at a temperature of 450°F. and after removal from the oven it was allowed to cool and was then washed with warm water.

The coating produced in this way was generally similar in appearance and properties to the coating formed on the steel sheet referred to in Example 1.

This procedure has the advantage that it avoids the mixing of the zinc dust and the liquid vehicle before same are applied to the surface to be coated.

Alternatively the zinc dust and the liquid vehicle may be simultaneously applied to the surface preferably by means of a spraying device in which separate streams of the vehicle and the of the zinc dust are intimately mixed.

In general it may be stated that different ingredients of the coating mixtures described herein may be separately applied to a surface to form the requisite mixture in situ or said ingredients may be admixed in a spray immediately prior to their application to the surface.

**EXAMPLE 3.**

To a liquid vehicle prepared in the manner and from the ingredients described in Example 1, there was added about 10% by weight of a mixture of approximately equal parts of magnesium oxide and calcium hydroxide.

This example was used as described in Example 1—that is to say, it was intimately mixed with an equal part by weight of zinc dust and was then brushed onto the surface of a steel sheet.

The coated sheet was allowed to stand at normal temperature for a period of 12 hrs. at the conclusion of which it was found that the coating had been converted to the substantially insoluble condition. The inclusion in the mixture of magnesium oxide and calcium hydroxide had obviated the formation of a significant proportion of soluble alkali in the coating and it was therefore unnecessary to wash it as in the foregoing examples.

This composition is therefore particularly useful in circumstances where it is inconvenient or impracticable to subject the coated article to heat treatment.

Furthermore, owing to the absence of substantial amounts of soluble alkali in the coating, it is particularly suitable as a base for a paint or other finish coat.

Whilst as above stated it is possible to dispense with the heat treatment when magnesium oxide and calcium hydroxide are included in the mixture, it is preferred, when practicable, to employ the heat treatment in order to consolidate the coating.

It will be clear from the foregoing that it is not essential to include borax in the mixture, particularly when it is desired to form the coatings on concrete and plaster.

Furthermore, where magnesium oxide and calcium hydroxide are used in the mixture, quite satisfactory coatings may be formed on concrete even if the bicarbonate is omitted. This result is probably due to the presence of sufficient carbonates in the concrete surface.

The proportions of magnesium oxide and calcium hydroxide may be varied considerably and either may be used without the other. Other basic oxides and hydroxides may also be employed in substitution for or in addition to magnesium oxide and calcium hydroxide.

**EXAMPLE 4.**

A liquid vehicle was prepared in the manner and from the ingredients specified in Example 1.

A corresponding proportion by weight of zinc dust was then intimately mixed with the vehicle and in addition a proportion of commercial powdered graphite equal to 4% by weight of the zinc, was incorporated therein.

The mixture was then brushed thickly onto the surface of a strip of spring steel after which the coated strip was subjected to a heat treatment at a temperature of 450°F. for a period of 12 hrs.
The coatings so produced had antifriction and corrosion resisting properties.

This form of the invention is particularly suitable for the formation of coatings on the leaves of automobile suspension springs. Such coatings may also be advantageously employed on other sliding parts and shaft bearings.

The proportion of the graphite and the quality thereof may vary within fairly wide limits depending largely on the purpose for which the coating is required. In the case of lead springs the proportion of graphite may advantageously be about 4% by weight of the zinc, as in the above described example, though 10% or more could be used if desired. In the case of a coating for a shaft bearing, the proportion of graphite may, in some cases, be as low as or even less than 0.5% by weight.

In lieu of mixing all the ingredients before applying them to the articles to be treated, the graphite and/or zinc dust may be sprayed onto the articles either after the liquid vehicle has been applied thereto or simultaneously with the application of the liquid vehicle. Furthermore, the zinc dust and graphite may be admixed and may be applied to the surface without previous admixture with the liquid vehicle.

Lead-bearing protective coatings may be formed by employing finely divided suboxide of lead (Pb₃O) preferably containing an appreciable proportion of metallic lead, in lieu of the zinc dust referred to in the preceding examples, the preparation and application of the material and the heat treatment of the coating being carried out substantially in any manner already described. The temperature at which the heat treatment is carried out when lead suboxide is used may advantageously be in the region of 200°F., though this temperature may be varied considerably. Preferably the coating is rubbed as by means of a wire brush immediately following the heat treatment and before it has cooled materially.

A further application of the invention resides in the formation of sound absorbent coatings for various purposes, such e.g as on the interior surfaces of steel panels employed in the bodywork of closed motor vehicles.

In this application of the invention it is preferred to use a smaller preparation of the metallic coating agent and to incorporate in the mixture one or more ingredients such as cork dust, the presence of which will conduce to the formation of a softer coating.

It has previously been indicated that the compositions and methods of this invention may be employed in the formation of articles of manufacture. For example, a mixture prepared substantially in the manner described in preceding Example 2 may be placed in a mould of suitable shape, such material then being preferably but not necessarily subjected to a high pressure to increase its density and to cause it to closely conform to the contour of the mould.

The pressed article is then permitted to dry at a relatively low temperature following which it is subjected to a heat treatment as previously described in order to complete the reaction and convert the material from a water-soluble to a substantially water-insoluble condition. If desired, an inert filler may be included in the mixture.

This form of the invention is applicable to the manufacture of relatively thin articles, such e.g. as stereotype blocks, liners for bearings, and the like.

In a modification the ingredients may be mixed preferably with an excess of water, the mixture then being permitted to dry or set. The dry mixture is then broken up into a granular or powdered condition and is used as a thermo-setting composition which may be placed in moulds, compressed and converted to the substantially insoluble condition upon the application of heat thereto.

Though preferred forms of the invention have been described herein, it will be obvious that modifications and variations within the general spirit and scope thereof may be readily effected by those skilled in the art and I therefore do not wish to be understood as confining this specification to the particular examples and proportions previously described as I desire the specification to be accorded the widest interpretation consistent with the advance made in the art.

Having now fully described and ascertained my said invention and the manner in which it is to be performed, I declare that what I claim is:

1. In the formation of silicated compositions preparing a mixture comprising a finely divided metal and/or metal compound
and an aqueous solution of a silicate and converting the mixture to a substantially insoluble condition in the presence of carbon dioxide.

2. In the formation of silicated compositions, preparing a mixture comprising a finely divided metal and/or metal compound and an aqueous solution of a silicate and a suitable bicarbonate or carbonate and heating the mixture.

3. In the formation of silicated compositions, preparing a mixture comprising finely divided zinc, an aqueous solution of a silicate and an alkaline bicarbonate.

4. In the formation of silicated compositions, preparing a mixture comprising one or more finely divided metals, an aqueous solution of a silicate and a bicarbonate and drying said mixture.

5. The formation of silicated compositions according to any preceding claim wherein the said silicate comprises sodium silicate and/or potassium silicate.

6. The formation of silicated compositions according to any preceding claim wherein approximately one to two parts by weight of said finely divided metal or metals and/or compounds thereof is used for each part of the said solution.

7. The formation of silicated compositions according to any preceding claim wherein the mixture is heated to a temperature of about 200°F. or more.

8. In the formation of silicated compositions, preparing a mixture comprising finely divided zinc and an aqueous solution of sodium silicate and sodium bicarbonate and heating the said mixture, the sodium silicate and sodium bicarbonate being approximately in the proportion of 100 parts by vol. of aqueous solution of sodium silicate 1.4 specific gravity to 12 parts by vol. of aqueous solution (saturated at 60°F.) of sodium bicarbonate.

9. In the formation of silicated compositions, preparing a mixture comprising one or more finely divided metals and/or compounds thereof, an aqueous solution containing a silicate, a bicarbonate or carbonate and a borate, and drying the said mixture.

10. In the formation of silicated compositions, preparing a mixture comprising one or more finely divided metals and a liquid vehicle containing a soluble silicate, a bicarbonate or carbonate and borax.

11. In the formation of silicated compositions, preparing a mixture comprising one or more finely divided metals and/or oxides and/or carbonates thereof, finely divided graphite or the like and an aqueous solution of a silicate.

12. The formation of silicated compositions according to Claim 12, wherein a bicarbonate is included in the said mixture.

13. The formation of silicated compositions according to Claim 12 or 13, wherein a borate is included in the said mixture.

14. The formation of silicated compositions according to Claim 12 or 13, wherein borax is included in the said mixture.

15. The formation of silicated compositions according to any ofClaims 10 to 15 inclusive, wherein the said mixture includes one or more basic oxides and/or hydroxides.

16. The formation of silicated compositions according to any of Claims 10 to 15 inclusive wherein the said mixture includes magnesium oxide and/or calcium hydroxide.

17. The formation of silicated compositions according to any of Claims 10 to 15 inclusive wherein the said mixture includes magnesium oxide and calcium hydroxide together being approximately equal to 10% by weight of the liquid vehicle.

18. The formation of silicated compositions according to any of Claims 10 to 15 inclusive wherein magnesium oxide and calcium hydroxide mixed in approximately equal parts by weight are included in the mixture.

19. The formation of silicated compositions according to any of Claims 10 to 15 inclusive wherein the mixture is heated to a temperature of about 200°F. or more.

20. In the formation of a coating on a surface, providing on the surface, a mixture containing an aqueous solution of a silicate, and one or more finely divided metals and/or compounds thereof, and converting the coating to a substantially insoluble condition in the presence of carbon dioxide.
22. In the formation of a coating on a surface, providing on the surface a mixture containing an aqueous solution of a silicate, a bicarbonate or carbonate and one or more finely divided metals and/or compounds thereof, and converting the coating to a substantially insoluble condition.

23. In the formation of a coating according to Claim 21 or 22, heating the said coating to a temperature of about 200°F. or more.

24. In the formation of a coating on a surface, providing on said surface a mixture containing zinc dust, a solution of sodium silicate and a bicarbonate and subjecting the coating formed thereby to heat treatment in order to convert same to a substantially insoluble condition.

25. The formation of a coating according to any of Claims 22 to 24 inclusive wherein the said ingredients are intermixed prior to applying them to the said surface.

26. The formation of a coating according to any of Claims 22 to 24 inclusive wherein the finely divided metal and/or compound thereof is applied to the surface separately from the application thereto of the other ingredients.

27. The formation of a corrosion-resisting coating on iron or steel according to any of preceding Claims 21 to 26 inclusive.

28. In the formation of a coating on a surface, providing on the surface a mixture comprising one or more finely divided metals and/or compounds thereof, an aqueous solution containing a silicate and a borate and converting the coating to a substantially insoluble condition in the presence of carbon dioxide.

29. In the formation of a coating on a surface, providing on the surface a mixture containing one or more finely divided metals and/or compounds thereof, finely divided graphite or the like and an aqueous solution of a silicate and a borate and converting the coating to a substantially insoluble condition in the presence of carbon dioxide.

30. The formation of a coating according to Claim 28 or 29 wherein sodium or potassium bicarbonate is dissolved in the said solution.

31. The formation of a coating according to Claim 28, 29 or 30, wherein the said silicate comprises sodium or potassium silicate.

32. The formation of a coating according to any of Claims 28 to 31 inclusive, wherein the said coating is heated to convert same to said substantially insoluble condition.

33. The formation of a coating according to any of Claims 28 to 32, wherein a borate is included in the said coating.

34. The formation of a coating according to any of Claims 28 to 32, wherein borax is included in the said coating.

35. In the formation of a coating according to any of the Claims 28 to 34 inclusive, incorporating one or more basic oxides and/or hydroxides in the mixture.

36. In the formation of a coating according to any of the Claims 28 to 34 inclusive, incorporating magnesium oxide and/or calcium hydroxide in the said mixture.

37. In the formation of a coating according to any of the Claims 28 to 34 inclusive, incorporating magnesium oxide and calcium hydroxide in the mixture in approximately equal parts by weight.

38. In the formation of a coating on a surface, providing on said surface a mixture containing zinc dust and a solution of sodium silicate, sodium bicarbonate and borax, and heating the said mixture.

39. In the formation of a coating on a surface, providing on said surface a mixture containing zinc dust, finely divided graphite and a solution of sodium silicate, sodium bicarbonate and borax, and heating the said mixture.

40. The formation of a coating according to Claim 38 or 39 wherein said sodium silicate, sodium bicarbonate and borax are provided approximately in the following proportions:–,

100 parts by vol. of aqueous solution of sodium silicate 1.4 specific gravity.

12 parts by vol. of aqueous solution (saturated at 60°F.) of sodium bicarbonate; and

6 parts by vol. of aqueous solution (saturated at 60°F.) of borax.

41. The formation of a coating according to Claim 38, 39 or 40, wherein approximately one to two parts by weight of zinc dust is used for each part of said solution containing sodium silicate, sodium bicarbonate and borax.
42. The formation of a coating according to any of Claims 28 to 41 inclusive wherein the said mixture is heated to a temperature of about 200°F. or more.

43. The formation of a corrosion-resisting coating on iron or steel according to any of preceding Claims 28 to 41 inclusive.

44. In the formation of a coating on a surface, providing on said surface a mixture containing zinc dust and an aqueous solution of alkaline silicate, magnesium oxide and calcium hydroxide.

45. In the formation of a coating according to Claim 22, 28 or 38, incorporating an inert filler in the said coating mixture.

46. In the manufacture of moulded bodies, compressing in a mould a mixture in accordance with any of Claims 1 to 7 inclusive, and subjecting the compressed material to heat to convert same to a substantially insoluble condition.

47. In the manufacture of moulded bodies, compressing in a mould a mixture in accordance with any of Claims 10 to 19 inclusive, and subjecting the compressed material to heat to convert same to a substantially insoluble condition.

48. In the formation of articles, preparing a mixture in accordance with any of Claims 1 to 7 inclusive, drying the mixture and converting the dried mixture to a granular or powdered condition for use as a thermosetting moulding material.

49. In the formation of articles, preparing a mixture in accordance with any of Claims 10 to 19 inclusive, drying the mixture and converting the dried mixture to a granular or powdered condition for use as a thermosetting moulding material.

50. A silicated composition produced in accordance with any of Claims 1 to 9 inclusive.

51. An article provided with a coating produced in accordance with any of Claims 21 to 27 inclusive.

52. A silicated composition produced in accordance with any of Claims 10 to 20 inclusive.

53. An article provided with a coating produced in accordance with any of Claims 28 to 45 inclusive.

54. The method of forming a coating on an article substantially as hereinbefore described.

55. The method of forming a silicated composition substantially as hereinbefore described.

Dated this 16th day of July, 1937.

VICTOR CHARLES JOHN NIGHTINGALL.

By his Patent Attorneys,
CLEMENT HACK & SON, ASHTON & WHITE.

Witness—N. Lambert.
ZINC-SILICATE TYPE COATINGS

C. L. O'NEILL

It is proposed to discuss the merits of Zinc-Silicate Coatings, but, in particular, the specific coatings manufactured by Dimet Pty. Ltd. These coatings are applied in Australia under the trade name “Galvanite”. They are long-term corrosion resistant zinc coatings which give a performance equivalent to high quality hot-dip galvanising. Protection is given by a galvanic mechanism.

COMPOSITION

Galvanite is not made of the salt “Zinc Silicate” but is essentially a mixture of metallic zinc powder in a sodium silicate vehicle. Most of the zinc remains in metallic form. Galvanite is not a “Zinc-rich Paint” which has an organic vehicle. Zinc-Silicate coatings are entirely inorganic and therefore not subject to degradation by ultra-violet light.

METHOD OF APPLICATION

Like all other high quality long-term coatings, surface preparation is very important. and particularly so for the Zinc-Silicate type. Top quality acid-descaling, or sand or grit blasting, is required. Blasting is by far the best preparation as it gives a fully cleaned and roughened surface for maximum adhesion. With blasting there is no limit to the size of the object which can be prepared and there is the added advantage that work can be carried out in-situ.

The Galvanite is applied cold, as is paint. The pigment and vehicle are mixed just prior to application and the mixture is normally applied by brush and spray, but occasionally by dipping or pouring. The water content normally dries from Galvanite within a few minutes, but the coating is still soluble at this stage. To render the coating insoluble, one of the two following methods is adopted-

1. For normal factory-applied coatings the work is baked in an oven for several hours at 400°F. There is uniform heating and cooling and therefore no danger of distortion of fabricated steel articles. Even multi-vane fan runner blades may be treated without losing the balance of the fan.

2. Curing by the application of a chemical solution to the dried coating is a more recent advance which has superseded earlier unreliable air-dried methods. The solution is merely brushed or sprayed on and the coating is rain-proof within a few minutes. This method opens up reliable field treatment which is a necessary adjunct to the baking type.

Principal applications for the curing type “Galvanite” is on reinstatement of field welds, large objects too big for transport to the works, or any other objects which for some reason cannot be baked.

Well formulated chemical curing types are suitable for most applications for which the baking type is used, including sea-water immersion. They have the same corrosion resistance as the baked coating.

GENERAL RESISTANCE

Galvanite has an excellent resistance to atmospheric weathering. One of the first commercial jobs ever carried out with this type of coating was by Dimet in 1942/3 on the Morgan to Whyalla pipeline in South Australia. This 240 mile pipeline is still in excellent condition following only its original application of one coat.

It is also very suitable for marine atmospheres and immersion, and also has good anti-fouling properties.

Being wholly inorganic, it has an excellent temperature resistance. Good performance can be obtained over long terms at temperatures of 750°F. Short periods up to 1100°F also do not affect the coating.

It is resistant to continuous immersion in neutral and alkaline salts and also is unaffected by organic solvents and petroleum products.
It has a light grey matt finish, is very tough, and has such excellent adhesion that it must be blasted or ground away if it has, by necessity, to be removed from a coated surface.

Galvanite is completely non-combustible at all temperatures, has good thermal conductivity due to the intimate contact between the metallic zinc particles. This property, together with its corrosion resistance, makes the coating very suitable for heating or cooling coils where maintenance of high heat transfer rates is necessary.

**NUMBER OF COATS**

Usually only one coat is applied and is at the rate of approximately 1.0 oz. zinc per sq. ft. of surface area. Two coats are advised for continuous marine immersion.

**WELDING AND BRAZING**

The coating may be welded and brazed readily. The strength of the weld is not impaired in any way by the presence of the zinc. Due to the heat resistance of the coating there is also very little damage to coated areas immediately adjacent to the weld.

**APPLICATIONS**

Typical types of work to which these coatings are applied are as follows:

Pipes, pressure vessels, refrigeration equipment, fans, ducting, window frames, trash screens, steel chimney stacks, wrought iron work, road and rail tankers, shipping, marine buoys, storage tanks, structural steel, etc.

**GALVANITE COMPARED WITH GALVANISING AND METAL SPRAYING**

(The factors mentioned do not necessarily apply to both galvanising and metal spraying.)

With Galvanite–

(i) there is no heat distortion in the treatment of complex fabricated articles,

(ii) work of any size can be treated as both baking and chemical cure types of Galvanite are available,

(iii) the coating is applied evenly over the surface, without dross or dag formation. This is most necessary when free contact must be maintained between mating surfaces, e.g., on opening sashes of steel window frames,

(iv) field reinstatement, if necessary, may readily be carried out with the same type of coating.

(v) Galvanite compares very favourably in cost with competing materials. For example, for equivalent protection by zinc metal spray, the cost would be approximately 50% more. (As Dimet also uses metal spraying, such comparative costs are readily obtained.)

This coating was invented in Australia and is now being applied in the United States under licence. The fact that during 1958 five times the quantity of zinc-silicate coatings was applied in the U.S.A. compared with Australia, is ample evidence of its unique character and use in industrialised countries.

In conclusion, it should be stated that Galvanite is not a cure all. If galvanising or zinc spray will do the job satisfactorily, then so too will Galvanite, but with the many advantages outlined earlier.
CORROSION PROTECTION TREATMENTS
In 1954, the Bridge Division of the Country Roads Board prepared fourteen steel test panels treated with one of the following corrosion protection treatments —

<table>
<thead>
<tr>
<th>4 plates.</th>
<th>4 plates.</th>
<th>6 plates.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel surface wire-brushed, Two coats red lead primer. Two coats of aluminium finishing paint. Conventional C.R.B. paint system. This type of treatment was the method commonly used by the C.R.B. in 1954.</td>
<td>Steel surface sand blasted to Commercial finish, Two coats of red lead primer, Two coats of aluminium finishing paint. Conventional C.R.B. paint system.</td>
<td>Steel surface sand blasted to white metal finish. Treated with an inorganic zinc coating consisting of fine zinc powder in a sodium silicate vehicle.</td>
</tr>
</tbody>
</table>

Test panels were attached to the girder flanges of three bridges, each representing a different corrosion environment.

EXPOSURE SITES
San Remo Bridge — Bridge connecting the Victorian Mainland with Phillip Island at San Remo. The Bridge is exposed to the ocean and subjected to salt spray. Corrosive conditions are severe and greater than normally encountered in Victorian bridgeworks.

Barwon River Bridge — Princes Highway West — Geelong
This bridge crosses the Barwon River approximately 12 miles from the sea at Geelong. Light industry is located along the river close to the bridge. Corrosive conditions: light to moderate.

Sunday Creek Bridge — Hume Highway near Seymour
This bridge is located north of the Great Dividing Range near the township of Seymour. Corrosive conditions: light.

METHOD OF ATTACHMENT TO BRIDGES
The test plates were attached to the bridges by galvanised steel connections and each test plate isolated from the connections by means of rubber washers. The test plates were hung vertically from the bridge girders except for one set of three plates which were attached horizontally to the Sunday Creek Bridge girders.

PERFORMANCE OF TEST PLATES
Figures 1 to 5 over indicate the arrangement of the test plates on the three bridges and their performance after approximately eight years of service. After photographing and examination the test plates were replaced on the respective bridges and further performance will be noted and recorded in the future.

CONCLUSIONS
Although the scope of the above field tests on the corrosion protected of steelwork is limited, the following conclusions can be made —

(a) The order of performance to date of the three corrosion treatments tested in all cases —
   1. Sand blasting and inorganic zinc coating.
   2. Sand blasting and conventional four coat paint system.
   3. Wire-brushing and conventional four coat paint system.

(b) The conventional four coat paint system when subjected to severe corrosive conditions such as those encountered at San Remo, is inadequate.

(c) In bridge girders, upper horizontal surfaces are more severely attacked than vertical surfaces and become the criterion in determining the suitability of a corrosion protection treatment.
The Role of Metallic Zinc in Zinc Rich Paints

D. G. THOMAS,† R. T. COX,† AND B. A. RICHARDSON*  

INTRODUCTION

In recent years there has been a substantial increase in the amount of zinc-rich paint, i.e., paint pigmented with zinc dust, produced in Australia. To some extent this has been due to increased production on the part of a few manufacturers who concentrate their activities in a specialised field. There has also been increased interest on the part of the larger paint manufacturers who are regarded normally as being in the architectural field. An increasing number of enquiries has also been received from smaller companies who wish to add a zinc dust paint to their line of products.

It was apparent that a bewildering number of vehicles was being used or proposed and investigations in various parts of the world had indicated that not all vehicles were suitable for use in zinc-rich paints. It also became apparent that, for certain applications, there could be marked variations in the resulting zinc-rich paint due to variation in such factors as particle size of the zinc dust, the size distribution, the metallic zinc content of the dust, and the degree of oxidation of the surface of the particles.†

The action of zinc in a paint film in protecting steel is not fully understood. Current theories are briefly examined before discussing the practical aspects of the use of accelerated tests in assessing some of the variables listed below.

MECHANISM OF CORROSION PROTECTION

The mechanism of corrosion protection which is applicable to a zinc-rich paint is not identical to that which is operative in the case of zinc that has been applied by galvanizing or spraying. In these latter cases virtually all the zinc is consumed before rust appears on the substrate. In other words, full cathodic protection has been operative throughout the entire life of the coating. Once the coating has failed the rate of rusting is rapid. In a paint film, unlike a galvanized or sprayed coating, zinc is not in continuous contact with the substrate, the actual area of contact being determined by the diameter of the zinc particles and their packing. As long as zinc is in contact with the substrate cathodic protection will be afforded to the substrate but will disappear once this contact has been lost. If it is assumed that 50% of the total zinc present in the paint film dissolves sacrificially before the iron-zinc contacts are broken, a film of weight 30 mg./sq.cm., which is equivalent to film thickness of 2 to 3 mil., could supply a current of 5 microamp./ sq.cm. required to give full cathodic protection to steel immersed in sea-water for a period of some three months only. Films of this weight have given service lives of two or more years.

Two possibilities exist for the explanation of this phenomenon. Both are dependent on the fact that zinc-rich films, on immersion in electrolyte, form zinc corrosion products in situ. As such paint films, in the unexposed condition, have been shown to be porous, the zinc corrosion products form and remain in the film. Initially the effective iron-zinc corrosion cell, shown schematically in Figure 1, is effectively an iron/zinc/electrolyte cell, i.e., the value of the resistance R is effectively the ionic resistance of the electrolyte. The corrosion reaction liberates Zn$^{++}$ and OH$^{-}$ ions and these form zinc-hydroxy or zinc aqueous corrosion products in the pores of the paint film to the exclusion of the electrolyte. The net result is that the value of R in Figure 1 increases, eventually attaining a value corresponding to the resistance of the paint film.

The increased resistance of the paint film has two effects. Firstly it limits the current flowing in the iron-zinc cell and, secondly, it limits the current that can flow in the iron corrosion cell. The rates of zinc dissolution and the rate of corrosion of iron are both effectively decreased. Thus the demand for, and the supply of cathodic protection are diminished at the same time.

* Electrolytic Zinc Co. of A/sia Ltd
† Formerly with Electrolytic Zinc Co. of A/sia Ltd.
Pass and Meason have shown that, after a few days’ immersion, the resitive layers formed on the paint surface cause the cathodic protection of adjacent bare areas to cease. Because of this it has been argued that the cathodic protection of the substrate must also cease. However, in the bare areas the iron corrosion cell will be fully operative since there will be no high resistance layer present between the locally anodic and cathodic areas. Consequently the demand for cathodic protection will remain constant whilst, because of the formation of resistive layers on the zinc-rich paint film, the supply of cathodic protection will decrease. The point will soon be reached where the protection currents are too small to cancel the iron corrosion cell currents – and rusting will occur. At the substrate, however, the supply of protective currents although diminished may well be large enough to completely cancel the diminished iron corrosion currents.

The two possibilities can thus be stated as follows:–

1. Cathodic protection of the substrate fails rapidly, subsequent protection being afforded solely by the high resistance of the paint film inhibiting the iron corrosion currents.

2. Cathodic protection of the substrate lasts for the whole life of the film, the demand for cathodic protection decreasing with time due to the increased resistance inhibition of the iron corrosion currents.

An additional effect of the build up of zinc corrosion products in the paint film is that the permeability to water and oxygen will decrease. Fresh paint films are, in general, so permeable that both water and oxygen can be supplied to the substrate, so that the cathodic reaction can proceed at the same rate as for bare steel immersed in the same electrolyte. As the permeability, particularly to water, decreases it may well be that the supply of water to the substrate may fall to a value which is insufficient to maintain the rate of the cathodic reaction. This, in turn, has the effect of decreasing the demand for and, by restricting the reaction rate in the iron-zinc cell, of decreasing the supply of cathodic protection.

**THE ANODIC TEST**

It would be expected that the ability to cathodically protect the substrate would be influenced by the particle size distribution of the zinc dust as this would determine the contact area between zinc and iron. This is only one of many parameters that could profitably be studied. One of the major difficulties in the way of carrying out such a study is the lack of a generally acceptable accelerated test. The alternative to such a test is to embark on a programme of actual exposure tests, a long tedious process which can delay the release of improved products. In addition, if the programme is to include a large number of variables, the method is not entirely suited to produce final results that can be shown to be statistically significant.

Of the accelerated tests only the salt spray method finds any favour and has not been accepted without considerable reservation.

Recently a new anodic test has been developed by Consolidated Mining and Smelting Co. of Canada and has aroused much interest. In this test the amount of zinc available to afford cathodic protection is measured. The test, in a modified form, has been used to determine the effect of pigment mean size for a polystyrene and a silicate vehicle as well as to determine the effect of film thickness. Additionally, a series of paints was tested and the results compared to those obtained from atmospheric exposure tests.

In the anodic test the zinc painted panel is immersed in a salt water filled cell, parallel to a bare steel panel. An external voltage is applied between the panels in such a direction as to drive zinc into solution. It has been found that a greater degree of reproducibility is obtained if only one face of the test panel is painted, the reverse side and the edges being sprayed with a thick coat of insulating paint. The electrical circuit is shown in Figure 2. The bare steel panels are all connected to the negative terminal of a 12v accumulator, the painted panels being connected, via individual 3300 ohm resistors, to the positive terminal. These resistors fix the current in each cell; since the cell resistance is much less than 3300 ohms and the cell e.m.f. is much less than 12v., the cell current is about 3.7mA.
Each cell is provided with a reference electrode consisting of a cadmium rod immersed in a pH 4.45 acetic acid/sodium acetate solution. The buffer solution is connected to the test cell electrolyte by a saturated KCl/Agar salt bridge. The potentials of the test panels are automatically monitored, intermittently. Each reference electrode is connected to one of 50 contacts on a post office uniselector switch. A driven wiper contact connects each point in turn to a recording voltmeter. The arrangement permits up to 50 painted panels to be tested simultaneously. If less than 50 cells are in use the unused voltage measurement points are short-circuited to the negative battery terminal.

**Variation of Accelerated Life with Pigment Particle Size: Polystyrene Vehicle**

Figure 3 shows accelerated life/coating weight curves for 4 paints, made from polystyrene pigmented with superfine zinc dust of average particle size 2.4, 2.8, 3.7 and 4.8 microns respectively as determined by the air permeability method. The pigmentation was 1.8 g/c.c. of vehicle in each case as recommended by the vehicle manufacturer. The curves drawn are rough fits by eye. Results for three other particle sizes, 2.5, 3.0 and 4.2 microns were scattered amongst the points shown on Figure 3 and have been omitted for the sake of clarity.

It is clear that for a polystyrene vehicle the accelerated lifetimes, and therefore the percentages of available zinc, are not greatly sensitive to pigment mean particle size over the range 2-5 microns as determined by the Fisher air permeability method.

**Variation of Percentage Available Zinc with Pigment Particle Size: Silicate Vehicle**

In Figure 4 is shown the percent available zinc against Fisher size of the zinc dust in a baking type of silicate vehicle. There is an improvement in available zinc as the pigment size is reduced from 4.2 to 2.7 microns. Further reduction in particle size resulted in a decrease in available zinc. This decrease may be, in part, a real decrease due to decreasing particle size and, in part, a decrease due to the increasing oxide content of the dust. It is usually found that the metallic zinc content of a dust decreases slightly with decreasing particle size.)

The curve in Fig. 4 has been drawn to fit the panels that had a coating weight of 15±2 gms. (i.e. .029±.004 gm. cm.\(^{-2}\)), each point being the mean value from two determinations. The points for panels with a heavier coating, 21±3 gm. all lie below this line. In other words, the thicker the paint film the smaller the percentage of the zinc available to provide cathodic protection. This result was thought to be of sufficient importance to warrant further investigation.

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**Fig. 2: Anodic Test Electrical Circuit**

**Fig. 3: Effect of particle size on accelerated life-coating weight curve for polystyrene vehicle.**
Variation of Accelerated Life With Coating Thickness

Since the percentage of available zinc had been already shown to decrease with increasing film thickness for a silicate vehicle a polystyrene vehicle was chosen for this series of tests.

Figure 5 shows two typical curves for polystyrene vehicle pigmented with dust having Fisher particle sizes of 2.4 and 3.7 microns. The curves are clearly non-linear since the slopes decrease with increasing thickness. The non-linearity implies that the percentage of available zinc which is proportional to the life, coating weight ratio varies with coating weight, becoming less for thicker coatings. A paint in which the available zinc was independent of the coating thickness would give a straight line through the origin of the life v. coating thickness graph. Two such straight-lines, for 10% and 20% available zinc, are drawn in Figure 5.

The practical importance of the non-linearity of the accelerated life v. coating weight graph is that the available zinc should be determined at constant film thickness. The effect of film thickness can be assessed, however, from the time value obtained in the anodic test and this could well be a more suitable value to use. Rischbieth and Marson\(^6\) have published detailed experimental results showing that, for silicate paints immersed in sea water, the corrosion-free life was reasonably proportional to the coating thickness. It is suggested that the amount of zinc available for cathodic protection is simply that which is in direct contact with the substrate and that this is independent of film thickness. The percentage available zinc will therefore decrease with increasing film thickness. If the anodic test simply measures the amount of zinc available to provide cathodic protection and this is constant it would, at first sight, seem reasonable to assume that the accelerated life v. coating thickness curves of Figure 5 would approach a limiting value for the accelerated life. There is little indication of this in Figure 5 for coating weights up to 0.15 g/sq. cm. (5 mil.). Whilst the geometry is different to that for a naturally corroding paint film the possibility of resistance and permeability limitations due to the in situ formation of zinc corrosion products should not be overlooked.

Fig.4. Effect of Particle Size on Percent Available Zinc for Silicate Vehicle.

Fig 5. Effect of Coating Thickness on Accelerated Life for Polystyrene Vehicle.
Correlation of Available Zinc With Service Life.

A series of panels was prepared from commercially available or laboratory formulated paints and exposed on the roof of the Research Laboratory at Risdon, Tasmania. These panels were prepared from 10 gauge mild steel and both surfaces were grit blasted, using No. 14 grit, to give a "white" metal surface. The painted panels were allowed to dry for a minimum of three days before being placed on the exposure rack. After a further two weeks a scribe line was drawn across the front surface of the painted panel, cutting through to the base metal.

All the paints were applied by brush to give as heavy a coat as possible without allowing the wet film to sag or run.

The results of exposure for 6 and 12 months, together with the available zinc (determined from separately prepared panels) are given in Table 1.

Considerable variation is found in the percentage available zinc for the various vehicles, ranging from zero for some chlorinated rubber formulations to 25% for the silicate vehicle. It would be anticipated from this that the chlorinated rubber formulations would give inferior results in the exposure tests and that there would be a graduated response, the silicate formulation giving the most satisfactory response. This is basically the case: paints having less than c. 10% available zinc failed to prevent rust formation in the scribe line at 6 months, those with greater available zinc were all successful in preventing such rust formation after 12 months.

The results with respect to rusting of the substrate are not so clear cut. Paints with available zinc of less than 10% failed to prevent such rusting with the exception of Paint C which was completely successful with an available zinc as low as 2.0%. Paints E and H, a polystyrene with 11.4% and a 2-pack epoxy with an available zinc as high as 17.7% respectively, failed to prevent rusting of the substrate between 6 and 12 months.

The variation of available zinc with vehicle type can be explained on the basis that some vehicles are more efficient wetting agents than others. Thus chlorinated rubber, being a good wetting agent, will give a low available zinc. As chlorinated rubber also has good insulating properties, a well formed film will give resistance inhibition of the iron corrosion cell currents. This could well account for the protection of the substrate by Paint C. At the other end of the scale, the silicate vehicle reacts with the pigment particles and this may influence the area of contact between particles and between particles and substrate.

The agreement between the results from the anodic test and those from exposure trials to date is sufficiently

<table>
<thead>
<tr>
<th>Paint No.</th>
<th>Vehicle Type</th>
<th>Available Zinc, %</th>
<th>Results of 6 months' exposure</th>
<th>Results of 12 months' exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Chlorinated Rubber</td>
<td>0.0</td>
<td>Rusting in scribe line.</td>
<td>Bad rusting in scribe line. General overall surface rusting. Many rust spots on back of panel.</td>
</tr>
<tr>
<td>B</td>
<td>Chlorinated Rubber</td>
<td>0.2</td>
<td>Bad rusting in scribe line, breakdown at the edges. Some rust spots on front surface.</td>
<td>Bad rusting in scribe line, 100% edge breakdown, rust spots on front surface and some rust spots on back of panel.</td>
</tr>
<tr>
<td>C</td>
<td>Chlorinated Rubber</td>
<td>2.0</td>
<td>Rusting in scribe line.</td>
<td>Slight rust in scribe line.</td>
</tr>
<tr>
<td>D</td>
<td>Alkyd</td>
<td>10.2</td>
<td>Rust in scribe line. Some edge breakdown. Several rust spots on surface.</td>
<td>Rust in scribe line, 100% edge breakdown. Rust spots on front and back surfaces.</td>
</tr>
<tr>
<td>E</td>
<td>Polystyrene</td>
<td>11.4</td>
<td>No breakdown evident.</td>
<td>Rust spots on both faces, more severe on back.</td>
</tr>
<tr>
<td>F</td>
<td>Vinyl Copolymer</td>
<td>11.2</td>
<td>No breakdown evident.</td>
<td>No breakdown evident.</td>
</tr>
<tr>
<td>G</td>
<td>Polystyrene</td>
<td>13.1</td>
<td>No breakdown evident.</td>
<td>No breakdown evident.</td>
</tr>
<tr>
<td>H</td>
<td>2-pack Epoxy</td>
<td>17.7</td>
<td>No breakdown evident.</td>
<td>A few surface rust spots.</td>
</tr>
<tr>
<td>I</td>
<td>Silicate</td>
<td>25.0</td>
<td>No breakdown evident.</td>
<td>No breakdown evident.</td>
</tr>
</tbody>
</table>
close to warrant further investigation of the test. On the other hand the discrepancies observed are sufficiently important to indicate that some other factor, or factors, may also be involved. It is this consideration that has led the authors to commence a series of accelerated tests, using a single vehicle only, and deliberately varying each factor. The distinct possibility of interactions between different factors existing has necessitated the use of a statistically designed experiment. It is vitally important that, in such work, the effects of all the factors and their interactions be estimated. As there are many factors the number of test panels required would be unmanageable if each factor were varied over the whole range likely to be met with in practice but there are statistical designs available that permit the evaluation of all factors and first-order interactions, with a manageable number of test panels.

**SIZE DISTRIBUTION OF ZINC DUST**

One of the variables which might be expected to influence the performance of a paint, as previously stated, is the size distribution of the pigment. There are indications that this is so in the case of a silicate vehicle, from the variation in available zinc. McKenzie\(^1\) has also pointed out its importance with respect to the physical properties of the paint. Further, when comparing a series of paints, unless the size distribution effect is known, it is difficult to assess the results in terms of other variables and be confident that the results are not in part due to variations in size distribution.

A further factor to be considered is that where a paint formulation is at or near the pigment critical volume concentration small changes in particle size distribution may have relatively large effects on such features as the mechanical strength and the mode of water (electrolyte) uptake of the film.

Whilst it is a relatively simple matter to measure the mean particle size, unless the dust consists of spheres of equal diameter the distribution cannot be specified by a single parameter. The following work was carried out to determine the parameters required to specify the distribution.

Whilst the Fisher air permeability is extremely useful for determining the mean size quickly it was felt that a more absolute method was required to enable the particle size distribution to be determined. Consequently a microscope technique was developed for this purpose.

A series of dusts was examined and the cumulative size distribution based on counts of 1300 particles obtained (Fig. 6). The cumulative distribution obtained, when plotted against a logarithmic abscissa proved to be symmetrical about the 50% point (Fig. 7). This indicates that the actual distribution is log-normal and if the cumulative log-normal curve is plotted on log-probability paper a straight line results (Fig. 8).

The log-normal function has the form:

\[
N(x)dx = \frac{0.4343}{\sqrt{2\pi} \cdot \log S} \cdot \exp\left[-\frac{1}{2} \left(\frac{\log x - \log G}{\log S}\right)^2\right] \cdot dx \quad \ldots \ldots \ldots (1)
\]

where \(G\) is the geometric mean diameter and \(\log G\) is the mean value of \(\log X\); and \(\log S\) is the log-geometric standard deviation and is the standard deviation of \(\log x\) about \(G\); all logs are to the base 10.

From (1) it follows directly that the distribution is completely determined by \(G\) and \(\log S\). In Fig. 8, \(G\) is the value of the diameter for which the graph crosses the 50% level and \(\log S\) is the horizontal distance, in log units, between the 15.87% and the 50% levels.

![Fig. 6: Cumulative size distribution based on a count of 1,300 particles.](image)

![Fig. 7: Cumulative log size distribution.](image)
Where the size distribution, based on a numerical count, is log-normal it can be shown mathematically that the size distribution by weight is also log-normal and is related to the numerical distribution by

$$\log G_w = \log G + 6.909 \log^2 S$$

$$\log S_w = \log S \quad \ldots(2)$$

where $G$ and $\log S$ have the same meaning and the suffix $w$ refers to the size distribution by weight. Since $\log S_w = \log S$ the number and weight distribution curves are parallel when drawn with log abscissa. The weight curve is displaced by the right of the numerical curve by a distance of $6.909 \log^2 S$.

Similarly the distribution of surface area amongst the particle sizes is parallel to the numerical distribution curve but displaced to the right by a distance of $4.606 \log^2 S$.

Several other zinc dusts have been examined in a similar manner and found to approximate to the log-normal distribution. The greatest discrepancy occurs for particles smaller than 1 micron. This is possibly due to the unreliability of the microscopic technique for such small particles. The figures for particles less than one micron were discarded and a value assumed that would turn the graph into a straight line.

**CONCLUSION**

Much has still to be learned of the actual mechanism(s) by which a zinc-rich paint protects the substrate. The use of the anodic test, possibly using the “time to failure” rather than the “available zinc” expressed as a percentage of the total zinc in the dried film, taken in conjunction with actual exposure trials, may well throw some further light on this subject. Great care must be taken in any such work to ensure that observed effects can be related to the controlled variations in the factors under study and not to chance variations in other factors.

There can be little doubt that the mechanism of protection afforded by zinc-rich paints differs considerably from that afforded by continuous massive zinc coatings, e.g., galvanized and sprayed surfaces. This difference can be attributed to the increasing resistance of the paint film as any discontinuities in the film become blocked with the zinc corrosion products. It would appear that the ability to provide protection to adjacent areas of bare steel for considerable time is a function of the available zinc as measured by the anodic test. It is also apparent that the ability to protect the substrate can be achieved with very little available zinc. This gives credence to the idea that resistance inhibiting plays a major role in the protection afforded by zinc-rich paints.

One of the factors which, theoretically, can influence the contact area between zinc and iron is the particle size distribution of the zinc dust. This has been shown to be substantially log-normal with a slight positive skew. In the distillation process it may be difficult to produce powders having the same mean size but different distributions (i.e., constant values of $G$ but different values of $\log S$) but a knowledge of the distribution is a necessary prerequisite to any study of the possible effects of particle size distribution.

**REFERENCES**

This paper is based on a lecture to a meeting of the Australasian Corrosion Association, Melbourne held in May, 1967.

Zinc Dust Pigmented Paints

F. MARSON

INTRODUCTION

"Blue Powder", a crude zinc dust, is formed as a by-product in the production of metallic zinc. Its composition is variable, the total zinc content rarely exceeding 92 per cent., a fair proportion of this being in the form of zinc oxide. This zinc dust was used in the earliest zinc dust pigmented paints described by Mallet in 1840; it was still being used when zinc pigmented paints were introduced for marine use in 1911. However, this crude zinc dust is too variable in composition and metallic zinc content for consistent successful use as a pigment. Zinc dust produced by the more recently developed volatilisation process is to be preferred. With this process the zinc vapour is condensed in an inert atmosphere under controlled conditions. The better pigment grades produced by this process contain 99 per cent or more of zinc, about 97 per cent being present as metallic powder. In addition, it has been possible to produce zinc dusts with an average particle size of 2.5 to 3.0 microns with a maximum particle size of the order of 10 microns. These new zinc dusts improve the properties of zinc rich paints so markedly that they have become relatively common, and, with the advent of many new paint vehicles, they have led to a great variety of zinc dust paints, ranging in performance from very poor to excellent.

Unfortunately, the user rarely has the means of determining either the suitability or quality of a new paint, other than by testing it under practical conditions. This process of trial and error is to be recommended but it is time consuming. However, the classification proposed below is a useful guide in predicting the performance of reasonably well formulated zinc dust paints, applied as uniform coats to sand-blasted steel with a maximum profile height not greater than one third of the coating thickness.

CLASSIFICATION SYSTEM

The first step is to split the paints into three main groups on an electrochemical basis. Fortunately, for practical purposes, it is possible to substitute the volume of zinc in the film, or more approximately the weight of zinc in the film, for the potentials quoted below.

Group I. – Paints which are poorly conductive, so that their mode of protection of the substrate is similar to that of conventional paints. Paints with a zinc content of less than 60 per cent by weight normally fall in this group.

Group II. – Paints which are reasonably conductive, having an initial potential difference with respect to the calomel half cell of less than -0.68 volts. Although these paints cannot protect an exposed area of the steel substrate for any great length of time, paints with potentials of -0.65 volts have been shown to afford protection to a bare area for periods of up to a month, even in sea water. Group II paints usually have zinc contents of between 60 and 80 per cent.

Group III – Conductive paints with potentials below -0.68 volts and preferably below -0.74 volts. These paints will initially protect steel in a similar way to hot dip galvanising. They need to contain over 80 per cent by weight of zinc. However, with this group of paints, each vehicle has a maximum zinc content which cannot be exceeded without a loss in performance. For example, epoxy based paints normally perform poorly when loaded with more than 85 per cent by weight of zinc.

As the vehicle used to bind the pigment particles together can have a marked effect on performance a further subdivision must be made: this time into the four major types of vehicles:

Group A – Organic vehicles readily affected by alkali, such as linseed oil and alkyd resins.

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* Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, Melbourne, Australia

Group B – Solvent based organic vehicles such as vinyl and chlorinated rubber.
Group C – Chemically cured, chemically resistant vehicles, such as epoxy and urethane resins.
Group D – Inorganic vehicles of the alkali silicate, phosphate and ethyl silicate types.

The vehicle classification is based on the ability of the vehicle to withstand the environment. The films should be resistant to moisture and to the alkali generated when zinc is sacrificed to protect the substrate, and of course the vehicle should not react deleteriously with the zinc itself. Most vehicles in Classes A and B either break down in the presence of alkali or the film loses adhesion to the substrate. Vehicles belonging to Classes C and D are similar in performance to each other, the zinc content of the film normally overriding differences in vehicle performance.

By combination of these two subdivisions, 12 classes of paints are possible. For currently formulated and applied coatings at equivalent film weights, exposed in severe environments, the following order of merit is suggested: —

III D > III C > II D > II C > I D > I C > III B > II B > I B > III A > II A > I A

Increasing the zinc content of a paint normally increases the potential difference with respect to steel, up to a limiting value, and so improves the ability of the film to protect the steel substrate by a cathodic protection mechanism. It is probable that the self-healing mechanism of zinc dust paints also improves with increasing zinc content. At very high loadings, dependent upon the vehicle, the mechanical properties of the film suffer and the protective value of the coating decreases. For silicate vehicles the desirable zinc content is usually above 90 per cent by weight, and for most epoxy and urethane coatings is usually above 80 per cent.

The suggested order of performance of various types of zinc dust pigmented paints needs comparison with experimental data to confirm the ideas on which it is based.

**EFFECT OF ENVIRONMENT**

Flack\(^3\) exposed 12 different formulations of zinc dust paints, applied under laboratory conditions to sand blasted steel panels using hot dipped galvanised iron as a control, to a range of severe environments. Table 1 shows the vehicle type, the zinc content and the proposed classification based upon both the vehicle used and the zinc content. The fourth column shows an average relative protection rating under three marine environments, salt fog, aerated and stagnant sea water immersion while column five shows the average rating when exposed to 100 per cent relative humidity and to stagnant and running fresh water. The ratings used have given equal weight to the occurrence of corrosion over the film as a whole, and at scribe lines and edges. This seems a reasonable balance for structural steel work. A value of 100 represents no failure; a completely rusted surface is represented by 0. Thus a panel with no corrosion on the main body of the film but 50 per cent corrosion present at the scribe line or edges is rated as 75; a test panel with no corrosion at the scribe line or edges of the test panel but with 25 per cent general corrosion present is rated as 87.5. The ranking order, best 1, worst 12, is also given. The ethyl silicate paint was marginally better than galvanised iron, and the two higher zinc content alkali silicates were in the same class. The two urethane paints also performed well. At the bottom end of the scale was the linseed oil paint.

Figure 1 illustrates the relationship between the corrosion protection rating and the classification for fresh water and marine environments. The better paints do not differ much in corrosion rating between the two environments whereas the poorer paints do. The proposed classification is therefore substantially confirmed by data obtained by exposure in severe environments.

Munger\(^4\) has rated vehicles on the basis of the percent protection afforded to V shaped grooves cut in zinc rich paint films exposed to 100% humidity as follows:- Zinc silicates and phosphate silicates, 100; galvanised iron, 95; a modified silicate, 85; ethyl silicate, 70; chlorinated rubber, 60; and epoxy, 40. Unfortunately, formulation details were not recorded, but results suggest that the inorganic vehicles are superior to the organic ones.
Thus, when zinc dust paints are to be used without overcoating in severe environments, inorganic paints with zinc contents of over 80 per cent by weight are best followed by high zinc content paints based on chemically cured, alkali resistant vehicles.

### INORGANIC VERSUS ORGANIC COATINGS

Inorganic zinc rich paints protect steel by a unique mechanism:

1. When first applied the film appears to act for a short time as a barrier coating in a similar manner to normal paints.
2. Being pervious, water and dissolved salts can enter the film; cathodic protection then protects the steel.
3. Zinc corrosion products are formed on and in between the zinc particles and also on the substrate, leading to anodic passivation.
4. The film of basic zinc salts then hardens and forms a self sealing barrier.

In sea water immersion we have found a marked increase in the electrical resistance of the film, much of this being concentrated at the surface of the film. When lightly scratched the resistance drops and the potential rises to a value sufficient to protect the steel. Sealing of the exposed surface can occur within a few hours, restoring the electrical resistance to its original value.

Perhaps it is this unique

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### Table 1. COMPARISON OF ZINC DUST PAINTS (EXPERIMENTAL RESULTS AFTER V. FLACK)

<table>
<thead>
<tr>
<th>Vehicle Type</th>
<th>% Zinc by Weight</th>
<th>Classification</th>
<th>Relative protection rating</th>
<th>Salt fog, aerated &amp; stagnant sea water</th>
<th>100% Humidity; running and stagnant fresh water</th>
<th>Average Protection Rating</th>
<th>Rank- ing Order</th>
<th>550°F to 65°F Quench test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Silicate Self Cure</td>
<td>92</td>
<td>IID</td>
<td>91</td>
<td>98.8</td>
<td>95</td>
<td>3</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td>Ethyl Silicate</td>
<td>91</td>
<td>IID</td>
<td>100</td>
<td>99.7</td>
<td>99.9</td>
<td>1</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td>Sodium Silicate Chemical Cure</td>
<td>91</td>
<td>IID</td>
<td>93</td>
<td>99.2</td>
<td>96</td>
<td>2</td>
<td>Excellent</td>
<td></td>
</tr>
<tr>
<td>Polyurethane</td>
<td>91</td>
<td>III</td>
<td>70</td>
<td>88</td>
<td>85</td>
<td>8</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>Polyurethane</td>
<td>83</td>
<td>III</td>
<td>91</td>
<td>97-5</td>
<td>94</td>
<td>4</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>Epoxy</td>
<td>80</td>
<td>IIIC</td>
<td>87</td>
<td>81</td>
<td>84</td>
<td>6</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>Sodium Silicate Baking type</td>
<td>78</td>
<td>IIID</td>
<td>70</td>
<td>92</td>
<td>81</td>
<td>7</td>
<td>Not tested</td>
<td></td>
</tr>
<tr>
<td>Inorganic (one pack) type unknown</td>
<td>49</td>
<td>ID</td>
<td>53</td>
<td>77</td>
<td>65</td>
<td>8</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>Epoxy Ester</td>
<td>86</td>
<td>IIIB</td>
<td>42</td>
<td>72</td>
<td>57</td>
<td>9</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>Epoxy</td>
<td>55</td>
<td>IC</td>
<td>38</td>
<td>45</td>
<td>42</td>
<td>10</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>Chlorinated Rubber</td>
<td>69</td>
<td>IIIB</td>
<td>27</td>
<td>47</td>
<td>32</td>
<td>11</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>Linseed Oil</td>
<td>61</td>
<td>IIA</td>
<td>1</td>
<td>28</td>
<td>15</td>
<td>12</td>
<td>Fail</td>
<td></td>
</tr>
<tr>
<td>Hot Dip Galvanising</td>
<td>100</td>
<td>-</td>
<td>99.7</td>
<td>99.8</td>
<td>99.8</td>
<td>-</td>
<td>Fail</td>
<td></td>
</tr>
</tbody>
</table>

0-Complete failure. 100-No corrosion

---

Fig. 1: Comparison of relative protection rating with proposed classification and order of merit.
mechanism which enables these paints to outperform most, if not all, conventional paint systems. If we accept this, why are so many organic zinc primers used? Part of the answer lies in the advantages and disadvantages of each type of coating.

The advantages of the organic compared with the inorganic coatings are:

1. They are less critical of surface preparation.
2. They can be applied over a wide range of temperature.
3. Organic solvents permit a wide variety of application techniques.
4. Many do not rely on humidity and/or temperature to cure properly.

Their disadvantages are:-

1. The solvent is a fire hazard.
2. On outdoor exposure they weather in a manner similar to conventional paints and frequently have a tendency to chalk, crack and check.
3. They can blister in areas of high humidity or under conditions of water immersion.
4. They may be adversely affected by solvents.
5. Their heat resistance is usually below 300°F.

Inorganic vehicles have a corresponding for and against listing. Their advantages are:-

1. Zinc is chemically part of the film and is highly conductive.
2. There is usually a chemical bond to the steel substrate.
3. They are largely unaffected by sunlight and a wide range of temperatures.
4. They resist most organic solvents.
5. Their chemical resistance is better than galvanising and often better than organic coatings.

Their disadvantages are:-

1. They must be applied to clean steel; sand blasting to white metal is essential.
2. They frequently show poor adhesion to metals other than steel and zinc.
3. Many require the application of a chemical curing agent or specific conditions of temperature and/or humidity to cure properly.

From the information given above it should be possible to determine which type of zinc dust paint to use for a particular application. Thin gauge body metal would be difficult to sand blast so that organic primers would be most suitable. The ability to withstand temperatures of up to 600°F and thermal shock make the inorganic coatings highly suitable for chimney stacks. This is confirmed by the final column in Table 1, which shows the effect of a quench cycle. Only inorganic systems passed this test; even the galvanised iron control failed. In general, good zinc rich paints can be used in lieu of galvanised iron but, as with the latter, strong acids and alkalis should be avoided.

Fig. 2 shows the average service life expectancy, based mainly on a paper by Keithler, of a number of inorganic zinc rich paints without overcoats in a range of environments. The results of sea water exposure trials in Sydney Harbour of a range of single pack sodium silicate based paints are also shown in Figure 2. Here the first sign of corrosion is taken as indicating failure.

Keithler’s service lives are very good; two mil of coating giving an estimated life of 15 years in rural, 12 years in light industrial, 10 years in light coastal, 8 years in severe coastal and 6 years in heavy industrial and fresh water immersion.
environments. The high sulphur dioxide content of the heavy industrial environment was probably responsible for the relatively rapid breakdown. Exposure tests carried out by DSL at Cape Schanck, Victoria, confirm Keithler's results for a light coastal environment.

However, these results assume that the paints are reasonably well formulated and are applied to well prepared steel surfaces having a maximum profile height no greater than one third of that of the thickness of the coatings. Incidentally, sea water immersion trials over a range of formulations of the air drying silicates\(^6\) showed that the time taken for the first sign of corrosion to appear was directly proportional to the weight of zinc per unit area, to a significance level of 0.1 per cent, so that the straight line relationships shown in Fig. 2 may well be correct.

From these service life predictions it appears that zinc rich paints would be suitable for protecting almost any steel work with the possible exception of that subjected to complete sea water immersion. Suggested uses, in addition to chimney stacks, are for coating pipe lines, bridges, structural steel work, ships' bilges, linings and exteriors of tanks and, when overcoated for decorative purposes, ships' superstructures. In addition, many inorganic films are exceptionally tough and abrasion resistant when fully cured and this has led to their use for coating ore rail trucks, steel decking and gantries.

The vehicles used in paints for overcoating zinc rich paints must not be affected by alkaline corrosion products at damage points. Epoxy, urethane, coal tar epoxy, coal digested pitch epoxy, vinyl resin and chlorinated rubber in particular have been found suitable, but care must be exercised if amine cured epoxy paints are employed because the zinc reacts with the amine resulting in undercured coatings.

Organic based zinc rich paints are suitable for use with organic overcoat making up for any lack of durability of the primer. They have great potential as shop or welding primers. Provided the film thickness is maintained at 0.5 mil, or at the most 1.0 mil, they can provide adequate protection for 6 months to a year; the paints have little or no effect on weld strengths of steels other than some high tensile steels if the welding technique is suitably modified. Zinc rich primers for car body metals have been produced which have satisfactory spot welding characteristics. The choice of vehicles is difficult and depends partly on the system to be used for overcoating. Epoxy based paints have been used in the ship building industry, and Wilson & Zonsveld\(^7\) have described the requirements for such coatings, including details of welding and weld strengths, surface preparation and specifications for the zinc rich epoxy based primer. The great advantage of the higher zinc content primers for use in fabrication is that some protection is given to the substrate even at damage points. Final painting can therefore proceed with little or no further surface preparation when fabrication is complete because there is virtually no corrosion. In addition, any areas which cannot be painted after fabrication will have a measure of corrosion protection.

One recent application of organic zinc rich paints with which DSL has been associated was for priming the chassis of a new army truck to protect it during fabrication and in transit, a much better performance being obtained than with the system used previously. Another recent use was as a primer for landing craft being constructed in tropical Queensland. It is hoped that a virtually corrosion free hull will be obtained prior to final paint finishing.

**PAINTING OF GALVANISED IRON**

One of the lesser known applications of zinc rich paints is for painting galvanised iron. In a severe environment K. Tator\(^8\) has estimated that it becomes economically desirable to paint normal galvanised iron after an average period of 2½ years. Excellent results have been obtained using paints containing 80 per cent zinc dust and 20 per cent zinc oxide. These are moderately high zinc content paints made to the formula given in U.S. Specification TT-P-641-C. Three types, one based on a linseed oil vehicle, another on a linseed modified phthalic alkyd resin vehicle, and a third on a 100 per cent phenolic resin spar varnish, are described in this specification. The first two types normally require no surface treatment other than a wash down. Two coats are usually applied, and a finishing coat is only required when the environment is severe or for decorative purposes. The American Iron & Steel Institute\(^9\), in both three year and five year exposure tests, found these paints the best available for painting galvanised iron.
This brief review of the uses of zinc rich paints is not exhaustive, and the number of ways in which they are used will increase as confidence in them grows.

BIBLIOGRAPHY

Abrasion Resistance of Inorganic Zinc Silicate Coatings

D. W. DONALD and F. E. WORSNOP

SYNOPSIS
An exploratory series of Taber Abraser tests on commercial inorganic silicate coatings has indicated significant differences between coating types. In descending order of abrasion resistance are baked coatings, water based self cured coatings and solvent based self cured coatings, with the last group covering a very substantial range of abrasion resistance.

INTRODUCTION

Over the past decade inorganic zinc silicate coatings have come of age. From the situation where the complexities of their curing techniques limited them to specialised usage, they have become widely accepted on projects associated with the mineral development age in Australia.

The recent spectacular increase in acceptance has followed the development of the self curing types with the resulting simpler application and wider interest by non-specialised coating companies.

There are now four basic types of genuine inorganic zinc silicate coatings available, classified by their curing mechanisms, and all four are currently widely used in Australia. Little has been published on selection criteria for these coating types and there appears to have been very little attempt to quantify the differences which are known to exist.

The three fundamental characteristics which have made inorganic zinc silicate so useful for coating structural steel have been the outstanding protection obtainable, the physical ability of the coating to resist damage in transport, handling and erection, and the inherent economy of a single coat system.

These characteristics together have made inorganic zinc silicates almost the universal protection for non-immersed steel exposed to marine environments in the major developments in Northern Australia. The single coat gives economical protection for many years and the resistance to damage permits surface preparation to be carried out where labour costs are most favourable, that is, at the steel fabrication plant.

Assessment of the relative protection of the types of inorganic zinc available is a vexed question and the authors are not aware of any valid comparison tests which have yet run for a long enough period. Accelerated tests, generally salt spray tests, have little acceptance because of the lack of proven correlation with field performance. Even salt spray tests require many months of patient operation to produce failure of well formulated coatings.

Inorganic zinc silicates are broadly classified into categories, as follows:

1. Baked Coatings

The baked or stoved inorganic zinc silicates are formed from a mixture of metallic zinc dust and a water solution of an alkali silicate. These coatings use low ratio sodium silicate solutions (e.g. Na₂O : SiO₂ – 1:2.1 Molar) and require baking to convert to a water insoluble condition within an acceptable time. This is the original inorganic zinc silicate formulation and was patented in 1937.

These coatings are still widely used in specialised situations such as the exterior surfaces of above-ground water reticulation pipes.
2. Post Cured Coatings

As higher ratio alkali silicates became available it was found that curing could be accomplished by neutralising the applied coating with a post applied acid wash. This is the coating type which has basically earned the world wide reputation of inorganic zincs and is still used in considerable quantity particularly in shipbuilding.

3. Self Cured Water-Borne Inorganic Zinc Silicates

With further advances in silicate technology still higher ratio alkali silicates have become available. Potassium silicate is preferred to sodium silicate and reliable self curing coatings have been available since about 1964. Attempts to increase ratios still further have so far resulted in instability of the water solution. Lithium silicates are available at a molar ration of 1:4.75, with excellent curing rate but the improvement in curing rate does not seem to have counter-balanced the additional cost of lithium silicate.

The self curing water borne silicates are widely used in Australasia. They cure reliably provided that climatic conditions during application permit a reasonable drying rate of a water film, without freezing, and provided that the coating can remain dry for an initial few hours.

4. Self Curing Solvent-Borne Inorganic Zinc Silicates

These products consist principally of metallic zinc dust in a solvent solution of an alkyl silicate, usually one of the commercial forms of ethyl silicate and are the subject of a U.S. Patent filed in 1959.\(^2\) Adjustment is made to the pH of the alkyl silicate so that hydrolysis of the silicate occurs, with loss of alcohol, when the applied coating is exposed to humid air. The alcohol evaporates leaving a coating consisting of zinc dust in a silica matrix.

Curing is reliable and rapid under climatic conditions where humidity is available for reaction. Temperatures below freezing can be tolerated. Unless humidities are sufficiently high these coatings will remain soft for substantial periods and shelf life may be short, depending on the method of hydrolysis chosen. These coatings are likewise widely used in Australasia.

**CONSIDERATION OF ABRASION TEST METHODS**

The overall resistance of a coating to handling damage can be expected to depend on three factors, the resistance to abrasion, the resistance to plastic deformation, and the adhesion of the coating to the substrate.

### Table 1: RESULTS AT 1500 WEAR CYCLES

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thickness</th>
<th>Wear Cycles</th>
<th>Weight Loss</th>
<th>Density</th>
<th>Calculated Volume Loss</th>
<th>Calculated Thickness Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAKED COATING:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 1 A</td>
<td>3.0 mils</td>
<td>1500</td>
<td>0.03 gms.</td>
<td>4.43 gms/cc</td>
<td>0.0068 cc</td>
<td>0.09 mils</td>
</tr>
<tr>
<td>B</td>
<td>3.0</td>
<td></td>
<td>0.02</td>
<td>4.43 gms/cc</td>
<td>0.0045</td>
<td>0.06</td>
</tr>
<tr>
<td>SELF CURED WATER BORNE:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W 1 A</td>
<td>3.3 mils.</td>
<td>1500</td>
<td>0.02 gms.</td>
<td>4.31 gms/cc</td>
<td>0.0046 cc</td>
<td>0.06 mils</td>
</tr>
<tr>
<td>B</td>
<td>3.4</td>
<td></td>
<td>0.04</td>
<td>4.31 gms/cc</td>
<td>0.0092</td>
<td>0.12</td>
</tr>
<tr>
<td>W 2 A</td>
<td>2.7</td>
<td></td>
<td>0.07</td>
<td>4.14 gms/cc</td>
<td>0.017</td>
<td>0.2</td>
</tr>
<tr>
<td>B</td>
<td>2.5</td>
<td></td>
<td>0.06</td>
<td>4.14 gms/cc</td>
<td>0.014</td>
<td>0.2</td>
</tr>
<tr>
<td>W 3 A</td>
<td>2.9</td>
<td></td>
<td>0.05</td>
<td>4.03 gms/cc</td>
<td>0.012</td>
<td>0.2</td>
</tr>
<tr>
<td>B</td>
<td>3.1</td>
<td></td>
<td>0.02</td>
<td>4.03 gms/cc</td>
<td>0.005</td>
<td>0.06</td>
</tr>
<tr>
<td>SELF CURED SOLVENT BORNE:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 1 A</td>
<td>1.8 mils.</td>
<td>1500</td>
<td>0.07 gms.</td>
<td>4.08 gms/cc</td>
<td>0.017 cc</td>
<td>0.2 mils</td>
</tr>
<tr>
<td>B</td>
<td>1.9</td>
<td></td>
<td>0.06</td>
<td>4.08 gms/cc</td>
<td>0.015</td>
<td>0.2</td>
</tr>
<tr>
<td>S 2 A</td>
<td>6.2</td>
<td></td>
<td>0.25</td>
<td>3.88 gms/cc</td>
<td>0.064</td>
<td>0.8</td>
</tr>
<tr>
<td>B</td>
<td>5.3</td>
<td></td>
<td>0.17</td>
<td>3.88 gms/cc</td>
<td>0.043</td>
<td>0.6</td>
</tr>
<tr>
<td>S 3 A</td>
<td>2.6</td>
<td></td>
<td>0.62</td>
<td>4.14 gms/cc</td>
<td>0.15</td>
<td>1.9</td>
</tr>
<tr>
<td>B</td>
<td>3.5</td>
<td></td>
<td>1.16</td>
<td>4.14 gms/cc</td>
<td>0.28</td>
<td>3.6</td>
</tr>
</tbody>
</table>

**CONSIDERATION OF ABRASION TEST METHODS**

The overall resistance of a coating to handling damage can be expected to depend on three factors, the resistance to abrasion, the resistance to plastic deformation, and the adhesion of the coating to the substrate.
The authors' general observations over many years have indicated that all inorganic zincs have such a high degree of adhesion to properly prepared steel that peeling of the coating from the substrate is virtually non-existent in practical situations. Likewise plastic deformation is not found to any practical degree. It therefore seems a valid inference that handling damage in a practical situation would result only from abrasion mechanisms, either from rubbing actions or from high point loadings.

The decision was made to carry out abrasion tests as a basis for assessing damage resistance. Possible techniques already in use in coatings assessment were pencil hardness tests and controlled attrition by means of a grinding wheel or similar.

The pencil hardness test is a go no-go test using a series of pencils of ascending hardness up to 6H. However, it was found that many of the coatings achieve hardnesses above 6H and the test was discarded as being insufficiently discriminating.

An attrition test widely used is Federal Test Method No. 141, Method 6192, using the Taber Abraser. Preliminary trials showed that even the hardest coatings could be abraded at a measurable rate using this instrument and it was decided to use the Taber Abraser to accumulate results.

The Taber Abraser uses a rotating test plate, under a standard load. The number of cycles can be varied to suit the hardness of the material being tested. Details of the coating preparation and of the test used are given in Appendix I.

Two methods of assessing coating performance are available, the Wear Index calculated from weight loss measurements, and the Wear Cycles calculated from thickness loss measurements.

Both sets of measurements were taken during the tests but since many of the coatings are extremely hard, the thickness loss measured was of the order of tenths of thousands of an inch in most cases. Many of the thickness loss measurements were quite variable and it was concluded that the accuracy required was probably beyond that of the measuring equipment available. For this reason it was decided to rely on weight loss measurements since these had a higher inherent degree of accuracy.

However, the only way in which results can have practical meaning is in the form of thickness loss. In order to convert to thickness loss it is necessary to have a knowledge of densities of the coatings.

Table 2: RESULTS AT 5000 WEAR CYCLES

<table>
<thead>
<tr>
<th>Coating</th>
<th>Wear Cycles</th>
<th>Weight Loss</th>
<th>Calculated Volume Loss</th>
<th>Calculated Thickness Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAKED COATING:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B IA</td>
<td>5000</td>
<td>0.05 gms</td>
<td>0.011 cc</td>
<td>0.1 mils</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>0.05</td>
<td>&quot;</td>
<td>0.1 &quot;</td>
</tr>
<tr>
<td>SELF CURED WATER BORNE:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W 1 A</td>
<td>5000</td>
<td>0.07 gms</td>
<td>0.016 &quot;</td>
<td>0.2 mils</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>0.12</td>
<td>&quot;</td>
<td>0.4 &quot;</td>
</tr>
<tr>
<td>W 2 A</td>
<td>&quot;</td>
<td>0.15</td>
<td>&quot;</td>
<td>0.5 &quot;</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>0.13</td>
<td>&quot;</td>
<td>0.4 &quot;</td>
</tr>
<tr>
<td>W 3 A</td>
<td>&quot;</td>
<td>0.14</td>
<td>&quot;</td>
<td>0.5 &quot;</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>0.21</td>
<td>&quot;</td>
<td>0.7 &quot;</td>
</tr>
<tr>
<td>SELF CURED SOLVENT BORNE:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 1 A</td>
<td>5000</td>
<td>0.21 gms</td>
<td>0.051 cc</td>
<td>0.7 mils</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>0.20</td>
<td>&quot;</td>
<td>0.6 &quot;</td>
</tr>
<tr>
<td>S 2 A</td>
<td>&quot;</td>
<td>0.51</td>
<td>&quot;</td>
<td>1.7 &quot;</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>0.36</td>
<td>&quot;</td>
<td>1.2 &quot;</td>
</tr>
<tr>
<td>S 3 A</td>
<td>2000</td>
<td>0.79</td>
<td>&quot;</td>
<td>2.4 &quot;</td>
</tr>
<tr>
<td>B</td>
<td>1590</td>
<td>1.20</td>
<td>&quot;</td>
<td>3.7 &quot;</td>
</tr>
</tbody>
</table>

The authors' general observations over many years have indicated that all inorganic zincs have such a high degree of adhesion to properly prepared steel that peeling of the coating from the substrate is virtually non-existent in practical situations. Likewise plastic deformation is not found to any practical degree. It therefore seems a valid inference that handling damage in a practical situation would result only from abrasion mechanisms, either from rubbing actions or from high point loadings.

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However, the only way in which results can have practical meaning is in the form of thickness loss. In order to convert to thickness loss it is necessary to have a knowledge of densities of the coatings.
### Table 3: EFFECT OF HUMIDITY

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thickness</th>
<th>Wear Cycles</th>
<th>Relative Humidity</th>
<th>Weight Loss</th>
<th>Calculated Volume</th>
<th>Calculated Thickness Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 1 C</td>
<td>3.3 mils.</td>
<td>5000</td>
<td>52.2±2.5</td>
<td>0.04 gm</td>
<td>0.009 cc</td>
<td>0.1 mil</td>
</tr>
<tr>
<td>D</td>
<td>2.9 &quot;</td>
<td>&quot;</td>
<td>52.2±2.5</td>
<td>0.04 &quot;</td>
<td>0.009 &quot;</td>
<td>0.1 &quot;</td>
</tr>
<tr>
<td>B 1 E</td>
<td>2.9 &quot;</td>
<td>&quot;</td>
<td>70±2</td>
<td>0.09 &quot;</td>
<td>0.020 &quot;</td>
<td>0.3 &quot;</td>
</tr>
<tr>
<td>F</td>
<td>3.0 &quot;</td>
<td>&quot;</td>
<td>70±2</td>
<td>0.11 &quot;</td>
<td>0.025 &quot;</td>
<td>0.3 &quot;</td>
</tr>
</tbody>
</table>

### BAKED COATING:

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thickness</th>
<th>Wear Cycles</th>
<th>Relative Humidity</th>
<th>Weight Loss</th>
<th>Calculated Volume</th>
<th>Calculated Thickness Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 1 C</td>
<td>3.3 mils.</td>
<td>5000</td>
<td>52.2±2.5</td>
<td>0.04 gm</td>
<td>0.009 cc</td>
<td>0.1 mil</td>
</tr>
<tr>
<td>D</td>
<td>2.9 &quot;</td>
<td>&quot;</td>
<td>52.2±2.5</td>
<td>0.04 &quot;</td>
<td>0.009 &quot;</td>
<td>0.1 &quot;</td>
</tr>
<tr>
<td>B 1 E</td>
<td>2.9 &quot;</td>
<td>&quot;</td>
<td>70±2</td>
<td>0.09 &quot;</td>
<td>0.020 &quot;</td>
<td>0.3 &quot;</td>
</tr>
<tr>
<td>F</td>
<td>3.0 &quot;</td>
<td>&quot;</td>
<td>70±2</td>
<td>0.11 &quot;</td>
<td>0.025 &quot;</td>
<td>0.3 &quot;</td>
</tr>
</tbody>
</table>

### SELF CURED SOLVENT BORNE:

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thickness</th>
<th>Wear Cycles</th>
<th>Relative Humidity</th>
<th>Weight Loss</th>
<th>Calculated Volume</th>
<th>Calculated Thickness Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 2 C</td>
<td>3.4 mils.</td>
<td>5000</td>
<td>52.2±2.5</td>
<td>0.21 gm</td>
<td>0.054 cc</td>
<td>0.7 mil</td>
</tr>
<tr>
<td>D</td>
<td>3.2 &quot;</td>
<td>&quot;</td>
<td>52.2±2.5</td>
<td>0.21 &quot;</td>
<td>0.048 &quot;</td>
<td>0.6 &quot;</td>
</tr>
<tr>
<td>S 2 E</td>
<td>3.3 &quot;</td>
<td>&quot;</td>
<td>70±2</td>
<td>0.30 &quot;</td>
<td>0.077 &quot;</td>
<td>1.0 &quot;</td>
</tr>
<tr>
<td>F</td>
<td>3.1 &quot;</td>
<td>&quot;</td>
<td>70±2</td>
<td>0.24 &quot;</td>
<td>0.062 &quot;</td>
<td>0.8 &quot;</td>
</tr>
</tbody>
</table>

### DENSITY OF INORGANIC ZINC COATINGS

Dealing with more conventional coating types which dry to homogenous pore-free films, density can be calculated from a knowledge of the formulation and of the densities of the materials used. Alternatively, measurement of the density of the wet coating and of the amount of volatile driven off during drying will give an accurate result.

Inorganic zinc silicates are known to be porous to varying degrees and it is therefore necessary to make a direct determination of coating density.

The method chosen for density determination was a displacement weighing method, using mercury as the displacement fluid. Mercury was used because its high negative contact angle made entry into the coating pores an unlikely possibility and because its density gave higher sensitivity. The details of the method used are given in Appendix II.

### ABRASION TEST RESULTS

The first series of tests were carried out on a selection of coatings, using 1500 wear cycles, and these are given in Table 1. Film thickness, weight losses, film densities, calculated volume losses, and calculated thickness losses (on the basis of an abraded area of 30.6 sq. cm.) are given in order. A and B are duplicates in each case.

The results of these tests were in very general agreement with impressions from practical situations and were regarded as encouraging. However, the thickness losses, with the exception of coating S3, were quite small and accordingly it was decided to carry out a further series of 5000 wear cycles in an attempt to develop more meaningful assessments. These further results are given in Table 2.

These results follow the same trends as the results from 1500 wear cycles. In general the rate of wear appears to have diminished after the first 1500 cycles but the accuracy and reproducibility are not good enough to quantify this difference. Note that product S3 has been abraded through to the steel substrate at 2000 and 1590 cycles.

At this stage it was decided to check three factors, with further tests. These were:

1. Reproducibility of the test using panels of the baked coating. The baked coating was chosen because its curing mechanism is under close control.

2. Effect of coating thickness. Product S2 had been inadvertently applied at 6 mils, about double the normal thickness. Solvent borne inorganic zins are sensitive to thickness and tend to show surface mud cracking at about this thickness. While this coating appeared to be free of mud cracking it was suspected that some surface weakening might have occurred causing some reduction in abrasion resistance. Fresh panels were prepared at about 3 mils.

3. Effect of humidity. Empirical testing had indicated that inorganic zinc silicates were softer when wet and it was decided to run comparisons on the two coatings selected, at different humidities.
The tests carried out to date had been at a relative humidity of 50% ± 5%.

Results of this further series of tests are shown in Table 3.

Finally some results were obtained from a private communication from American sources using one identical coating (W1), a post cured coating (P1), and a solvent borne coating not included in our series (S4). These results are given in Table 4.

No information is available on relative humidity during these tests.

**COMMENTS ON THE RESULTS**

Bearing in mind the very wide range of abrasion resistance indicated from these results the reproducibility of the test on the same plate, from plate to plate, and from laboratory to laboratory, appears to be adequate for use to draw general conclusions.

The accuracy of the test is not high and does not warrant results being reported beyond two significant figures.

Relative humidity appears to affect abrasion resistance, with better resistance at lower humidities. No reason can be offered for this result but it is consistent with the authors’ previous general impressions.

Film thickness appears to be important, as would be expected and should be controlled within normally specified limits for most useful comparisons.

**CONCLUSIONS**

Significant differences in abrasion resistance, and by inference, in practical damage susceptibility, are confirmed.

A wide range of abrasion resistances has shown up amongst the solvent borne coatings. The coatings chosen represent only a proportion of commercially available coatings, particularly of the solvent borne type, and may not necessarily be indicative of the whole field.

To better illustrate the range of results we have converted the thickness losses to wear cycles per unit of thickness, that is the number of standard Taber cycles needed to wear through the usually specified thickness of these coatings, that is, 3 mils. Using the results from Table 2 and averaging pairs, we obtain the following rounded off results.

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>Wear Cycles per 3 mils</th>
<th>Calculated Thickness Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baked</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Water borne self cured</td>
<td>25–50</td>
<td></td>
</tr>
<tr>
<td>Solvent borne self cured</td>
<td>2–25</td>
<td></td>
</tr>
</tbody>
</table>

Of interest for future work would be further investigation of effect of humidity, thickness variation, the rate of wear at increasing depth in the coating, and a wider cover of commercial coatings available.

It is the intention of the authors to carry out further work on these aspects, with the hope of gaining a better understanding of the coatings.

---

Table 4: RESULTS FROM AMERICAN SOURCES

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>Wear Cycles</th>
<th>Weight Loss</th>
<th>Dry Film Density</th>
<th>Calculated Volume Loss</th>
<th>Calculated Thickness Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>SELF CURED WATER BORNE:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P 1</td>
<td>1500</td>
<td>0.10 gm</td>
<td>5.11</td>
<td>0.020 cc.</td>
<td>0.3 mils</td>
</tr>
<tr>
<td>POST CURED COATING:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W 1</td>
<td>1500</td>
<td>0.04 gm</td>
<td>4.31</td>
<td>0.0092 cc.</td>
<td>0.12 mils</td>
</tr>
<tr>
<td>SELF CURED SOLVENT BORNE:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*S 4</td>
<td>500</td>
<td>1.18 gm.</td>
<td>3.57</td>
<td>0.33 cc.</td>
<td>4.2 mils</td>
</tr>
</tbody>
</table>

*Note: This coating failed at 500 cycles.*
REFERENCES

3. Ameron Corrosion Control Division.

APPENDIX I

Test Method:
Federal Test Method No. 141 (Method 6192)

Method of Application:
Air atomised spray.

Method of Ageing All Films:
Exposure to weather for three weeks.

Type of Abrasive Wheel:
Calibrase CS-17.

Pressure of Wheel Against Coating:
1,000 gms.

Relative Humidity During Test:
50% ± 5% (unless otherwise noted).

Test Plates:
Mild steel plate 4" x 4" x ¼". This thickness was chosen to avoid distortion of the plates during blasting. It was felt that distortion could result in uneven running of the plate on the test apparatus.

Surface Preparation:
Grit blast to Australian Standard CK9.4 Class 3.

APPENDIX II.

COATING DENSITY DETERMINATION USING MERCURY DISPLACEMENT

The technique used is similar to the standard method for determining density from weighing in air and weighing in water.

Water is unsuitable for this particular purpose because the coatings are porous and would absorb water, giving an erroneous result.

Mercury was investigated because of its excellent non-wetting properties and the belief that it would not penetrate the pores in the coatings. However, in order to ensure good surface wetting and the absence of occluded air bubbles on the surface of the specimen being weighed, it was decided to immerse the specimen in the mercury under vacuum.

Any mercury entering the pores of the coating under these conditions could be expected to remain there after removal at atmospheric pressure. A check weighing indicated nil mercury pick up even during evaluation and the technique was adopted.

All density determinations were carried out using mild steel shims, pre-weighed, and then coated on both faces.

In order to sink the specimen in the mercury, it is necessary to use a tungsten sinker and to correct the volume of the sinker for temperature variations in the mercury.

Calculations involved in this method are:

Weight of shim in air –W
Weight of sinker in mercury –WS
Weight of sinker + shim in mercury –WSF

Shim volume = \( \frac{WS + W - WSF}{13.53 \ (\text{@} 25^\circ \text{C.})} \)

Then: Dry film volume = Coated shim volume – shim volume.

The coating weight is determined from normal weighing in air and the density calculated in the usual way.
THE STRUCTURE OF INORGANIC Zn-RICH COATINGS EXAMINED
WITH OPTICAL AND ELECTRON MICROSCOPY

by

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ABSTRACT

Inorganic Zn-rich coatings consist of more than 70% by dry weight of
Zn dust and sometimes small concentration of other inert pigments in a
matrix, usually of silica. The coatings have a good performance record for
the protection of steel in open air exposure and marine environments, which
has been claimed to be due to cathodic protection. This view is based
mainly on case histories of practical systems and scratch tests on
specimens on weathering racks. It seemed therefore desirable to study the
morphology and structure of coatings, which had been exposed to a variety
of environmental conditions, in order to determine which factors influence
the effectiveness and lifetime of the coatings. For this purpose coatings
were sectioned and examined with optical and electron microscopy.

INTRODUCTION

Over the last 20 odd years Zn-rich inorganic coatings have gained a
firm hold in the market as both primers and complete systems for the
corrosion protection of steel, mainly for structures for which hot dip
galvanising is not economical because the individual members are too large
or it is desirable to apply the protection after on site construction. The
development of this type of coating started in the mid 1930’s. Early
patents filed in Australia and later elsewhere described a coating
formulation containing metallic dust pigments, including Zn dust in a
vehicle consisting of aqueous alkali silicate solutions; the coating being
mixed just before use in a ratio of about 20 pounds of pigment to six pints
of the vehicle.

In early commercial applications superfine grade of Zn dust only was
used in a solution of commercial "alkaline" grade sodium silicate (Na2O:SiO2
= 1:2). These formulations had the disadvantage that the useful pot life
after mixing of the ingredients was limited, being terminated by sudden
frothing due to hydrogen evolution. In addition the applied coatings had
to be baked at 120 - 320°C to render them insoluble. The cured coatings
although hard and tough had a tendency to become brittle and lose adhesion
to the underlying steel.

Later improvements of the properties of the coatings were achieved by
the use of special Zn dust with a more space filling particle size
distribution, the addition of lead compounds and oxidising agents and the
use of less alkaline silicates or alkyl silicates as vehicles for the
pigments. In this way it was possible to formulate coatings which become
insoluble in water by air drying or by chemical curing achieved by brush or
spray application of an acid reacting salt solution in a non aqueous
solvent.
The coatings which now have the widest applications are the self-curing types, which fall into two main categories:

(a) **Self-curing water-borne types:**
These are coatings based on the high ratio types of alkali metal silicates. Best curing rates are achieved with the highest possible alkali metal silicate ratio. Although very good results have been achieved with lithium silicate \((\text{Li}_2\text{O}:\text{SiO}_2 = 1:4.75)\) due to the relatively high cost of lithium silicate, potassium silicate \((\text{K}_2\text{O}:\text{SiO}_2 = 1:3.89)\) has been more widely used. Coatings of this type have been available since approximately 1965.

(b) **Self-curing solvent-borne types:**
These coatings are based on a solvent solution of alkyl silicates, usually ethyl silicate. Adjustment is made to the pH of the ethyl silicate solution, so that hydrolysis occurs with the loss of ethyl alcohol, when the applied coating is exposed to humid air. The alcohol evaporates leaving a coating consisting of Zn dust in a silica matrix containing no metal ions. These coatings have been available since 1959.

The performance of inorganic Zn-rich coatings is usually claimed by manufacturers to be due to the cathodic protection of the steel surface by the zinc. This claim is based mainly on rack exposure tests of specimen coatings and on case histories of practical systems, the most notable of which in this country is the 240 mile pipeline from Morgan to Whyalla in South Australia. This pipeline was coated in 1942 and was still in perfectly serviceable condition more than 20 years later and is now in a state where some sections have to be recoated.

The effective lifetime varies strongly with exposure conditions and ranges from \(\frac{1}{2}\) to 2 years for marine immersion to 20 years or more for open air exposure. This suggested that it is not merely the amount of zinc available for cathodic protection which is important for successful corrosion prevention with such coatings but that the proper development of coatings after curing plays an important role. In order to investigate this supposition, the internal morphology and structure of freshly cured and exposed coatings have been studied by examining the external surfaces and cross sections of the coatings with optical and electron microscopy.

**EXPERIMENTAL**

**Types of Samples**

Samples of coatings were taken from the following main groups:
1. Freshly cured coatings without any outdoor exposure,
2. open air rural and light industrial exposure of up to 7 years,
3. overcoatings put on primers after 6 - 9 months exposure,
4. marine exposure up to 5 years,
5. coatings which had undergone accelerated laboratory tests.

**Specimen Preparation**

The samples were self-curing, water-borne or solvent-borne type coatings on a mild steel base, which took the form of panels, 75 mm x 130 mm x 3 mm, or lengths of 25 mm angle iron. Panels were used for weather rack exposure at various sites and angle iron for marine exposure at the Australian Corrosion Associations Marine Test Station at Point Cook, Victoria, where they were attached to a wooden pier.
After removal from the test site the surfaces of the coatings were inspected optically with the naked eye and aided with a low powered microscope, to select apparently representative and special areas for closer study. Such areas were then cut off the samples with a hack saw. If the surface was mainly of interest the cut off pieces were examined directly at higher magnification with optical microscopy or after being coated with a conducting film of carbon, with scanning electron microscopy. However, if the underlying morphology and structure was of interest, the cut off pieces were mounted edge on in polyester resin and later ground and polished until features of interest emerged at the surface. Most sections were prepared normal to the coating thickness, but sometimes taper sections were prepared by mounting the cut off pieces in the resin at an inclination of 30° to 10°.

The sections were ground and polished using standard metallographic techniques, first on SiC abrasive papers (Nrs. 320 - 600) and finally with diamond paste (6µ - 1µ) on a wheel with oil or kerosene as lubricant. In some instances water could be used as lubricant for the polishing on paper, but for specimens which had been exposed to marine conditions or accelerated laboratory tests, the use of non-aqueous lubricants throughout the preparation was absolutely essential. Care had to be taken to avoid moisture pick up when prepared sections were stored, as this would lead to preferential corrosion of exposed metallic particles of zinc near the steel. Initially a layer of a harder metal was deposited in vacuum onto the outer surface of a coating and the thickness of the deposited metal was then increased further by electro-deposition. Later on it was found that rounding off of the coating at the outside could be sufficiently avoided by mounting specimens with the coatings facing each other at a suitable separation. This was preferred especially for analytical examination.

**Examination of Specimens**

Specimens were examined with a Bausch and Lomb metallographic microscope at magnifications of up to 1000x at normal incidence. Polarised light was found to be useful to distinguish between rust and zinc corrosion products. Scanning electron microscopy was carried out in a JEOL - USM3 at 15 - 20 KV with a final magnification mostly at up to 600x, but in selected areas at up to 5000x. Before examination in the scanning electron microscope, specimens were carbon coated in a conventional high vacuum chamber. The elemental composition across the thickness of a coating or at special points within a coating and the distribution of particular elements in coatings were examined with an EDAX energy dispersive X-ray analyzer attached to the scanning electron microscope. The powdered matrix and thin flakes of broken up coatings were also examined in transmission in a Philips EM 200 electron microscope being operated at 100 KV.

**OBSERVATIONS AND INTERPRETATIONS**

**General**

In this section we describe first the appearance of new coatings and then of coatings which have undergone different outdoor exposures. The appearance of coatings after accelerated laboratory testing is the theme of a separate paper in this conference.

Because they are easier to obtain and they are pictorially more pleasing and of better definition, we shall reproduce here mostly micrographs taken on the scanning electron microscope. However, we wish to stress that in all cases optical and electron microscopy have been used as complementary techniques.
New Coatings after Curing

In Figure 1 we show a section through the entire thickness of a freshly cured solvent-borne (ethyl-silicate) coating on a mild steel base. While in Figure 2 we show part of a section through a freshly cured water-borne (potassium silicate matrix) coating. Neither of these coatings has been exposed outdoors.

The dark contrast at the top of Figure 1 is the plastic embedding material which consists of low atomic number elements and thus has a low secondary electron yield. At the top surface of the coating the presence of a layer of electro deposited copper is indicated by a wavy line of very light contrast. In the coating the most obvious features are the circular shaped sectioned particles of metallic zinc which are light grey in contrast. It is noted that the matrix in these coatings is nearly transparent so that particles of metallic zinc which are embedded deep within the matrix are also revealed. The latter are of a slightly darker grey, than the particles that are intersected. Particles of filler material within the coating are easily recognised because they differ in shape (crescent or unevenly rounded) and contrast (darker) from particles of metallic zinc. The mild steel (near the bottom of Figure 1) is a shade darker in contrast than the zinc particles. The sand blasted steel surface is very rough with deep holes that are sometimes covered by folded over strips of steel. The lighter contrast along the steel coating interface is due to a step down in level from the harder steel base to the softer coating. Examination of large numbers of micrographs like that in Figure 1 has shown that the contrast between the coating and steel is always very good. The coatings interlock very well without leaving cavities at the interface and smooth out even very rough surfaces. Usually metallic zinc particles are packed right up to the steel surface and only occasionally are deep cavities in the steel filled with matrix material only. When the matrix is an alkali-silicate (Figure 2) it is much darker in contrast. Thus, in sections of such coatings metallic zinc particles are revealed only when they are either intersected or are at least close to the surface of the section. The greater opacity of the alkali matrix makes it possible to examine the morphology of the matrix without having to metallise the sections.

Examination of fractured coatings has shown that the matrix encapsulates the zinc particles with a thick skin. In Figure 2 one can see that in between larger particles there are often cavities left in the coating. Occasionally such cavities may be large (>25 \( \mu \)m across) and shaped irregularly, but more commonly the cavities are smaller (<3 \( \mu \)m across) and round. Sometimes curtain like sheets of matrix material span gaps between separate zinc particles. Transmission electron microscopy of ground up coatings has shown that the solidified matrix itself is very porous. Initially it is rather structureless, but after ageing (of the order of 3 weeks) its appearance is that of a rigid framework permeated with very small cavities and channels. Electron diffraction shows that after this time the matrix exhibits a high degree of crystallinity.

The zinc particles appear smooth at up to about 1000x magnification but rough at 3000x. Microscopy of zinc dust used for coating formulations showed that loose powder particles sometimes are very irregularly shaped. The surface of the particles is usually covered with an oxide layer. This layer is very thin, of the order of 50 nm, for smooth spherical particles, but the surface of irregularly shaped zinc particles is often covered with heavy clumpy oxide. The oxide layer is the result of the manufacturing process used in this country. Coating manufacturers do not mind the oxide layer being present as it extends the pot life of formulations without affecting the usually expected performance of coatings.
There is no evidence of segregation of zinc particles across the coating thickness. The zinc particles appear closely packed and randomly distributed. Contact between adjacent zinc particles is frequent in the sections, hence very common in three dimensions. However, this contact usually leaves essentially intact the oxide film at the surface of a particle.

Coatings after 7 Years Open Air Exposure

As an example of how coatings change over long periods of exposure we show in Figure 3 part of a section of a coating which was exposed for 7 years on a weather rack in light industrial atmosphere. The following description of the state of coatings after this time is based on the examination of a large number of specimens.

Examination of Figure 3 shows that some of the metallic zinc particles have been corroded in parts. The extent of corrosion can be determined as the original outline can often be ascertained because the position of the initial oxide layer on a particle is marked by a slight groove in the section (slightly darker contrast) The zinc corrosion products have generally been accumulated in the surrounding matrix (e.g. compare contrast in space between metallic zinc particles in Figures 2 and 3 and Figures 1 and 3). The presence of zinc corrosion products in the matrix after exposure was confirmed with X-ray spectroscopy of sections and electron diffraction of ground up coatings. Not only is the matrix itself permeated with zinc corrosion product but also some of the actual cavities have been filled with zinc corrosion products.

In scanning electron micrographs the surface of a coating appears rough and weathered after 7 years of exposure (Figure 4). Optical microscopy with polarised light showed that there is still some metallic zinc left in the outermost layer of such a coating. But examination of sections revealed that the outermost part of the coating consists of a skeleton of matrix permeated with zinc corrosion products and containing spherical holes. The holes are the original sites of zinc particles. The metallic zinc has been corroded and the corrosion products have been lost as they appear to be less resistant to leaching than the matrix when it is permeated with corrosion from ducts.

In the outer 1/7th of the original coating thickness most of the metallic zinc is converted into corrosion products but the central parts of large zinc particles often remain uncorroded buried in corrosion products. In the outer 1/3rd of the coating most zinc particles have been at least partly attacked, but in the inside 2/3rds of the coating, only a few zinc particles, apparently at random show signs of attack. There are occasionally areas where the attack has penetrated further than the outer 1/3rd of the coating and never was any rust observed at the steel coating interface except when the rust appeared to have been contained in a very deep crevice and was not removed by the abrasive blasting. Any such rust pockets appeared not to be actively growing under a cured coating. In general, after this time of exposure the matrix is completely permeated by corrosion products, except for a few pockets, sparsely distributed.

Open Air Exposure for Less than 7 Years

In Figures 5a and b we show sections through samples of coatings that were put onto inorganic zinc-rich primer after the former had been exposed for 6 months. Before top coating the primers were cleaned by sweep blasting (Figure 5a) or by wire brushing (Figure 5b). The top coats were then exposed for another 4 months to light industrial atmospheric conditions. As illustrated in Figure 5b the more usual development of the top coat during the first few months of exposure is the formation of a
definite layer of corrosion products near the outer surface of a coating but occasionally the zinc corrosion products permeate immediately deeper into the coating (Figure 5b). Generally the advancement of corrosion products into the interior of the coating is such that they reach the coating steel interface within about 2 years of exposure under open rural or light industrial atmospheric conditions.

**Attack on Zinc Particles**

If one examines the attack on zinc particles one finds that the attack on very large particles is usually uneven and that the extremely small particles are often not attacked at all even after long times of exposure. The attack on large particles is often due to their size being so extreme that they extend through the larger part of the coating thickness to close under the outer surface. This is illustrated in Figure 6 where the corrosion of the very large particle is most extensive near the surface. The presence of such particles is generally deleterious for a coating because the volume of the surrounding matrix is insufficient to accept all the zinc corrosion products. This causes the coating to swell and form cracks to the surface. Figure 6 also illustrates that very fine zinc particles may remain unattacked close to a fast corroding particle. The uneven attack on large zinc particles is not always due to a change in environment across the surface of the particle, but may also be the result of the particle consisting of different grains. This is illustrated in Figures 7a, b. The polarised light used for the optical micrograph (Figure 7b) reveals that the large zinc particle shown in the scanning electron micrograph of Figure 7a consist of different grains and that the attack on the particle is limited to certain grains only. At present we do not yet know if this type of variation in attack is associated with variations in impurity content of different grains in particles.

**Effect of Damage to Coatings**

When specimens exposed to rural or light industrial atmospheres are scratched there is a very slight amount of rust visible in the scratch, but this does not develop any further. Examination of sections across scratches with polarised light showed that a large part of the steel surface in the scratch becomes covered with zinc corrosion products (Figure 8). Examination of sections of specimens which were only coated in parts (Figure 9) showed that, as the coating ages the zinc corrosion products extend onto the bare areas and rust is observed only at some distance from the original edge of the coating.

**Marine Exposure**

The development of coatings on exposure is similar for marine conditions, but in this case it proceeds on an accelerated scale. This is illustrated in Figures 10a, b and c, which show sections through a specimen at the high (Figure 10a), intermediate (Figure 10b) and low tide level (Figure 10c) after 1½ years exposure at Point Cook, Victoria. Examination of the Figures shows that after this time the matrix is completely compacted and filled with corrosion products at the high tide level. There is a distinct layer near the outer surface of the coating where the corrosion of zinc particles is more extensive.

At the intermediate tide level (Figure 10b) leaching of the outer surface has removed zinc corrosion products from the original sites of zinc particles down to about half of the original coating thickness, and only about 1/3 of the original coating still consists of metallic zinc particles in a compacted matrix.

At low tide level (Figure 10c), the coating has lost all metallic zinc particles in certain areas. This has lead to the dissolution of iron. But
it is noteworthy, that the coating is not undercut at the edges. Rust is
formed in the coating and is to a large extent retained there. Optical
microscopy showed that the rust reduces the leaching of zinc corrosion
products from the original sites of metallic zinc particles. This effect
is also noticeable in Figure 10c, because the thickness of the coating is
greater on the left hand side than on the right hand side where there is
still a layer of zinc particles left near the steel surface.

SUMMARY AND CONCLUSION

The main points of the above descriptions can be summarised as
follows:

1. The Zn dust used in coatings usually contains some Zn oxide. This is
   present in particulate form or covers the outside of Zn particles.
   Most particles of Zn carry only a thin oxide skin but some carry thick
   oxide layers.

2. The coatings effectively even out surface irregularities and interlock
   with the underlying steel without leaving voids. Zn-particles are
   evenly distributed but inaccessible crevices at the steel surface
   often contain matrix material only.

3. Cured coatings consist of a framework of Zn particles which are in
   contact. The solidified matrix forms a skin around the Zn particles
   or extends in form of lamellae across gaps between them.

4. The solidified matrix itself is porous. When broken up samples of
   matrix are examined with transmission electron microscopy, the matrix
   of a 1 day old coating appears nearly structureless and amorphous, but
   in a 3 week old coating it consists of flakes with a high degree of
   crystallinity.

5. When coatings are scratched the exposed steel does not rust and
   eventually becomes covered by Zn corrosion products, thus remaining
   protected although all the metallic Zn in the vicinity has been used
   up. In undamaged areas of coatings Zn particles near the surface
corrode first. The corrosion products fill the pores and voids in the
surrounding matrix; thus, under open air exposure, a definite layer of
corrosion products is built up over the initial 1 - 3 months. Not all
metallic Zn is used up to fill the voids and pores in the adjacent
matrix, nor do all Zn particles corrode at similar rates, nor is the
rate generally constant over the surface of a single particle.

   With continued exposure the corrosion product layer extends deeper
   into the coating and generally reaches the steel surface after about
   1½ to 2 years. However, the advance of the layer is uneven and after 7
years pockets in the matrix unfilled by Zn corrosion products may
still persist near the steel surface.

   When the matrix seems to be saturated with corrosion products, only Zn
particles near the surface are extensively corroded but those well
inside the coating are usually much less attacked. The filling of the
matrix is therefore due mainly to the inward diffusion of corrosion
products rather than the advancement of a corrosion front. The
corrosion products thus form a barrier which hinders access of
reactants.

6. Coatings usually contain "oversize" particles (50 μm diam.), which
   constitute weak spots. The surrounding matrix cannot absorb all the
corrosion products and cracks usually extend from such particles to the outer surface.

7. After all of the matrix has been filled with corrosion products usually about 60% of the original metallic Zn content still remains in the coating. This corrodes, or is lost as such, as the coating erodes from the outside. Corrosion products leach out preferentially from the sites occupied originally by the Zn particles, so that the outside of the coating consists of a skeleton of matrix filled with corrosion products. The life time of a coating seems to be determined mainly by its resistance to erosion because it takes about 2 years to fill the matrix whereas coatings have been reported to provide protection for 20 years or more. For the greater part of the life time, the sites of Zn particles are thus actually weak spots in the coating.

8. Coatings exposed to a marine environment behave similarly but on an accelerated time scale, the life times of coatings ranging from 0.5 to 2 years for immersion to 10 years for marine atmosphere. When in a marine environment coatings become perforated, they do not lift off. However, the rust which is formed stains the coating and visually the deterioration seems to be worse than it really is. Examination of cross sections shows that although appreciable areas of steel may be exposed, Zn particles in the surrounding coating still appear to provide cathodic protection.

Two main conclusions may be drawn from this work:

i. This type of coating acts mainly as a barrier. In addition it provides cathodic protection in case of mechanical damage.

ii. Present day coatings contain more Zn than appears to be necessary for the protection of the underlying steel. One should therefore examine how the Zn content can be reduced without impairing the effectiveness and lifetime either by replacing some Zn by cheaper materials or by altering the structure of coatings.
Figure 2: SEM micrograph. Part section through Zn-rich coating of potassium silicate type. The coating is cured but not exposed. Magnification: a) 1000x, b) 3000x.

Figure 3: SEM micrograph. Part section through Zn-rich coating of potassium silicate type after 7 years exposure in light industrial atmosphere. Magnification: 1000x.

Figure 4: SEM micrograph. Surface of Zn-rich coating of potassium silicate type after 7 years exposure in light industrial atmosphere. Magnification: 1500x.
Figure 5: SEM micrograph. Cross section through top coat of potassium silicate type applied over a primer of the same type. The primer, after 6 months exposure in a light industrial atmosphere has had different surface treatments before topcoating. Topcoat exposure 4 months in light industrial atmosphere; top, primer wire brushed; bottom, primer sweep blasted. Magnification: 900x.

Figure 6: SEM micrograph. Effect of over-large Zn particle on a coating of potassium silicate type. Note the crack passing from the particle to the surface. Very small Zn particles are not corroded at all. Magnification: 500x.
Figure 7: Rate of corrosion of Zn particles varies with different subgrains, upper SEM micrograph, magnification 900x, lower optical micrograph with polarised light, magnification 750x.

Figure 8: Optical micrograph taken with polarised light of cross section through scratch in Zn-rich coating (potassium silicate type) after 3 years exposure in light industrial atmosphere. Magnification: 190x.

Figure 9: SEM micrograph. Through Zn-rich coating of potassium silicate type. The coating covers only part of the steel, exposure is 3 years light industrial atmosphere. R denotes position of rust. Magnification: 500x.
Figure 10: SEM micrograph. Cross section through Zn-rich coatings of potassium silicate type on mild steel after 2 years exposure at marine test station at Point Cook in Victoria. Upper, near high tide level, middle, at intermediate tide level, lower, near low tide level. Magnification: 600x.
AN ELECTRON MICROSCOPE STUDY OF THE STRUCTURE OF INORGANIC Zn-RICH COATINGS AFTER ACCELERATED TESTING

by
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Abstract

A method of accelerated testing used in practice, is to apply a potential and pass a current between a specimen of a coating and a steel counter electrode in an aqueous electrolyte. The electric charge used up to the point where the potential at the coating indicates that bare steel is exposed to the electrolyte is then supposed to be a measure of the amount of zinc available in the coating for cathodic protection of the steel.

Examination of metallographic cross sections of coatings which had undergone such accelerated tests in seawater in the laboratory has shown that, compared with specimens which had been simply immersed in seawater from a pier, very little of the zinc corrosion products is retained in the matrix after testing. Furthermore, when the accelerated tests are continued until the coating breaks down completely, the nature and distribution of rust differ from that obtained on specimens immersed in seawater.

INTRODUCTION

Inorganic Zn-rich coatings were first introduced in 1939 (1). Since this date, four distinct types of coating have been developed and used in Australia. The differences are essentially related to the curing mechanism and the four types can be broadly divided into categories as follows:

1.) Baked water-borne.
2.) Post-cured water-borne.
3.) Self-curing water-borne.
4.) Self-curing solvent-borne.

These coatings have been used as single coats, usually specified 62.5 - 75 microns dry film thickness. However, they are sometimes overcoated with organic top coats to give additional protection.

OBSERVATIONS AND INTERPRETATIONS

Performance Testing of Inorganic Zn-rich Coatings.

The performance of inorganic Zn-rich coatings in preventing corrosion has been established by exposure testing and observing field applications over a period of years. Examples of the performance of single coat applications are shown in Table I.
A site of particular interest, in regard to exposure testing, is the Australasian Corrosion Association's Marine Test Station at Point Cook, Victoria. Here coated angle iron specimens, 3 meters long, are attached to the side of a jetty. Various sections of the specimens are exposed to a marine atmosphere, splash, tidal and marine immersion conditions. Thus four separate zones of varying severity are encountered on the same angle iron specimen. Figure 1 shows a typical angle iron specimen after removal from the site. The four exposure zones are indicated along the length of it. Tests on coatings have been carried out at this station over the last 20 years. Break down of a coating usually proceeds in the following general manner. Failure first occurs in the tidal zone and proceeds from there first down into the immersion zone and then into the splash zone and finally into the atmospheric zone. First failure is usually detected visually in the tidal zone after ½ - 2 years and in the atmospheric zone after about 10 years.

As normal life times of coatings under rural and light industrial atmospheric exposure conditions range from 20 to 30 years, it is obvious that marine conditions cause the inorganic zn-rich coatings to fail most rapidly. While the use of organic top coats extends the life considerably in the most severe tidal, immersion and splash zones, the desirability of having improved formulations for these conditions which give satisfactory service without organic topcoats is quite obvious. For this development work, the time needed to establish performance data by field testing is lengthy and substantial delays occur before sufficient data can be accumulated and new or modified formulations can be introduced commercially. It would therefore be of advantage to have a reliable accelerated test method for this type of coating.

Accelerated Testing of Inorganic Zn-rich Coatings.

The 5% ASTM salt fog test has been used as an accelerated test for such coatings but Garoutte and Hutchinson (2) quote: "There are those who believe that if an inorganic zinc primer lasts 1000 hours in a 5% ASTM salt fog cabinet, it is acceptable for use. It has been our experience that the best inorganic zinc primers last more than 5000 hours in this test, while many inorganic zinc primers that last 1000 hours will fail completely by 2000 hours. The best inorganic zins are tested in the field after laboratory testing". A time of 5000 hours (about 30 weeks) is quite a lengthy accelerated test and the desirability of having a test that produces results in a considerably shorter time is apparent.

When electrode potentials of the specimens at Point Cook are periodically monitored against an Ag/AgCl reference electrode, the value of the potential is initially close to that of zinc. The potential gradually changes with time and becomes steady as it approaches that of iron. As the latter value is attained, rust spots in the coating can be detected visually. In Figure 2 the potential is plotted against the exposure time for three coatings, illustrating the best and worst results observed as well as the normal result observed for most inorganic zn-rich coatings. As there appears to be a correlation between the time for the potential to change from that corresponding to zinc to that corresponding to iron and the first appearance of rust when carrying out tests at Point Cook, it seemed desirable to investigate whether the life of a coating could be predicted from an accelerated test first proposed by Craw for these coatings (3).

In the procedure proposed by Craw (3) a potential is applied to drive a current between a coated specimen and a steel counter electrode in an electrolyte consisting of synthetic or natural seawater. The electric
charge used up to the point where the potential of the coated specimen corresponds to that of iron is taken as a measure of the amount of zinc available for cathodic protection. Further, the time taken for the potential to change is defined as the "accelerated life" of coatings. Tests were carried out using this method with natural seawater as an electrolyte. After initial experiments with varying current densities, the value of the latter was standardised to 1 mA dm$^{-2}$, as this value caused coatings of proven good performance in the field to fail in 14 - 27 days during accelerated testing. The results of the accelerated tests were then compared with performance tests of coatings at the Point Cook test site. As angle iron test specimens are difficult to coat uniformly and because the specimens at Point Cook are sometime subject to damage, it was decided to record the time to general failure in the tidal zone. In this way any slight failures due to extraneous causes were eliminated. The results recorded in Tables II and III have been obtained on this basis.

Examination of the Tables reveals some correlation between the time taken to failure at Point Cook and by the accelerated tests. Coatings with metallic zinc contents of at least 72% are regarded as giving satisfactory performance. The coating with the lower metallic zinc content, viz 42.3% is regarded as an inferior inorganic Zn-rich coating. The general philosophy of formulating in the past has been that the higher the zinc content in an inorganic coating, the longer lasts the protection against corrosion.

From a commercial point of view it may be desirable to use extenders to reduce the costs of coatings with the higher metallic zinc contents and still provide corrosion protection of acceptable standards. To evaluate this approach standard, self-curing potassium-silicate coatings were modified with extenders to give metallic zinc contents of 52% and 65% respectively. These modified coatings were then evaluated using the accelerated tests and exposure at Point Cook. In these results there is an anomaly, because it would have been expected that the coating 2 (see Table III) would have failed somewhere between 4 to 14 days.

**Microscopic Examination of Inorganic Zn-rich Coatings.**

It has been shown that exposure of Zn-rich coatings leads to the formation of barrier layers which reduce access of moisture and air to the underlying steel (4) and that the development of the barrier layers can be examined with optical and electron microscopy. Using the techniques and specimen preparation described elsewhere (4) the structure of coatings was examined with microscopy after natural exposures and after accelerated testing. The self-curing water-borne potassium silicate type of coating was chosen for this work because this coating type has been most extensively examined before (4).

Typical cross sections through coatings which have failed in marine exposure tests and in accelerated tests in sea water are shown in Figures 3a and b respectively. In both cases the tests were continued until the value of the potential of the coated specimen, measured against an Ag/AgCl reference electrode, was very close to the value corresponding to iron, i.e. to the point of visual failure in the tidal zone for the marine exposure. The appearance of the surfaces of such specimens is, with respect to roughness and cracking, entirely consistent with the information contained in the micrographs of sections. However, it is only by the inspection of sections that it is possible to obtain a true picture of the physical state of a coating and of the amount and distribution of metallic zinc remaining within a coating after a given exposure.
Examination of a range of electron and optical micrographs provided the following general picture of coatings tested to the point of failure:

i) **Marine Exposure (Fig. 3a)**: The coatings are generally reduced to about 1/3 of their original thickness. In most areas the outside of the coating consists of a skeleton of matrix containing holes which mark the sites of zinc particles which were completely consumed. From these sites the zinc corrosion products were then lost preferentially by leaching and dissolution. Metallic zinc particles and dense matrix saturated with zinc corrosion products still exist near the steel surface except in areas where the corrosion has penetrated the whole thickness of the coating. In these areas rust has been retained in the coating and this has reduced the loss of zinc corrosion products from the sites of metallic zinc particles.

ii) **Accelerated Testing (Fig. 3b)**: During accelerated testing in seawater in the laboratory the original thickness of the coating is maintained, but the surfaces show cracks which penetrate deep into the coating. Metallic zinc particles are still numerous throughout the thickness of a coating, but from some sites particles have partly or completely disappeared. The matrix is generally not compact and has a leached stringy appearance. Usually there is a narrow region close to the surface of the steel where the metallic zinc has been more extensively corroded and from where more zinc particles have been lost than from near the outer surface of a coating. The cracks which are visible in the sections are also obvious in micrographs taken of the surface (Fig. 4a). Other surface features, which are typical of specimens which have been through accelerated tests but are not observed after normal exposure are pits and craters (Fig. 4b). The sizes of pits and craters are typically from a few tenths of a millimetre across to a few millimetres across in extreme cases. These pits and craters become obvious to the naked eyes shortly after specimens are removed from the test solution because they are the sites where brown rust quickly starts to accumulate.

**Development of Pits and Craters During Accelerated Testing.**

The way in which pits or craters form during accelerated testing is illustrated in Figures 5a to d. At first some part of a coating is slightly lifted like a hinged lid (Fig. 5a). In sections (Fig. 5b) it is seen that the lid usually does not extend through the whole thickness of the coating. In addition one can see transverse cracks which are usually wider at the underside of a lid. The cracks indicate that a lid is being pushed upwards usually only at a few points and tends to break up into smaller fragments. Although points of contact can sometimes be seen in sections, it is not obvious where the upward forces reside. At higher magnification (Fig. 5c), it can be seen in sections that zinc particles near the gap between the lid and the rest of the coating are generally corroded more extensively than in the lid itself. In old craters which have lost their lids (Fig. 5d) large nodules can often be observed. When a lid, which is still firmly held in the coating, is removed with the aid of fine tweezers, which sometimes requires considerable force, it is possible to observe in the bottom of the resulting crater nodules which expose cleaved surfaces (Fig. 6a) and matching sets of nodules with cleavage faces can be seen on the underside of the removed lid. X-ray microprobe analysis reveals only calcium at the cleavage face of nodules (Fig. 6b) while mainly iron and zinc are observed on the general area at the bottom of the crater and at the underside of the lid (Fig. 6c). The elemental X-ray analysis was carried out with an energy dispersive detector which did not allow detection of elements with an atomic number less than that of sodium. However, as no other element
that could be combined with the calcium could be detected there is strong
evidence that the nodules consist mainly of calcium carbonate. The
formation of this compound can be envisaged in the following way. With
accelerated testing the cathodic reaction takes place with the coating
itself. As this reaction in some form or other removes hydrogen ions the pH
may be locally increased considerably in the coating. This may result in
the precipitation of calcium carbonate. In addition zinc corrosion products
will not be precipitated and thus the coating will be very weak. At present
the knowledge about the distribution of craters and their initial
development have not yet been sufficiently examined to say which local
conditions in freshly cured coatings constitute weak spots for crater
formation. However, as this form of breakdown is limited to accelerated
testing by applying a potential there is little economic incentive to
examine this point further.

SUMMARY

The above reported results show that although the accelerated tests
reproduce the order of failure of real exposure tests, and thus appear to
be as good as any accelerated test can be expected to be, this agreement is
quite fortuitous because:

1.) When the potential of the coating attains the value corresponding to
that of iron only about 30% of the original zinc content has been used
up and it has been shown elsewhere (4) that, when this amount of zinc
has been corroded under normal exposure conditions, all the matrix is
filled with zinc corrosion products and the coating is most effective
as a barrier.

2.) Optical and electron microscopy of cross sections of coatings after
accelerated testing have shown that the zinc corrosion products are
not retained in the matrix and this is opposite to what happens under
natural weathering conditions and marine exposure. A true acceleration
of the natural weathering is therefore not produced by the accelerated
test in its present state of development.

CONCLUSIONS

It is recommended that for any accelerated test under consideration
the microscopic examination of cross sections be employed to ensure that
the same physical structure is produced by the accelerated test as is
produced by the natural weathering process. If this is achieved it is
considered that such an accelerated test could be applied to forecast the
long term behaviour of coatings with confidence.

At present the outlook that reliable accelerated tests can be devised
and proved in the near future is very slim. The present authors have
therefore started work involving exposure tests of a series of different
formulations which are being exposed to a light industrial atmosphere. In
these tests the run-off from the samples is collected and analysed
periodically. It is hoped to detect defects in coatings from the appearance
of certain ions in the run-off.
REFERENCES

(1) Australia Patent 104,231

(2) Garoutte, J. D. and Hutchinson, M.
“Coating Problems Encountered in the Refining Industry and their Solution”

(3) Graw, D. A.
“The Determination of Available Zinc in Zinc Rich Paint Films”
Consolidated Mining and Smelting Co. of Canada Ltd., April 1958.

(4) Jaeger, H. and Sherwood, R. G.
“The Structure of Inorganic Zn-rich Coatings Examined with Optical and Electron Microscopy”
To be published 6th International Congress on Metallic Corrosion, Sydney December 1975.
TABLE I: Examples showing the performance of single-coat inorganic Zn-rich coatings.

<table>
<thead>
<tr>
<th>TYPE OF EXPOSURE</th>
<th>COATING TYPE</th>
<th>SITE</th>
<th>LIFE-TIME+</th>
<th>PROJECT</th>
<th>YEAR COATED</th>
<th>SUBSEQUENT MAINTENANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>RURAL</td>
<td>Baked Water Borne</td>
<td>Morgan-Whyalla Pipeline South Australia</td>
<td>1942</td>
<td>Some maintenance needed 1975</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Post Cured Water Borne</td>
<td>Murray I Penstocks Snowy Mountains N.S.W.</td>
<td>1964</td>
<td>NIL</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Self Cured Water Borne</td>
<td>Exterior of 9,000,000 litres water storage tank 250 km inland from Dampier Western Australia</td>
<td>1969</td>
<td>NIL</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Self Cured Solvent Borne</td>
<td>214 cm diameter Water Main Warragamba N.S.W.</td>
<td>1952-3</td>
<td>Was overcoated with aluminium spar varnish initially, to give better appearance. Has been subsequently recoated with aluminium spar varnish to maintain appearance.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>INDUSTRIAL</td>
<td>Baked Water Borne</td>
<td>Brooklyn VIC</td>
<td>Greater than 14 years</td>
<td>56 x 60 tonne capacity Rail Coal cars. N.S.W.</td>
<td>1965</td>
<td>NIL</td>
</tr>
<tr>
<td></td>
<td>Post Cured Water Borne</td>
<td>Brooklyn VIC</td>
<td>Greater than 14 years</td>
<td>30 wheat storage silos Pt. Adelaide SOUTH AUST.</td>
<td>1962</td>
<td>Some maintenance needed on exposed seaward side 1975</td>
</tr>
<tr>
<td></td>
<td>Self Cured Water Borne</td>
<td>Brooklyn VIC</td>
<td>Greater than 11 years</td>
<td>Exterior of Ammonia Tanks at a fertilizer Factory Brisbane QLD</td>
<td>1969</td>
<td>NIL</td>
</tr>
<tr>
<td></td>
<td>Self Cured Solvent Borne</td>
<td>Brooklyn VIC</td>
<td>Greater than 10 years</td>
<td>1.8 metre diameter Chimney Stack at a cement company Adelaide SOUTH AUST.</td>
<td>1969</td>
<td>NIL</td>
</tr>
<tr>
<td>MARINE ATMOSPHERE</td>
<td>Baked Water Borne</td>
<td>Pt. Cook VIC</td>
<td>10 years</td>
<td>Wharf Superstructure Pt. Latta Tasmania</td>
<td>1967</td>
<td>NIL</td>
</tr>
<tr>
<td></td>
<td>Post Cured Water Borne</td>
<td>Pt. Cook VIC</td>
<td>10 years</td>
<td>$8,000 dwt. bulk carrier &quot;Cluha Capricorn&quot; (Hatch coamings, hatch covers &amp; ballast tanks)</td>
<td>1971</td>
<td>NIL</td>
</tr>
<tr>
<td></td>
<td>Self Cured Water Borne</td>
<td>Pt. Cook VIC</td>
<td>10 years</td>
<td>Wharf Superstructure Cape Lambert W. AUST.</td>
<td>1970</td>
<td>NIL</td>
</tr>
<tr>
<td></td>
<td>Self Cured Solvent Borne</td>
<td>Pt. Cook VIC</td>
<td>Greater than 6 years</td>
<td>Shiploader &amp; Stockpile Gantry Eden N.S.W.</td>
<td>1968-69</td>
<td>NIL</td>
</tr>
</tbody>
</table>

+ TIME TO THE FIRST APPEARANCE OF RUST
TABLE II

Time to Failure of Standard Zn-rich Coatings after Accelerated Testing and after Marine Exposure at Point Cook, Victoria.

<table>
<thead>
<tr>
<th>Type of Coating</th>
<th>Metallic Zinc (%)</th>
<th>Time to Failure (Days)</th>
<th>Accelerated Test</th>
<th>Exposure at Point Cook</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-curing Solvent-borne (1)</td>
<td>42.3</td>
<td>2½</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Self-curing Water-borne</td>
<td>85.0</td>
<td>14</td>
<td>180 - 240</td>
<td></td>
</tr>
<tr>
<td>Self-curing Solvent-borne (2)</td>
<td>72.0</td>
<td>25</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>Self-curing Solvent-borne (3)</td>
<td>79.0</td>
<td>27</td>
<td>270 - 330</td>
<td></td>
</tr>
<tr>
<td>Self-curing Solvent-borne (4)</td>
<td>Unknown</td>
<td>27</td>
<td>270 - 330</td>
<td></td>
</tr>
<tr>
<td>Baked Water-borne</td>
<td>80.0</td>
<td>23</td>
<td>330 - 410</td>
<td></td>
</tr>
</tbody>
</table>

TABLE III

Time to Failure of Modified Zn-rich Coatings after Accelerated Testing and after Exposure at Point Cook, Victoria.

<table>
<thead>
<tr>
<th>Type of Coating</th>
<th>Metallic Zinc (%)</th>
<th>Time to Failure (days)</th>
<th>Accelerated Test</th>
<th>Exposure at Point Cook</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-curing Solvent-borne (1)</td>
<td>42.3</td>
<td>2½</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Modified Self-curing Water-borne (1)</td>
<td>52.0</td>
<td>4</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Modified Self-curing Water-borne (2)</td>
<td>65.0</td>
<td>17</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Self-curing Water-borne</td>
<td>85.0</td>
<td>14</td>
<td>180 - 240</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1: Coated angle iron specimen after marine Exposure. The Specimen is 3 m long. The exposure zones are indicated at the right of the specimen.
Figure 2: Plot of potential of coated specimen versus exposure time at Point Cook Test Station;
\( \Delta \) worst result, 3 months to first rust,
\( O \) normal result, 8 months to first rust,
\( x \) best result, 24 months to first rust.

Figure 3: SEM micrographs of cross sections of failed coatings on mild steel; a) failed during marine exposure, b) failed during accelerated testing in seawater in the laboratory.
Magnification: 600x.
Figure 4: SEM micrographs of surfaces of coatings after failure during accelerated testing; a) cracks, b) example of pit in coating. Magnifications: a) 1500x, b) 400x.

Figure 5: Details of formation of pits during accelerated testing; a) part of a coating lifts like a hinged lid, b) c) cross sections through raised lids and coatings, d) interior of pit after lid has been lost, note the largish nodules. Magnifications: a) 150x, b) 150x, c) 600x, d) 600x.
Figure 6: SEM micrograph of crater produced by lifting off lid with tweezers a) and elemental x-ray analyses b), c). The analysis shown in b) is of the cleavage face of a nodule, the one shown in c) is of the general area at the bottom of the pit. Magnification: a) 700x.
TESTING OF INORGANIC ZINC-RICH ANTICORROSION COATINGS IN DIFFERENT ATMOSPHERES

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INTRODUCTION

In previous work on inorganic zinc-rich coatings test specimens have been examined with both optical and electron microscopy, X-ray elemental analysis and electron or X-ray diffraction (1),(2),(3). These examinations have shown that the protective action of this type of coating results extensively from the interaction with the environment to which a coating is exposed. Zinc corrosion products, which are formed, are largely retained in the matrix where they fill pores and voids and thus limit the access of air and moisture to the underlying steel.

In order to increase our understanding of the formation of barrier layers and examine the extent to which the metallic zinc in the coatings provides cathodic protection to the underlying base metal, it appeared to be desirable to obtain more information about the influence of changes in the environment on coatings formulated with different matrices. Test panels, which were coated with various formulations, were therefore exposed to light industrial atmospheric conditions at Brooklyn in Victoria, Australia and to marine atmospheric and intermittent submersion conditions at the Australasian Corrosion Association’s marine test station at Point Cook in Victoria, Australia. In addition, test panels were subjected to accelerated testing in a salt fog cabinet (4) or under submerged conditions by applying an electrical potential between the panel and an uncoated mild steel electrode in an aqueous electrolyte (2).

EXPERIMENTAL AND TECHNIQUES

A potassium silicate matrix coating, which has been used commercially since 1965, was first selected because of its proven record of good performance in practical situations (FORMULATION 1). Three other potassium silicate formulations with reduced zinc content (FORMULATIONS 2, 3 and 4) and one with a lithium silicate matrix (FORMULATION 5) were also included. The latter was chosen because previous testing has suggested that this type of coating performs better than FORMULATION 1. However, because of higher costs, lithium silicate based coatings have not been used widely commercially.

Before preparing exposure panels, the metallic zinc in the formulations was determined in accordance with the procedure laid down in BS 3982: 1966, Appendix B, Method 2. The results were as follows: FORMULATION 1, 86%; FORMULATION 2, 76%; FORMULATION 3, 71%; FORMULATION 4, 64%; FORMULATION 5, 88%. The panels used were mild steel 15.2cm x 7.6cm x 0.16cm. Surface preparation was by abrasive blast cleaning in accordance with AS 1627, Part 4-1974 to a Class 3 standard. Application of the coatings was by conventional spray to a dry film thickness of approximately 75 micrometers. At Brooklyn, where some of the panels were part of an exposure series that has already been reported (3), they were mounted inclined in 31cm diameter glass funnels so that they were facing north. At Point Cook, the panels
were attached vertically to the northerly side of a jetty running about west - east. The panels subjected to marine atmospheric conditions were approximately 200 meters from the shore. At Point Cook panels were exposed for up to 4 years, but at Brooklyn exposure times extended to 7 years. Accelerated testing in the salt fog cabinet was extended for up to 1050 hours. The current density for accelerated testing under submerged conditions was 1 mA/dm\(^2\) and the electrolyte was seawater (2).

Panels were examined with all the methods used in (1), (2) and (3). However, here we concentrate on X-ray diffraction to show that this method is very suitable to fingerprint crystalline corrosion product distributions for different environmental conditions and determine the corrosion products and metallic zinc at different levels in a coating which enables one to reliably predict the further lifetime. Coatings were examined in the as-exposed state and after successive surface layers had been ground away on 1200 grade wet and dry emery paper using filtered power kerosene to wash away the debris. For the results summarised here in Tables 1 to 4, the diffractometer, a Siemens Kristalloflex 805, was operated as follows: Anode, Co, voltage 30 KV, current 30 mA, K-beta filter Fe, slit setting .3, .3, .3, .15. The X-rays were detected with a scintillation counter, measured with a ratemeter (time constant 2 s, sensitivity 2x10\(^3\) pulses/s) and recorded with a Siemens Kompensograph III. The mode of operation was 20/0 and the angular scan rate was 0.5° 20/min. However, to fit the metallic zinc peaks onto the recorder chart for most of the traces, the zinc peaks were scanned at a rate of 5.0° 20/min. Since all formulations had a similar size distribution of metallic zinc particles, the relative zinc content in different traces can simply be obtained from a comparison of the height of a particular metallic zinc peak. It is best to choose the peak resulting from crystal planes with 2.30 Å spacing, because the one resulting from 2.09 Å spacing often still exceeded the chart and the peak resulting from 2.46 Å spacings coincides with a strong zinc oxide peak. When the angle 2\(\theta\) exceeded 15°, specimens were rotated; the area examined with X-rays was the slightly in excess of 2 cm\(^2\).

RESULTS AND INTERPRETATIONS

Examination of Table 1 shows that the trace of the zinc dust used in the formulations reveals two small peaks resulting from zinc oxide besides the three prominent peaks corresponding to metallic zinc. Although not shown here, an applied coating of FORMULATION 1 exhibits, for the first few weeks of exposure, traces very similar to that shown for the zinc dust. However, after that time other peaks appear indicating the formation of crystalline corrosion products. At present it is not possible to ascribe these newly appearing peaks to definite compounds of zinc. However, the distributions of peaks observed are characteristic of the type of exposure and the matrix used in the formulation. As seen in Table 1, in the case of FORMULATION 1, after 4 years exposure, there is a greater variation of corrosion products formed and a greater amount of metallic zinc is used up in the marine atmosphere than is the case in the light industrial atmosphere. Whereas in the case of FORMULATION 5, the differences are much less marked. Thus the marine atmosphere is much more severe on inorganic zinc coatings than is a light industrial atmosphere and a lithium silicate based coating appears to be the more durable coating in the more aggressive environment. As seen in the two bottom traces, where some peaks are labelled SiO\(_2\), this method readily detects zinc extenders, provided they are crystalline. The admixture of non-crystalline extender could be detected with X-ray diffraction only by a reduction of the height of the metallic zinc peaks and an increase in the background, which would not be accurate especially if coatings have been exposed for some time.
TABLE 1.

X-RAY DIFFRACTION

COMPARISON OF 4 YEARS EXPOSURE TO INDUSTRIAL AND MARINE ATMOSPHERE

<table>
<thead>
<tr>
<th>FORMULATIONS 1, 2, 3</th>
<th>POTASSIUM SILICATE MATRIX</th>
</tr>
</thead>
<tbody>
<tr>
<td>FORMULATION 5</td>
<td>LITHIUM SILICATE MATRIX</td>
</tr>
</tbody>
</table>

FORMULATIONS 2, 3 CONTAIN SILICA EXTENDER

ZINC DUST USED IN FORMULATIONS

FORMULATION 1: INDUSTRIAL ATMOSPHERE

FORMULATION 5: INDUSTRIAL ATMOSPHERE

FORMULATION 5: MARINE ATMOSPHERE

FORMULATION 2: MARINE ATMOSPHERE

FORMULATION 3: MARINE ATMOSPHERE

INTENSITY in arbitrary units

ANGLE 2θ in degrees
From Table 2 it is seen that when exposed coatings are abraded, peaks of corrosion products are gradually removed, suggesting that the products form in the outer layers and move into the bulk of a coating over a period of several years. The lowest trace in Table 2 shows a peak characteristic of metallic iron, indicating that after this number of strokes the mild steel base can be detected. When FORMULATION 1 coatings which have been exposed to marine conditions are abraded (Table 3), not only do the zinc corrosion peaks detected at the exposed surface disappear, but new peaks become prominent. Now it is not until 32 strokes of abrasion, that the metallic zinc peaks return to near the height shown in the zinc dust trace in Table 1. This indicates a marked variation in the corrosion product distribution in the coatings and a substantial consumption of metallic zinc throughout much of the thickness of the coating. The comparison of these traces with the lowest one in Table 3 illustrates the severity of the marine tidal area compared with the marine atmosphere. When natural marine exposure is compared with accelerated testing, the salt fog cabinet or under submersion (Table 4) it becomes apparent that the product distribution resulting from the tests is radically different again. This indicates that the accelerated tests in no way simulate natural exposure conditions (compare also Tables 1 and 4) and that results of such tests should be viewed with caution. This conclusion is entirely consistent with that deduced previously from microscopic observations (1),(2).

PRACTICAL CONSIDERATIONS

As it is now about 35 years since the early applications of these types of coatings, many situations will arise in the near future where coatings are still apparently sound and protecting to the underlying steel, but the coating is approaching the end of its lifetime because much of the metallic zinc has been used up. Thus the questions that arise are:

i) Should deterioration be allowed to proceed to the point where rusting of the underlying steel makes it necessary to use costly abrasion before a new long-life protective system could be applied?

ii) Could an organic top coat be applied at a most appropriate time and thus prolong the lifetime of the coating system with less costly surface preparation?

It is suggested that the techniques reported here applied to samples cut from actual field structures could well assist in making the necessary decisions.
<table>
<thead>
<tr>
<th>TABLE 2.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-RAY DIFFRACTION</td>
</tr>
<tr>
<td>DEPTH OF CORROSION OF COATINGS EXPOSED 7 YEARS TO INDUSTRIAL ATMOSPHERE</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angle 2θ (in degrees)</th>
<th>Depth Intensity in arbitrary units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
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</tr>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>

*ALL CURVES FORMULATION 1 ON MILD STEEL*
TABLE 3.
X-RAY DIFFRACTION
DEPTH OF CORROSION IN COATINGS EXPOSED 4 YEARS TO MARINE ATMOSPHERE

<table>
<thead>
<tr>
<th>Intensity in arbitrary units</th>
<th>Angle 2θ in degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
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<tr>
<td>5</td>
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<td>4</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
</tr>
</tbody>
</table>

Formulation 1: Marine Atmosphere
Exposed Surface
Abraded 3 strokes on 1200 paper
Abraded 4 strokes on 1200 paper
Abraded 8 strokes on 1200 paper
Abraded 16 strokes on 1200 paper
Abraded 32 strokes on 1200 paper

Formulation 1: High Tide Level
2.5mm Abraded 3 strokes on 1200 paper
TABLE 4.

X-RAY DIFFRACTION

COMPARISON OF DIFFERENT MARINE EXPOSURES AND ACCELERATED TESTS

<table>
<thead>
<tr>
<th>INTENSITY in arbitrary units</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>5</td>
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<td>4</td>
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<tr>
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</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>0</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>ANGLE 2Θ in degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>

FORMULATION 1 MARINE ATMOSPHERE 4 yrs

FORMULATION 1 HIGH TIDE LEVEL 2.5 yrs

FORMULATION 1 1.35m ABOVE HIGH TIDE LEVEL 2.5 yrs

FORMULATION 1 1032 hrs SALT SPRAY

FORMULATION 1 784 hrs SALT SPRAY

FORMULATION 1 ACCEL TEST IN SEA WATER TO IRON POTENTIAL

FORMULATION 1 ACCEL TEST IN SEA WATER EXTENDED AFTER IRON POTENTIAL

20Å 10Å 5Å 3Å 2Å 1Å

2Å 3Å 5Å 10Å 15Å 20Å 30Å 40Å 50Å 60Å 70Å 80Å 90Å 100Å

2Å 3Å 5Å 10Å 15Å 20Å 30Å 40Å 50Å 60Å 70Å 80Å 90Å 100Å

FORMULATION 1

FORMULATION 1

FORMULATION 1

FORMULATION 1
CONCLUSIONS

X-ray diffraction has been demonstrated as a useful technique for the examination of inorganic zinc-rich anticorrosion coatings. As well as being of value for the developmental and testing work, it is suggested that the technique could also assist with field problems and thus enable more accurate and economic coating recommendations to be made.

REFERENCES


SUMMARY
The history and development of water borne inorganic zinc silicate coatings are reviewed. Curing problems are discussed and it is shown how the use of lithium silicate can reduce these problems. Experimental work is described, using a blend of potassium and lithium silicate and some extender in the powder component, which indicates how most of the advantages of lithium silicate are retained without incurring a prohibitive cost increase.

INTRODUCTION
With current worldwide concern regarding environment protection and energy conservation, it seems that Australia will follow the lead of overseas countries such as U.S.A. and Japan and that the trend to high solids, solventless and water borne coatings will gather momentum during the 1980's.

In the case of water borne inorganic zinc silicate coatings, they are far from being new. The original water borne inorganic zinc silicate coating was patented in 1937 (1) and this coating is still in use today for specialised applications. There can be no doubt that water borne inorganic zinc silicate coatings have a proven record of good performance since their earliest applications in the late 1930's.

It is also true that the curing mechanism, involving the conversion of a water soluble vehicle to a water insoluble state, has presented practical difficulties to applicators. If these coatings are subject to rain, dew etc. before water insolubility has been achieved they wash off the surface and re-work must then be carried out by the applicator.

The early applications of water borne inorganic zinc silicate coatings involved the application of heat to convert the silicate to an insoluble state. In the 1950's the technique of post curing, which involved the subsequent application of an acidic curing solution to achieve water insolubility, was developed. Further improvements came in the mid 1960's with advances in silicate technology when "high ratio" sodium and potassium silicates became available. The higher the molar ratio of silica to alkali oxide, the greater is the tendency for the coating to cure to a water insoluble state of its own accord.

Since 1965 we have had practical self curing, water borne inorganic zinc silicate coatings but, variation in times needed to reach a water insoluble state has also been a criticism of such coatings. Table 1. shows the times to become water insoluble for such a coating under various conditions of air temperature and relative humidity. However, self curing, water borne inorganic zinc silicate coatings also have advantages over solvent borne ethyl silicate types. These advantages are as follows:

1) **High Zinc loading** - Metallic zinc content in the dry film when determined by analysis (2) can be as high as 85% where as the comparable figure for solvent borne ethyl silicate types is 78%. The traditional approach to inorganic zinc silicate technology has been that the highest possible metallic zinc content is consistent with best performance. However, fairly recent work (3) (4) indicates some reduction in metallic zinc content may be possible, provided that the extender particles are of appropriate size and are properly distributed within the film.
2) **Abrasion resistance** - The use of the Taber Abraser to investigate the abrasion resistance of inorganic zinc silicate coatings has been previously reported (5) and since this time, we have seen the advent of the Australian Standard 2105-1978. The better abrasion resistance obtainable with water borne types in comparison to solvent borne types as reflected is the allowable weight losses after 5000 cycles with 1000 gm load, specified by this standard i.e. 0.2 gm and compared with 0.4 gm.

3) **Absence of all organic solvents** - Advantages occur here in the following areas:
   
a) Environment protection.  
b) Energy conservation.  
c) Industrial toxicology  
d) Cost.

4) **Shelf life stability** - The liquid part of solvent borne, ethyl silicate inorganic zinc silicate coatings is usually intrinsically unstable and gelling occurs in the container after a period of 6 - 9 months. On the other hand water borne silicates, even though the ratio may be high, usually remain stable for at least 2 years.

5) **Coverage** - It is usually possible to obtain higher coverages from water born types. The following is a typical comparison:-

   Water Borne Type - Theoretical coverage at 25 micrometres 27.0 sq. m/litre.  
   Solvent Borne Type - Theoretical coverage at 25 micrometres 20.6 sq. m/litre.

Thus, to further exploit these advantages of water borne inorganic zinc silicate types, the desirability of overcoming the long standing criticism of being "unreliable" in attaining water insolubility becomes obvious. This paper covers how some improvements can be brought about without an increase in cost.

**Raw Material Considerations:** - "High Ratio" commercial grades of potassium and sodium silicate have been available for 15-20 years at molar ratios of silica:alkali oxide of about 3.9:1. Attempts to increase this ratio with the common alkali metals results in unacceptable shelf life stability but it is possible to obtain acceptable shelf life stability with lithium silicate at higher ratios.

By using lithium silicate with a molar ratio SiO₂:Li₂O in excess of 4:1 the times for the coating to become water insoluble are approximately half the times quoted in Table 1. except under low temperature, high air relative humidity conditions.

In addition there are performance advantages in the use of lithium silicate. When subjected to a severe practical test such as applying at 75 micrometres dry film thickness to 3 metre long angle iron test pieces and exposing at the Australian Corrosion Association's Marine Test Station at Point Cook, Victoria, it is found that a lithium silicate based coating will last about four times as long as any other inorganic zinc silicate coating before the first sign of failure, which is inevitably in the tidal zone, occurs.

Further, more recent work (4) by x-ray diffraction has shown a lithium silicate based coating to be much more durable than a potassium silicate based coating after four years exposure in the marine atmosphere at Point Cook.
So, there are real advantages in the use of lithium silicate but the big disadvantage is its increased price. The price of the basic lithium silicate raw material is $1.27 per kg more expensive than potassium silicate. In terms of an applied cost per square metre, a lithium silicate based coating in comparison with a potassium silicate based coating results in a price increase of 16%.

Commercially, the use of lithium silicate based coatings has been restricted and only used in the most severe situations where the additional cost can be justified. Such a situation occurs in ships cargo/ballast tanks and lithium silicate based coatings have performed successfully in this service for about seven years.

So, the problem becomes one of how to obtain the advantages of lithium silicate but not incur the prohibitive cost increase.

**Experimental Results and Practical Implications:**

1) Blends of lithium silicate with potassium silicate. A high proportion of lithium silicate in such a blend results in instability with precipitation occurring. However, if the stability of a range of blends is monitored until stability of about 9 months is achieved, this is regarded as a practical shelf life and the blend is considered optimum.

2) Water insolubility times on an inorganic zinc silicate coating based on the optimum blend of lithium and potassium silicate, are shown in Table 2. A comparison of the results in Table 1 with the results in Table 2 shows that under intermediate atmospheric conditions there is still a real advantage in using a lithium silicate/potassium silicate blend in comparison with potassium silicate alone. Under high temperature - low relative humidity conditions the time to attain water insolubility with the lithium/potassium blend type of coating is considerably reduced whereas with the potassium silicate type this time is considerably increased. It is also of interest to note that conditions of high temperature and low relative humidity are difficult conditions for the curing of solvent borne inorganic zinc silicate coatings. The low temperature - high relative humidity situation is a difficult one for any water borne coating. When the water content of the air approaches saturation, it is difficult for water to evaporate from an applied film. For this reason drying and curing times become lengthy under these conditions and this is therefore a problem area for a lithium/potassium blend type of inorganic zinc silicate coating as well as all other water borne coatings.

3) In practice, the application of protective coatings to structural steel is often carried out outdoors. There are weather restrictions on such operations as abrasive blasting must be performed in the first instance and abrasive blasted steel will deteriorate if subject to rain, dew etc. Under workable weather conditions abrasive blasted steel is often warm due to being in direct sunlight as well as due to warmth generated by the blasting operation. A potassium/lithium silicate blend type of inorganic zinc silicate coating could be applied to steel in this situation and cure very rapidly. Due to the steel being warm, water will evaporate very quickly and this slightly elevated temperature will accelerate the curing reaction, as indicated in Table 2. Thus, what is a problem area for both ethyl silicate and potassium silicate types of inorganic zinc silicate coatings is resolved with the new coating.

4) While a price reduction is achieved by the use of a blend, the use of any lithium silicate at all will result in some increase in comparison to potassium silicate. This situation can be eliminated by a minor inclusion of extender in the powder component of the coating. Figures 1 and 2 are
photomicrographs of a coating containing extender and not containing extender. The distribution of extender particles within the zinc dust and any change in the distribution of the zinc dust particles is readily seen.

Other work has shown that the extender appears to act as inert spaces within the coating and the distribution of zinc particles around these spaces is similar to the coating not containing extenders. In this way the normal protective action of the coating can still take place around these inert spaces.

5) Another two aspects that need to be considered for the potassium/ lithium blend type of inorganic zinc silicate coating containing extender are:-

a) Metallic zinc content in the dry film AS2105 = 82%

b) Abrasion Resistance AS2105 = 0.22 gm. mean.

In the case of metallic zinc content, the fact that the figure obtained does not meet the requirements of AS2105 is not regarded as serious, as the distribution of zinc dust and extender particles as seen in Figure 2 is considered satisfactory.

With abrasion resistance, the figure obtained is just outside the requirements of AS2105. The coating surface burnishes, as does the surface of all inorganic zinc coatings with good abrasion resistance. This, coupled with the fact that the result is only just outside the requirements of AS2105 means the down grading of abrasion resistance is only very marginal.

CONCLUSION

Once the initial stage of evaporation of water from the film has occurred, it has been shown that with the newly developed coating, much faster rates of achieving a water insoluble state occur than is the case with present generation water borne inorganic zinc silicate coatings. Indeed it cures better than solvent borne ethyl silicate inorganic zinc silicate coatings under certain atmospheric conditions.

With these improvements, coupled with the fact that the price of the newly developed coating is now comparable with present day inorganic zinc silicate coatings, greater commercial use of water borne inorganic zinc silicate coatings can be expected in the future.

REFERENCES

TABLE 1 Time for potassium silicate based coating to become water insoluble at various temperatures and relative humidity.

<table>
<thead>
<tr>
<th>Time to become Water insoluble (Hrs)</th>
<th>Temperature (°C)</th>
<th>Relative Humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6½</td>
<td>15</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>2½</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>2½</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>6½</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

TABLE 2 Time for potassium/lithium silicate blended coating to become water insoluble at various temperatures and relative humidity.

<table>
<thead>
<tr>
<th>Time to become Water insoluble</th>
<th>Temperature (°C)</th>
<th>Relative Humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour 40 minutes</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>17 minutes</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>5 minutes</td>
<td>60</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 1: Photomicrograph of inorganic zinc coating without extender.

Figure 2: Photomicrograph of inorganic zinc coating containing extender.
Inorganic Zinc Coatings
Ivan Baxter ICI Dulux

Comparison with Galvanising
Inorganic zinc silicate coatings contain zinc metal held in an inorganic vehicle binder and are referred to in AS2105-1992. Marketing hype to sell galvanising has tended to detract from the real benefits of inorganic zinc.

Under any given situation, the rate of loss of zinc metal in an electrolyte is constant whether it is zinc in a galvanised coating, zinc in an inorganic zinc coating applied to a steel substrate or a sacrificial anode attached to a steel structure. The galvanic cell produced in say, salt water electrolyte is the same for galvanising or inorganic zinc with both producing electrical energy and zinc corrosion products, including zinc carbonate. These corrosion products become dense and rather impermeable barriers, frequently called white rust, which seals off the zinc metal. This layer forms on top of a galvanised surface, but in contrast it is deep within the pores and voids of the silicate matrix, further enhancing the binders’ lock out properties.

When exposed to a flowing electrolyte such as salt water, the protective basic zinc carbonate layer is simply eroded from the surface, exposing fresh zinc metal to simply corrode again. Clearly the layer of protective zinc corrosion product is easily eroded or removed from a plain galvanised surface. Under the same conditions, the protective zinc salts are locked and somewhat protected from the flow because they are deep within the silicate matrix of the inorganic zinc coating. This physical barrier or matrix slows down the rate of zinc loss and so extends the useful life of the inorganic zinc coating. It can therefore be said, inorganic zinc coatings are able to protect steel, in severe environments such as found on jetties and off-shore structures, over much longer periods than galvanising. As the exposure site moves further away from the coastline, so the difference between the two methods of protection evens-out and the decision becomes largely economic.

A Concrete Analogy
If inorganic zinc coatings are classed as paint, then application problems will occur which could easily be avoided. The physical behaviour of the coating is more analogous to concrete than it is to paint. Liquid paint coatings are homogenous mixtures, whereas inorganic zinc is more concrete-like with heavy aggregates and lots of void spaces.

Keep it Stirred: It is often said that inorganic zincks can be likened in rheology to sand in a bucket of water and it is for this reason why the coating must be continually stirred during application otherwise a uniform distribution of zinc dust cannot be obtained.

Avoiding Topcoat Blistering: Because of the spherical shape of the zinc particles and the small amount of silicate binder to fill the space between the spheres, the dry film can be expected to contain some 27% void space. The voids tend to be discrete and with time will be mostly filled with zinc corrosion product.

If topcoated too early, solvent will be trapped in the voids and may give rise to blisters in the topcoat as the solvent tries to escape. This can be overcome in several ways:

- Allow the zinc pigment to corrode and fill the void spaces.
- Apply a deep penetrating seal or tie-coat.
- Allow a light application of the topcoat material, allowing time for the solvents to evaporate and the coating to dry before building to full thickness.
- Choose a slow setting or slow drying topcoat which will remain open or wet sufficiently long for all the volatiles to evaporate and penetrate deep into the structure of the inorganic zinc.

Self Recoat/Repairs: Unless a concrete pour is worked well after placement it will be more dense the bottom and tend to be more friable at the top.

Similarly in inorganic zinc, and particularly if applied at very high film builds, the silicate binder migrates to the bottom of the coating leaving the top in a friable or underbound condition.

Since the coating is underbound at the top level, it is physically less strong than at lower levels. This will give rise to poor bonding with topcoats, split coating, mud cracking and a powdery surface.

When an increase of film build is required or repair needed, this migrating phenomenon of the silicate solution must be considered.

Because of the porous open nature of the coating, some of the silicate solution from the repair coat will rapidly migrate into the layer beneath, leaving the repair underbound or friable.

The loss of silicate solution can be offset by increasing the liquid content of the repair coat, usually by about 12½%. The increased liquid will migrate into the lower coating leaving the repair coat correctly bound and strongly adhering.
Inorganic Zinc Silicate Coatings

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Formerly Technical Manager, Protective Coatings and Deep Sea Marine Research and Development Laboratory Taubmans Pty Ltd, Yeronga, Queensland - Now retired.


Summary
Silicate film formers have been known for over a century and metallic zinc as an anticorrosive coating for about 150 years. It was not until the 1930's that the two components were combined in an Australian invention and the first major use of an inorganic zinc silicate paint applied in 1941.

A great deal of development work has occurred since then. Huge volumes have been produced throughout the world, but mainly in North America and Australia for the protection of steelwork in marine and protective coatings. There is no doubt zinc silicates are the major paint in combating corrosion, used either as a single coat protective, or as a primer for high performance topcoats. This paper puts into perspective their types, chemistry, formulations and performance.

Introduction
Inorganic zinc silicates have become the first choice of protective coatings to be applied direct to prepared steel where a high level of corrosion protection for severe atmospheric conditions is required. There is increasing use of a single coat of inorganic zinc silicate in environments that are not chemically aggressive. Where such conditions do exist, inorganic zinc silicates are still often used as the primer and protected themselves by high performance topcoats, which are readily applied, such as epoxies.

<table>
<thead>
<tr>
<th>Table 1 - Electrochemical Series</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>Gold Au$^{3+}$</td>
</tr>
<tr>
<td>Mercury Hg$^{2+}$</td>
</tr>
<tr>
<td>Silver Ag$^{+}$</td>
</tr>
<tr>
<td>Copper Cu$^{2+}$</td>
</tr>
<tr>
<td>Hydrogen H$^+$</td>
</tr>
<tr>
<td>Lead Pb$^{2+}$</td>
</tr>
<tr>
<td>Tin Sn$^{2+}$</td>
</tr>
<tr>
<td>Nickel Ni$^{2+}$</td>
</tr>
<tr>
<td>Iron Fe$^{2+}$</td>
</tr>
<tr>
<td>Chromium Cr$^{2+}$</td>
</tr>
<tr>
<td>Zinc Zn$^{2+}$</td>
</tr>
<tr>
<td>Aluminium Al$^{3+}$</td>
</tr>
<tr>
<td>Magnesium Mg$^{2+}$</td>
</tr>
<tr>
<td>Sodium Na$^+$</td>
</tr>
</tbody>
</table>

Table 2 shows three metals, zinc, aluminium and magnesium, may dissolve preferentially to steel.

<table>
<thead>
<tr>
<th>Table 2 - Potential developed by zinc rich coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substrate</strong></td>
</tr>
<tr>
<td>Steel</td>
</tr>
<tr>
<td>Steel</td>
</tr>
<tr>
<td>Steel</td>
</tr>
<tr>
<td>Steel</td>
</tr>
<tr>
<td>Zinc</td>
</tr>
</tbody>
</table>

The potential measured by Mayne (1) is shown in Table 2.

Table 2 shows that when a zinc rich paint film is immersed, an electrical potential is set up between the film and the steel substrate. A zinc rich paint develops the same potential as a zinc plate and hence will protect steel. Magnesium and aluminium paints do not show any cathodic protection properties, having essentially the same potential as steel and it is theorised that this is due from: *Corrosion Australasia*, Vol. 19, No. 2, pp 4 - 8, (April 1994).
to both metal particles being covered with oxide layers, which are not conductive and which effectively insulates them from the steel substrate. Zinc oxide is an electronic conductor.

If the zinc is to dissolve out preferentially to the steel, then the metal particles must be in electrical contact with one another. Hence there must be a high proportion of zinc dust in zinc paints. The resistivity versus metal loading is shown in Table 3 (Elm (2), (3) and Pass (4)).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Resistivity (Ohms/square inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic Zinc (% by weight)</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>1270</td>
</tr>
<tr>
<td>90</td>
<td>40</td>
</tr>
<tr>
<td>85</td>
<td>250</td>
</tr>
<tr>
<td>80</td>
<td>1050</td>
</tr>
<tr>
<td>75</td>
<td>29,000</td>
</tr>
</tbody>
</table>

Table 3 shows there is essentially little difference in the electrical resistivity at concentrations between 80 and 95% of zinc. As the zinc ‘corrodes’, insoluble basic zinc salts are formed at the water/zinc interface and the electrical potential gradually falls. However if this insulating layer is removed by abrasion or if the film is scratched, the potential returns to the original value as shown in figure 1 (5).

**Figure 1: Potential/time curve for zinc rich coating.**

**pH Value**

Since zinc is an amphoteric metal, it will dissolve in both acids and alkalis, and the actual corrosion rate is shown in Figure 2. From this it can be seen that the corrosion rate appears to be acceptable in the range from pH 6 to 12.5, where a stable film is produced.

**Figure 2: pH versus corrosion rate.**
The initial film formed on zinc surfaces is zinc oxide and zinc hydroxide, the latter is converted to basic zinc carbonate by carbon dioxide present in the air.

\[
\begin{align*}
2\text{Zn} & \rightarrow 2\text{Zn}^{2+} + 4e^- \quad \text{anode} \\
2\text{H}_2\text{O} + \text{O}_2 + 4e^- & \rightarrow 4\text{OH}^- \quad \text{cathode} \\
2\text{Zn}^{2+} + 4\text{OH}^- & \rightarrow 2\text{Zn(OH)}_2 \\
2\text{Zn(OH)}_2 + \text{CO}_3^- & \rightarrow \text{Zn(OH)}_2\cdot\text{ZnCO}_3
\end{align*}
\]

The basic zinc carbonate and zinc oxide film is very protective and is responsible for the excellent resistance of zinc to ordinary environments. In industrial environments sulphur dioxide and nitrogen oxides result in the formation also of zinc sulphite, zinc sulphate and zinc nitrate, which are soluble and are washed off by rain, and so continuously exposing a fresh zinc surface. In marine environments, zinc has good protection providing it is some hundred metres or more from the shoreline. As will be discussed later, inorganic zinc silicates have excellent protection in marine atmospheres.

**Zinc Dust**

The zinc dust used in zinc silicates today complies with the requirements shown in AS 2105-1992 (Inorganic Zinc Silicate Paint) clause 2.3.

<table>
<thead>
<tr>
<th>Component</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total zinc (as Zn)</td>
<td>98.0% min.</td>
</tr>
<tr>
<td>Metallic zinc (as Zn)</td>
<td>94.0% min</td>
</tr>
<tr>
<td>Total lead (Pb)</td>
<td>0.2% max. by mass</td>
</tr>
<tr>
<td>Total cadmium (Cd)</td>
<td>0.1% max</td>
</tr>
<tr>
<td>Total iron (Fe)</td>
<td>0.05% max</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.0005% max</td>
</tr>
</tbody>
</table>

Zinc dusts with average particle size 5-9 micrometres are generally used. Due to the high rate of reactivity between polysilicate and zinc dust, the larger surface area microfine grades 2-4 micrometre particle size, are not recommended. Use of this finer particle size zinc may result in reduced pot life and premature gelation of the vehicle, which can lead to poor wetting of steel surfaces, and excessive mud cracking at higher film thicknesses.

AS 2105-1992 clause 3.2 requires the metallic zinc content of a dry film of inorganic zinc silicate, determined by AS 1580:504.1 (metallic zinc content by the hydrogen evolution method):

- Type 1 (baked) 80% minimum
- Type 2 (post cured) 85% minimum
- Type 3 (self cured) 85% minimum
- Type 4 (alkyl) 77% minimum
- Type 5 (preconstruction primer) 60% minimum

Despite the high zinc content, the silicate binder has sufficient strength to bind and hold the pigment and also provide good adhesion and flexibility. This is because of the high weight (zinc SG 7.1), but low bulk of zinc dust pigment.

**Silicates**

Alkali water based silicates have been known and used since the 1850s. They are based on sodium, potassium and lithium, usually in the form of solutions and general formula M₂SiO₃. It is the ratio of SiO₂:M₂O that is important and which varies widely. Sodium silicate with molar SiO₂:Na₂O ratios less than 2.5 are used for the manufacture of detergents and cleaners. Adhesive, binder and deflocculant applications depend on the presence of polysilicate ions and have ratios from 2.5 to 3.8.

The binding mechanism in the molecular unit SiO₂₅, the tetrahedral unit coordination group [SiO₄²⁻] and its tendency toward complex polymerisation into chains, networks and frameworks are fundamental facts on which the structural study of these networks is based. That is the nature of the Si–O–Si bonds. The degree of polymerisation of silicate solutions increases with decreasing cation-to-SiO₂ ratio, that is increasing silica concentration. Silicon (or silica) has the ability to polymerise with oxygen in branched or cross-linked siloxane bond systems to form a three dimensional network of siloxane bonds:

\[
\begin{align*}
\text{OH or K} & \quad -\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \\
\text{OH or K} & \quad -\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} -
\end{align*}
\]

Polymerisation with higher ratios of silica give higher molecular weight branched and cross-linked siloxane bond Si–O–Si systems (6).
The alkali silica solutions consist mainly of SiO$_2^-$ and HSiO$^-$ ions and in higher ratio SiO$_2$-M$_2$O, an increasing proportion of the silica forms silicate polymer-ions or charged particles:

```
K     K
|     |
O     O

HO – Si – O – Si –
|     |
O     O

HO – Si – O – Si –
```

This accounts for the outstanding adhesion of zinc silicates to steel.

The curing mechanism of zinc silicates relies on the presence of salts as a ‘catalyst’ for polymerisation of polysilicates. In alkaline pH, the negatively charged silicate ions repel each other, however in the presence of salts the charge repulsion is reduced, allowing aggregation and gelling of silica.

Nauman and Debye (7) measured the following molecular weights (expressed as anhydrous SiO$_2$) and concluded that at ratios less than 2.0 there are no polymers or particles, but at higher ratios, increasing amounts are present.

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>Average Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$:Na$_2$O</td>
<td></td>
</tr>
<tr>
<td>0.48</td>
<td>60</td>
</tr>
<tr>
<td>1.01</td>
<td>70</td>
</tr>
<tr>
<td>2.03</td>
<td>150</td>
</tr>
<tr>
<td>3.32</td>
<td>325</td>
</tr>
<tr>
<td>3.90</td>
<td>400</td>
</tr>
</tbody>
</table>

While in a potassium silicate solution of 3.8 molar ratio, Brady, Brown and Huff (7) found an average molecular weight of 2000.

**Polysilicates**

Silicates with SiO$_2$:M$_2$O ratios of 4:1 to about 25:1 are usually referred to as polysilicates. However above about 4:1 ratio, sodium and potassium silicates require additions of the corresponding free alkali for solubility. Such polysilicates are unsuitable for use as inorganic zinc silicates. Compositions of SiO$_2$:Li$_2$O ratios from 4:1 to 25:1 are soluble and stable (8).

When used in zinc silicates, further polymerisation occurs due to dehydration (evaporation of water from an applied film) and a reduction in pH. Linking of polymerised silica particles occurs to form branched chains and cross linking into a three dimensional network.

The reaction that results in the increase in molecular weight involves the condensation of silanol groups at siloxane chain bonds.

```
|   |   |
O | O |
|   |   |
Si – | Si – |
|   |   |
OH → O + H$_2$O
|   |   |
OH – Si –
```

**Baked Inorganic Zinc Silicate**

The credit for the invention of inorganic zinc silicate paint goes to Victor Charles Nightingall, an Australian Engineer who first pigmented a sodium silicate solution with zinc dust as recorded in British patent 505,710 May 1939 and later followed by Canadian patent 406,902, 1942 and US patents Nightingall, Victor 2,440,969, May 1948 and 2,462,763 Nightingall and McDonald, 1949.
The first recorded field use was in 1942 on a portion of the above ground Woranora water pipeline in Sydney, followed by the above ground Morgan to Whyalla pipeline completed in 1944. The coating consisted of 19 pounds of sodium silicate, a small amount of sodium bicarbonate, to which was added 20 pounds of zinc dust and 2 pounds of red lead. After vigorous mixing, the coating was brush applied to the steel pipe, prepared free of mill scale by pickling. The pipe was then heated for approximately 30 minutes to a temperature between 150°C and 250°C (9).

Nightingall discovered that carbon dioxide was required to polymerise the silicic acid deposited (9) when the coating was heated, hence the inclusion of sodium bicarbonate. Also as the temperature is raised, hydroxyl groups in the silicate condense to form siloxane bonds and water is evolved.

The red lead addition imparts a degree of pot life by delaying or preventing when dry the evolution of hydrogen by reaction with the zinc dust at the high pH.

Baked silicates are still in limited use today being specified on some above ground water pipes and on vertical holding posts for bridge guard rails.

Post Cured Alkali Zinc Silicate

This type of coating came into being when it was necessary to find a method of curing a zinc silicate other than by baking, and so enabling a more general field use of this type of coating.

Sodium silicate solutions of ratios SiO$_2$:Na$_2$O from 2.86:1 to 3.75:1 have been used. The pigment portion is zinc dust alone or zinc dust plus some red lead. To cure the applied coating, that is to polymerise the silicate and to make the coating no longer water soluble, the pH is reduced by the application of an acid solution, so in effect this is a three package system.

Figure 3 from Iler (10) shows the general effects of pH on polysilicic acids. Curve ABC represents the behaviour of silica in the absence of salts, while curve DEF shows the general behaviour when an electrolyte is present at concentrations above 0.2 to 0.3 N. This is likely in the application of the acid solution, as the acid used is usually phosphoric acid. The ‘salt’ lowers the ionic charge on the particles.

Figure 3: The effect of pH on the gelling of silica sols. Curve A-C sols in the absence of sodium salts; D-F in the presence of sodium salts.
Thus from Figure 3 which shows the ‘catalyst’ effect of salts on the gelling of polysilicic acid, the use of the acid solution produces ample salts. Iler (16) states that metal silicates are precipitated from alkali polysilicates, using the corresponding metal salts. With zinc salts formed, zinc silicate is produced. Some of the possible reactions that may occur are shown:

\[
\text{Zn} + \text{ZnO} + \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \downarrow \\
\text{SiO}_3^{2-} \text{silicate ions} \\
\text{HSiO}_3^- \text{acid solution} \text{H}^+ + \text{Si(OH)}_4 \text{(silicic acid)} \\
\text{H}_2 + \text{Na}_2\text{ZnO}_2 + \text{zinc salts} + \text{sodium salts} \\
\text{sodium zincate} \downarrow \\
\text{colloidal silica + zinc silicate}
\]

It seems likely that the final applied film is a porous, heterogenous coating, containing metallic zinc, zinc oxide, zinc silicate, colloidal silica (highly polymerised silica), free sodium silicate, water of crystallization, sodium phosphate and zinc phosphate.

Post cured inorganic zinc silicates have been used as primers for structural steel but their principal use was as a single coat tank lining for petroleum products in new tankers and land based tanks (17). This type of coating is described in US patents Nos. 2,509,875 and 2,440,969 and Australian patent No. 166,694.

Self Cured Alkali Zinc Silicate

Elimination of the need for an acid wash solution with the post cured type led to the development of the self cured inorganic zinc silicate. Here higher ratio SiO$_2$ : M$_2$O ratios are required using either potassium or lithium silicates.

The main potassium silicate solution in use has a 3.9 to 4.1:1 SiO$_2$ : K$_2$O molar ratio, while the main lithium silicate solution has a 4.8:1 SiO$_2$ : Li$_2$O molar ratio. To reduce the higher cost of lithium silicate, a widely used coating uses a combination of sodium and lithium silicates. This silicate solution is made using sodium hydroxide, lithium hydroxide, silica gel (an anhydrous powder consisting of a coherent, rigid three-dimensional network of contiguous particles of polymerised silica having a particle size ranging from 1 to 100 nm in diameter) as the source of silica, water and reacted for several hours at 70 to 90°C.

The film formation and curing to water insolubility is the same as for the post cured type (except no acid wash is used). There are still ample ‘salts’ available from the high pH of 11-12 of these silicate solutions. The main drawback is its slower cure due to the reliance on good weather conditions, such as low humidity and high ambient temperatures, to enable water to evaporate from the film.

Adverse weather such as high humidity and low ambient temperature results in slower curing and an applied coating could have a water insolubility ranging from one hour to 24 hours, or longer. Outdoors, exposure to rain before it is cured damages the film, as fresh water leaches out un polymerised silicates from the film. Contact with salt or sea water has the opposite effect, since salts, as shown, are ‘catalysts’ for curing. Many tonnes of steel have had to be reblasted and recoated due to early exposure to rain or heavy dew.

From the early 1960's, to the late 1970's, this type of zinc silicate, despite the above problems of cure, was the workhorse primer of the protective coatings industry, with extensive usage on atmospheric structural steel, from offshore oil rigs and platforms, to land usage requiring long term corrosion protection. Applicators began to blast and prime under cover, so primed steelwork was protected until cured.

Used as a primer, dry thicknesses range from 50-90 μm, then topcoated with epoxy, chlorinated rubber, vinyl and polyurethane systems as appropriate.
As a single coat, long term protective dry thicknesses of 100 to 150 μm are now recommended. In the Gulf of Mexico, there are oil rigs with 10 years protection to date, being afforded by a single coat of water based zinc silicate.

There are sections of steelwork with coastal exposure in Victoria with 20 years protection. Delahunt (18) reports on 12 to 15 years (some sections 17 years) protection from 75 μm dry thickness, on an Exxon oil refinery at Okinawa.

This proven long term protection is no doubt due to the continuing polymerisation of unreacted silicic acid and condensation of hydroxyl groups. This matrix of inert colloidal silica protects the zinc dust which it binds together. In marine atmospheres, salt accelerates this polymerisation. While on the zinc silicate surface, also shielding the underlying free zinc (which remains dormant until the film is damaged), is an inert inorganic barrier of zinc corrosion salts. These are:

- ZnO – Zinc Oxide
- Zn(OH)\(_2\)ZnCO\(_3\) – Basic Zinc Carbonate

and in coastal/marine environments:

- ZnO ZnCl\(_2\) – Zinc Oxychloride
- Zn(OH)\(_2\) ZnCl\(_2\) – Basic Zinc Chloride

Topcoating soon after priming with zinc silicate paint with, for example, 125 to 175 μm dry thickness of high build catalysed epoxy, prevents the continuing polymerisation of silicic acid and the surface formation of the above zinc salts.

High ratio water based zinc silicates to a large extent have overcome the slower cure of the ‘original’ self cured products. The ‘high ratio’ types use a potassium silicate solution with a 4.8 to 5.3:1 SiO\(_2\):K\(_2\)O ratio, originally developed by NASA, one formula being (19):

- Potassium silicate solution 21.0% wt
- Methyltrimethoxysilane 0.6% wt
- Zinc dust 78.4% wt

Further improvement led to its commercialisation in the mid 1980’s, and because of anti-pollution regulations, this zinc silicate ultimately will supplant the solvent based alkyl silicates.

The ‘high ratio’ means increased silica and rapid cure. Water insolubility occurs very soon after the applied film is dry, generally within 15 to 30 minutes and extremely hard after 2 hours, ready for topcoating if required. Early water ponding should be avoided. This may cause attack on the zinc metal from the formation of potassium hydroxide. Any wonder with water clean up and this advantage of rapid cure, the water based zinc silicates are back. The great advantage of water based self cured inorganic zins is their water clean up and zero VOC, that is they are environmentally acceptable as they contain no organic solvents. However, from about the mid-1970’s to the present day, the major inorganic zins used are those based on alkyl silicate containing organic solvent.

**Alkyl Zinc Silicates**

For the past 15 to 20 years, ethyl zinc silicates have been the dominant product used, since moisture is essential for curing. Provided the applied film has air dried for 20 to 30 minutes, the coating is very tolerant of inclement weather and rain aids curing and will not damage the coating. Applicators coating steel outdoors, can thus use such a product with confidence.

Hydrolysed ethyl silicate zinc dust primers date back to the late 1940’s and were used in Europe. Early US patents covered ethyl silicate and zinc dust paints.

Other alkyl types have been used such as isopropyl and butyl from which the corresponding alcohol is evolved on hydrolysis, but ethyl alcohol, despite the low flash point (10°C), is the principle type used. Ethyl alcohol is completely miscible with water, ideal for hydrolysis and it has a high threshold limiting value of 1000 ppm, so has low toxicity.

The starting point is ethyl ortho silicate, a monomeric product with a composition of (C\(_2\)H\(_4\))\(_3\)Si. The raw material used by paint manufacturers is a polyethyl silicate containing about 40% silica with a general configuration:

\[
\begin{align*}
\text{OC}_2\text{H}_5 & \quad \text{OC}_2\text{H}_5 & \quad \text{OC}_2\text{H}_5 \\
\text{H}_2\text{C}_2\text{O} & \quad -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si} & \\
& \quad \text{OC}_2\text{H}_5 & \quad \text{OC}_2\text{H}_5 & \quad \text{OC}_2\text{H}_5
\end{align*}
\]
Paint manufacturers raise the hydrolysis to about 70% by the addition of water, using a amount of acid, usually hydrochloric, as a catalyst, plus a water miscible solvent.

The amounts of water and acid must be carefully calculated and controlled for optimum shelf life, mixed pot life and mud crack tolerance. Too high a quantity of each will reduce these. Too little results in slower curing of the applied coating.

Antisag agents plus inorganic extenders to minimise mudcracking on drying such as talc, clay, mica, silica, etc. are dispersed in. The amounts and second component zinc dust quantity are adjusted so the final mixed product meets the AS 2105 type 4 zinc requirement. Shelf life of the liquid component due to gradual hydrolysis in the container is limited to about six months.

During application, humidity in the air completes the hydrolysis of ethyl groups, the polysilicic acids formed polymerise in the same manner as the alkali silicates. The overall reaction can be simply illustrated:

\[
\text{Si(OC}_2\text{H}_5)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH} \\
(\text{silica}) \quad (\text{ethanol})
\]

**Single Pack Alkyl Zinc Silicate**

This product was an innovative development in the early 1980’s. It used a hydrolysis less than that with the two pack ethyl types hence curing of the applied film was somewhat slower under the same conditions. Extraneous water was carefully excluded during manufacture and the can stability exceeded 12 months. During application, hydrolysis of remaining ester groups from humidity moisture-cured the coating in a similar manner to the two pack product.

The advantage of the single pack zinc silicate was just that: single pack, with the zinc dust predispersed by the manufacturer. In addition, application especially by airless spray was superb, no dry overspray at all and a mud crack tolerance of 200 \(\mu\)m dry, allowing good applicator latitude in the fillets of structural steel.

The main drawback with the alkyl zinc silicate coatings is, if there is inadequate moisture for curing, that is hydrolysis of remaining ester groups, because of low humidity, the film will be dry because of solvent evaporation, but be only partially cured. In many instances, painting is the last in the engineering priorities of a project, or an applicator has limited space and steel delivery must not be delayed, so the primed steel is topcoated. If the zinc silicate is not fully cured, its abrasion resistance is reduced, although, depending on service conditions, corrosion resistance, while not optimum, will probably be satisfactory.

**Friction Grip Joints**

Inorganic zinc silicates are the only paints that are suitable for application to the mating surfaces of friction grip joints used in high strength bolted connections. Organic coatings all have some lubricity that a coated joint would fail in service. Left unpainted, bare steel joints would rust and unsightly rust stains would disfigure the structure. Testing of an inorganic zinc silicate paint to ensure suitability is carried out in accordance with Appendix A of AS 1511. The testing specification ensures that the creep deformation of the coating due to both the clamping force of the bolt and the service load joint shear, are such that the coating will provide satisfactory performance under sustained loading. The minimum acceptable slip factor value is 0.35, however most zinc silicates have a value around 0.50

**Heat Resistance**

For use on mild steel surfaces used as construction material for stacks, kilns, incinerators, furnaces, ductwork and piping operating above about 100°C, inorganic paint coatings give the best protection. This is due to their resistance to expansion and contraction from fluctuating temperatures, the destructive attack from oxygen on organic coatings and shock from rain.

Inorganic zinc silicates can be used to 400°C. To prevent continued formation of zinc oxide, zinc silicate is used as the primer and topcoated with silicone acrylic paint to 200°C and pure silicone paint to 480°C (20).

**Tank Lining**

Inorganic zinc can be used as the liner on bulk tanks which are used for the storage of solvents such as alcohols, aldehydes, esters, ethers, glycols, ketones, aliphatic and aromatic hydrocarbons and gasolines. Chlorinated solvents which may hydrolyse in the presence of some water and produce hydrochloric acid, are unsuitable. Aviation fuels are generally not stored due to the likelihood of zinc absorption which is not permitted by aviation authorities.

The tolerance to particular solvents should be checked with the zinc silicate manufacturer.
Conclusion

If zinc dust was available in a range of attractive colours, a one coat of inorganic zinc silicate paint would give long term protection to many facilities. Nevertheless, engineers, owners and specifiers should give serious thought to the cost effectiveness of a functional grey colour of a single coat of alkali water-based self-cured inorganic zinc silicate for areas where aesthetics are unimportant and there is no likelihood of chemical attack.

In coastal exposures where much of our industry, especially export mining projects, are located, salt catalyses the polymerisation of unreacted silicic acid groups, increasing the molecular weight and thus protection by the silicate matrix. Combined with the surface protection afforded by zinc corrosion products, and its environmental attractiveness, water based zinc silicates are back in favour.

When used as a primer and suitably topcoated, inorganic zinc silicates have a proven record of long term, 10 to 20 years, atmospheric corrosion protection of steelwork. The newer high ratio water based zinc silicate offers the advantage of water clean up and same day topcoating.

Whether used as a primer or as a single coat protective, inorganic zinc silicates have an assured continuing future and should be the first consideration in the selection of the most appropriate paint system.

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INORGANIC ZINC OR GALVANIZING: 
CHOOSING THE IDEAL CORROSION PROTECTION FOR STRUCTURAL STEEL

by
R A Francis

1. INTRODUCTION

Inorganic zinc silicates coatings and hot dip galvanizing are widely used for corrosion protection of structural steel, where they provide long life protection in a variety of atmospheric environments. As they are both used in similar situations, it may appear at first that the two coatings directly compete with one another. However, investigation of their properties and features show that the two are generally complementary, and one coating usually is clearly preferred in any given situation. Often the specifier should not try to determine which of these coatings should be used for the entire assignment, but rather look at each piece of the job and decide which process best lends itself to the task at hand. This paper looks at the features of both these coatings, comparing them and showing the situations where each can be used. Further information on galvanizing is given in [1], on inorganic zinc coatings in [2,3] and on a comparison between the two is given in [4,5].

Inorganic zinc silicates and hot dip galvanizing both rely on the exceptional ability of zinc to provide corrosion protection. Being more active than steel on the galvanic series, zinc will corrode in preference to steel when the two are in electrical contact and placed in an aggressive environment. When steel connected to zinc are both exposed to a corrosive medium, such as at an edge or damaged area on a zinc-coated item, the zinc will preferentially corrode providing cathodic protection to the steel. This is the key feature of zinc and the reason for its widespread use in the protection of steel. But it has other important properties as well. Its corrosion rate is usually very low, of the order of 0.5 to 3 microns per year in most (non-acidic) atmospheric environments, around one to ten per cent of that of steel. A coating of 70 microns or more, as is the case with most inorganic zinc or galvanized coatings, will therefore last at least twenty years, often much longer. A third feature, especially with the inorganic zinc silicates, is that the zinc corrosion products are largely insoluble and tend to block the pores in the coating, further slowing corrosion.

However, while zinc provides excellent protection in many environments, it is not suitable in others. Zinc coatings generally should only be used in neutral environments and show high corrosion rates in acidic and strongly alkaline environments. Figure 1 shows how the corrosion rate of zinc varies with pH and generally no zinc coating should be used outside the range of pH 6 to 12, although inorganic zinc silicates are often given an upper limit of pH 10 as strong alkalinity can react with the silicate binder. Zinc coatings have been used with some success in submerged conditions, both fresh and sea water, but generally are not recommended under continually wet conditions. Hot fresh water, above around 60 deg C is especially corrosive to zinc. Zinc coatings are not normally used in underground applications, unless only short term protection is required, or the soil is especially dry. In these environments, different coatings must be used, or consideration could be given to the use of corrosion-resistant materials or cathodic protection, or some combination of these. But in dry, intermittent wet and dry, humid, marine and many other atmospheric zones, zinc coatings excel.

The most attractive aspect of both galvanizing and inorganic zincs is that they both provide exceptionally long-life performance. This means that the structure will probably not require much maintenance, with resulting cost savings as well as reduced scaffolding, dust, conventional paints and other hazardous aspects of maintenance.

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Even if maintenance is required, these coatings do not allow rust creep or undercutting underneath them and maintenance is relatively easy. Certainly, field abrasive blasting should not be required during maintenance. This undercutting resistance cannot be over-emphasised since the majority of organic coating failures under severe corrosive attack is by this mechanism. There is increasing evidence, from laboratory and field experience, that the undercutting resistance of top coated zinc coatings is significantly less than for those that have not been top coated. Even so, zinc coatings can be maintained easily and economically and at a time suitable to the facility owner.

2. HISTORY

Both coatings have been around for a long time. The word ‘galvanizing’ started to appear in the mid 1830s although the actual process appeared soon after the first commercial smelting of zinc was developed in the mid 1700s. Galvanizing was originally used with small articles, although bath size and resultant article size increased throughout the 1800s. Developments have continued until the present, improving the quality of the coating and increasing bath size. Inorganic zinc coatings were invented in the late 1930s by Melbourne engineer Victor Nightingall, who wanted a protective zinc coating which was not limited by the need to fit the item to be protected in a galvanizing bath. However, his initial product did require heating which limited application. A later development required application of an acidic curing solution but it was not until early 1960s with the development of self-curing solvent-borne and water-borne coatings that inorganic zinc coatings really became a widely used means of corrosion control.

Figure 2: Microscopic cross section of coating produced by (a) hot dip galvanizing and (b) Inorganic zinc silicate (after [2]).

3. COATING

3.1 Nature of the coating

While both coatings rely largely on zinc to provide protection, the nature of the coating is quite different. When the steel item is dipped in the molten bath of zinc to form a galvanized coating, the zinc reacts with the steel to form a series of steel-zinc alloys as shown in Figure 2(a). The layer nearest the steel interface is around 25% iron, followed by an alloy of 11% iron, a phase containing about 8% iron and an outer layer of almost pure zinc. The iron-zinc alloys are harder than steel, giving resistance to abrasion and heavy loading. Small amounts of lead and tin in the bath give the characteristic spangle finish to the coating. Some compositions of steel result in a dull grey finish but there is negligible difference between coating life provided by either type of finish. The thickness of the coating depends on the rate the item heats up, which in turn depends largely on the section thickness. Steel around 2 mm thick has at least 50 microns of zinc, while steel of 5 mm thickness has a coating of at least 85 microns. For heavier sections, the thickness is greater. Thicker coatings are produced with steels of higher silicon content and by abrasively blasting the steel, although these will have a rougher surface and poorer appearance. Immersion time, double dipping, bath chemistry and temperature, etc., have little effect on coating thickness so that a galvanizer generally has little control over the final thickness of the coating. An oxide and carbonate layer will form on the surface and the zinc metal generally corrodes fairly slowly. The galvanizing discussed in this paper is after-fabrication galvanizing, often called batch hot dip galvanizing, or simply, hot dip galvanizing. It is covered by AS 1650 [6], although the standard is under revision and will be given a new number when released. Continuous galvanizing, used on wire, sheet and some structural products has a much thinner coating and subsequent lesser life.
The inorganic zinc silicate coating is completely different. The coating consists of small spheres of zinc metal surrounded by a matrix of silicate (see Figure 2(b)). The surface has a distinctive dull grey, matt finish. The silicate and zinc combine to provide a hard, abrasion resistant surface, although this may take some time to develop, depending on ambient conditions. Both inorganic zinc and galvanized surfaces under normal conditions are largely equivalent in abrasion or impact resistance, although some thick galvanized coatings can be brittle. There is some reaction between the zinc and silicate and the steel surface and the silicate, but the amount of reaction is quite small. The coating is largely mechanically bonded to the steel surface, which is why a blast cleaned surface with a suitable profile is required. Unlike the galvanized coating, an inorganic zinc surface is quite porous and water will soak into the coating. However, the corrosion reaction proceeds very slowly due to the protective nature of the zinc corrosion products which fills the void spaces in the silicate matrix, thereby slowing the cathodic reaction. As a result, zinc is largely corroded away slowly from the exposed outer surfaces only.

There are two distinct types of inorganic zinc coatings in use today, the water-borne or alkali silicates and the solvent-borne or alkyl silicates. They are covered by AS/NZS 3750.15 [7] (formerly AS 2105) where the water-borne are referred to as Type 3, the solvent-borne as Type 4 and the newer high-ratio water-borne as Type 6. According to the standard, Type 3 and Type 6 have at least 85% zinc in the dry film, while Type 4 have at least 77% zinc in the dry film. The water-borne types generally have better corrosion resistance, due to the fact that they are harder, have a higher zinc loading and can be applied at a higher film thickness. These types have the edge in environmental impact and safety as they have no VOC (volatile organic compound) component. However, the alkyl silicates are easier to apply and more forgiving of slightly poorer surface preparation, although they still require a class 2½ blast. Both the solvent-borne and water-borne can experience problems with curing. The solvent borne require a certain minimum relative humidity to cure as they absorb moisture in the curing process. On the other hand, alkali silicates need dry conditions to cure. Both types can mudcrack if applied too thickly, although the water-borne formulations can be applied at much greater thicknesses. Applicators need to have special training to properly apply inorganic zincons, especially water-borne formulations, and owners should ensure thorough inspection of surface preparation and application. But given the exceptionally long life that can be achieved, this adds little to the long-term cost. There are a range of inorganic zinc silicate coatings available, but the following discussion is confined to those materials with a high zinc loading in the dry film. Coatings with a lower loading, while providing good protection is some environments, do not provide the excellent protection of the higher zinc content coatings.

3.2 Coating Application

Hot dip galvanizing involves immersing the object to be coated in a bath of molten zinc. The zinc flows over the entire surface exposed to the molten metal, providing complete protection. Before it can be coated with zinc, the surface must be thoroughly clean. This is usually achieved by dipping in a caustic bath to remove grease and oil, followed by a wash in fresh water. The second cleaning stage is to pickle the item in acid to remove rust and scale, again followed by a water wash. The item is then dipped in a flux bath to prevent oxidation and ensure the molten zinc adheres to the surface. After the zinc coating, the item is usually quenched in a water bath containing a small amount of chromate. The chromate stops the reactive surface reacting with moisture causing ‘white rust’, a largely innocuous but visually unappealing corrosion product which forms on freshly galvanized surfaces under damp conditions. The item is then ready to go into service.

In contrast, inorganic zinc silicate coatings are applied by spray gun, in a similar manner to paint coatings. Again the surface must be thoroughly cleaned and this is achieved by abrasive blasting to a high standard, at least Class 2½ or preferably a Class 3. The liquid coating material is prepared by thoroughly mixing zinc powder with the silicate binder. The mixture must be continuously agitated during application. The coating is applied using conventional, or more commonly these days, airless spray equipment. It is best carried out in a shop, but can be applied with care in the field using ordinary equipment. Application is similar to other paints, but special skills are required by the painter. For example, the thickness must be closely controlled and weather conditions for application and curing must be closely monitored. Depending on the type of inorganic zinc coating and weather conditions, the coating usually dries and cures fairly quickly and there is usually little delay in putting the item into service.

The totally different application procedures obviously have a significant influence on coating selection. Most importantly, an item to be galvanized must be able to fit into the bath, whereas there is no limit to the size of the item which can be coated with inorganic zinc. In the major population centres, large galvanizing baths are now available and items up to about 12 metres in length can be easily treated. With double end dipping, where one end is dipped in the bath, removed and the other end similarly treated, items 18 metres or so in length can be coated. However, double end dipping is not without disadvantages and should not be carried out unless necessary. Not only is it significantly more expensive due to complex handling requirements, but it can distort items due to the temperature gradient along the item and it often results in an ugly ‘tide mark’ at the centre of the item. Dross or dag formation can occur on galvanized surfaces which can be a problem when aesthetics or tolerances are important. Design and geometry can have other effects on galvanizing. The pickling acids and zinc must be able to flow across all surfaces and there must not be any air pockets or, not only will there be bare spots, but dangerous explosions could occur. There are other detailing constraints with hot dip galvanizing, as
venting and drain holes must be provided. Cross-sectional thickness is also important. A thin section will heat up and cool down much faster than a thick section so an item containing different cross sections can distort. Similarly, heavily welded assemblies may warp. Galvanizing cannot be carried out if the item is made of mixed materials, unless it can be easily dismantled. Galvanizing cannot be used to coat only certain parts of an item, such as externals of pipework or box sections. If the item is to be welded after galvanizing, damaged areas will have to be repaired and protection in these areas will be poorer than intact areas and there will be aesthetic considerations as the repair can never be made invisible. A large welded structure really must be coated with inorganic zinc on site for best protection. Finally, items containing cold-bent features can show strain ageing after galvanizing, although this is rarely a problem. Any specifier wanting to galvanize an unusual shape should discuss the coating process with the galvanizer to ensure it can be carried out safely and without problems.

There can also be application problems with inorganic zinc silicate. Perhaps the major problem is accessibility of all areas that must be coated. The blasting nozzle and spray gun must be able to reach all areas. Long-handled brushes or mops can be used for coating application over small areas, but their efficacy is questionable. Even the best painters cannot apply a coating uniformly across the entire surface and there are likely to be regions where coating is not applied to the correct thickness. Thin edges and small diameter items are difficult to paint uniformly, and thin sections cannot be blast cleaned. Finer abrasives and lower pressures can be used, but sections less than a couple of millimetres cannot be safely blasted without distortion. Coatings applied in the field are naturally subject to the vagaries of the weather, whereas galvanizing as a shop-applied process is unlikely to have delays for this reason. Against this, a zinc-rich coating may be able to be applied during fabrication in a shop at any time, without disrupting construction schedules.

Summarising from the application point-of-view, one coating will often be preferred. An item with lots of awkward surfaces to coat should be galvanized, as long as the zinc can flow through the item. A large structure must be coated with inorganic zinc, whereas small items are ideally galvanized. There must a local galvanizer available to carry out the work if that is the coating of choice, but coating with inorganic zinc silicate is a complex undertaking and cannot be carried out except by skilled blaster/coaters. It is a good idea to consider the surface treatment at the design stage of a steel structure, as the choice of coating will have a bearing on the design details.

### 3.3 Coating life

Zinc coatings largely depend on their thickness to provide protection in a given environment, and the thicker the coating, the greater the protection. Hot dip galvanizing and other metallic zinc coatings have been investigated over many years and there is a reasonably accurate picture of the life that can be expected from them. Regardless of the method of application, metallic zinc coatings show a linear increase in life in a given environment. Figure 3 shows the life obtained from metallic zinc coatings in different environments [8]. For a hot dip galvanizing coating of around 85 microns, the coating should last 25 to 30 years in a rural environment, 15 to 20 years in a marine environment (less for beach front) and around 10 years in an industrial environment. Anecdotal evidence suggests a longer life than these figures is likely, especially in less severe environments. Furthermore, many hot dipped galvanized coatings are thicker than 85 microns and the life should be proportionally longer.

![Figure 3: The effect of thickness and environment on the life of a zinc coating.](image-url)
Determining the life of an inorganic zinc silicate coating is not as simple. Such coatings are rarely as uniform in thickness, there is considerable variation in the behaviour of the different inorganic zinc silicate types and surface preparation standards are critical. These and other reasons mean that inorganic zinc silicate coated structures show far more variation than hot dip galvanized coated items and, not surprisingly, the life of such coatings is difficult to predict. For a coating of the same thickness, it has been claimed that, because it is porous, contains less zinc metal per unit area and contains silicate binder, the life should be less than the equivalent hot dip galvanizing coating of solid zinc of the same thickness. However, the silicate binder contributes to the corrosion protection of the inorganic zinc silicate coating. The inert silicate matrix surrounds the zinc particles considerably slowing down their dissolution. This silicate provides chemical resistance and restricts oxygen and water access to the zinc and, although the zinc particles still corrode away with time, this occurs at a far slower rate than the fresh zinc layer (even with a thin protective oxide or carbonate) on the hot dip galvanized surface. Munger [2] considers this is the major reason inorganic zinc silicate gives 'significantly' longer life than hot dip galvanizing of the same thickness but does not quantify this figure. Berger [9] also believes inorganic zinc will outlast galvanizing in some situations and gives examples. Salt spray exposure tests also tend to show inorganic zinc as giving superior life, but these do not represent real-life situations and such data are misleading and best ignored. Anecdotal evidence where inorganic zinc silicate and hot dip galvanizing are exposed to the same environment also confirms the better protection of inorganic zinc silicate. A much longer life for a properly applied coating of inorganic zinc silicate to a well-prepared surface is not unreasonable. However, this is not the entire story.

Liquid applied coatings tend to be thinner at edges due to difficulties in application, although inorganic zinc coatings contract far less on curing than other coatings. Invariably such coatings break down first in these areas. Zinc coatings do provide galvanic protection to edges and the thin edge effect is far less than with non-zinc coatings. But these areas are still their weak spot. So even with a significantly longer life in the flat areas, a coating of inorganic zinc silicate will probably break down at the edges much sooner than the flat areas. This tends to negate the improved life of the inorganic zinc silicate over hot dip galvanizing on flat areas. A unique feature of hot dip galvanizing is that the coating is as thick at the edges as the main body of the item. This is one of the most important features of a hot dip galvanizing coating. So an item without edges, such as a tank or pipeline, is an ideal candidate for inorganic zinc silicate while an item with many edges would be an ideal candidate for hot dip galvanizing. Once again, the two coatings are complementary.

Table 1 from work published regularly in NACE ‘Materials Performance’ [10] gives lives for galvanized coatings very close to the above figures. This work considers both inorganic zinc and galvanizing give roughly identical lives, 25 to 30 years in a milder environment, with about half this in more severe environments. This work gives a slightly better performance by inorganic zinc silicate in the marine environment. Szokolik [11] has assessed the performance of single coat inorganic zinc silicate systems on a number of bridges and other structures in a range of environments in Victoria. He found the water borne coatings in rural/urban environments were in excellent condition after more than thirty years exposure, and solvent-borne coatings in marine/light industrial exposure were still in perfect condition after 20 years exposure. Hot dipped galvanized coatings in light marine and light industrial exposure were in perfect condition after 28 years. He considered all coatings would continue to provide protection for another 10 or 20 years. Clearly, the figures given in Table 1 are conservative, especially for Australian conditions.

Table 1: Life to first maintenance in years for the two coatings in different environments [10].

<table>
<thead>
<tr>
<th>System</th>
<th>Mild/Rural</th>
<th>Moderate (industrial)</th>
<th>Seacoast marine</th>
<th>Severe heavy industrial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 2½/ 75 μm IZS</td>
<td>27</td>
<td>17</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>Hot Dip Galvanize</td>
<td>27</td>
<td>17</td>
<td>13</td>
<td>12</td>
</tr>
</tbody>
</table>

IZS: Inorganic zinc silicate.

Some suggested lives of inorganic zinc silicate and hot dip galvanizing coatings from AS/NZS 2312: 1994 [12] are given in Table 2. Looking initially at the figures given for hot dip galvanizing, these lives are significantly shorter than quoted above. The solvent-borne inorganic zinc shows significantly poorer performance than the galvanizing, and this code effectively does not recommend solvent-borne inorganic zinc silicate for any application (up to 5 years for a mild/moderate environment only), and recommends the thicker water-borne coating for a reasonable life in most environments except industrial. It appears that AS/NZS 2312:1994 gives very conservative figures which bear little resemblance to actual lives for either galvanizing or inorganic zinc and such figures are probably best ignored.
Table 2: Life to first maintenance in years of inorganic zinc and hot dip galvanizing coatings from AS/NZS 2312:1994.

<table>
<thead>
<tr>
<th>System</th>
<th>Environment</th>
<th>Mild/Moderate</th>
<th>Tropical</th>
<th>Industrial</th>
<th>Marine</th>
<th>Severe marine</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP1A</td>
<td>Class 2½/ 65-75µm IZS-SB</td>
<td>5 - 10</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>LP3</td>
<td>Class 2½/ 100-150µm IZS-WB</td>
<td>10 - 20</td>
<td>10 - 20</td>
<td>NR</td>
<td>10 - 20</td>
<td>10 - 20</td>
</tr>
<tr>
<td>GZ</td>
<td>Hot Dip Galvanize</td>
<td>10 - 20</td>
<td>10 - 20</td>
<td>2 - 5</td>
<td>5 - 10</td>
<td>NR</td>
</tr>
</tbody>
</table>


4. ECONOMICS

Many situations will lend themselves to one system or the other for practical reasons, and cost alone would rarely be a deciding factor between the options. However, an economic analysis may be required in some situations. Comparing the cost of the two coatings is difficult because of the differences between them and the fact that they are priced completely differently. Galvanizing is generally priced by the tonne, while coating with inorganic zinc is priced by the square metre. Figure 4 compares the cost of items galvanized to those coated with inorganic zinc as a function of surface area per tonne, which is inversely related to section thickness. This figure has been calculated from costs for using inorganic zinc taken from Table D1 in AS/NZS 2312 [12] for 75 microns of coating over a class 3 surface which gives around $15 per square metre for 10 square metres per tonne to around $20 per square metre for 40 square metres per tonne. A cost of $400 per tonne has been taken for galvanizing. Other sources such as Appendix A3 in [13] will give slightly different costs, but the trends are similar. While these costs give only a rough idea, they clearly show that galvanizing becomes more economically beneficial as the section thickness decreases so the item has more surface area per unit weight. Therefore, fasteners and similar small items with large surface area are ideal for galvanizing. Coating with inorganic zinc becomes more economic as the section thickness increases and the surface area per tonne decreases. As a result, large, heavy items tend to lend themselves to coating with inorganic zinc. These figures can only give a rough indication as, for example, handling difficulties can influence the price. The price for galvanizing varies considerably depending on the item that is coated. A simple item to be galvanized which requires little extra preparation, with simple handling requirements, and short residence times in the bath, may cost less than $400 per tonne. A complex item that is difficult to handle and requires special preparation, such as double dipping, may be well over $1000 a tonne. There can also be considerable variation in price per square metre of coating with inorganic zinc if complex handling is required. Painting of small sections will result in considerable overspray, partly accounting for increased cost with higher surface area ratios. However, depending on section thickness, one form of coating will clearly become more economic than the other. In fact, the two coatings can be combined on the same project to realise considerable savings. If the prices in Figure 4 are applicable, light sections with more than about 25 square metres area per tonne (section thickness below around 5 mm) should be galvanized, while heavier sections (section thickness above around 5 mm) should be coated with inorganic zinc silicate, all other considerations being equal.

Figure 4: Cost per square metre for galvanizing and coating with inorganic zinc as a function of surface area.

5. TOPCOATING

Both coatings provide excellent protection in many environments and do not normally need subsequent topcoats, nor should such coats be applied unless necessary. In fact, there is increasing evidence that, at least in some situations, a topcoated inorganic zinc silicate system has a lesser life than the same inorganic zinc without the subsequent coating. The suggested reason is that the top coat limits the amount of zinc available for providing
galvanic protection at scratched or other damaged areas. One would imagine a similar situation will occur with galvanized coatings. Another suggestion is that the inorganic zinc must be allowed to age so that the porosity is filled in (or a seal coat applied) prior to top coat application for enhanced coating life, a situation which rarely occurs in practice. Nevertheless, there are situations, such as for aesthetics, for safety colours, for added protection, etc. where subsequent coating is required. It cannot be stressed enough if colour is required, or the environment is not suitable for zinc primers, there are numerous other coating systems that can be considered (see, for example, 12, 14). However, it must be recognised that there will be situations where galvanizing or inorganic zinc will require, or the specifier will desire, subsequent coating. It is possible to obtain inorganic zincs in 'environmental' tints, such as dark greens or browns which can be considered when structures must blend into the landscape although unpigmented inorganic zinc and galvanizing will usually weather to a dull finish which may be environmentally acceptable.

Galvanizing does not lend itself well to subsequent coating, although it can be successfully carried out if care is taken. Paint flaking from galvanizing is common due to the smooth surface, contamination on the surface or an incompatible coating. The surface must be degreased, thoroughly cleaned, ideally brush blasted and special etchants or etch primers are often specified. However, the use of etch primers is no longer recommended for galvanized surfaces as unreasonable control over film thickness is required. Only certain coatings are compatible with galvanizing. The best coating for galvanizing is usually a non-inhibitive two-pack epoxy primer, as long as the surface has been degreased and ideally brush blasted. This and other coating systems for galvanizing are given in [12].

By contrast, inorganic zinc is relatively easy to topcoat, especially the solvent-borne types, although again compatible coatings must be used. Its surface readily accepts many different paint coatings to provide colour or additional protection. Topcoats soak into the inorganic zinc silicate surface and bond to the surface, providing strong and reliable adhesion. Unlike coatings over galvanizing, paint flaking from an inorganic zinc coating is virtually unknown. It is not without problems however. Solvent-borne coatings must be properly cured before topcoating or the zinc can split, but full cure is not easy to determine. The porosity can cause blistering or bubbling of fast drying topcoats and a thin wash coat or tie coat is often used to avoid this problem. Despite these problems, inorganic zinc has been successfully topcoated with many different types of organic coatings and, when properly carried out, should be without difficulties. If subsequent coating is desired or necessary, inorganic zinc is preferable to galvanizing.

6. QUALITY ASSURANCE AND INSPECTION

Quality assurance of galvanizing is relatively simple and, generally if the final product looks acceptable, it probably will be. If the pickling and other cleaning and surface preparation requirements are not correctly carried out, the zinc will not adhere to the surface and bare spots will be apparent immediately the work is withdrawn from the molten zinc. As long as there are no air pockets, zinc should flow over the entire surface. The galvanizer has little control over thickness and there is little risk of the coating being too thin or thick. Quality assurance of galvanizing is usually limited to visual inspection and measurement of the film thickness.

Application of inorganic zinc coatings will require much more care in quality assurance. The product can be controlled, and coatings should meet formulation or performance standards such as AS/NZS 3750.15 [7] or APAS (Australian Paint Approval Scheme) approval. Quality assurance of surface preparation and application can be more difficult, and will add to the price. The environment must be monitored, the surface must be blast cleaned to a high standard, the coating properly mixed, carefully applied to the correct thickness and allowed to properly cure under the correct conditions. With a properly worded specification and careful inspection by the owner, or an efficient quality assurance programme in place by the applicator, this should be achieved. But, unlike galvanizing, a finish that looks acceptable may lack proper surface preparation, for example, and not provide the desired protection. Inspection is important with application of inorganic zinc adding to cost, unlike galvanizing which is essentially self-inspecting.

7. WELDING

Because there is no size limit to items to be coated with inorganic zinc silicate, welding is not usually a problem as coating will normally be carried out after fabrication completion. But even if welded, inorganic zinc generally does not cause significant problems. Thin film inorganic zinc primers of 15 to 25 microns with a lower zinc loading are commonly used as preconstruction primers where they can provide protection during fabrication and be safely welded through by most methods without hazards or reduction in weld strength or speed. Full thickness inorganic zinc coatings (75 microns or more) can be welded without any loss of strength in many situations, but high-speed production welding can produce some porous welds. Manual welding, however, will usually provide welds with equivalent strength to uncoated steels with proper welding procedures. Similarly, items should be welded before galvanizing, but welding may be necessary after fabrication due to the size limit of items which can be galvanized. As with inorganic zinc, limited tests have shown that mechanical properties are not significantly changed by the presence of a galvanized layer as long as welding rate is not too high to allow burn-off of the zinc. However,
because of possible health hazards from the evolution of fumes from coated and non-coated steels, welding fume control measures must be adopted [15].

8. SPECIAL PROPERTIES AND APPLICATIONS

Table 3 provides a summary of some of the properties, features and applications of the two types of zinc coatings. As noted in this paper, there are slight differences between some properties of the solvent-borne and water-borne inorganic zins, which may be important.

Table 3: Summary of properties and features of galvanizing and inorganic zinc coatings.

<table>
<thead>
<tr>
<th>Property</th>
<th>Galvanizing</th>
<th>Inorganic zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness/toughness</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Abrasion resistance</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Max temperature - dry</td>
<td>200 - 250°C</td>
<td>400°C</td>
</tr>
<tr>
<td>Resistance to:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Marine environments</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>• Humidity</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>• Oil and solvents</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>• Acid</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>• Alkali</td>
<td>OK below pH 12</td>
<td>OK below pH 10</td>
</tr>
<tr>
<td>• Fungi, mould, etc</td>
<td>Unaffected</td>
<td>Unaffected</td>
</tr>
<tr>
<td>• Fire</td>
<td>Resistant</td>
<td>Resistant</td>
</tr>
<tr>
<td>Coating Application:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Minimum surface preparation</td>
<td>Pickle</td>
<td>Class 2½ blast</td>
</tr>
<tr>
<td>• Can suffer warpage during application</td>
<td>Possible</td>
<td>No</td>
</tr>
<tr>
<td>• Typical thickness (microns)</td>
<td>50-150</td>
<td>50-200</td>
</tr>
<tr>
<td>• Thickness at corners and edges</td>
<td>Same or greater</td>
<td>Same or less</td>
</tr>
<tr>
<td>• Temperature/ humidity requirements for cure</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>• Ease of topcoating</td>
<td>Complex</td>
<td>Acceptable</td>
</tr>
<tr>
<td>• Inspection (QA) requirements</td>
<td>Simple</td>
<td>Complex</td>
</tr>
<tr>
<td>• Ease and appearance of repair</td>
<td>Complex and poor</td>
<td>Simple and good</td>
</tr>
<tr>
<td>Applications:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Faying surfaces</td>
<td>Must be roughened</td>
<td>Acceptable</td>
</tr>
<tr>
<td>• Small items - fasteners, etc</td>
<td>Ideal</td>
<td>No</td>
</tr>
<tr>
<td>• Large or existing structures</td>
<td>No</td>
<td>Ideal</td>
</tr>
<tr>
<td>• Complex structures</td>
<td>Complete coverage</td>
<td>Difficult</td>
</tr>
</tbody>
</table>

Inorganic zinc coatings, unlike organic coatings, have high slip coefficients and may be safely applied to the faying surfaces of tensioned bolted steelwork connections. Hot dip galvanized surfaces should have faying surfaces of friction-grip bolted connections lightly blasted or otherwise roughened to increase friction. (Slip factors for various surface treatments are given in Table C9.3.3.2 of [16]). Both coatings can resist high temperatures, with inorganic zinc resisting temperatures near the melting point of zinc, and hot dip galvanizing withstanding somewhat less than this. Both coatings will withstand temperature shocks and both are unaffected by radiation and can be used in nuclear power plants. Both coatings are very hard and tough with excellent abrasion resistance, although the solvent-borne inorganic zins show lower resistance than the water-borne types. Both coatings are completely inorganic and provide excellent resistance to UV light and most organic solvents and petroleum products.

Light, general purpose steelwork can be more economically galvanized than coated with inorganic zinc. This includes fasteners, handrails, ladders, stair treads, etc. Grating is an ideal candidate for galvanizing because of the complex shape, difficult access and the need for good abrasion resistance. Complex fabricated assemblies with difficult blasting and painting access may be at risk of poor coating operations and difficult inspection and would lend themselves to hot dip galvanizing. Narrow diameter piping (less than about 65 mm diameter) is ideally galvanized. Above ground water piping can use either coating unless specific identification colours are required. Hot water piping that is to be insulated should never be coated with any zinc-based coating, as the inevitable hot water beneath the insulation will cause rapid corrosion. Many other examples of galvanized steel are available, including transmission towers and other electrical structures, road and rail furniture, small bridges, concrete reinforcement, farm equipment and building components. These have generally shown excellent performance.
Inorganic zinc primers have been used on virtually every conceivable steel structure, new or old, on the ground, at sea or in a shop. Applications include pipelines, power plants, transmission towers, coal washeries, road and rail bridges, ships, wharf facilities, offshore platforms and oil rigs and tanks (interior and exterior depending on contents). Many of these also have shown excellent performance after decades of exposure.

9. CONCLUSIONS

This paper has attempted to provide some guidelines as to the merits and uses of inorganic zinc silicate coatings and hot dip galvanized coatings. There is no simple answer to the question, ‘which is best?’, as both have advantages and disadvantages. Generally, they should be considered as complementary coatings. Both provide excellent protection in a range of atmospheric environments, as long as it is not acidic or strongly alkaline. Both provide similar protection, with galvanizing having the advantage on complex items with many corners and edges, and inorganic zinc superior for large flat sections such as tanks and above-ground pipelines. Galvanizing has a limit to the size of the item which will fit in the galvanizing bath, while there is no limit to the size of items which can be coated with inorganic zinc. Galvanizing is cheaper for small objects and inorganic zinc more economic for larger objects. Quality assurance requirements are simpler for galvanizing, but inorganic zinc provides a better surface for subsequent painting. Each project should be considered on its environment, shape, size and scheduling to determine which form of corrosion protection is optimal. With such an evaluation, the best system can be selected.

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11. REFERENCES

A Comparison of the Corrosion Behaviour of Inorganic Zinc and Conventionally-Coated Bridges

R A Francis, Consultant, Ashburton, Victoria and A Szokolik, Consultant, Sale, Victoria

SUMMARY: The condition of the coatings on a number of steel bridges in the region around Melbourne was investigated. The condition of the coatings showed that single-coat inorganic zinc silicate gave significantly better performance than conventional multi-coat inhibitive systems, up to three times the life or more. Maintenance of the inorganic zinc coatings was also far easier. This work also showed a major weakness of the ASTM D610 method of assessing coating condition.

Keywords: Bridge coatings, inorganic zinc silicate, ASTM D610 coating assessment.

1. INTRODUCTION

The condition of the coatings of a number of steel bridges in the Melbourne metropolitan and surrounding areas was investigated. The original investigation was commissioned by BHP Integrated Steel Marketing Group to generate information for a bridge coating guide, produced by one of the authors (1). This paper looks at the results of this survey with a view to try to quantify differences between protection given by coating systems used, and to assess the applicability of the usual method used of measuring degree of coating breakdown, especially as it applies to inorganic zinc silicate coatings.

Most information on coating lives is obtained from exposing test panels to either laboratory accelerated testing, or atmospheric exposure at specific sites. Such tests can give valuable results, but there will always be doubt about applicability to real structures in a variety of environments. The survey on which this paper is based, using actual structures in a range of real environments, should be able to give a more realistic guide to coating performance. In practice however, there are many problems associated with analysing actual structures, as compared to test panels. Some of the problems include:

• Records are rarely available of original system, maintenance, inspection results, etc. Maintenance painting is the major problem, as a number of these bridges have clearly been spot painted, or given a complete coat to parts of the structure at some stage since construction.

• Actual structures are subjected to a range of micro-environmental and design features which means the coating is not uniformly subjected to its environment. For example, horizontal surfaces will be wet for a longer period of time than vertical surfaces and subjected to higher corrosivity. Sheltered items are not subjected to the corrosive action of rain, but deposited salts and dirt will not be washed off, and corrosivity may be increased.

• The coatings will be applied at a much greater variation in thickness than would occur on test panels and there is greater likelihood that surface preparation and coating application may not have been as good as for test panels.

• Coatings used may change formulations over the period of time investigated and coatings used in the past may no longer be used. Many new coatings have been introduced over the 50 or so years covered by this survey. In fact, many of the coating systems used in this survey were based on red lead primer, which has now been phased out. However, it is worth noting that modern developments in coatings have concentrated on producing coatings that are safer to apply, and have less environmental impact, than earlier formulations. Newer developed coating will not necessarily have better corrosion resistance.

Despite these difficulties, the results are worth investigating and should provide useful information as to coating performance.
2. CORROSIVITY OF THE ENVIRONMENT

While the bridges surveyed were spread over a quite large geographical area, corrosivity of the macro-
environment would be fairly consistent, and not be very high. A thorough study of the corrosivity of the
Melbourne metropolitan area some years ago (2) found that the corrosivity was relatively constant over the area,
around 10-25 microns carbon steel per year for first year. Higher rates were found on the shore of Port Philip
Bay from the marine influence, but this influence extended no further inland than about one kilometre. None of
the bridges were this close to the bay. The bridges in the country were a significant distance from the sea and no
marine influence would be expected. A few were in the Latrobe Valley region of the state, known for the
presence of significant power generation facilities, but these burn low sulphur fuel and corrosion rates in the
valley would be expected to be similar to the metropolitan area. These corrosion rates would put the macro
environment of the bridges in the upper end of ISO 9223 category C2, perhaps extending into category C3.

Local or micro-environmental effects would probably increase corrosion rates. These bridges pass over major
roads, freeways and railways, and it would be expected that transport pollutants, especially diesel combustion
products, would increase corrosivity. However, this pollutant is not a major contributor to metallic corrosion, and
its effect would be expected to be small. Design features would also influence corrosivity, with horizontal
surfaces having a greater time of wetness, and retaining dirt and dust, so showing greater corrosivity than vertical
surfaces. Unwashed regions, such as inner beams, are generally considered to show higher corrosion rates than
surfaces that are regularly washed, such as outer surfaces, but this effect is relatively minor away from major
sources of corrosion, such as sea salt or acid rain. For these structures, unwashed interior sections would
probably show lower corrosivity than external sections.

In summary, all bridges are in a similar corrosion environment, and micro-environmental and design influences
on corrosion would probably have the same effect on all. The environment is not particularly corrosive, but still
allows a comparison to be made. Absolute lives for structures in different environments from these cannot be
accurately extrapolated from the data presented in this paper. However, there is no reason to believe that the
relative performance of the coatings would not be similar in other environments.

3. THE COATING SURVEY

All but one of the bridges surveyed was constructed with steel I-beams, or similar construction (see Figure 1),
the one exception being of box girder construction. Surface condition has been assessed solely on the degree of
coating breakdown and subsequent rusting. The evaluation has been carried out using the well-known standard
ASTM D-610 (Degree of Rusting), also published as SSPC Vis 2, where a numerical number from 1 to 10 is
assigned based on the percentage of the surface rusted. The scale is logarithmic, with each percentage of rust 10
times that of the preceding grade. The higher the rating, the less the rust. A rust grade of 10 to 8 indicates the
coating is almost intact, a rating of 8 to 6 indicates some weathering, 6 to 4 indicates a thoroughly weathered
coating, and a rating less than 4 indicates heavily rusted steel. The logarithmic scale for characterising
breakdown is used because coating breakdown tends to accelerate with time. ISO 4628-3 (Designation of degree
of rusting) uses a similar method of evaluation where grade Ri 0 is equivalent to D-610 rating 10 (no rust), Ri 3
is equivalent to D-610 rating 6 (one per cent rust) and Ri 5 (40 to 50 per cent rust) is between D-610 ratings 1
and 2. Both these type of standards were developed for evaluating small test specimens and are difficult to use
for actual structures. The weaknesses will be discussed later on.

Chalking, discolouration, dirt accumulation, rust staining and other deterioration modes have not been
considered. It is considered that this is valid as these modes are far less serious than coating breakdown.

The coated surfaces of the steel bridges were investigated. A thorough visual examination was made, looking at
surfaces that were likely to break down: the horizontal flange surfaces (top and underside), edges and webs. The
outer beams were recorded separately from inner beams. Bracing was also investigated where present. A
comprehensive coating thickness survey was also carried out using an electronic dry film thickness gauge.
Readings were taken on inner beams and on outer beams. Minimum, maximum and average thicknesses and
number of readings taken were recorded. A summary of some of the results is given in the Appendix. The table
shows only minimum dry film thickness reading, as this is known to be the parameter commonly associated with
coating breakdown. Between about 20 and 100 readings were taken in each region.
Figure 1: Bridge at Keilor, showing girder construction, coated with water-borne inorganic zinc.

To enable trends to be determined, the main results have been plotted in Figures 2 to 5. The condition of the inorganic zinc coated structures is plotted as a function of age of the structure in Figure 2 and as a function of minimum dry film thickness in Figure 3. Figures 4 and 5 plot the same trends, but for the red lead and micaceous iron oxide (MIO)/Aluminium pigment systems.

Figure 2: Condition of inorganic zinc coated bridges as a function of age

Figure 3: Condition of inorganic zinc coated bridges as a function of minimum measured DFT
4. RESULTS OF THE SURVEY

Sixteen bridges were coated with a single-coat water-borne inorganic zinc coating, ranging in age from 3 to 37 years. All surfaces were extremely hard and about half showed a tightly adhering layer of white zinc corrosion product. Average thicknesses ranged from 95 to 190 microns, although individual readings ranged from 35 microns to 375 microns. Despite some very high readings, no mudcracking was observed on any surface. Most of the structures showed little breakdown, with 80% of the surfaces having an ASTM rating better than 9.5. Where breakdown was observed, it was mainly associated with edges of the beams, and the tops of flanges. Breakdown was generally associated with areas which had been missed at the time of original application, or thin areas (see Figure 6).

![Figure 4: Condition of red lead/MIO or red lead/Aluminium coated bridges as a function of age](image)

![Figure 5: Condition of red lead/MIO or red lead/Al bridges as a function of minimum measured DFT.](image)

Only one structure was protected with solvent-borne inorganic zinc, a bridge 22 years old. While a single structure does not allow definite conclusions to be drawn, it is interesting to compare its performance with the water-borne materials. From Figure 2 it appears to perform significantly poorer for its age than the water-borne counterpart, but this is not necessarily true. In fact, its poorer performance is most likely due to rather low minimum film thicknesses. The regions of rust breakthrough were associated with areas of low film thickness. Interestingly, the maximum thickness measured was 336 microns, with a number of readings above 150 microns but, as with the water-borne product, no mud cracking was observed.
Seventeen structures were coated with a red lead based system, most with an aluminium pigmented top coat, the rest an MIO top coat, both of unknown resin base (probably oil or alkyd phenolic). The age of these coatings is between 10 and 50 years. Most of the bridges had been subjected to some maintenance painting, usually the surfaces of the outer beams. These bridges showed far poorer performance than those coated with inorganic zinc. Figure 4 shows there is a slight relationship between age and condition, with condition deteriorating with age. However, this relationship is not conclusive, as one structure over 30 years old is in better condition than many younger structures. Figure 5 shows that there is little relationship between minimum film thickness of the structure and its condition. The minimum dry film thickness was between about 60 and 120 microns, with conditions ranging from very good to poor. Rust breakthrough for these coating systems is by a different mechanism than with the inorganic zinc. Areas of breakdown are not necessarily associated with thin areas, but appears to be random, probably as a result of surface defects. Furthermore, rather than breakdown occurring at particular sections, such as top flanges, it is universal in its extent (see Figure 7).

One bridge was protected with a zinc phosphate/ chlorinated rubber system. It was only one year old, and applied quite thickly so not surprisingly was in excellent condition. One bridge had a solvent-borne inorganic zinc primer with 2 coats of epoxy MIO. Isolated rusting was observed on the underside flanges and edges, mainly as a result of poor application techniques. Where properly applied, the system was performing well. With such coatings being carried out relatively recently, such performance is not surprising and no real conclusions can be drawn from these two examples.
5. DISCUSSION

The survey clearly shows the superiority of the inorganic zinc systems. The multi-coat system showed a far greater degree of coating breakdown and rust-through than the inorganic zinc system. Breakdown of the inorganic zinc is generally apparent only in those areas where thickness is insufficient. Figure 3 shows that if dry film thickness had been kept above about 75 microns, conditions would have been even better. Indeed, only one sample with a minimum greater than 75 microns showed any breakdown, and it was still ASTM D-610 Rating 9 with over 20 years exposure.

The breakdown of the two types of coatings shows clearly the limitations of the ASTM D-610 rating system. This limitation has been discussed in an earlier paper looking at the performance of inorganic zinc coatings on offshore platforms (3). The ASTM D-610 system assumes that breakdown will occur over a surface in a scattered manner. While this is often the case with conventional coatings, inorganic zinc coatings tend to break down in localised areas, usually where coating thickness was inadequate. This difference is very important in maintenance programs, as localised breakdown is far easier to maintain than scattered breakdown. For example, a surface with 10 per cent scattered breakdown would need complete coating removal and coating reinstatement, but 10 per cent breakdown in one localised area could easily be fixed by spot repair. In fact, localised breakdown will be far easier and cheaper to repair than scattered breakdown, whatever the amount.

As discussed above, environmental differences did not appear to have a significant effect on coating performance. Micro-environmental effects would probably be more important, with the inner beams not being subjected to the washing effect of rain. However, outer surfaces have had more frequent maintenance for aesthetic reasons so this would mask any difference in performance between inner and outer surfaces because of micro-environmental effects.

As mudcracking was not observed on any beam coated with inorganic zinc, even with thicknesses of more than 300 microns, it would appear that keeping film thicknesses low to avoid mudcracking is unnecessary. Measuring dry film thickness according to AS 3894 Part 3 or SSPC PA-2 allows dry film thicknesses as low as 20 per cent below the minimum specified. Under such a regime, to ensure no figure falls below 75 microns, it is recommended that all inorganic zinc coatings be applied to a minimum of 100 microns. While mud-cracking will probably be more likely as the specified minimum increases, this risk can be reduced by other means. For example, mud cracking probability appears to depend on formulation, and products used should meet standards such AS/NZS 3750 Part 15. Furthermore, inorganic zinc coatings do require skill in application, and only applicators trained in its use should apply this product. While mud-cracking would appear to be a serious problem, it must be remembered that zinc will galvanically protect bare steel some millimetres from the edge of a coating, and such cracking is far less of a problem than might appear. Furthermore, zinc corrosion products are likely to fill cracks. This survey shows that low thickness certainly reduces the protective life of an inorganic zinc, and it is considered this risk is far more serious than small amounts of mud cracking.

Even allowing for the presence of dry film thickness readings below the desirable figure, the inorganic zinc coatings have shown predictable performance. Figure 2 shows coating deterioration varies with time in a similar manner to that discussed by Appelman (4). There is an apparent threshold or induction period during which no breakdown is observed, followed by a roughly constant deterioration. Looking at the worst possible case for the inorganic zinc, the induction period seems to be about 15 to 20 years (as suggested by Appelman for a mild environment) followed by a very low maximum deterioration rate of one ASTM unit per 5 years. This mathematical relationship can be used to estimate future breakdown, and can be used for maintenance programs. For example, if it is desired to carry out maintenance when a rust rating of 6 (1 per cent rust) is achieved, then this would be carried out after 35 years. These figures can also be used to estimate the amount of breakdown which may occur if delay to maintenance programs are required, and repainting is deferred. With inorganic zinc in this environment, the structure could be left for at least five years before breakdown equal to one ASTM unit would occur. Had dry film thickness been kept above 75 microns, the threshold may have been thirty or forty years or more before breakdown commenced.

Because of the great amount of scatter, attempting to model breakdown of the red lead/ MIO or aluminium systems would be very imprecise. The threshold (if one exists) appears to be between 0 and 10 years, significantly lower than for the inorganic zinc systems. Rate of breakdown may be as high as one ASTM unit every 2.5 years, double that of the maximum for the inorganic zinc. However, as with the inorganic zinc coatings, rate of breakdown is probably much lower than this. But there is little doubt that the threshold time for the conventional coatings is far less than for the inorganic zinc. In practice, these beams should have been repaired at a much earlier degree of breakdown, but because of the presence of lead-containing paint, it is more economic to allow the coating to completely degrade and remove it completely. It would appear that the inorganic zinc system provides at least three time the protection of the conventional system, and breaks down at about half the rate of the conventional system.
As well as the significant improvement in coating life obtained by the inorganic zinc coating over conventional systems and localised rather than scattered breakdown, the zinc coating offers a number of other important advantages. Where the inorganic zinc coating has broken down, it is solely by rusting. Unlike other coatings, it does not suffer breakdown by chalking, blistering, underfilm rusting, or other modes of failure. This makes assessment easier as no weighting needs to be given to different breakdown modes. For example, a conventional coating may show rust over 1 per cent and blistering over 2 per cent of the surface. Is this better, worse or the same as a coating with rust over 2 per cent and blistering over 1 per cent of the surface? These judgements are not required with inorganic zinc. Secondly, rusting on a zinc-coated surface is far less damaging than rust on a conventionally-coated surface. The rust tends to remain on the surface when zinc coated whereas corrosion grows into the steel surface on a conventionally-coated surface. This makes surface preparation for repair much simpler. Thirdly, once formed, the rust tends to grow more slowly on zinc-coated steel compared to a conventionally-coated surface. Finally, as pointed out above, maintenance on a zinc-coated structure can be delayed before maintenance. The big advantages of conventional coatings is the range of colours and gloss level available, compared to the dull grey only obtainable with zinc. This was not an issue with these bridge coatings, as aluminium or MIO pigments tend to limit appearance possibilities. In fact, the grey colour is often preferred for such structures by architects and engineers. Table 1 summarises these features of inorganic zinc and multi-coat systems.

<table>
<thead>
<tr>
<th>Property</th>
<th>Inorganic zinc</th>
<th>Multi-coat, inhibitive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition of degraded surface</td>
<td>Rust localised &amp; limited</td>
<td>Rust scattered and widespread</td>
</tr>
<tr>
<td>Urgency for repair</td>
<td>Can be delayed</td>
<td>No delay</td>
</tr>
<tr>
<td>Depth of rusting</td>
<td>Surface only</td>
<td>Can pit</td>
</tr>
<tr>
<td>Required repair surface preparation</td>
<td>Spot repair</td>
<td>Probably complete removal</td>
</tr>
<tr>
<td>Amount of breakdown before repair</td>
<td>~2%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Coating life (before first breakdown) in studied environment</td>
<td>25-30 years</td>
<td>0-10 years</td>
</tr>
<tr>
<td>Colour and gloss</td>
<td>Grey, flat</td>
<td>Range possible</td>
</tr>
</tbody>
</table>

6. CONCLUSIONS

- Within the studied environment, a single coat inorganic zinc silicate coating provides far superior protection to a conventional coating system of a red lead primer with an aluminium or MIO top coat. A life of at least twenty years, possibly forty, before first major maintenance is easily achievable with inorganic zinc in this environment. Compared to a conventional system, the inorganic zinc could provide three times or more life before maintenance. If the minimum dry film thickness was kept above 75 microns, it would appear that durability of the inorganic zinc could be even better. Also, the inorganic zinc coating broke down in localised regions with defined boundaries, so would be much easier to maintain than the multi-coat system.

- The well-known ASTM D-610 system for rust grading is adequate for assessing breakdown of coatings which degrade uniformly across the surface, such as the conventional multi-coat system. It is less applicable for the single-coat inorganic zinc system which breaks down in a more localised manner. It indicates that significantly larger areas require maintenance than is, in fact, the case. As well as grading according to amount of the coating degraded, breakdown should also be identified as either scattered or localised.

- The relative predictability of breakdown of inorganic zinc coatings makes maintenance planning easier. In this survey, no breakdown was observed for about 25 years, then the coating degraded by one ASTM unit for each five years thereafter. If the level of breakdown when maintenance is required is known, maintenance work can be planned more easily with the inorganic zinc coating.

7. REFERENCES


8. ACKNOWLEDGMENT

The authors gratefully acknowledge the support of Frank Rapattoni and BHP Steel for commissioning the survey described in this paper.

APPENDIX: SUMMARY OF COATING CONDITION OF BRIDGES SURVEYED.

(a) Bridges coated with water-borne inorganic zinc.

<table>
<thead>
<tr>
<th>ID</th>
<th>Location</th>
<th>Age</th>
<th>Outer Surfaces</th>
<th>Inner Surfaces</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Min DFT (µm)</td>
<td>ASTM Condition</td>
<td>Min DFT (µm)</td>
</tr>
<tr>
<td>1a</td>
<td>Keilor - West Carriageway</td>
<td>17</td>
<td>58</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>1b</td>
<td>Keilor - East Carriageway</td>
<td>17</td>
<td>84</td>
<td>10</td>
<td>56</td>
</tr>
<tr>
<td>2a</td>
<td>Jackson Ck - West Carriageway</td>
<td>11</td>
<td>75</td>
<td>10</td>
<td>37</td>
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<tr>
<td>2b</td>
<td>Jackson Ck - East Carriageway</td>
<td>11</td>
<td>61</td>
<td>10</td>
<td>53</td>
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<tr>
<td>4</td>
<td>Footscray</td>
<td>3</td>
<td>NM</td>
<td>10</td>
<td>NM</td>
</tr>
<tr>
<td>7a</td>
<td>Laverton - New</td>
<td>20</td>
<td>113</td>
<td>10</td>
<td>113</td>
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<tr>
<td>9</td>
<td>Werribee</td>
<td>37</td>
<td>37</td>
<td>8</td>
<td>35</td>
</tr>
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<td>Werribee</td>
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<td>53</td>
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<td>46</td>
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<tr>
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<td>10</td>
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<td>Morwell</td>
<td>6</td>
<td>53</td>
<td>10</td>
<td>53</td>
</tr>
<tr>
<td>25a</td>
<td>Spotswood - North Carriageway</td>
<td>27</td>
<td>61</td>
<td>10</td>
<td>63</td>
</tr>
<tr>
<td>25b</td>
<td>Spotswood - South Carriageway</td>
<td>27</td>
<td>96</td>
<td>10</td>
<td>66</td>
</tr>
<tr>
<td>27</td>
<td>Greensborough</td>
<td>11</td>
<td>48</td>
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<td>59</td>
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<td>28</td>
<td>St Albans</td>
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<td>10</td>
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<td>Spotswood</td>
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<td>59</td>
<td>10</td>
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</table>
(b) Bridges coated with Red Lead primer and Aluminium or MIO top coat.

<table>
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<th>ID</th>
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<th>Outer Surfaces</th>
<th>Inner Surfaces</th>
<th>Comments</th>
</tr>
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<td>ASTM Condition</td>
<td>Min DFT (µm)</td>
</tr>
<tr>
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<td>Coburg</td>
<td>28</td>
<td>110</td>
<td>6</td>
<td>110</td>
</tr>
<tr>
<td>7b</td>
<td>Laverton - Old</td>
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<td>NM</td>
<td>3</td>
<td>NM</td>
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<tr>
<td>19</td>
<td>Yallourn</td>
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<td>NM</td>
<td>2</td>
<td>NM</td>
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<tr>
<td>20</td>
<td>Yallourn North</td>
<td>&gt;50</td>
<td>NM</td>
<td>3</td>
<td>NM</td>
</tr>
<tr>
<td>21</td>
<td>Moe</td>
<td>30</td>
<td>67</td>
<td>4</td>
<td>78</td>
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<tr>
<td>22</td>
<td>Moe</td>
<td>29</td>
<td>NM</td>
<td>4</td>
<td>NM</td>
</tr>
<tr>
<td>23b</td>
<td>Dandenong - Old section</td>
<td>&gt;50</td>
<td>NM</td>
<td>7</td>
<td>NM</td>
</tr>
<tr>
<td>24</td>
<td>Canterbury</td>
<td>11</td>
<td>NM</td>
<td>4</td>
<td>NM</td>
</tr>
<tr>
<td>26a</td>
<td>Tullamarine - South Overpass</td>
<td>31</td>
<td>97</td>
<td>9</td>
<td>89</td>
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<tr>
<td>26b</td>
<td>Tullamarine - Mid Overpass</td>
<td>31</td>
<td>99</td>
<td>5</td>
<td>106</td>
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<tr>
<td>26c</td>
<td>Tullamarine - North Overpass</td>
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<td>65</td>
<td>4</td>
<td>109</td>
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<tr>
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<td>Glengarry West</td>
<td>&gt;50</td>
<td>NM</td>
<td>1</td>
<td>NM</td>
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(c) Bridges coated with other systems

<table>
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<td>Min DFT (µm)</td>
<td>ASTM Condition</td>
<td>Min DFT (µm)</td>
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<td>39</td>
<td>9</td>
<td>39</td>
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<tr>
<td>10</td>
<td>Werribee - Zn Phos primer + 2x Chlorinated Rubber</td>
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<td>239</td>
<td>10</td>
<td>239</td>
</tr>
<tr>
<td>18</td>
<td>Morwell - IZS primer plus MIO top coat</td>
<td>&lt;5</td>
<td>NM</td>
<td>10</td>
<td>NM</td>
</tr>
<tr>
<td>23a</td>
<td>Dandenong - Org Zn/Al paint</td>
<td>14</td>
<td>92</td>
<td>7</td>
<td>82</td>
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</tbody>
</table>

(NM: Not measured)
WATER BASED INORGANIC ZINCS – PERFORMANCE vs PRACTICABILITY

E Hemmings and N Demirdjian

Summary: There are currently a number of significant events being played out in the Australian Corrosion Protection Industry all related to inorganic zinc specification and usage. In summary the industry has changed considerable over the last 5 years. The results of those changes is the current unsatisfactory situation with regard to inorganic zinc specifications.

Keywords. Inorganic zinc, water-borne, specification, water resistance

1. INTRODUCTION

There are currently a number of significant events being played out in the Australian corrosion protection industry, all related to inorganic zinc specification and usage.

The first is the formation of the Zinc Rich Coatings Council with membership of the paint companies, zinc dust manufacturers, some other raw material suppliers and coating application associations. The formation of this group is quite remarkable in the Australian situation where paint companies have been more competitive than cooperative. We probably have to thank the APMF (Australian Paint Manufacturers Federation) for initiating this group.

Secondly, there is considerable disagreement between the galvanizing industry representatives and those of the paint companies on the committee dealing with the revision of AS/NZS2312 standard for protecting steel in atmospheric environments. The disagreement centres around the life expectancy to first maintenance for inorganic zinc coatings and galvanising.

A third factor in this whole scene is the current recession in the global economy which has led to the demise of Pasminco, the sole zinc producer in Australia. It has also led to the reduction in prices for hot dip galvanising as Australian galvanisers have competed against imported galvanised steel. Likewise, engineering consultancies have looked for lower cost systems as the investment in new resource projects have sought to keep the cost of capitalisation low to make projects viable in a market with low commodity prices.

And fourthly there has been a significant change in the source of technical specifications to the Australian paint industry. I suspect that this is a worldwide phenomenon driven by outsourcing of technical expertise in large chemical and mining companies. Very few now have resident coatings or corrosion experts. Likewise paint companies have reduced their technical costs by reducing technical staff. Globalisation has also led to centralisation of research and development personnel in European or American sites with a consequent decrease in the understanding of the chemistry of coatings here in Australia.

Another factor has been the constriction in the Australian blast cleaning and coating industry. Employees have been drastically reduced and a number of companies have closed their doors. Associations like the BCCA and AIPC have never been weaker in supporting their industry.

2. CURRENT SITUATION AND HOW WE GOT THERE

The current situation with regard to inorganic zinc coatings is as follows. Where heavy duty coatings are required in a marine environment and where aesthetics are not a significant issue then there is a preference by coating consultants to specify a single coat of high ratio water based inorganic zinc coating. This is usually to a dry film thickness (DFT) of either 100 to 150 microns or a minimum of 150 microns.

This system originated with the entry to the coatings industry in the USA of a company called Inorganic Coatings. This company acquired the rights to a 1979 NASA patent for the production of what was called “High Ratio” water borne inorganic zinc coatings. The NASA patent essentially took the existing self-curing alkali silicate technology that had been around since the 1960’s and, with the use of colloidal silica increased the ratio...
of silicate to alkali metal composition in the silicate binder. The result of this advance was to produce a water based silicate binder for zinc powder that achieved film hardness and water insolubility faster and enabled the application of thicker films in one coat.

Although the owners of Inorganic Coatings were not great chemists they were exceptional marketers and with phrases such as “instant cure” and “lifetime protection” managed to convince the industry that they had developed a new coating that would revolutionise the corrosion protection industry. Several factors were in their favour; one being the emergence of the environmental legislation in the USA restricting the use of solvent based coatings. The 100% water content of “High Ratio Inorganic Zinks” gave them a receptive audience. In addition they enlisted the services of “Chuck” Munger of Ameron fame to promote the benefits of this product. (1)

For clarity we should point out that an arbitrary figure has been chosen in the AS/NZS 3750.15 standard of a mole ratio of minimum 4.7:1 silica to alkali metal ratio as defining “high ratio” or Type 6 products. In this paper we are referring to such coatings as conform to this definition.

This technology was brought to Australia through two avenues. Valspar Coatings took up a license to sell but not manufacture the coatings and Taubmans, Valspar’s then licensee, also saw the potential and imported the products from Inorganic Coatings. Alex Szokolik on a fact finding tour of Esso USA operations was introduced to the technology and brought it back to Australia. Alex also was informed that the film thickness should be one single coat at 125 to 175 microns. Alex did some laboratory evaluations as detailed in his article in the 1992 JPCL (2) which confirmed the performance of this system and hence it was specified for offshore work and on the coating specification for the new Esso offshore oil and gas platforms built in 1992.

The higher film thickness did cause some problems and particularly so with Inorganic Coating’s IC531 product. Several alternatives were trialled by Transfield and the dry time and resistance to mud cracking in corners and channels were prime criteria in that evaluation.

It is fair to say that this system saved Esso considerable expense in their coating maintenance budget and has worked well for them particularly offshore where the non-flammable aspect of the water based zinc was a significant benefit. It is also accurate to say that the enthusiasm for the system by Alex Szokolik and his ability to argue the case for this system was successful in increasing adoption of the system and its specification for many major projects throughout Australia.

This system has now been in use for nearly 10 years and it is time to review its use and success. Hence the reason for this paper.

3. CHEMISTRY OF WATER BORNE INORGANIC ZINC COATINGS

The alkali silicate solution is mixed with the zinc dust and applied to the surface. The zinc is hydrolysed and reacts with the silicic acid to form a polymeric structure.
Figure 1: Chemistry of Zinc Silicate Formation from Alkali Silicate Binder

Figure 1 is taken from “Inorganic Zinc Coatings: A Review” by Charles G. Munger (1), with an intermediate step included to show formation of free alkali.

Self cured alkali silicates cure initially by the evaporation of water from the coating. This concentrates the water soluble silicate binder leading to condensation and precipitation of the basic zinc silicate and polymerised silica matrix. Ultimate hardness is achieved with ongoing polymerisation of silicate particles with time. A consideration during this process is the formation of an alkali metal hydroxide as the zinc replaces the alkali metal on the silicate. If water ponding or dew occurs on the coating during this period the silica matrix can be re-dissolved and leached from the coating with the highly alkaline solution. Under normal cure conditions the hydroxide reacts with carbonic acid as carbon dioxide is absorbed from the air and a neutral surface is achieved.

Type 4 solvent borne zinc silicates, whilst approaching from a different route, end up with the identical chemical polymer structure. I have not seen any explanation as to why an inorganic zinc coating should have different properties because of the origin of the silica matrix.

4. PERFORMANCE OF WATER BORNE INORGANIC ZINC COATINGS

The prime purpose for any corrosion protection system is to provide corrosion protection and if it can be done at minimum cost and maximum life then all the better.

The Morgan to Whyalla Pipeline is of course the Australian icon for inorganic zinc coatings with it still protecting the pipeline now after nearly 60 years. The coating used there was a water based alkali silicate but it was baked to achieve cure. It is also important to emphasise that the success of this coating system is equally due to a regular maintenance program and that any points of corrosion have been touched up over the years.

The key performance characteristics of water-borne coatings are excellent corrosion protection, excellent adhesion, excellent hardness, and excellent resistance to corrosion undercutting. This has been attested to many times. Alex Szokolik’s presentations and papers give extensive laboratory testing and field case histories substantiating this performance. (3)

Many papers have demonstrated the superior abrasion resistance of self curing water borne zinc silicates over solvent borne ethyl silicates. Using a Taber abraser, the coating removed in 100 cycles will usually be double for the solvent borne product (4). However, what is the significance of this test to the real world? I would suggest little and there is every evidence that solvent borne inorganic zinc silicates have for many years been transported quietly successfully with little wear or chain damage. The additional abrasion resistance of water-borne zincs is not required when all we really want is corrosion protection.

Other than abrasion resistance and elimination of solvents, water based zinc coatings have no other performance attributes that would render them superior to a solvent based inorganic zinc. However, a driving force in the use of water borne zinc silicates has been the life expectancies attributed to them in AS/NZS 2312-1994 as shown in Table 1.
Table 1: AS/NZS 2312 - 1994 Life Expectancies of Zinc Coatings

<table>
<thead>
<tr>
<th>Code</th>
<th>Coating</th>
<th>DFT microns</th>
<th>Mild</th>
<th>Moderate</th>
<th>Tropical</th>
<th>Industrial</th>
<th>Marine</th>
<th>Severe Marine</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP1-A</td>
<td>Solvent or water borne inorganic zinc</td>
<td>65 - 75</td>
<td>5 - 10</td>
<td>5 - 10</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>LP3-A</td>
<td>Water borne inorganic zinc</td>
<td>100 - 150</td>
<td>10 - 20</td>
<td>10 - 20</td>
<td>10 - 20</td>
<td>NR</td>
<td>10 - 20</td>
<td>10 - 20</td>
</tr>
<tr>
<td>ZN100</td>
<td>Hot spray zinc</td>
<td>100</td>
<td>10 - 20</td>
<td>10 - 20</td>
<td>10 - 20</td>
<td>2 - 5</td>
<td>5 - 10</td>
<td>2 - 5</td>
</tr>
<tr>
<td>GZ</td>
<td>Hot dip galvanising</td>
<td>85</td>
<td>10 - 20</td>
<td>10 - 20</td>
<td>10 - 20</td>
<td>2-5</td>
<td>5 - 10</td>
<td>NR</td>
</tr>
</tbody>
</table>

NR – not recommended

The result of this standard was to promote the use of the “high ratio water borne zinc” in a single coat system. Note that the nominal thickness was 125 microns. Along with “not recommended” statement on solvent borne zinscs there was also a favourable correlation between the life expectancies of hot dip galvanising and water borne inorganic zinc.

Rob Francis comments (5) that “AS/NZS 2312:1994 gives very conservative figures which bear little resemblance to actual lives for either galvanising or inorganic zinc and such figures are probably best ignored.”.

Table 2 gives the life expectancies of the coatings systems in the new draft standard.

Table 2: AS/NZS 2132 2001 Revision Draft Life Expectancies

<table>
<thead>
<tr>
<th>System</th>
<th>Old Code</th>
<th>Coating</th>
<th>DFT microns</th>
<th>Very Low</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
<th>Very High Industrial</th>
<th>Very High Marine</th>
<th>Inland Tropical</th>
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<tbody>
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<td>IZS1</td>
<td>MP1-A</td>
<td>Solvent borne inorganic zinc</td>
<td>75</td>
<td>25+</td>
<td>15-25</td>
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<td>25+</td>
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<td>HDG85</td>
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<td>Hot dip galvanising</td>
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<td>25+</td>
<td>25+</td>
<td>25+</td>
<td>15-25</td>
<td>2-5</td>
<td>5-15</td>
<td>25+</td>
</tr>
</tbody>
</table>

These are the life expectancies recommended by the sub-committee in 2000. This draft standard again gives a strong bias towards the performance of water borne Type 3 and 6 alkali zinc silicates.

This is obviously a point of contention and the purpose of my paper is not to air my position on this issue. As can be seen even these changes still give considerable weight to water based zinc silicates in comparison with the solvent borne system. One reason is the difficulty in identifying case histories for solvent borne zinc silicates in the more severe environments. With the damming comment given to solvent borne Type 4 zinc silicates in previous AS2312 standards it is no wonder that they were not used without topcoats in more aggressive environments.

The conclusion is that water borne silicates are harder but other than specialised uses such as coal wagons, that has little bearing on performance for corrosion protection of structural steel.

5. PRACTICABILITY OF WATER BORNE INORGANIC ZINC COATINGS

5.1 Literature Comments on Cure Problems

How practical are water borne inorganic zinc coatings? It is interesting to quote from a Vessey industry newsletter of 1969 (6). This was written as part of the promotional benefits for introduction of the new solvent borne inorganic zinc Zinorg Zincite G, and it said of the previous water borne self-curing silicate type that “applications frequently have to be held up or done over because of high humidity conditions or unexpected showers which cause almost immediate failure – a costly inconvenience”. The most telling comment was that
which I will repeat “which cause almost immediate failure”. This is currently the same experience many applicators of high ratio water borne zinc coatings are currently experiencing.

In John Biddle’s article given at the 1993 ACA Conference at Newcastle (7), he says in reference to conventional water borne zinc coatings “Many tonnes of steel have had to be re-blasted and re-coated due to early exposure to rain or heavy dew”. There is no doubt that water borne inorganic zincs, whether high ratio or low ratio, are susceptible to the influence of high humidity and low temperature.

The difficulties experienced previously with water borne alkali silicate zinc coatings has been lost in time as people experienced in their use have left the industry or died. It is interesting to note that David Donald in his paper in 1980 (8) states “When the water content of the air reaches saturation, it is difficult for water to evaporate from the applied film. For this reason drying and curing times become lengthy …and this is therefore a problem area for a lithium/potassium blend type of inorganic zinc silicate coating.”

What is becoming increasingly clear is that alkali silicates are very susceptible not only to water contact after application but also high humidity at low temperatures during the curing process.

5.2 Cure Times Determined by Mike Moore

As a result of 6 months work by Mike Moore with a qualified chemist at Vessey, he produced Table 3 and Table 4 showing weather parameters for suitable application of Vessey’s high ratio water borne zinc. Two things to notice; firstly the work was done at a thickness of 100 microns not 150 microns as commonly specified and that the “full cure test” was resistance to the water insolubility test given in AS3750.15.

<table>
<thead>
<tr>
<th>RELATIVE HUMIDITY%</th>
</tr>
</thead>
<tbody>
<tr>
<td>STEEL TEMP. ºC</td>
</tr>
<tr>
<td>ZONE A</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>35</td>
</tr>
<tr>
<td>40</td>
</tr>
</tbody>
</table>

| ZONE B |

It was recommended that application be should not be undertaken in Zone A or B.
Table 4: Full Cure Time (hours) for WB IZS (100 microns dry film thickness)

<table>
<thead>
<tr>
<th>RELATIVE HUMIDITY%</th>
<th>STEEL TEMP.°C</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZONE A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16.00</td>
<td>17.00</td>
<td>18.00</td>
<td>22</td>
<td>25</td>
<td>28</td>
<td>33</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.75</td>
<td>13.00</td>
<td>13.75</td>
<td>18.00</td>
<td>21</td>
<td>23</td>
<td>28</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>8.25</td>
<td>10.00</td>
<td>12.00</td>
<td>17.00</td>
<td>18.5</td>
<td>21</td>
<td>24</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>6.29</td>
<td>8.00</td>
<td>9.75</td>
<td>12.50</td>
<td>16.00</td>
<td>18.00</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>4.75</td>
<td>6.50</td>
<td>8.00</td>
<td>11.00</td>
<td>12.75</td>
<td>15.25</td>
<td>18.00</td>
<td>19.00</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>3.50</td>
<td>4.25</td>
<td>6.50</td>
<td>8.50</td>
<td>13.25</td>
<td>13.00</td>
<td>15.00</td>
<td>16.50</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2.75</td>
<td>4.00</td>
<td>5.00</td>
<td>6.25</td>
<td>9.25</td>
<td>12.00</td>
<td>13.00</td>
<td>15.00</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>2.00</td>
<td>2.25</td>
<td>3.75</td>
<td>5.50</td>
<td>7.50</td>
<td>9.00</td>
<td>9.50</td>
<td>12.50</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.25</td>
<td>2.00</td>
<td>2.75</td>
<td>3.50</td>
<td>4.50</td>
<td>7.00</td>
<td>8.75</td>
<td>9.00</td>
</tr>
</tbody>
</table>

It was recommended that application be should not be undertaken in Zone A or B.

5.3 Water Resistance.

Another difficulty is the term “water resistant”. In most cases it is undefined and applied in many different ways throughout the literature. It is used to describe resistance to rain as tested with a shower applied to a coated panel in the old AS 2105. The AS 2105 test is a tap-water spray for 2 minutes then allow to recover for 24 hours. Water resistance is also the term used to describe the AS/NZS 3750.15 test for High Ratio water borne zincs of applying wet cotton wool to a score line through the coating and after 30 minutes the cotton wool is removed and allowed to recover for 24 hours. It is rarely used as a guide as to when the coating is resistant to ponding water or dew or rain during transport.

A better test may be to do an immersion test in tap water and define resistance to immersion as the criteria for “water resistance”. This would obviously extend the “resistance to water “times from hours to days. In other words in adverse conditions the coating would have to be protected from dew or rain for days, this would be somewhat impractical.

It needs to be recognised that, just because the water has evaporated from the coating, this does not mean that the coating is cured and is resistant to re-dissolution. There is still considerable cross-linking to proceed and this reaction continues for many weeks and even years. Secondly, the water resistance of the coating has been poorly established in the Australian Standard AS/NZS 3750.15. The test given there was one developed for a particular problem being experienced during the Esso Bass Strait platform construction during the early 90’s when again a serious failure occurred with the water borne product. We have found that a coating that passes this test is still very susceptible to the effects of dew or rainwater on the coating.

The old AS 2105 standard used a simulated rain test by subjecting the coating to a shower of running water and then also giving it a recovery time.

Zones A and B in Table 3 and Table 4 would have been much larger if cure to water immersion had been used.

5.4 Current Laboratory Work.

Two factory batches of a high ratio Type 6 inorganic zinc were tested to AS3750.15 qualifying tests with results given in Table 5.
Table 5: Results of AS/NZS 3750.15 Tests

<table>
<thead>
<tr>
<th></th>
<th>Clause 2.6.3 Handling Time</th>
<th>Clause 2.6.7 Water Insolubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch A</td>
<td>Pass H pencil hardness in 90 minutes.</td>
<td>Pass, no loss of coating integrity.</td>
</tr>
<tr>
<td>Batch B</td>
<td>Pass H pencil hardness in 90 minutes.</td>
<td>Pass, no loss of coating integrity.</td>
</tr>
</tbody>
</table>

The cure conditions under the standard are 23°C and 60% relative humidity. As can be seen both batches passed the AS/NZS 3750.15 standard for cure for Type 6 products.

In order to simulate the field conditions more closely where powdery zinc coating was being experienced, the water insolubility test was modified. The wet cotton wool was placed on the zinc coating at various times after application and allowed to remain in place for 16 hours followed by a 24 hour recovery time. This test was conducted under a low temperature condition as well with the results given in Table 6. The coating was applied at a DFT of 150 to 160 microns. Recovery time was also reduced to 4 hours.

Table 6: Results of modified water insolubility tests

<table>
<thead>
<tr>
<th>Cure time before application of wet cotton wool</th>
<th>Test</th>
<th>23°C 58% RH</th>
<th>6°C 50%RH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recovery Time 4 hours</td>
<td>Recovery Time 72 hours</td>
<td>Recovery Time 4 hours</td>
</tr>
<tr>
<td>7 Days</td>
<td>Pencil Hardness pH</td>
<td>HB 10</td>
<td>HB 10</td>
</tr>
<tr>
<td>3 Days</td>
<td>Pencil Hardness pH</td>
<td>HB 10</td>
<td>HB 10</td>
</tr>
<tr>
<td>5 hours</td>
<td>Pencil Hardness pH</td>
<td>HB 11</td>
<td>HB 11</td>
</tr>
<tr>
<td>3 hours</td>
<td>Pencil Hardness pH</td>
<td>B 11</td>
<td>B 11</td>
</tr>
<tr>
<td>2 hours</td>
<td>Pencil Hardness pH</td>
<td>2B 10</td>
<td>B 11</td>
</tr>
<tr>
<td>1 hour</td>
<td>Pencil Hardness pH</td>
<td>2B 10</td>
<td>B 11</td>
</tr>
<tr>
<td>30 minutes</td>
<td>Pencil Hardness pH</td>
<td>4B 10</td>
<td>2B 9</td>
</tr>
</tbody>
</table>

Shortened cure times and recovery times, as well as lower temperatures, have a significant effect on cure of the coating. Unfortunately we did not have equipment to enable humidity variations.

The work was repeated using four high ratio products commonly used in the industry. The wet cotton wool was placed on the coating after 5 hours cure and left in place for 16 hours. There is some variation but essentially all products suffer from water immersion or dew attack on the coating, even though all coatings are hard before application of the wet cotton wool. This is confirmed from field reports of the performance of other products in the market place.

It was decided to check the effect of a 2 coat system to achieve 150 microns DFT as compared to a 1 coat application. The 2 coat system was applied with a 24 hour recoat time. Wet cotton wool was applied after 5 hours cure and left in place for 16 hours. The results are given in Table 7. Again we can conclude that application by two coats rather than a single coat to achieve the 150 microns neither improves nor detracts from water resistance.
Table 7: Water resistance of two coat system.

<table>
<thead>
<tr>
<th>Test Region</th>
<th>Test</th>
<th>23°C 58% RH</th>
<th>6°C 50% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 Coat System</td>
<td>2 Coat System</td>
</tr>
<tr>
<td>Dry Area of Panel</td>
<td>Pencil Hardness</td>
<td>3H</td>
<td>3H</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Wet Area</td>
<td>Pencil Hardness</td>
<td>2B</td>
<td>2B</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 8 shows work done by Dupont with lithium silicate based inorganic zinc broadly indicating the effect of temperature and humidity on cure, with resistance to water immersion indicated as “absolute cure”. Their test for absolute cure is given in Appendix A.

Table 8: Cure Rate of a Typical 3-mil (75 µm) Polysilicate Zinc-Rich Primer Coat

<table>
<thead>
<tr>
<th>Humidity&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Temperature&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Initial Cure</th>
<th>Max. Dry Abrasion Resistance</th>
<th>Top Coat Readiness</th>
<th>Absolute Cure&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate</td>
<td>Moderate</td>
<td>3/4</td>
<td>2</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>Low</td>
<td>High</td>
<td>1/3</td>
<td>1/2</td>
<td>2</td>
<td>3-1/2</td>
</tr>
<tr>
<td>Low</td>
<td>Low</td>
<td>1</td>
<td>5</td>
<td>20</td>
<td>78</td>
</tr>
<tr>
<td>High</td>
<td>High</td>
<td>1/3</td>
<td>1</td>
<td>2-1/2</td>
<td>4</td>
</tr>
<tr>
<td>Low</td>
<td>Low</td>
<td>3</td>
<td>10</td>
<td>36</td>
<td>144</td>
</tr>
</tbody>
</table>

<sup>a</sup> Low = 20/50% RH, Moderate = 40/60% RH, High = 60/90%

<sup>b</sup> Low = 2/10ºC, Moderate = 10/32ºC, High = 32/52ºC

<sup>c</sup> Under most severe conditions - not to be confused with cure rate under normal conditions.

This was then transposed into a graph (Figure 2) which shows the relationship of water evaporation in the initial film forming reaction to resistance to water immersion. Resistance to water immersion takes some time after the loss of water out of the film and as can be seen in the above table at high humidities and low temperatures can be an inordinately long period.

Figure 2: Typical Cure Timetable for a Polysilicate Zinc-Rich Primer Coating

Note: The tap-water immersion test represents most severe curing conditions and should not be confused with normal curing conditions. Intimate contact of the primer coat with fresh water decreases the rate of
polymerization, and the fresh water leaches out the unpolymerized silicates from the coating, weakening the zinc-to-silicate bonds. This increases the cure time. (9)

The fallacy of recovery times is only appreciated when dealing with practical issues of transporting steel on an uncovered truck with carpet used between layers of steel to protect against abrasion damage. Fabricators demanding steel urgently, coating hard to the touch, uncovered truck, rain, carpet, abrasion and finally coating completely removed from the steel when it reaches site. The real world rarely allows for a recovery period.

The effect of film thickness is demonstrated by the Ameron Data Sheet for Dimetcote ® 21-5 as in Table 9 below.

<table>
<thead>
<tr>
<th>Time to water insolubility @ 70% RH (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 microns</td>
</tr>
<tr>
<td>150 microns</td>
</tr>
<tr>
<td>225 microns</td>
</tr>
</tbody>
</table>

Cure for continuous water contact @ 70% RH (hours)

| 75 microns | 12 | 24 | 48 | 72 |
| 150 microns | 24 | 36 | 72 | 120 |
| 225 microns | 36 | 72 | 120 | 180 |

Ameron use an in-house test for time to water insolubility but essentially it is similar to the AS2105 shower test. Compare the time to water insolubility of 30 minutes at 21°C to water contact 120 hours (5 days) at 4°C and 150 microns and one can understand the problems facing industry with current specifications for high ratio water borne zinc coatings.

There is no doubt that low temperatures and wet conditions with possibly relative humidities of 70% can permanently lead to a powdery film, one in some cases so soft that it can be rubbed off with finger pressure.

Unfortunately the Australian industry is no longer able to investigate these reactions thoroughly, having neither the required equipment nor the resources to fund such an investigation. The monetary return is nil for such an investment of scarce people resources.

Table 10 and Table 11 show the results of the United States Federal Highways Commission “Dew Condensation Test” on a high ratio water based zinc silicate applied at 75 microns DFT. (10)

Table 10: Dew Condensation Test

<table>
<thead>
<tr>
<th>Drying Time (hours)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>21°C, 58% Relative Humidity</td>
<td>Coating is soft and can be removed by rubbing.</td>
</tr>
<tr>
<td>4</td>
<td>Coating is soft and can be removed by rubbing.</td>
</tr>
<tr>
<td>8</td>
<td>Coating is soft but cannot be removed by rubbing.</td>
</tr>
<tr>
<td>24</td>
<td>Coating is soft but water insoluble. Zinc salts evident.</td>
</tr>
<tr>
<td>48</td>
<td>Coating is slightly soft but water insoluble. Zinc salts evident.</td>
</tr>
<tr>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>
Table 11: Comparison of times to Water Insolubility and Water Immersion Service

<table>
<thead>
<tr>
<th></th>
<th>32°C</th>
<th>21°C</th>
<th>10°C</th>
<th>4.4°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to water insoluble @ 70% RH (minutes)</td>
<td>15 – 45 min</td>
<td>30 – 120 min</td>
<td>45 – 180 min</td>
<td>60 – 270 min</td>
</tr>
<tr>
<td>Time to water immersion resistance @ 70% RH (hours)</td>
<td>12 – 36 hr</td>
<td>24 – 72 hr</td>
<td>48 – 120 hr (2 – 5 days)</td>
<td>72 – 180 hr</td>
</tr>
</tbody>
</table>

The range results from evaluating a number of commercial products.

The Federal Highways Department then state “based on this data, the most favourable environmental conditions for proper curing of most self-cure water borne inorganic zinc coatings (high ratio) include relative humidities of less than 70 % and temperatures of at least 21°C. Conditions to avoid (higher probability for improper cure) include relative humidity higher than 70%, temperatures lower than 4.4°C and stagnant air flow conditions. Any combination of these three conditions would be even more likely to cause improper cure of self-cure WB-IOZ coatings.” (10) (page 12).

The achievement of film thicknesses as high as 150 microns only compounds this problem. The longer the film takes to dry, the more opportunity for damage from dew, high humidity or rain. On flat plate with few corners or nodes, a single coat at this thickness can be easily achieved with no mud-cracking and a sound corrosion- and damage-resistant film. And, provided the correct weather conditions are prevailing at the time, a film which is also resistant to water damage.

5.5 Failure Modes:

Even a sound film is susceptible to damage by ponding water. A suggested scenario is that during the cure of alkali silicate coatings potassium and/or sodium silicate is released as part of the condensation reaction giving a residual pH of 12 on the surface. In dry conditions this reacts with carbon dioxide in the atmosphere to produce carbonate on the surface. This can take several days depending again on temperatures. If rain is allowed to pond on the surface then this alkali dissolves and, as the water evaporates, can produce a pH as high as 13 to 14. There are two effects from this; firstly zinc being amphoteric is attacked with the production of soluble sodium or potassium zincalate. In addition, zinc potential reversal also takes effect and at high pH’s zinc becomes more noble than iron and at any small pinholes or thin areas the steel rusts prodigiously as small pinpoint regions of steel try to protect a very large zinc surface.

A literature search has not revealed any theories on what causes a powdery zinc coating when high humidity prevails during the cure process. What we do know is that it happens all too frequently. The result of a water affected coating is a coating that has no abrasion resistance or resistance to damage. It has to be removed with high-pressure water blast (2000 psi) and reinstated. This is at no small cost and with the small margins existing in the supply and application of inorganic zinc turns a small profit into a large loss to both supplier and applicator. Nearly every major project has experienced this type of failure and loss at to one degree or another. The industry is in no position to sustain these losses.

There was some suggestion that 150 microns of water based inorganic zinc is a competitive alternative to hot dip galvanising; however if it has to be applied in two coats then that is not the case. Hot dip galvanizing is currently quoted in Western Australia at $400 to $500 per tonne. The cost of applying two coats of water borne inorganic zinc to 150 microns DFT is $600 to $700 per tonne compared to $350 to $450 per tonne for a single coat system at 75 microns of solvent borne inorganic zinc. If we are relying on water borne zinc silicates to save the blast coating industry then were going to be very disappointed.

6. ALTERNATIVE APPROACHES

Is there an alternative that satisfies the desires of owners and specifiers to obtain a low cost, long lasting protective coating for their steelwork and one that gives assurance of trouble free application?

There are a number of approaches, one being the recent development of a water borne zirconium silicate coating. This has been shown to achieve water resistance even faster than the lithium silicate high ratio systems thus reducing the window for water sensitivity. Ameron have taken out a US patent 5,888,280 already for this product which is in field test now. This will have the benefit of continuing to offer an environmentally-friendly water borne product but with reduced chance of failure. Ameron have also been working on cure additives to further avoid faulty results. (11).

Another approach is the use of a Type 4 solvent borne zinc silicate that may successfully be applied in two coats to achieve a minimum of 150 microns DFT. This is currently being done in Western Australia and recently on
the outside of a water tank at Wallsend near Newcastle. This system has a 14 day recoat window compared to the 24 hour re-coat window for water borne high ratio zins. Also, solvent borne inorganic zins do have early water resistance to rain and dew, as well as to high humidity. A twin tank alongside the new tank at Wallsend has had the same two coat system of solvent borne zinc and still remains free of after 25 years service.

7. CONCLUSIONS

The specification of 150 microns of water borne inorganic zinc coatings should cease. To continue to specify this system is to place a demand on the industry that almost certainly condemns it to monetary losses. The specification should at least be 100 to 125 microns DFT and if the performance benefits of water borne high ratio zinc is desired then the offer should be made that solvent borne system can be used when weather conditions become unacceptable for the water borne zinc.

Once we were ignorant of the faults of high ratio water borne zinc coatings but that is no longer the case. Such coatings, whether high ratio or not, are subject as the Vessey Release said to “irrecoverable breakdown of the binder system rendering the applied coating totally useless.” This has now been confirmed by our own laboratory work and the United States Federal Highways Department.

For environmental and safety reasons offshore, the use of water borne zinc silicate coatings will continue and it is hoped that in the future we will have more cure tolerant water borne zinc coatings available. At the moment allowances must be made for the applicator to cease painting when adverse conditions could occur.

8. APPENDIX A: Dupont Absolute Cure Test for Polysilicate Zinc Rich Primers

Panel removed from conditions cabinet, partially immersed 1 hr in 24°C tap water, air-dried 2 hr, and abraded 100 cycles with Taber Abrader (CS-17 wheels at 1000g loading per wheel). Coating must remain hard after the exposure to water immersion. (9)

9. BIBLIOGRAPHY:

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6 Vessey News Review No. 26 1969. Edited by Dr. Ernest Haeman.
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9 Dupont Technical Bulletin Lithium Polysilicate 242557A (9/94)
SUMMARY: The term "zinc-rich coatings" includes a wide range of paints which have significantly different binder types and curing mechanisms, and which differ in their response to ambient climatic conditions, such as temperature and humidity, at time of application and during the subsequent curing interval. An understanding of the different curing mechanisms is essential to be able to assess the impact of climatic conditions on the cure and subsequent coating performance. This paper examines how the different types of zinc-rich coatings cure and how these may be affected by ambient climatic conditions. A review of common problems experienced due to adverse conditions is also presented.

Keywords: Inorganic zinc, climatic conditions, ethyl silicate, potassium silicate, relative humidity, epoxy zinc, moisture cured urethanes

1. INTRODUCTION

The Zinc Rich Coatings Council (ZRCC) regards zinc rich coatings as any liquid-applied paint in which the principal pigment ingredient is zinc dust. Due to the wide range of resin vehicles used in the protective coatings industry, this definition encompasses a wide range of different types of resin binders. The most common binders for zinc-rich coatings are those based on inorganic alkali-metal silicates, ethyl silicate, two-pack epoxies, moisture-cured polyurethanes and single pack binders such as epoxy ester, polystyrene and chlorinated rubber.

Each of these resin binders has its own particular curing mechanism, and each curing mechanism is variably affected by the ambient climatic conditions that prevail at the time, and shortly after, application.

Coating manufacturers generally publish the broad range of suitable conditions for their products, although the consequences of straying beyond the published range of conditions are not often made clear. It is also not often stressed that the optimum range of conditions can occupy a quite narrow band within the published figures.

While it is generally appreciated that it is desirable for ambient conditions to be optimal at time of coating application, this does not always eventuate. Many coatings types merely suffer increased curing (drying) intervals if temperatures are low, and it is not uncommon for coating application to proceed despite the conditions being less than optimal with an acceptance of extended cure times.

However, for some zinc-rich coatings adverse climatic conditions affect not only the time to cure, but can have a significant impact on the final composition and performance of the paint film. In fact, in some instances too much or too little moisture in the surface layer of air can result in physico-chemical processes that alter the fundamental chemistry of the coating.

It is therefore important that the impact of climatic conditions on the cure of coatings be fully understood, to allow the correct coating or coating conditions to be specified or selected for a particular project, and to allow project supervisors to make informed decisions should adverse conditions prevail.

1.1 Climatic Conditions

The three main climatic factors that need to be considered when examining the curing of protective coatings are temperature, humidity and the rate of atmospheric transport away from a surface.

1.2 Temperature

All chemical reactions are affected by temperature, which can determine whether or not a reaction will proceed at all (threshold temperatures) and the rate of reaction, with increased temperatures generally associated with
increased reaction rates. This generally applies to coating that cure by chemical reaction such as two-pack epoxies and moisture-cured urethanes, and affects not only the cure-related properties such as touch dry time, recoat time or time to handling, but also affects the time for which the paint remains workable, referred to as pot-life.

Temperature also has a direct influence on the rate of evaporation of solvents, which are either organic or aqueous liquids. The volatility and hence rate of evaporation of all solvents increases with rising temperatures. Temperature is therefore often the main consideration when dealing with single-pack coatings that cure simply by evaporation of the solvent, usually referred to as lacquer cure.

In the case of coatings that cure by a process that requires reaction with water, the temperature can have a double impact, by regulating the rate of reaction as well as controlling the availability of moisture in the film. These often act in opposite ways, with increased temperature increasing the rate of reaction, but also reducing the amount of moisture that might be present in or adjacent to the paint film at a particular time after application. In such cases, the rate of evaporation of water is critical to achieving successful outcomes.

The most critical temperature measurement is that of the paint itself, from immediately after application until the required degree of cure is reached. This will often equate closely with surface temperature, which can be conveniently measured prior to paint application using a surface thermometer. It is therefore common practice for manufacturers or specifiers to place limits on the allowable upper and lower surface temperatures.

However, it should be borne in mind that the surface temperature can and usually does change after paint has been applied, either as a direct consequence of the application (eg. cooling due to solvent evaporation drawing the latent heat of evaporation from the substrate), as a response to changing ambient conditions (changes in air temperature, effect of direct sunlight or wind-chill factors) or due to night time clear sky radiation. Therefore, although conditions may be satisfactory at time of application, this is no guarantee that they will not become adverse before the coating reaches the required cure.

The temperature of the paint from the time it is readied for application until it reaches the surface may also be important, especially if the coating cures by chemical reaction. This will affect the pot-life, and may also play an important role in the extent of pre-reaction that occurs. The paint temperature also affects the viscosity which in turn affects the rheology of the paint in application equipment including flow through paint lines and levelling off brushes and is therefore a factor in the degree of thinning that is required. Cold paint requires more thinners than warm.

The air temperature, conveniently measured using a dry-bulb liquid-in-glass thermometer, does not have a direct impact on the cure, but has important indirect consequences including its impact on substrate temperature and its inter-relationship with humidity, as will be discussed below.

1.3 Humidity

Humidity is a measure of the amount of moisture vapour in a mixture of gases. Humidity is often measured and considered as either the absolute humidity or the relative humidity.

1.3.1 Absolute Humidity

The absolute humidity is the total amount of moisture in a mixture of gases at any given time and is usually expressed either as a % by weight or in terms of weight per volume (eg. g/m$^3$). For any given temperature and pressure, there is an upper limit to the amount of moisture that can be present in the gas mixture and at that limit, the gas is said to be saturated with moisture. This is referred to as the saturation concentration or the saturation moisture content.

The saturation moisture content is not dependent on the nature of the gases present, and occurs when the partial pressure of the water vapour in the gas mixture equals the vapour pressure of water at that temperature. Absolute humidity values may be read off psychometric charts which are frequently published in chemical engineering handbooks and similar almanacs.

At normal atmospheric pressures, the saturation concentration at 25°C equals 2.1 % w/w or 24 g/m$^3$, while at 50°C it equals 8.7 % w/w or 83 g/m$^3$. 
Table I: Saturation Humidity at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Saturation Concentration (g/m$^3$)</th>
<th>Saturation Moisture Content (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>0.8</td>
<td>9.9</td>
</tr>
<tr>
<td>14°C</td>
<td>1.0</td>
<td>12</td>
</tr>
<tr>
<td>20°C</td>
<td>1.5</td>
<td>19</td>
</tr>
<tr>
<td>25°C</td>
<td>2.1</td>
<td>24</td>
</tr>
<tr>
<td>50°C</td>
<td>8.7</td>
<td>84</td>
</tr>
</tbody>
</table>

If a saturated gas mixture is cooled or compressed, the saturation concentration will decrease and moisture will condense out of the mixture, as free droplets (mist) or on surfaces (dew).

If a given gas mixture with a given moisture content below the saturation concentration is heated or cooled, the absolute moisture will not vary until the temperature falls below that at which the actual concentration equals the saturation concentration.

The absolute moisture content can be used to calculate the amount of moisture in a given volume of air that may be available for reaction. If the absolute moisture content is known, it can also be used to calculate the dew point of an air mixture, by reference to psychometric charts.

However it is not easy to measure the moisture content of air direct, and this parameter is usually calculated indirectly by measuring air temperature and relative humidity.

1.3.2 Relative Humidity

Relative Humidity (RH) is a term used almost exclusively in association with atmospheric air, and refers to the amount of moisture vapour in air as a percentage of the saturation concentration at a particular temperature. It follows that any value of relative humidity does not indicate the actual moisture content of air unless the air temperature is also known.

Unlike the absolute humidity, the relative humidity of a given air mixture does change as the temperature is changed. At atmospheric pressure and 25°C, the relative humidity of air containing moisture at 12 g/m$^3$ is 50%.

If this mixture is cooled to 20°C, the relative humidity is increased to 70%. At 14°C, the mixture will be saturated, and the relative humidity will be 100%. This is called the dew-point, and further cooling will result in condensation of moisture from the air.

If the temperature is further reduced to 10°C, 2.1 grams of moisture will condense out of each cubic metre of air.

Conversely, heating this mixture leads to a rapid reduction in the relative humidity. At 50°C, the relative humidity of this mixture is only 14%!

Table II: Effect of Falling Temperature on Relative and Absolute Humidity

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Relative Humidity (%)</th>
<th>Absolute Humidity (g/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>25°C</td>
<td>50</td>
<td>12</td>
</tr>
<tr>
<td>20°C</td>
<td>70</td>
<td>12</td>
</tr>
<tr>
<td>14°C</td>
<td>100</td>
<td>12</td>
</tr>
<tr>
<td>10°C</td>
<td>100</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Relative humidity can be easily determined, whether in a laboratory or in the field, by using wet bulb and dry bulb thermometers (a whirling sling psychrometer). From the air temperature and relative humidity, all other factors can be calculated from psychometric charts, including the dew point and the absolute moisture content.

By itself, the relative humidity can indicate the risk of the surface temperature falling below the dew point. At high relative humidity, there is a significant risk that if either the air temperature or the surface temperature falls, moisture will condense from the air. This could result in moisture settling on a newly applied paint film and if this has not yet reached full moisture resistance, damage can ensue.
Relative humidity also influences the rate of evaporation of water and other solvents from an applied paint. The rate of evaporation of moisture from a paint film will be slow if the relative humidity is high, so that paints that rely on evaporation of moisture to cure will cure more slowly at high relative humidity. Conversely, at low relative humidity the rate of moisture evaporation will be high, and paints that require the presence of moisture within the film may be starved of this essential reactant.

The rate of evaporation of organic solvents is also affected by the relative humidity, so that even lacquer drying single-pack solvent borne paints cure more slowly at high relative humidity. For this reason, it is usual industry practice to limit the relative humidity at time of paint application to 85%.

1.4 Rate of Atmospheric Transport

A freshly applied paint film will undergo liquid/vapour exchange with the layer of air immediately over it. If the exchange is evaporative, it is possible that the surface layer of air can become saturated with the evaporating species even though the bulk air may remain quite unsaturated. If this occurs, the rate of further evaporation is limited by the rate of transport of the corresponding vapour away from the surface.

Natural atmospheric transport of gases in static conditions is by diffusion, which is a relatively slow process. However if conditions are not static, the surface air itself can be transported away and replaced by fresh, unsaturated air. This can occur at much faster rates than diffusion, and can occur from natural mixing due to wind or convection, or induced mixing, i.e. ventilation.

Under static atmospheric conditions, ventilation is generally extremely beneficial to curing of paints which rely on evaporative loss of moisture or solvents. If high humidity is also of concern then the ventilation should be achieved by introducing dehumidified air.

2. INORGANIC ZINC SILICATES

Inorganic zinc silicate coatings, when cured, consist of discrete particles of zinc dust bound together in a matrix consisting mostly of silica (SiO$_2$) but which also contains smaller amounts of oxides, silicates and other salts of zinc and iron. On aging and weathering, additional inorganic corrosion products of zinc accumulate in the pores of the paint film, typically forming from the outer surface.

Although the end-product is essentially the same, there are two different ways of creating the inorganic zinc silicate film.

2.1 Water-Borne Inorganic Zinc Silicates

2.1.1 Curing Mechanism

Water-borne inorganic zinc silicates (WB-IZS) are applied as a dispersion of zinc dust in a liquid binder which is itself an aqueous solution of an alkali metal silicate (i.e. lithium, sodium or potassium silicate). It is not possible to create solutions of silica by itself, and the usual way of making useful water-borne products based on silica is to co-dissolve it with alkali metal hydroxides to form water-soluble alkali metal silicates. For zinc rich coatings, the alkali metal is usually potassium and/or lithium (1).

When mixed with zinc dust and applied as a coating, the alkali metal is displaced from the matrix by zinc, and on further water loss precipitates out as the alkali metal hydroxide. As the alkali metal is displaced, the growing matrix of zinc and zinc/iron silicate gradually becomes increasingly more insoluble and water resistant.

However this reaction is to some extent reversible if moisture again becomes available, and one of the main risks to the performance of WB-IZS coatings is the presence of alkali metal hydroxide in the film shortly after application. This water soluble alkali metal hydroxide will redissolve if the film is re-wetted and then has the potential to re-solubilise the precipitated silicate matrix, or to dissolve some of the zinc dust.

If the wetting is severe such as in a prolonged downpour, the alkali metal hydroxide is simply washed out of the film without causing any significant damage to the silicate matrix. However if discrete droplets of water form on the film, this can create spots of a highly alkaline solution which can attack either zinc or the binder itself, with significant impairment of performance. Recoating the WB-IZS with itself can also lead to resolubilisation of the matrix by the alkali metal hydroxides. Thus a small amount of wetting may be worse than prolonged inundation. The coating cannot be said to be fully resistant to water until the alkali metal hydroxides are no longer present.

Two modes of failure often associated with impaired curing of WB-IZS are spot rusting with blistering of the coating, or an excessively soft film that does not harden with age. The exact mechanisms by which these defects develop have not yet been fully explained.
With time, the alkali metal hydroxide will react with atmospheric carbon dioxide to convert it into a carbonate. However this reaction requires a small amount of atmospheric moisture to proceed and does not occur at a very low humidity, and the time for this to happen is usually not known or is indeterminable.

Alkali metal carbonates are also water soluble but do not form highly alkaline solutions, and cannot redissolve the silicate matrix. Therefore permanent water resistance occurs only when the alkali metal hydroxides are either washed out or converted to carbonates. High ratio WB-IZS coatings have a lower proportion of the alkali metal, and therefore reach the first stage of water resistance more quickly, but while the hydroxides remain present, the coatings remain susceptible to moisture damage.

All of the necessary reactions can continue over extended periods, and WB-IZS coatings often reach their optimum hardness after weeks or months rather than days. With time and repeated wetting, ultimately the alkali metal carbonates are also lost from the film. The surface is not usually fully neutral until a number of months have passed.

2.1.2 Effect of Climatic Conditions

One of the initial curing stages for WB-IZS is the evaporative loss of moisture, and this will be retarded by low temperature and high relative humidity. Therefore if the surface temperature is less than 15°C, or if the RH is more than about 70%, moisture loss will be slow and the time to handle will be relatively long. On the other hand, at low RH and higher temperatures, the dry-to-handle time will be very short which make this coating a favourite in warm, arid regions.

After the coating is dry to handle, it quickly reaches a stage of water-resistance when tested using a wet-sponge method (2). However at this stage the hydroxides may still be present, and if the coating undergoes light wetting, such as after light rain or if subject to dew, droplets of the highly alkaline solution can form on its surface with dire consequences. This alkalinity (if still present) can be detected by use of pH paper or phenolphthalein indicator (3). A fully cured, mature film of WB-IZS has an essentially neutral pH.

In general terms, ideal conditions for the application of WB-IZS coatings are a surface temperature of 20 to 25°C, and an RH of between 40% and 50%. Under these conditions, curing to water resistance can be achieved in about 2 hours.

At higher surface temperatures, evaporative loss can occur too quickly for a sound film to form over the surface leading to porosity and a coarse, powdery surface. At lower temperatures, the development of water resistance will be slower, and the risk increases that the coated surface may be subjected to condensation, dew or sprinkling rain. If these are considered likely, the coated steel should be kept under-cover or the environment dehumidified.

High humidity will slow down the evaporation of moisture, while low humidity will enhance the loss of water but may retard the carbonation of the metal hydroxides.

Conditions to avoid are a combination of low temperatures and high humidity. Severe changes in conditions may also be detrimental. If a WB-IZS is applied at favourable surface temperatures and very low RH, the conversion of hydroxide to carbonate can be very slow, so that if conditions suddenly change to allow condensation, the alkaline droplets may form even days after application and damage the paint.

Manufacturers published figures for application conditions (summarised in Ref: 2.) suggest a temperature range of 5 to 45°C and RH of between 25 to 90%. This is now considered to be too wide, and includes regimes of low temperature or high humidity that can seriously impair the curing of these paints.

Overcoating a WB-IZS before the hydroxides or carbonates are lost will trap these soluble materials beneath the subsequent coat and can lead to osmotic blistering. However WB-IZS are best left without top-coating and this situation should not commonly arise.

The challenge for specifiers is that, at the time of writing a specification, it is usually not known when or where steel is to be coated, so that the likely ambient conditions cannot be considered when selecting a coating. This is even more significant if generic specifications are used over a range of different projects.

In order to prevent an applicator being forced to apply WB-IZS under climatic conditions where it is not likely to be able to achieve satisfactory cure times, provision should be made by specifiers to allow solvent borne ethyl silicate coating to be used in their place whenever such conditions prevail.
2.2 Solvent Borne Ethyl Silicate Zinc Coatings

2.2.1 Curing Mechanism

The starting point raw material for the binder used in solvent borne ethyl silicate zinc coatings is ethyl orthosilicate, the molecules of which on average contain five silicon atoms joined by siloxane (Si-O-Si) linkages. The other twelve valence sites are occupied by reactive alkoxide groups (Si-O-Alkyl, where the alkyl is typically ethyl). By itself, this material could react in the presence of moisture to form a solid silica matrix, but the curing would take too long to be of practical use.

During manufacture of the binder, the ethyl ortho-silicate molecules are partially pre-hydrolysed by adding some water under controlled conditions, to produce a more reactive material which does cure at a practical rate when mixed with zinc and applied to steel surfaces (4).

This pre-hydrolysis involves the reaction of some of the Si-O-Alkyl linkages with water to split off the alkoxide group (which converts to the corresponding alcohol and evaporates) and form silanol groups (Si-OH). Silanol groups are reactive to each other and, under neutral or alkaline conditions, two silanol groups can condense to produce the siloxane (Si-O-Si) linkage. However this reaction is deliberately inhibited at this point by creating slightly acidic conditions.

When mixed with zinc dust, the acidic conditions cease to exist and the silanol groups readily condense to begin forming a continuous silica matrix.

Each condensation reaction between two silanol groups also liberates one water molecule. This liberated moisture can then hydrolyse another alkoxide group and so allow the reaction sequence to proceed to full cure. As long as the initial amount of water added during the pre-hydrolysis stage exceeds that required for the hydrolysis of 50% of the alkoxide groups present, the curing of the ethyl silicate does not require any additional external moisture.

However, if the moisture liberated by the silanol condensation is lost from the film by evaporation, it cannot participate in further reactions.

2.2.2 Climatic Conditions

Low relative humidities are generally unfavourable for the curing of solvent borne ethyl silicates, regardless of the temperature. At low temperatures and low RH, the reactions are severely retarded and curing will be very slow, while at higher temperatures and low RH, an increase in the reaction rate will be off-set by increasing moisture loss from the film, so that overall the cure remains retarded.

Surface temperatures of 20 to 25°C and a relative humidity above 75% are ideal for ethyl silicates, while at temperatures below 15°C and a relative humidity less than 50% curing may be unacceptably slow, with extended handling or overcoating times.

It has, in fact, been shown that if the relative humidity remains at 40% during the initial curing period, regardless of the temperature, full cure may never be achieved (4).

Very high RH, above 90%, does not impact negatively on the curing mechanism, but may retard evaporation of the alcohol solvent and may also increase the risk of early exposure to wetting from condensation or rain.

Overcoating of ethyl silicate primers has been and remains a common industry practice. Since the top-coats used are mostly epoxies, curing of the zinc ceases after overcoating. If the ethyl silicate remains partially un-cured when overcoated, this will lead to increased susceptibility for splitting of the zinc under stress, which often manifests itself as extensive handling and erection damage.

It is generally recommended by manufacturers that for application of ethyl silicates which are to be overcoated, the RH must be above 50% and if left uncoated, at least 40%. However these figures are now considered to be too low, and if an ethyl silicate IZS is to be overcoated, the temperature at time of application should be at least 15°C and the relative humidity at least 60%, with the added proviso that any likely increase in the temperature should not see the RH falling below 50%.

Since these conditions cannot generally be assured at time of specifying, it is often considered preferably to use organic zinc rich coatings if overcoating is to be part of the coating system.

3. ORGANIC ZINC RICH COATINGS

3.1 Epoxy Zinc Rich Coatings

Epoxy zinc-rich coatings behave essentially the same as other epoxies. Most have medium to high volume solids, so solvent evaporation is a significant part of the curing process although the film builds are generally not
so high as to encourage solvent retention. Nonetheless, low temperature and high relative humidity can retard evaporation and prolong dry times.

After the solvent is lost, the coating cures by chemical reaction. The chemistry does not involve, nor is it directly affected by, moisture. There is, however, a possible side reaction of epoxy curing agents (notably polyamides and cyclo-aliphatic amines) with atmospheric moisture and carbon dioxide to form a quaternary amine carbonate salt (amine bloom) which remains moisture sensitive and can interfere with adhesion of subsequent coats of paint.

This usually occurs if the epoxy cure is retarded by low temperature and if the surface temperature is close to the dew point. Amine bloom was more commonly experienced on high build epoxies than on epoxy zinc primers, perhaps due to the presence of the zinc in the latter.

Traditionally, epoxies have shown poor curing rates at temperatures below 10°C, but over the last two decades rapid cure epoxy technologies have become firmly established and most manufacturers now have products suitable for low temperature application.

The relative lack of curing problems and the rapid, predictable overcoating intervals of epoxy zincs has seen them become the favoured product where overcoating is to be carried out.

### 3.2 Moisture Cured Urethanes

Zinc–rich primers with moisture cured urethane (MCU) binders have long been available and have formed the basis of multi-coat MCU paint systems since the 1980’s. However the very real advantages of MCUs, which are broad application conditions, long pot-life and fast curing, remained overshadowed by shelf-life problems, and it has not been until recent years that MCUs have been fully embraced by major manufacturers of protective coatings.

The resins used for MCU coatings are polyfunctional isocyanate prepolymers. The reaction mechanism for MCU curing involves first the reaction of one isocyanate group with water and subsequent loss of carbon dioxide to produce an amine.

$$\text{Isocyanate} + \text{water} \rightarrow \text{Intermediate} \rightarrow \text{Amine} + \text{carbon dioxide}$$

The amine is then free to react with a further isocyanate group to produce the carbamate linkage.

$$\text{Amine} + \text{isocyanate} \rightarrow \text{Carbamate linkage}$$

Therefore, one molecule of water is required for each of the cross-linking reactions that takes place. This moisture must be obtained from external sources, i.e. the atmosphere.

Isocyanate groups are highly reactive, and will react with available moisture, even at low temperatures. Published figures suggest that cure proceeds rapidly at relative humidity as low as 30%. If lower RH’s are experienced, curing additives are available.

Therefore, although dependent on atmospheric moisture for curing, MCU’s will cure under a wider range of climatic conditions than most other chemically cured coatings.

### 3.3 Lacquer Dry Zinc Rich Coatings

As the complexity of the curing system diminishes, the effects of climatic conditions become less significant. Lacquer dry coatings rely only on the evaporation of the solvent. Low temperatures and high relative humidity may reduce evaporation rates.

Since most lacquer dry coatings have low to medium volume solids, they rely on evaporation of the solvent to gain an increase in viscosity shortly after being applied, which in turn helps the coating cover sharp edges and allows good film build on vertical surfaces. Should solvent evaporation be significantly retarded, these coatings may fall away from edges or slump on vertical surfaces, resulting in low dry film thickness and a reduced level of protection.

However the composition of the dry film is not significantly influenced by climatic conditions during cure unless directly wetted before they become water resistant.
4. SUMMARY

With an increased understanding of the effect of climatic conditions on the curing of the various generic coating types used to formulate zinc rich coatings, it is possible to review the range of allowable conditions for each coating type.

The range of conditions for any particular coating recommended by coating manufacturers often does not discriminate between conditions that are "optimum" and those that are only just acceptable. The ramifications of applying coatings at or near the acceptable limits, or of straying outside these limits after application, need to be better understood and communicated to avoid failures or impaired coating performance.

A summary of optimum conditions and of conditions to avoid for the various coatings types is given in Table III.
### Table III: Summary of Climatic Conditions for Application of Zinc-Rich Coatings

<table>
<thead>
<tr>
<th>Product</th>
<th>Optimum Conditions</th>
<th>Avoid or Use Caution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Relative Humidity (%)</td>
</tr>
<tr>
<td>Inorganic Zinc Rich Coatings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water-Borne (Alkali metal silicates)</td>
<td>18 – 27</td>
<td>40 - 60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent Borne (ethyl silicate)</td>
<td>18 – 27</td>
<td>60 – 90</td>
</tr>
<tr>
<td>Uncoated</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>70 – 90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Topcoated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic Zinc Rich Coatings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Pack Epoxy</td>
<td>15 – 30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture Cured Urethanes</td>
<td>10 – 30</td>
<td>30 - 95</td>
</tr>
<tr>
<td>Single Pack (Lacquer Dry)</td>
<td>10 – 30</td>
<td>&lt; 90</td>
</tr>
<tr>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

**5. CONCLUSIONS**

In order to realise the very real performance and cost benefits that zinc-rich coatings offer over other protective systems for steel, attention must be paid to factors involved in their application. This is not a unique requirement for zinc rich coatings, since every industrial process must be correctly carried out for it to perform to expectations.

The range of generic coatings, and their different curing mechanisms, covered by the broad term of "zinc-rich coatings" are affected in different ways by factors such as climatic conditions at time of application and during the subsequent curing interval.

A sound understanding of how climatic conditions affect certain types of coatings can be used to avoid unfavourable conditions, or to select particular products most suited to the prevailing conditions.

Specifiers, project managers and coating supervisors should be aware of the likely impact of climatic conditions, and should have or be allowed sufficient flexibility to ensure products are not applied or cured under conditions that are likely to result in failure. Control over the prevailing conditions may be possible, such as delaying coating or providing dehumidification.

As a last resort, deviation from the specified product may be necessary to prevent otherwise avoidable failures. Changes to a specification are preferable to rigid enforcement of a specification that can only result in impaired coating performance.

**6. REFERENCES**


7. FURTHER READING
Sixty years of inorganic zinc coatings, ed. R.A. Francis, ACA, Mt Waverley (1999)


8. ACKNOWLEDGEMENT
This paper presents a summary of information gleaned from published industry literature and individual representations, including those made at an ACA NSW Technical Meeting held in Sydney in March 2002. In addition to the listed references, the contributions made by Gerry Pore, Ern Hemmings and Ted Riding in particular are acknowledged.
SUMMARY: The object of this paper is to provide an overview of the different types of zinc-based coatings that currently form the basis of high performance, multi-coat protective systems. The discussion is limited to catalysed epoxy, moisture-cured polyurethane and the alkali/alkyl silicate resin based zinc primers. The recent past, however, has seen an increase in the practice of overcoating hot dip galvanized (HDG) surfaces, thus HDG is also included in this discussion. The paper details the advantages and disadvantages of these systems and their relative performance with supporting evidence from case histories and accelerated laboratory testing. The information provided should make it easier to select the optimum protective coating systems for specific service conditions.

Keywords: zinc primer, hot dip galvanizing, coating systems

1. INTRODUCTION

Red lead primer based coating systems have built up a remarkable performance track record over some two centuries of applications. Their large scale use, however, came to quite a sudden stop in the 1950s and 60s when we became fully aware of the health hazards associated with their use, and when several different types of zinc-based primers became available to replace the red lead without affecting corrosion protection performance. The relatively new zinc coatings were versatile, had excellent application and physical characteristics, and were a better suited primer for the more sophisticated, high performance coatings coming onto the corrosion mitigation scene at that time. This paper describes the various types of zinc-based primers, including hot dip galvanizing, looking at properties, performance and selection issues.

2. THE COATING SYSTEM

Before the merits of the various zinc primer based coating systems are discussed, it may be of benefit to identify the various types of coating systems and have a short review of what constitutes a coating system and its elements.

The coating system seeks to optimise the principal properties and contributions of the major coating components, e.g. the binder (vehicle or film former), pigments, solvents and additives. A large variety of components and compounds are used, in countless combinations, to produce systems that best fit specific requirements. This gives us a tremendous flexibility when we need to design protective coating systems for any corrosive environment.

2.1. Basic Types of Coating Systems.

A coating system’s ability to provide corrosion protection may be enhanced by employing one or more of the three basic coating principles of impermeability, inhibition, and galvanic action. Thus, we identify the different kinds of systems by the type of protection they afford, e.g.:

1. **Barrier coating systems** utilize impermeable components to build a barrier between the substrate and the corrosive condition. Despite their simplicity, their performance is unequalled when it comes to the protection of steel structures and process equipment in severe marine and chemical environments, either in atmospheric, immersion or splash zone exposures.

2. **Inhibiting coating systems** utilize inhibitive pigments, such as zinc phosphate and to a lesser extent aluminium phosphate in the primer. The reactive phosphate pigments are activated by moisture penetration
and passivate the metal substrate at the primer/substrate interface, thus corrosion is inhibited. Their inhibiting value is questionable when they are used in strong resin based coatings such as epoxies where their solubility and mobility are curtailed. Still, when such coatings suffer mechanical damage the exposed substrate is effectively inhibited. The most beneficial characteristic of phosphate-pigmented primers is much-improved adhesion to non-ferrous substrates, adhesion that does not deteriorate with time.

3. **Galvanic, cathodic or sacrificial coating systems** utilize the galvanic nature of metallic zinc. These coatings are highly filled with finely divided metallic zinc dust that will cathodically protect the steel substrate. In other words, the zinc will corrode in preference (sacrificing itself) to the steel.

### 2.2. System Components

A coating system consists of three basic elements; primer, build (or intermediate) and finish (or top) coats (1).

#### 2.2.1. Primer Coats

The primer is universal for all anticorrosive coatings and is considered one of the most essential components of the coating system. It can be viewed as the system foundation, and as in the case of buildings, a faulty foundation may cause the collapse or break down of the system. The most important features and main purposes of primers are listed in Table 1.

<table>
<thead>
<tr>
<th>Feature &amp; Purpose</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion</td>
<td>Strong bond to substrate to stifle or retard the spread of corrosion. The best primers have both physical and chemical bonds to the substrate.</td>
</tr>
<tr>
<td>Surface Wetting</td>
<td>An ability to completely wet and obtain total contact with the surface to prevent the creation of voids at the primer/substrate interface. Water can accumulate in such voids and initiate the formation of corrosion cells.</td>
</tr>
<tr>
<td>Cohesion</td>
<td>High order of internal strength to withstand stresses from differential movement between the substrate and topcoats, or mechanical stress such as impact.</td>
</tr>
<tr>
<td>Weathering Resistance</td>
<td>To withstand the effects of weather on prolonged exposure before being top coated or when the topcoat is breached.</td>
</tr>
<tr>
<td>Intercoat bond</td>
<td>Strong bond to build coat, e.g. compatibility</td>
</tr>
<tr>
<td>Flexibility</td>
<td>Ability to withstand expansion and contraction of the substrate</td>
</tr>
<tr>
<td>Inertness</td>
<td>Resistance to corrosion and chemicals.</td>
</tr>
</tbody>
</table>

#### 2.2.2. Build (or Intermediate) Coats

The primary characteristics and purposes of build coats are listed in Table 2.

<table>
<thead>
<tr>
<th>Feature &amp; Purpose</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercoat Adhesion</td>
<td>Ensures a strong bond to the primer and to the topcoat, and ensures compatibility.</td>
</tr>
<tr>
<td>Cohesive Strength</td>
<td>Overcomes the strong intercoat adhesion forces.</td>
</tr>
<tr>
<td>Physical thickness</td>
<td>Improves many other essential coating properties, such as moisture vapour transfer rate, chemical resistance, electrical, abrasion, and impact resistance.</td>
</tr>
<tr>
<td>Physical strength</td>
<td>To resist mechanical stresses to which the system may be subjected in service.</td>
</tr>
<tr>
<td>Moisture Vapour Transfer resistance</td>
<td>Provides a more effective and impervious barrier in aggressive environments or when immersed.</td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>Improves protection in aggressive environments.</td>
</tr>
</tbody>
</table>
2.2.3. Finish (or Top) Coats

The finish coat is the first line of defence against weathering, aggressive chemicals, water and other corrosive elements in the environment. Finish coats provide a resinous seal over the build coats and the primer and perform several important functions. The most important features of finish coats are listed in Table 3.

<table>
<thead>
<tr>
<th>Feature &amp; Purpose</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Barrier &amp; Seal</td>
<td>Forming the first line of defence against the ingress of the corrosive elements in the environment.</td>
</tr>
<tr>
<td>Resistance</td>
<td>Provide resistance to chemicals, water, and weather.</td>
</tr>
<tr>
<td>Toughness</td>
<td>Provide a tough and wear-resistant surface.</td>
</tr>
<tr>
<td>Appearance</td>
<td>Provide an aesthetic appearance.</td>
</tr>
</tbody>
</table>

In some instances, the build coats may be used to provide the primary barrier to a corrosive condition, while the finish coat is applied for very different and specific purposes, for instance, to provide a non-skid surface, resistance to marine fouling or appearance alone.

2.2.4. Variations

It needs to be said that a "coating system" does not always contain all three components, i.e., primer, build coat and finish coat. This is true particularly where the main requirement is long-term protection. For example, inorganic zinc silicates and galvanising would be the most widely used single coat (sacrificial type) systems in the world where chemical resistance is not required. "Ultra High Build" epoxies and polyesters (coatings that can be applied to 750 microns or thicker in one coat) are widely used as single-coat (barrier type) systems for the protection of offshore oil and gas producing platforms and other marine structures, particularly the splash zone area.

3. ZINC BASED PRIMERS

Most of the zinc coatings used in high performance systems are based on liquid binders, such as epoxy, polyurethane or alkali/alkyl silicate resins. The filler component is almost entirely made up of finely divided zinc dust, which provides the galvanic protection that makes these coatings so useful in corrosion mitigation.

Galvanizing has been in commercial use for about 150 years and the catalysed epoxy and alkali/alkyl silicate resin based zinc coatings have been in commercial use for about 60 years. They built up an eminent track record of successful applications in a variety of mild to severe service conditions and in locations that extend from the desert to tropical and from the arctic to rural areas of the world. The catalysed resin based zinc coatings, in particular, have been exceptionally successful as primers in high performance coating systems.

In order to make the selection of the most suitable primer for specific service conditions, and the particular type of coating system being considered, it is necessary to know the main beneficial characteristics as well as any negative properties of the primers under discussion. Table 4, provides a summarised list of primer attributes. The effectiveness of each characteristic is ranked on a scale of very poor to excellent; the ranking is based on experience gained in the field, case histories and performance data from laboratory testing programs (1,2). The information provided in Table 4, also allows us to gauge how each primer candidate fits the essential requirements given in the previous tables.

4. BUILD AND FINISH COATS

Having examined the principal properties and features of zinc-based primers, as the foundation for high performance coating systems, it is appropriate to also examine the components, i.e. build and finish coats, that complete the composition of such systems. The two components will be considered under the one heading, because often the build coats are used for both functions, as build and as finish coats.

The majority of high performance systems used in Australia today are composed of zinc-based primers, catalysed epoxy resin based build coats and catalysed polyurethane, recoatable (PU-RC) resin based finish coats.

Note: It needs to be pointed out that there are great many case histories where protective systems based on zinc rich primers and vinyl or chlorinated rubber top coats have provided faultless protection to steel services in mild
to severe environments. The use of vinyl and chlorinated rubber based finish coats, however, is being phased out because of the very high volatile content of these coatings.

As a variation, the PU-RC finish coat is dropped and a combination of thin-film, lower solids and high-build, high-solids epoxies are used as the build/finish coats for protecting steel surfaces in severe marine and industrial environments. More likely than not, such coatings are compounded with inert fillers such as micaeous iron oxide, mica or glass flake to enhance the system’s resistance to weathering and moisture ingress. Special fillers, e.g. red oxide and zinc phosphate are used to improve corrosion resistance in addition to the strength and permanence of adhesion to the primer, particularly if the primer is HDG.

| CHARACTERISTICS & OTHER FEATURES | CATALYSED EPOXY ZINC | MOISTURE CURED POLYURETHANE ZINC | INORGANIC ZINC SILICATES | HOT DIP GALVANISE
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond to Substrate</td>
<td>Mechanical &amp; Chemical, VG</td>
<td>Mechanical &amp; Chemical, VG</td>
<td>Mechanical &amp; Chemical, VG</td>
<td>Mechanical &amp; Chemical, VG</td>
</tr>
<tr>
<td>Internal Adhesion (Primer to Body Coat)</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>Unpredictable, VP to VG</td>
</tr>
<tr>
<td>Flexibility</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Cohesive Strength</td>
<td>E</td>
<td>E</td>
<td>VG</td>
<td>G</td>
</tr>
<tr>
<td>Corrosion Resistance</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Galvanic Protection</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Weather Resistance</td>
<td>G</td>
<td>VG</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Chemical Resistance: pH6</td>
<td>VP</td>
<td>VG</td>
<td>VP</td>
<td>VP</td>
</tr>
<tr>
<td>pH8 to 10</td>
<td>VP</td>
<td>VP</td>
<td>VP</td>
<td>VP</td>
</tr>
<tr>
<td>Water Resistance - Immersion</td>
<td>F to G</td>
<td>F to G</td>
<td>F to G</td>
<td>F to G</td>
</tr>
<tr>
<td>Solvent Resistance</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Temperature Resistance</td>
<td>200-250°C Dry, VG</td>
<td>200-250°C Dry, VG</td>
<td>400°C Dry, E</td>
<td>400°C Dry, E</td>
</tr>
<tr>
<td>Physical Toughness</td>
<td>G</td>
<td>G</td>
<td>E</td>
<td>VG</td>
</tr>
<tr>
<td>Ease of Application</td>
<td>Moderate Skill Required</td>
<td>Moderate Skill Required</td>
<td>High Skill Required</td>
<td>Moderate Skill Required</td>
</tr>
<tr>
<td>Optimum Application Conditions</td>
<td>10°C to 50°C</td>
<td>60°C to 100°C</td>
<td>20°C to 25°C</td>
<td>20°C to 25°C</td>
</tr>
<tr>
<td></td>
<td>40 to 90% RH</td>
<td>75 to 80% RH</td>
<td>40 to 50% RH</td>
<td>55 to 90% RH</td>
</tr>
</tbody>
</table>

Catalysed epoxy resin coatings derive their success from their versatility. There are many chemically and physically different types of epoxy resins, depending on their derivation and molecular weight (3). There is also a variety of curing agents, hardeners, e.g. aromatic amines, polyamides, anhydrides etc, used to obtain epoxy coatings with different desirable features and properties. Thus, the coating chemist has at his disposal a number of variables to use, in countless combinations, to formulate protective coatings, enhancing particular characteristics to best-fit specific requirements.

Whilst moisture cured polyurethanes have been very successfully used overseas, particularly in the USA, they have not yet gained a wide acceptance in Australia. They are included in this discussion to provide a comparison and because they have certain beneficial features (4). Being moisture cured they are particularly useful in maintenance situations especially in high humidity, low temperature conditions.

The main characteristics and features of the build and finish coats are summarised in Table 5.

5. COATING ADHESION TO HDG

The grading given to attributes listed in Table 4 clearly shows that zinc based primers provide an excellent foundation for high performance, multi-coat systems. Specifiers of protective coatings, however, need to exercise a good measure of caution when prescribing the top coating of HDG, particularly if a strong and permanent adhesion between the HDG and the topcoats is to be achieved (5,6,7). Field performance data and laboratory test results indicate that to obtain such adhesion is a “hit & miss” affair even when exceptional
measures are taken to ensure the desired outcome. Such measures may include the correct choice of (HDG) surface preparation or pre-treatment and the appropriate build/finish coats.

The failure of intercoat adhesion may be viewed as a nuisance only, as in the case of peeling paint from galvanized guttering. Or it can lead to drawn out litigation and serious financial losses, when such failure occurs on large commercial or industrial projects. In most cases, it is very difficult (almost impossible) to determine, after the fact, the reasons for the failure. Was it because of incorrect specifications, poor or faulty workmanship on the part of the galvaniser/coating applicator or was it the result of faulty/inappropriate paint coating?

Table 5: Comparison of Build and Finish Coat Characteristics

<table>
<thead>
<tr>
<th>CHARACTERISTICS &amp; OTHER FEATURES</th>
<th>BUILD COATS</th>
<th>FINISH COATS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polyamide Catalysed Epoxy</td>
<td>Moisture Cured Polyurethane</td>
</tr>
<tr>
<td></td>
<td>Thin Film</td>
<td>High Build</td>
</tr>
<tr>
<td>Intercoat Adhesion</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Flexibility</td>
<td>VG</td>
<td>VG</td>
</tr>
<tr>
<td>Cohesive Strength</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Weather Resistance</td>
<td>G to VG</td>
<td>G to VG</td>
</tr>
<tr>
<td>Chemical Resistance:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid:</td>
<td>VG</td>
<td>VG</td>
</tr>
<tr>
<td>Alkali:</td>
<td>VG</td>
<td>VG</td>
</tr>
<tr>
<td>Salt:</td>
<td>VG</td>
<td>VG</td>
</tr>
<tr>
<td>Water Resistance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Splash:</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Immersion:</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Solvent Resistance</td>
<td>VG</td>
<td>G</td>
</tr>
<tr>
<td>Temperature Resistance</td>
<td>100-150 C, VG</td>
<td>100-150 C, VG</td>
</tr>
<tr>
<td>Physical Toughness</td>
<td>VG</td>
<td>VG</td>
</tr>
<tr>
<td>Ease of Application</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Optimum Application Conditions</td>
<td>10 C to 50 C 40 to 90% RH</td>
<td>10 C to 50 C 40 to 90% RH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) VP = Very Poor, P = Poor, F = Fair, G = Good, VG = Very Good, E = Excellent

As a matter of interest, Galvanizers Association of Australia recently acknowledged, that there is a perennial adhesion problem with top coated HDG by inviting paint manufacturers to participate in a review program to “address surface preparation and adhesion promoting primers….as essential to the success of duplex systems”.

Some examples of disastrous intercoat adhesion failure, related to top coated HDG, in recent times, include:

1. Mount Blackwood Telecom Tower near Townsville. The galvanized surfaces were treated with a proprietary etch solution followed by a non-inhibiting epoxy primer and two polyurethane finish coats. The work was performed in 1988-9 and within 12 months there was evidence of a massive intercoat failure. Conditions are tropical/rural.

2. South Esk River Bridge (Transport Tasmania), Launceston, built in 1993-4. The heavy-duty galvanized balustrades were top-coated with an etch primer and alkyd enamel system. Failure of the intercoat adhesion became evident in less than 12 months. Prevailing conditions are marine.

3. Cooling fins on large electric transformers at the Portland aluminium smelter, coated with an epoxy zinc phosphate primer followed by recoatable polyurethane finish coats. The system failed within 12 months. Prevailing conditions are industrial/severe marine.

4. Cairns Meyer Centre structural steelwork. The epoxy primer and recoatable polyurethane finish coats started peeling off the galvanized surfaces some 12 months after the project was completed. The shopping centre is a very large complex in the middle of the town. Refurbishment of the failed areas has been going on for some four years. The shopping complex is open seven days a week, which makes the refurbishment work extremely difficult. Conditions are urban.
5. NSW Railway Stations. Adhesion failure has been an ongoing problem with top coated galvanized structural steel work. Conditions are urban/industrial.

Undeniably, there are also many examples of successfully top coated galvanized steel projects, e.g. the original Melbourne Arts Centre spire; but there is always a measure of uncertainty associated with such projects.

6. COATING ADHESION TO ZINC-RICH PRIMERS

The intercoat adhesion is more reliable in the case of the high performance systems based on a catalysed epoxy or inorganic silicate zinc-rich primers. The best way to illustrate that zinc-rich primer based high performance systems do, in fact, provide long-term protection to steel surfaces in a variety of environments, is by way of reviewing some case histories. Table 6 below provides a number of case histories where zinc-rich primer based systems have been successfully protecting steel structures for 10 years or more. The handful of case histories listed in Table 6, represents hundreds of similar projects and is a snapshot of the performance that can be expected from the zinc-rich primer based systems.

Table 6: Zinc-Rich Primer Based Coating System Case Histories

<table>
<thead>
<tr>
<th>Project</th>
<th>System</th>
<th>Coating Type</th>
<th>DFT µm</th>
<th>Age, Years</th>
<th>Condition in 2002</th>
</tr>
</thead>
<tbody>
<tr>
<td>Port Adelaide Grain Silos, Bins &amp;</td>
<td>Coastal Marine/Light Industrial</td>
<td>IZS SB E-HB</td>
<td>75</td>
<td>19</td>
<td>Excellent. Some decorative deterioration of finish coat only</td>
</tr>
<tr>
<td>Structural Steel</td>
<td></td>
<td>PU-RC</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structural Steel</td>
<td>90% RH.</td>
<td>PU-RC</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal Conversion Plant, Morwell,</td>
<td>Mild Industrial</td>
<td>IZS-WB E-HB</td>
<td>75</td>
<td>10</td>
<td>Excellent Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td>Victoria</td>
<td>PU-RC</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Railway Bridge, Morwell,</td>
<td>Rural/mild Industrial</td>
<td>IZS-SB 2xE-MIO</td>
<td>75</td>
<td>12</td>
<td>Excellent. Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td>Victoria</td>
<td></td>
<td>250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCG Light Towers.</td>
<td>Urban</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>16</td>
<td>Excellent. Needed only PU refresher topcoat after 16 years.</td>
</tr>
<tr>
<td></td>
<td>PU-RC</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melbourne Tennis Centre</td>
<td>Urban</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>&gt;10</td>
<td>Excellent. Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td></td>
<td>PU-RC</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Offshore Oil/Gas production Platforms</td>
<td>Severe Marine</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>10-12</td>
<td>Very good - on tubular structural steel members.</td>
</tr>
<tr>
<td></td>
<td>2xE-HB</td>
<td>300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arch Bridge Over the Yarra River,</td>
<td>Urban/Light Industrial</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>15</td>
<td>Excellent. Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td>Melbourne</td>
<td>PU-RC</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PU</td>
<td>75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arts Centre Spire, Melbourne</td>
<td>Urban/Light Industrial</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>&gt;10</td>
<td>Excellent. Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td></td>
<td>PU-RC</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chute and Support Structure, Sugar</td>
<td>Marine</td>
<td>IZS SB E-MIO</td>
<td>75</td>
<td>9</td>
<td>Excellent. Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td>Australia, Mackay Port</td>
<td></td>
<td>150</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structural Steel, Kestrel Coal Mine,</td>
<td>Industrial</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>11</td>
<td>Excellent. Maintenance not required for at least 3 years.</td>
</tr>
<tr>
<td>Rio Tinto</td>
<td></td>
<td>200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Omega Communications Tower, South</td>
<td>Rural/Light Marine</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>&gt;15</td>
<td>Excellent. Only required minor maintenance of patch repairs during 20 years service.</td>
</tr>
<tr>
<td>Gippsland</td>
<td>PU-RC</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melbourne Exhibition Centre</td>
<td>Urban</td>
<td>E-ZR E-HB</td>
<td>75</td>
<td>&gt;7</td>
<td>Excellent. Maintenance not required for atleast 5 years.</td>
</tr>
<tr>
<td></td>
<td>PU-RC</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCG Light Towers</td>
<td>Urban</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>16</td>
<td>Excellent. Needed only PU refresher topcoat after 16 years.</td>
</tr>
<tr>
<td></td>
<td>PU-RC</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QPenos Australia pty Ltd, Sphere</td>
<td>Industrial</td>
<td>IZS-SB E-HB</td>
<td>75</td>
<td>6</td>
<td>Excellent. Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td>Refurbishment</td>
<td>PU-RC</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Snowy Mountains Authority, Geehi</td>
<td>Cold, High Humidity</td>
<td>ZR-PUMC</td>
<td>75</td>
<td>2</td>
<td>Excellent. Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td>Tunnel Steelwork</td>
<td></td>
<td>PUMC,MIO</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pasmicno Smelter, Port Pirie</td>
<td>Severe Industrial</td>
<td>ZR-PUMC</td>
<td>75</td>
<td>2</td>
<td>Excellent. Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PUMC,MIO</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Auckland Harbour Bridge, New Zealand</td>
<td>Marine</td>
<td>ZR-PUMC</td>
<td>75</td>
<td>6</td>
<td>Excellent Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PUMC,MIO</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell Petroleum, Brunel, Kefirev</td>
<td>Marine</td>
<td>ZR-PUMC</td>
<td>75</td>
<td>2</td>
<td>Excellent Maintenance not required for at least 5 years.</td>
</tr>
<tr>
<td>Steelwork &amp; Eiaumont</td>
<td></td>
<td>PUMC,MIO</td>
<td>200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The projects listed in Table 6, have been inspected in 2002 and most of them were found to be in excellent condition and unlikely to deteriorate to a point of needing maintenance in the next 5 years. In most cases any deterioration is usually limited to the finish coat only, as, for example, in the case of the MCG light towers where the finish coat chalked and weathered off in areas; but the primer and build coats were intact and there were no signs of rusting or loss of adhesion - an excellent performance after 16 years service.

7. LABORATORY TESTING

An accelerated laboratory testing program was undertaken by two major paint manufacturers to compare the performance of coating systems based on various zinc primers including catalysed epoxy zinc-rich, inorganic zinc silicates (solvent borne, water borne and high ratio) and galvanizing (hot dip, both bath and inline). The build coats were either a thin-film or a high-build catalysed epoxy and the finish coat in all instances was a catalysed polyurethane finish. Two types of build coats were included to determine if there was a difference in strength of adhesion, particularly after the test exposure. Altogether 20 coating systems were tested. A duplicate set of coated and scribed panels (the HDG panels were 1-2mm thinner than the rest of the test panels) were subjected to a standard salt spray test for 2000 hours.

Table 7 and Table 8 provide a list of the tested systems and a summary of results showing their performance in respect to scribe rusting, under creep, and strength of adhesion.

### Table 7: Summary of Salt Spray Test Results - Zinc Rich Primer Based Systems

<table>
<thead>
<tr>
<th>Coating System</th>
<th>Test Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scribe Rust, ISO 4628/3 (1)</td>
</tr>
<tr>
<td></td>
<td>Strength (MPa)</td>
</tr>
<tr>
<td>No.</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Coat (2)</td>
</tr>
<tr>
<td>1, 3 &amp; 5</td>
<td>E-ZR (50)</td>
</tr>
<tr>
<td>2, 4 &amp; 6</td>
<td>E-HB (125)</td>
</tr>
<tr>
<td>7</td>
<td>IZS-SB (50)</td>
</tr>
<tr>
<td>8</td>
<td>HRZ (50)</td>
</tr>
<tr>
<td>10</td>
<td>E-HB (125)</td>
</tr>
<tr>
<td>11</td>
<td>IZS-WB (50)</td>
</tr>
<tr>
<td>12</td>
<td>E-HB (125)</td>
</tr>
</tbody>
</table>

(1) Value of Rust Grade numbers: 0=0%, 1=0.06%, 2=0.5%, 3=1%, 4=8% & 5=40/50% Area Rusted
(2) Bracketed numbers denote dry film thickness in microns

Looking at the test results in Table 7 and Table 8, it becomes evident, that:

- Overall there is less rusting in the scribes of the panels coated with the HDG based systems. This result reflects the larger amount of zinc that is available in the HDG to perform the function of cathodic protection immediately upon exposure to the corrosive test conditions.

- The amount of under creep, extending from the edges of the scribe, is appreciably greater in the case of the HDG based systems than in the case of the zinc-rich primer based systems. This result suggests that the bond is weaker between the HDG and epoxy topcoats.

- The strength of bond between the zinc-rich primers and topcoats is significantly higher than between the HDG and topcoats. In addition to this symptomatic result, the adhesion further deteriorates when the system is exposed to the destructive elements in the environment. The results suggest that the type of body coat does not significantly affect bond strength. Interestingly, the type of pre-treatment given to the HDG surface before top coating also does not seem to guarantee that an acceptable and permanent intercoat adhesion will be achieved. In other words, the bond can be good or bad whether the pre-treatment was abrasive blasting, degreasing or nothing. This result, clearly confirms the unpredictability of intercoat adhesion HDG based coating systems.

- The adhesion strength test results, in the case of the zinc-rich primer based systems, exhibit some interesting and unusual features. For example, the bond strength increased markedly during the salt spray exposure in the case of the zinc-rich epoxy based systems. The bond remained practically the same in the case of the IZS-SB based systems. Bond strength deterioration appeared to be negligible in the case of the IZS-WB system, whereas the deterioration was, inexplicably, significant in the case of the HRZ system. Varying degrees of zinc splitting was the mode of adhesion failure, besides glue failure and separation between the zinc primer and build coat, in most cases of the zinc-rich primer based systems.

It is interesting to note that in the case of the HDG based systems, the adhesion test results from the coated panels exposed to the accelerated salt spray testing seem to reflect the performance of such systems in real life exposures exemplified by the case histories of the rapid adhesion failures listed above. In the case of the zinc-rich primer based systems, on the other hand, an imperceptibly slow deterioration of the finish coat only, takes place over 15 to 20 years exposure. In all the case histories investigated no evidence of adhesion failure was
found, even though it may be construed that zinc splitting, found to be a prominent feature of the mode of adhesion failure in the above salt spray test, is a point of weakness in the zinc rich primer based systems.

8. CONCLUSIONS
The data presented shows that multi-coat, high performance systems based on zinc primers, are indeed high performance systems that provide long-term protection to steel surfaces in a variety of corrosive environments ranging from mild to severe. The supporting evidence is based on long standing coatings technology, current accelerated laboratory test results and case histories from a cross section of exposures. The evidence also suggests that caution needs to be exercised when consideration is given to top coated hot dip galvanised surfaces because of the unpredictability of the strength and permanence of adhesion exhibited by such systems. The information provided in the paper should be helpful to specifiers and users of coatings when selecting protective systems for specific conditions.

9. ACKNOWLEDGEMENTS
The author is grateful to and thanks Ted Riding, Jotun Australia Pty Ltd and Jeffrey James and Jamie O’Brien, International Protective Coatings, for their assistance with the laboratory testing and for their helpful review comments.

10. REFERENCES
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METALLIC ZINC BASED COATING SYSTEMS – EVALUATION OF PERFORMANCE.

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¹CSIRO Industrial Research Services, ²PPG Protective & Marine Coatings, ³A & A Szokolik Consulting Pty Ltd.

SUMMARY: The paper details the results of a test program undertaken to compare the relative performance parameters of zinc rich coatings and galvanising. The test regime included long-term natural exposure and accelerated testing and was performed by CSIRO for the Zinc Rich Coatings Council, an industry body comprised of representatives of manufacturers of zinc rich coatings. The objective of the testing program was to generate comparative performance data on the inter-coat adhesion in systems based on zinc rich primers, on galvanized surfaces and on the general performance of un-topcoated metallic zinc based systems. The paper describes the test regime, discusses the results and draws appropriate conclusions about the performance of each system tested. The unbiased, practical information provided in the paper should be of great value to all involved in the use of protective coatings.

Keywords: Testing, inter-coat adhesion, performance, zinc rich, galvanized surface, prohesion, corrosion, coatings, corrosion prevention.

1. INTRODUCTION

Galvanizing has been, for a great number of years, a highly successful treatment to prevent corrosion of steel surfaces. Indeed, it has a long track record of providing effective corrosion protection in a wide range of environments ranging from mild rural to industrial and marine conditions. In recent times it has become popular with architects for commercial applications where, in most cases, it was top coated with an organic resin based system, such as acrylics, epoxies or polyurethanes. In many instances, the top coating was applied for aesthetic reasons only.

Engineers also have been specifying galvanizing as the corrosion prevention treatment for steel in more severe environments. In such situations, it is necessary to top coat with epoxy/polyurethane based systems to prevent the rapid consumption of the underlying pure zinc layer.

The increasing use of paint coatings on galvanized surfaces has led to an increase in the incidence of adhesion failures between the galvanized surface and the paint system. This has usually been attributed to the use of saponifiable resin coatings such as alkyd enamels or primers. However, there is evidence that non-saponifiable resin systems have also suffered adhesion problems over galvanized surfaces.

2. BACKGROUND

The Australian paint industry has spent much time; energy and money on research in an effort to find a practical and reliable solution to the inter-coat adhesion problem associated with top coated galvanized surfaces. Over the years a variety of remedies have been tried. They included allowing the galvanizing to weather, etching the galvanized surface with various acid salt solutions, roughening the zinc surface with emery paper or lightly abrasive blasting to applying a thin film of a vinyl butyral, zinc tetroxychromate etch primer and currently the use of either non-inhibitive or zinc phosphate two pack epoxy primers. The problem with all these remedies has been, and still is, that using them doesn’t give a 100% guarantee that sound, long-term adhesion has been achieved.
Massive inter-coat adhesion failures on a number of large projects are a well-documented fact. This supports the claim that obtaining long-term adhesion between galvanized surfaces and organic topcoats is a haphazard, hit and miss affair.

Some examples of disastrous intercoat adhesion failure, related to top coated hot dipped galvanizing (HDG), in recent times, include:

- Mount Blackwood Telecom Tower near Townsville, Queensland, tropical/rural conditions. The galvanized surfaces were treated with a proprietary etch solution followed by a non-inhibiting epoxy primer and two polyurethane finish coats in 1988-9. Within 12 months there was massive adhesion failure.
- South Esk River Bridge, Launceston, Tasmania. Built in 1993-4. Marine conditions. The heavy-duty galvanized balustrades were treated with an etch primer and top-coated with an alkyd enamel system. Failure at the galvanizing-to-coating interface became evident in less than 12 months.
- Cooling fins on large electric transformers at the Portland, Victoria aluminium smelter. Industrial/severe marine conditions. Coated with an epoxy zinc phosphate primer/recoatable polyurethane finish system. Adhesion failed within 12 months.
- Cairns Meyer Centre, galvanized structural steelwork, urban conditions. Coated with an epoxy primer/recoatable polyurethane system. Adhesion failed within 12 months. Located in the middle of the town, the huge shopping complex is open seven days a week. Refurbishment of the failed areas has been going on for some four years under extremely difficult conditions.
- NSW Railway Stations, galvanized structural steel work, urban/industrial conditions. Adhesion failure between the HDG and topcoats has been an ongoing problem.

Undeniably, there are also many examples of successfully top coated galvanized steel projects, e.g. the original Melbourne Arts Centre spire, but there is always a measure of uncertainty associated with such projects.

The consequence of such failures as listed above, and the search for whom or what is to blame for the disaster has consumed considerable personnel and financial resources. The first question asked by the architect or consulting engineer is: “Whose fault is this?” First the applicator is blamed and if he can prove that he has done everything in accordance with the coating manufacturer’s recommendations, then the manufacturer and his coatings are in the firing line and are said to be responsible for the failure. It is interesting to note that the role of the galvanized surface is rarely questioned. And the question: “Why was an unreliable coating system specified?” is almost never asked.

It is understandable then, that the coating manufacturers have become reluctant to recommend, let alone guarantee, top coating systems for galvanized surfaces. In contrast, the high performance systems based on a catalysed epoxy zinc rich or inorganic zinc silicate primers have a track record of having reliable intercoat adhesion and can provide long-term corrosion protection to steel surfaces in almost all environments. This evidence in itself, however, doesn’t seem to be sufficient proof to convince the specifying engineers or architects of the fact that, when service conditions warrant top coating, galvanizing the steel should not be the selected choice of primer for the coating system. Consequently, the coatings manufacturers decided that there was a need to provide independent evidence, under the auspices of the recently (2001) formed Zinc Rich Coatings Council (ZRCC) of the difficulties of coating galvanized surfaces. CSIRO’s Manufacturing and Infrastructure Technology (CMIT) Division was commissioned to conduct a comprehensive comparative accelerated and long-term natural exposure-testing program, evaluating corrosion performance and the over-coating of galvanizing and zinc rich coating primers for steel.

3. TESTING PROGRAM

It was decided that truly reliable data could only be obtained from actual long-term natural weathering at suitable site/s. However, due to the long time frame before any meaningful results were likely to be gained, a concurrent accelerated testing program had to be conducted.

3.1. Test/exposure conditions

3.1.1. Accelerated Laboratory Testing

Prohesion testing to ASTM G85 Annex A5 was agreed upon as the most suitable test protocol to accelerate the natural weathering of the coatings subjected to this test regime. Test panels were placed in a NATA accredited Q-Fog Cyclic Corrosion Tester (temperature and humidity controlled) test chamber. Cycles of one hour salt fog
and one hour dry off were used. A salt solution of 0.05% NaCl and 0.35% NH₄Cl at pH of 5.0 to 5.4 was required with a chamber temperature of 35±1.5°C.

Prior to placing the panels in the test chamber, the thickness of each system was measured and its adhesion was evaluated using AS 1580 408.5 (pull-off test) and AS 1580 408.2 (knife test). Panels were placed in the chamber and visually assessed at intervals of 2000 and 4000 hours. After 6000 hours the panels were subjected to the final assessment in which the following coating features were evaluated:

- Degree of corrosion in the scribe and on the panel surface, using AS/NZS 1580 481.3,
- Degree of blistering, using AS 1580 481.1.9, and
- Adhesion, using AS 1580 408.5 (pull-off test) and AS 1580 408.2 (knife test).

### 3.1.2. Natural Exposure

It was agreed that this type of testing should be long-term, at least 10 years. In order to accurately evaluate coating performance, it was agreed that the panels should be exposed at three sites that represent a range of environments likely to be experienced in Australia, i.e.:

- Inland Tropical: Category F (AS/NZS 2312) no equivalent ISO category exists
- High Corrosivity: Category D (AS/NZS 2312) equivalent to ISO C4
- Very High (Marine) Corrosivity: Category E-M (AS/NZS 2312) equivalent to ISO C5-M

CSIRO maintains a number of natural exposure sites accredited by NATA to AS 1580.457.1. They are located at Flinders and Highett (both in Victoria) and Darwin (Northern Territory) and were chosen as the preferred test sites.

The panels were exposed mid 2005 but at this stage it is still far too early to see any meaningful results. Consequently the subject of this paper is limited to the accelerated test regime and results. Relating accelerated and natural exposure testing results will be the subject of future papers.

### 3.2. Panel preparation

Mild steel panels 150 x 300 x 3mm were sourced and abrasively blasted to AS 1627.4 class Sa 2½ by a commercial abrasive blasting organisation. Panels were stored under clean new xylene solvent to prevent further oxidation and were then delivered to each coating manufacturer for system application.

Each coating manufacturer participating in the trial applied their own products in their own laboratories under a NATA certificate ensuring compliance with AS 1580.205.2 (or 205.4 airless spraying). Full traceability of product/s, formulation/s and film thicknesses was ensured. Panels were also backed and edge sealed. Once satisfactorily cured they were shipped to CSIRO’s Highett (Victoria) facility.

Panels destined for Prohesion testing were scribed through to bare metal using a carbide tipped cutting tool. Scribes were 100mm in length, centred on the panel and running parallel to the long edge of the panel. All test panels were prepared and tested in duplicate. In all, a total of 234 panels were prepared and placed under test.

### 3.3. Coating systems applied for testing

A range of systems was chosen to cover the most typical applications encountered in the field. Systems were also chosen to ensure at least two manufacturers were represented in each system in order to check consistency of product results across different suppliers. See Table 1 for a summary of systems applied.

Panels were labelled and placed on test. It was decided that the only truly reliable data to be achieved was from actual long-term natural weathering at suitable sites. However, due to the long time frame before any meaningful results were likely to be obtained, an accelerated testing program needed to be run concurrently.
Table 1: Generic test system details

<table>
<thead>
<tr>
<th>No.</th>
<th>Surface Preparation</th>
<th>1st Coat</th>
<th>2nd Coat</th>
<th>3rd Coat</th>
<th>Manufacturers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Type</td>
<td>DFT, µm</td>
<td>Type</td>
<td>DFT, µm</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>IZS-SB</td>
<td>75-100</td>
<td>A &amp; B</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>IZS-WB</td>
<td>75-100</td>
<td>B &amp; C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>IZS-HR</td>
<td>75-100</td>
<td>C &amp; A</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Abrasive Blast Clean to AS 1627.4 Class Sa2½</td>
<td>HDG-B</td>
<td>75-100</td>
<td>Galvanizers</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>HDG-IC</td>
<td>20-40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>EZ-2p</td>
<td>50-80</td>
<td>E-HB</td>
<td>100-150</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>EZ-2p</td>
<td>50-80</td>
<td>E-MIO</td>
<td>100-150</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>EZ-2p</td>
<td>50-80</td>
<td>ACC-L</td>
<td>30-50</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>HDG-B</td>
<td>75-100</td>
<td>ACC-L</td>
<td>30-50</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>HDG-B</td>
<td>75-100</td>
<td>ACC-L</td>
<td>30-50</td>
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<tr>
<td>11</td>
<td>Sweep Abrasive Blast Clean</td>
<td>HDG-B</td>
<td>75-100</td>
<td>ACC-L</td>
<td>30-50</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>HDG-IC</td>
<td>20-40</td>
<td>E-HB</td>
<td>100-150</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>HDG-IC</td>
<td>20-40</td>
<td>E-MIO</td>
<td>100-150</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>HDG-IC</td>
<td>20-40</td>
<td>ACC-L</td>
<td>30-50</td>
</tr>
</tbody>
</table>

Note 1 – Legend: DFT – dry film thickness
IZS-SB - Inorganic zinc silicate - solvent borne, conforming to AS3750.9 Type 4.
IZS-WB - Inorganic zinc silicate - water borne, conforming to As3750.9 Type 3.
IZS-HR - Inorganic zinc silicate – high ratio water borne, conforming to AS3750.9 Type 6.
HDG-B - Hot dip galvanized surface – batch, conforming to AS/NZS 4680.
HDG-IC - Hot dip galvanized surface – inline continuous, conforming to AS/NZS 4792.
EZ-2p - Epoxy zinc, 2-pack, conforming to AS 3750.9.
E-HB - Epoxy-high build, conforming to AS 3750.14.
E-MIO - Epoxy-micaceous iron oxide, conforming to AS 3750.14.
ACC-2p - Acrylic-2 pack, conforming to AS 3750.5.
ACC-L - Acrylic latex, conforming to AS 3750.16.

Note 2 - Participating manufacturers: Ameron, Jotun, Akzo Nobel, Dulux, Wattyl and Protec.

4. RESULTS AND DISCUSSION

After 6000 hours test exposure, the condition of the coating was assessed on each panel. The coating performance was determined (before and after exposure), by assessing coating features such as

- DFT as per AS 3894,
- Degree of corrosion in the scribe and on the panel in accordance with AS/NZS 1580 481.3,
- Degree of blistering as per AS/NZS 1580 481.3,
- Adhesion in accordance with AS/NZS 1580 408.5 Pull-off Test and 408.2 Knife Test.

Following are pertinent comments regarding the performance of each group of coating systems.

4.4. Single Coat IZS Systems

The performance of the IZS-SB system can be described as faultless as is illustrated by the photograph in Figure 1. There was no corrosion in the scribe or on the panel surface. There were no blisters and adhesion was excellent. This result is the same as that obtained in a previous test program reported by Szokolik (1).

The IZS-WB systems had no corrosion in the scribe but developed some corrosion on the panel surface; however most of this corrosion appeared to have resulted from “edge effect” and/or from poor application during test panel preparation. There were no blisters and adhesion was excellent.
The performance of the IZS-HR systems was unexpectedly poor, suffering corrosion in both the scribe and panel surface. The only explanation for this poor performance is that it is formulation related. There were no blisters and adhesion was good. Results of the final assessment after 6000 hours exposure are detailed in Table 2. Note: None of the coating systems showed any deterioration after 4000 hours exposure.

Table 2: Single Coat IZS Systems - Details of Test Results

<table>
<thead>
<tr>
<th>COATING SYSTEM</th>
<th>PERFORMANCE AFTER 6000 HOURS EXPOSURE</th>
<th>Adhesion Test – AS/NZS 1580</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT µm</td>
<td>Degree of Corrosion AS/NZS 1580 481.3</td>
</tr>
<tr>
<td>No.</td>
<td>Detail</td>
<td>Scribe</td>
</tr>
<tr>
<td>-----</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>1A</td>
<td>IZS-SB</td>
<td>110</td>
</tr>
<tr>
<td>1B</td>
<td>IZS-WB</td>
<td>136</td>
</tr>
<tr>
<td>2A</td>
<td>IZS-SB</td>
<td>96</td>
</tr>
<tr>
<td>2B</td>
<td>IZS-HR</td>
<td>125</td>
</tr>
<tr>
<td>3A</td>
<td>IZS-SB</td>
<td>101</td>
</tr>
<tr>
<td>3B</td>
<td>IZS-WB</td>
<td>76</td>
</tr>
</tbody>
</table>

1 The mode of failure is given in parentheses, where z/s = zinc/split (cohesive failure), tc/g = top coat/glue (no adhesion loss in coating), nf = no failure.
2 The maximum pull capacity of the Pull-off gauge was 3.5Mpa.

4.5. Un-topcoated HDG Systems

The HDG-IC coating was almost entirely consumed and the panel was covered with rust, see Figure 2. This result was not unexpected as the zinc DFT was very low and because galvanizing consists of pure zinc, which has a propensity to go into solution when exposed to more corrosive environments.

In contrast to the inorganic zinc coated panels, the HDG-B coating developed light rusting in the scribe and on the panel surface, again indicating that pure zinc is rapidly consumed in corrosive environments. In such conditions long term performance is entirely controlled by the thickness of the galvanize coating, in other words, the amount of zinc available for consumption.

Note: Both galvanized systems showed light rusting on the panel surface after 4000 hours exposure.
Figure 2: In-Line Galvanized coating before and after Prohesion testing.

Results of the final assessment after 6000 hours exposure are detailed in Table 3.

### Table 3: Un-topcoated HDG Systems - Details of Test Results

<table>
<thead>
<tr>
<th>No.</th>
<th>Detail</th>
<th>DFT (µm)</th>
<th>Degree of Corrosion AS/NZS 1580 481.3</th>
<th>Degree of Blistering AS/NZS 1580 481.2</th>
<th>Adhesion Test – AS/NZS 1580</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Scribe</td>
<td>Panel</td>
<td>Pull-off, 408.5, MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>4</td>
<td>HDG-IC</td>
<td>21</td>
<td>5</td>
<td>4-1</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>HDG-B</td>
<td>67.2</td>
<td>0</td>
<td>1-1</td>
<td>0</td>
</tr>
</tbody>
</table>

1 Tests couldn’t be performed, panels completely covered with rust layer.
2 The mode of failure is given in parentheses, where tc/g = top coat/glue.

4.6. Epoxy Zinc Primer Based Systems

All panels developed varying degrees of rusting in the scribe. Results of the final assessment after 6000 hours exposure are detailed in Table 4.

### Table 4: Epoxy Zinc Primer Based Systems - Details of Test Results

<table>
<thead>
<tr>
<th>No.</th>
<th>Detail</th>
<th>DFT, µm</th>
<th>Degree of Corrosion AS/NZS 1580 481.3</th>
<th>Degree of Blistering AS/NZS 1580 481.2</th>
<th>Adhesion Test – AS/NZS 1580</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Scribe</td>
<td>Panel</td>
<td>Pull-off, 408.5, MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>6E7</td>
<td>EZ-2p/E-</td>
<td>242</td>
<td>2</td>
<td>0</td>
<td>D, S₁</td>
</tr>
<tr>
<td>6E8</td>
<td>HB/ACC-2p</td>
<td>290</td>
<td>2</td>
<td>0</td>
<td>D, S₁</td>
</tr>
<tr>
<td>6F7</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.4 (100% z/s)</td>
</tr>
<tr>
<td>6F8</td>
<td>7D7</td>
<td>334</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7E7</td>
<td>EZ-2p/E-</td>
<td>360</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7E8</td>
<td>MIO/E-MIO</td>
<td>153</td>
<td>1</td>
<td>1-1</td>
<td>0</td>
</tr>
<tr>
<td>8F7</td>
<td>EZ-2p/ACC-</td>
<td>1</td>
<td></td>
<td>1</td>
<td>1-1</td>
</tr>
<tr>
<td>8F8</td>
<td>ACC-L</td>
<td>1</td>
<td></td>
<td>1</td>
<td>1-1</td>
</tr>
</tbody>
</table>

1 The mode of failure is given in parentheses, where z/s=zinc/split, tc/g=top coat/glue (no adhesion loss in coating), nf=no failure, g/d=glue/dolly (no adhesion loss in coating), m/m=MIO/MIO.
2 The maximum pull capacity of the Pull-off gauge was 3.5MPa.

Only one system developed light spot rusting on the panel surface, and only one proprietary system developed dense, fine blisters in the topcoat. The test results show that for all intents and purposes there was no deterioration of adhesion after 6000 hours exposure, regardless of the type of topcoat used. This can be plainly seen in the photographs showing the comparative performance of the EZ-based systems, see Figure 3.

Note: First signs of rusting became evident in some systems during assessment after 4000 hours exposure.
4.7. HDG-Batch Based Multi-coat Systems

The combined effects of corrosion and coating disbondment in and adjacent to the scribe was significantly worse than seen in the case of the epoxy zinc primer based systems. See Table 5 for details of assessment results after 6000 hours exposure. Work carried out elsewhere also indicates that deterioration of adhesion occurs between galvanized surfaces and topcoats when such systems are exposed to moderately/severely corrosive environments (2).

Table 5: Top Coated HDG-Batch Systems - Details of Test Results

<table>
<thead>
<tr>
<th>COATING SYSTEM</th>
<th>PERFORMANCE AFTER 6000 HOURS EXPOSURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Detail</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>9E7</td>
<td>HDG-B/E-HB/HB/ACC-2p</td>
</tr>
<tr>
<td>9E8</td>
<td></td>
</tr>
<tr>
<td>9F7</td>
<td></td>
</tr>
<tr>
<td>9F8</td>
<td></td>
</tr>
<tr>
<td>10E7</td>
<td>HDG-B/E-MIO/E-MIO</td>
</tr>
<tr>
<td>10E8</td>
<td></td>
</tr>
<tr>
<td>10D7</td>
<td></td>
</tr>
<tr>
<td>10D8</td>
<td></td>
</tr>
</tbody>
</table>

1 The mode of failure is given in parentheses, where z/tc=zinc/top coat, tc/gl=glue (no adhesion loss in coating), nf=no failure, m/m=MIO/MIO, ga/tc=galvanize/top coat, g/d=glue/dolly (no adhesion loss in coating).

Some rusting was evident in the scribe on all panels see Figure 4. Zinc salt (white rust) formation at the scribe and under the film immediately adjacent to the scribe affected the adhesion of even the epoxy coatings at the galvanizing to topcoat interface. One-third of the systems also showed minor to moderate rusting on the panel surface and two-thirds of the systems showed moderate to extensive blistering. The performance of the acrylic latex topcoat was poor. The Pull-off adhesion tests gave a mixed result; mode of failure was either between the zinc and topcoat or between the topcoat and adhesive. On the other hand, the Knife adhesion tests, gave a clear indication of deteriorating adhesion, see Figure 4.
4.8. HDG-Inline Coating Based Multi-coat Systems

The combined effects of corrosion and coating disbondment in and adjacent to the scribe was considerably worse than seen in the case of the HDG-B based systems, see Figure 5. The rusting on the panel surface and the degree of blistering was about the same as in the case of the HDG-B based systems. The Pull-off adhesion tests gave mixed results; mode of failure was either between the topcoat and adhesive, particularly in the case of the MIO topcoats or between the two layers of MIO. The Knife adhesion tests indicated that deterioration only occurred in one-third of the systems. The performance of the acrylic latex topcoat was poor. Results of the final assessment after 6000 hours exposure are detailed in Table 6.

Note: Scribe/panel corrosion and blistering became evident after 2000 hours, with further deterioration after 4000 hours exposure.

Table 6: Top Coated HDG-Inline Coating Systems - Details of Test Results

<table>
<thead>
<tr>
<th>COATING SYSTEM</th>
<th>PERFORMANCE AFTER 6000 HOURS EXPOSURE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Degree of Corrosion AS/NZS 1580 481.3</td>
</tr>
<tr>
<td></td>
<td>Scribe</td>
</tr>
<tr>
<td>12E7</td>
<td>HDG-IC/E-MIO/E-MIO</td>
</tr>
<tr>
<td>12E8</td>
<td>HDG-IC/E-MIO/E-MIO</td>
</tr>
<tr>
<td>12F7</td>
<td>HDG-IC/E-MIO/E-MIO</td>
</tr>
<tr>
<td>12F8</td>
<td>HDG-IC/E-MIO/E-MIO</td>
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<tr>
<td>12D7</td>
<td>HDG-IC/E-MIO/E-MIO</td>
</tr>
<tr>
<td>12D8</td>
<td>HDG-IC/E-MIO/E-MIO</td>
</tr>
</tbody>
</table>

1 The mode of failure is given in parentheses, where z/tc=zinc/top coat, nf=no failure, tc/g=top coat/glue (no adhesion loss in coating), g/d=glue/dolly (no adhesion loss in coating), m/m=MIO/MIO, ss/ga=steel surface/galvanize, ga/tc=galvanize/top coat.

2 The maximum pull capacity of the Pull-off gauge was 3.5MPa.
5. CONCLUSIONS

The above findings generate the following conclusions:

- A single coat of solvent borne inorganic zinc silicate system (No.1), conforming to AS1530.15 Type 4, at 75µm minimum DFT will provide excellent long-term protection to Class Sa2½ blasted steel surfaces. In a corrosive marine atmosphere as reproduced by the Prohesion test program, the best performing system was clearly the solvent borne inorganic zinc silicate; it performed better than the hot dipped galvanized system (No.5). Where aesthetics are not of significance, a single coat of solvent borne inorganic zinc silicate will be the most economical system to use. In addition it has the beneficial characteristic of being able to self-repair any damage that the coating may sustain during handling or in service (Figure 1 shows zinc salts sealing off scribe damage). The zinc rich epoxy or hot dip galvanize based multi-coat systems have no such ability because (due to the top coating) there is a shortage of zinc to effect self-repair (3).

- Where aesthetics are important and a topcoat system (e.g., Nos. 9&10) is required then the zinc rich epoxy primer conforming to AS 3750.9 Organic zinc-rich primer, Type 2, will provide excellent, permanent all round adhesion and corrosion protection to the steel substrate.

- The above test results clearly point to a tendency for adhesion to deteriorate during service at the zinc/coating interface, in the HDG-B and HDG-IC based systems despite the showing of excellent initial adhesion. Even though the galvanized surfaces were brush blasted, water appeared to have been able to react with the zinc to produce zinc salts that led to degeneration of adhesion between the galvanized surface and the topcoat.

6. REFERENCES

3 A. Szokolik, Sixty Years of Inorganic Zinc Coatings (ACA), pp88-97 (1999)
REPAIR OF SINGLE COAT INORGANIC ZINC SILICATE COATINGS

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* Connell Wagner, South Melbourne, Australia
# SA Water, Adelaide, Australia
+ VicRoads - GeoPave, Burwood East, Victoria

SUMMARY: A single coat inorganic zinc silicate coating system has proven to provide excellent performance in a range of applications for over sixty years. However, like all coating systems, maintenance is sometimes required. Because of its unique composition and special application requirements, inorganic zinc has been considered as a difficult coating to repair. As a result, a number of different methods for repair and maintenance of inorganic zinc coatings have been suggested. This paper describes the structure of inorganic zinc coatings, how they degrade and the issues that must be considered when repairing them. It looks at the results of some repair trials that have been carried out. Examples of repair methods used on above ground water pipelines in South Australia and on an overpass in Victoria are given. The work shows that, contrary to some claims, repair of inorganic zinc is not difficult and normal surface preparation and application methods can be used. There is no reason why such coating systems cannot be simply and economically repaired and continue to provide excellent long-term performance.

Keywords: coating, inorganic zinc silicate, maintenance, recoatibility, repair

1. INTRODUCTION

A single coat inorganic zinc silicate (IZS) coating system has been recommended and specified in a range of applications for over sixty years. In many situations, its performance has been shown to be superior to multi-coat systems. However, like all coating systems, maintenance is sometimes required. Because of its unique composition, inorganic zinc has been considered as a difficult coating to repair. This paper looks at issues regarding repair of IZS coatings, including:

- Existing views and opinions on IZS system repair
- Results of fundamental studies into breakdown of IZS coatings carried out in the 1970s
- The results of trials on recoating IZS
- Case studies of IZS repairs in South Australia and in Victoria

2. VIEWS ON REPAIR OF IZS COATINGS

A number of different methods for repair and maintenance of inorganic zinc coatings have been suggested and there is a wide variation in opinions. At one extreme, the view is that basically they are not able to be repaired and should be removed if degraded, as summarised in a paper comparing IZS to thermal spray coatings:

“...When used as a stand alone system, eg as a tank lining or on a chimney stack, repairs to damaged IZS require reblasting and reapplication. … Thermal spray coatings can be applied to itself which simplifies repairs where underbuilt areas are found.” (1)

However, others have not required such drastic preparation as requiring complete removal of the old coating. One repair procedure (2) recommends spot blasting to near white metal, although “small areas can be cleaned with needle guns. Reapplication may be by spray or brush, but spray is preferred. Freshly applied material can be
overlapped onto existing inorganic coating. The existing coating must be clean and free from all organic and inorganic contamination to ensure proper adhesion between coats.”

AS/NZS 2312 (3) provides guidance on the maintenance of protective coating systems, but little specific advice for IZS coatings. For the breakdown of an inorganic zinc silicate coating (not top-coated), repainting or repair is recommended when about 2% of the surface in any particular area shows signs of rusting. The recommended pre-treatment before repainting depends on the amount of breakdown, without distinguishing between different coating types. The standard nominates a number of coatings (not including IZS) which are compatible with aged IZS, but notes there are precautions required for surface preparation and application when recoating inorganic zinc rich coatings. However, it does not detail repair coating systems nor the specific precautions required for the repair coating.

The Coatings Guide for New Steel Bridges (4), which recommends a single coat water-borne inorganic zinc coating as the optimum coating for steel bridges, states that these coatings “should never need complete removal provided that adequate maintenance is carried out to ensure that coating breakdown and rusting does not exceed 5% of the total surface area at any stage.” The Guide briefly covers recoatability in Appendix 5, listing manufacturer’s recommendations. Interestingly, different coating suppliers recommend completely different surface preparation procedures for applying a new coat of water-borne IZS over an old coat of IZS. Two companies recommend high pressure water cleaning only, one company recommends a brush blast, and two companies require a brush blast and repair with epoxy zinc. No discussion of these widely divergent views is given in the document.

Clearly, there is no accepted best practice for overcoating aged inorganic zinc coatings. A range of procedures from power tool cleaning, high pressure washing, brush blasting and full removal have been suggested, and recoating with the same product, an epoxy zinc or other coating. If such divergent views exist within coating experts and suppliers, then it is not surprising that there is confusion amongst users. As a result, they may specify the drastic and expensive option of total removal, or the lesser protection offered by repair with epoxy zinc or other conventional system. It is quite possible this uncertainty could result in users specifying a lower durability system in the first place, as such a system is perceived to be easier to repair.

3. BREAKDOWN OF INORGANIC ZINC COATINGS

In order to develop the best method of repair of IZS, an understanding of the breakdown of such coatings is necessary, as their behaviour is different to other protective coatings. A cured coating of inorganic zinc, regardless of the original type, consists of zinc particles in contact, surrounded by a porous framework of silicate binder. With exposure to the atmosphere, the silicate matrix hardens, and zinc corrosion products fill the pores providing a barrier to moisture and oxygen. Unlike other coatings, IZS become more protective in the first year or two of exposure as the coating hardens and the pores become blocked. Contrary to popular belief, cathodic protection of the steel provided by corroding zinc particles is a minor contributor to the protection mechanism, operating only in damaged and thin regions of the coating.

Jaeger and Sherwood (5) investigated changes in the initial structure of an inorganic zinc coating (both solvent-borne and water-borne) examined, with no apparent differences in the structure of the cured film) after open air exposure in a light industrial environment for seven years. With exposure, the surface of the coating became rough and weathered but there was still some zinc present in the outermost layer. The metallic zinc particles in the outer layer corroded first and zinc corrosion products filled up the pores and voids within the matrix. In the outermost layer, there were holes where the zinc particles were originally, and these holes were filled with zinc corrosion products. Most zinc particles in the outer layer were at least partially attacked, but very few zinc particles were attacked in the inner two-thirds of the coating. With continued exposure, the zinc corrosion product layer extended deeper into the coating and reached the steel surface after 1½ to 2 years, when the matrix was almost completely permeated by zinc corrosion products. However, only the zinc particles at the coating surface were extensively corroded with those inside the coating less attacked. Jaeger and Sherwood concluded that the filling of the matrix was therefore due to inward diffusion of corrosion products from the outer surface, rather than corrosion of the zinc particles within the coating. The corrosion products formed a barrier, which hindered access of corrosive reactants. After further weathering, zinc corrosion products leached out from the sites at the coating surface originally occupied by zinc particles. After ageing, the outer part of the coating consisted of a skeleton of silicate matrix filled with corrosion products. This relatively short degree of weathering would have resulted only in the coating becoming lighter in colour due to build up of white zinc corrosion products within the coating. No iron corrosion products would have been apparent at this relatively early stage of weathering.

These investigators also looked at the structure of a coating after repair. An inorganic zinc coating was exposed for six months, cleaned by sweep blasting or wire brushing, and a new top coat applied and exposed (see Figure
Microscopic work showed a similar mode of attack to that described above, but the zinc corrosion products from the repair coating actually permeated into the original coating, reaching the steel interface within two years. There was no evidence from the test results of loss of adhesion between the old coat and repair coat. In fact, the presence of an interface appeared to have little effect on performance even though it was clearly apparent in the micrographs. The effect of the method of surface preparation was not discussed, although as Figure 1 shows, the interface is more apparent after wire brushing than brush blasting. This suggests brush blasting more effectively removes the weathered outer layer and would appear to be the superior method of preparation where the surface is heavily degraded or contaminated.

![Cross section through a repair potassium silicate coating (after 4 months exposure) applied to the same type of coating, originally exposed for 6 months. (a) Original coating wire brushed, (b) original coating sweep blasted. The arrows indicate the interface between the original and repair coatings. Original magnification 900x. (Ref 5).](image1.png)

These investigators also looked at the same type of coating exposed to a low tide sea water environment for comparison. This is not an environment where IZS would be specified, but enabled rapid degradation of the coating to occur, perhaps equivalent to decades of exposure in a normal atmosphere. As expected, in this case the zinc particles were extensively corroded in the entire layer although, as shown in Figure 2, zinc particles still exist. Dissolution of the iron substrate had commenced but the corrosion has not undercut the coating, as would occur in conventional coatings, and iron corrosion products were largely retained within the coating. Visually, the deterioration of the coating seems worse than it really is. The presence of the rust within the silicate matrix tended to reduce leaching of zinc corrosion products from the original sites of metallic zinc particles. With exposure to sea water, the zinc corrosion products that provided barrier protection with atmospheric exposure are lost by leaching and dissolution. Neither the marine environment nor the atmospheric environment appeared to have attacked the glassy silicate matrix.

![Inorganic zinc silicate coating after 2 years exposure to sea water at low tide. (Ref 5)](image2.png)

An owner would probably not require repair of an IZS coated structure unless there were regions showing red rust, that is having affected regions showing a local structure similar to that obtained after marine exposure. Red rust starts forming when the corrosion “front” reaches the steel surface and the steel starts corroding forming ferrous ions. Regions of low coating thickness will be the first to show this effect. The steel surface reacts with the oxygen and moisture causing the rust to form. Unlike zinc corrosion products, rust has a distinctive orange colour, and the steel corrosion products start filling the gaps within the silicate matrix. This gives the appearance...
that the surface is rusting, but in fact the rust is bound within the silicate matrix and is not the loose powdery material usually seen when steel corrodes. The amount of steel corrosion is quite small, and no pitting is apparent if this rusty region is blast cleaned from the surface. These patches of rust tend to grow very slowly as the coating weathers.

So, even if at first glance a degraded IZS coating looks like a badly rusted paint film, in fact there are features that mean the surface is in relatively good condition compared to a conventional paint film with the same degree of breakdown. The “rust” is in fact bound up within the silicate matrix and not as active, porous or non-adherent as normal rust. Any corrosion patches will slowly grow in area within the coating, rather than into the steel. Also, the corrosion is visible, unlike rusting on steel under a conventional coating where the invisible undercutting corrosion may be many times greater than the visible area. The unique nature of the corrosion of an IZS coated surface (the lack of undercutting is true for metallic zinc coatings as well) is the reason that such coatings can withstand a significantly greater degree of breakdown before maintenance is necessary (3), and can be left for a longer time without significant additional breakdown.

The first consideration with maintaining a degraded IZS coating then is that the breakdown is probably not as serious as it looks. If aesthetic issues are not important, little corrosion of the steel substrate is taking place, and any corrosion will be proceeding slowly. Maintenance may not be especially urgent. However, when aesthetic issues are important, maintenance is usually required when red rust appears, and this is discussed in the following sections.

4. TESTS ON RECOATING OF IZS

The main concern with recoating aged IZS systems is whether the repair coat will penetrate into existing coating, and whether there will be sufficient adhesion between the two coatings. As shown above, on a microscopic scale the repair coating appears to easily blend in with the existing coating. Tests have been carried out to determine if this also occurs in practice.

4.1 Recoating Adhesion Testing

Riding (6) reported the results of adhesion testing of a water borne IZS which had been exposed for 16 and 29 months, and then recoated with the same product after different types of surface preparation. Intercoat adhesion testing (Intersecting cut) was carried out on the front and rear of the test panels after a further 6 months and 12 months exposure after recoating. This trial made three important findings:

- The first finding was that the method of surface preparation (scrub with a brush, low pressure wash, scrub and wash, wash and sweep blast) made little difference to adhesion.
- The second finding was that adhesion improved significantly with time. After 6 months exposure, adhesion was poor on the front face of the panel exposed for 29 months, but improved after 12 months. Adhesion was good after 6 months for the panels originally exposed for only 16 months. There was little change after 12 months for these panels.
- The final finding was that adhesion on the back of the panel was significantly better for both initial exposure periods and subsequent exposure periods. This was believed to be due to accumulation of salts and more prolonged periods of condensation.

These results confirmed that IZS can be successfully applied to itself and perhaps most importantly, that adhesion will improve with time. The results also showed that the method of surface preparation was not critical, but it must be stressed that only limited weathering of the original IZS coating had taken place in this trial. This conclusion may not be applicable to heavily degraded coatings.

4.2 Repair Trials on Graham Street Overpass Beams

VicRoads, as manager of the Victorian arterial road network, has over 100 bridges and overpasses constructed from 1968 to the 1980s that were treated with a single coat of IZS. A survey carried out on a number of these some years ago (7) showed these to be in very good condition, especially compared to those coated with other coating systems. However VicRoads does have a number of bridges which show some break down of the inorganic zinc coating and needed to develop and trial appropriate procedures for their repair. A trial was set up in March 2003 using IZS coated beams on the Graham Street overpass, Port Melbourne (Figure 3), to assess methods of surface preparation and coating type to use. It is not the intention of this paper to describe the trial and its findings in detail, but rather record the results of tests where the aged IZS was prepared and coated with a new coating of IZS. The results with other coating types will be documented at a later date.

The four surface preparation methods trialed were low pressure water cleaning, pressure water cleaning with abrasive injection, sweep abrasive blasting and power tool abrading after pressure water cleaning. The surface
preparation was intended to clean and where appropriate roughen the surface of the zinc without removing any significant thickness of the zinc. The methods were chosen because they were either recommended by some paint manufacturers, or assessed as relatively simple site treatments for preparation of existing inorganic zinc silicate coating prior to recoat or topcoat. The surfaces prepared with these methods were overcoated with both solvent borne and water borne inorganic zins from major suppliers, following the individual manufacturer’s recommendations for application and film thickness. Preliminary examination was carried out after atmospheric exposure for 42 months. No rust or white zinc corrosion products were observed on any of the beams repaired with IZS. There were no observable differences between the IZS coatings applied over the different surface preparation methods. The adhesion and cohesion of the four solvent borne IZS coatings was tested using the knife test and all were found to be excellent (Figure 4). Water borne coatings appeared to perform similarly. This trial confirmed that IZS could be successfully applied to aged IZS, that the surface preparation method is not critical and that adhesion between the old and new coatings will not be a problem.

5. CASE STUDIES OF IZS REPAIR

5.1 Mannum Adelaide Pipeline Recoating
The 80 kilometre long Mannum Adelaide water pipeline was completed in 1958. Most of it was above ground and coated with heat cured IZS applied by brush to acid descaled steel with welded field joints reinstated with water borne IZS. There is no visible difference in the performance of the heat cured and field applied water borne coatings. Minor maintenance of the coating had been regularly undertaken by abrasive blasting and recoating of isolated locations of rust with both ethyl silicate and water borne IZS. Some sections were prepared by power tool cleaning and coated with a variety of products over the years and all have adequate adhesion and are providing acceptable performance. In 1987, twelve kilometres of the pipeline were low pressure water cleaned (LPWC) to remove dirt and chalked coating. Locations of rust were spot blasted using garnet abrasive and the whole pipeline was recoated with water borne IZS from two different suppliers. Cross-cut adhesion tests conducted soon after the first trial section was coated revealed less than full adhesion. Moreover, where surface preparation was inadequate and coating thickness excessive, poor adhesion resulted. However, a number of random tests after two years on both products indicated significantly improved adhesion. During water washing and subsequent abrasive blasting, some days elapsed between preparation and coating and concern was expressed regarding adhesion at locations where white rust had appeared on prepared surfaces. However, subsequent testing (after 2 years) at some of the known locations has not revealed reduced adhesion. After nine years, no peeling or flaking has been observed during random visual inspections (Figure 5).

5.2 Port Lincoln East Coast Pipeline
The above ground water pipeline on Eyre Peninsula along the coast from Port Lincoln to the Airport is laid within 100 metres of the coast. The pipeline was constructed in 1951 using factory applied heat cured IZS applied by brush to acid descaled steel with welded field joints reinstated with water borne inorganic zinc silicate. The pipe showed areas of brown staining and rust covering up to 5% of the pipe surface, largely restricted to the upper half of the pipeline. In mid 2007, the rusty regions were power tool cleaned using abrasive discs and a thin coat of water based IZS applied as a holding primer (Figure 6). This was followed by LPWC and application of 100 microns of water borne IZS applied to the upper two thirds of the pipeline. Adhesion testing after two weeks drying showed only moderate adhesion but, as discussed above, it is believed this will increase with further exposure.
5.3 Recoating of Duncans Road Overpass

An IZS coated overpass managed by VicRoads, Duncans Road overpass near Werribee, just south west of Melbourne, was rehabilitated in early 2007. The bridge was originally constructed using rolled sections in 1960, with the original coating being removed, the surface blast cleaned and re-coated with solvent-borne inorganic zinc in the late 1970s. By 2007, the girders exhibited red rust covering about 10 per cent of the surface in apparently random areas (Figure 7) and at expansion joints. Because of this random breakdown and the fact that the soffit was sheltered from the weather, it is assumed that breakdown was probably due to poor surface preparation or coating application, rather than weathering of the coating. However, the cause of the failure was not determined. In regions not affected by red rusting, the zinc was in good condition with a thickness of around 60 to 120 microns and showing good adhesion. Aesthetics were not important, so patch repair of the degraded regions was specified.

Affected regions were blasted to Sa2½ near white metal standard and surrounding regions brush blasted and feathered. No damage to surrounding areas from the abrasive was apparent. As discussed above, one of the advantages of a zinc-rich coating is that when it breaks down, there is no pitting on the steel substrate. This was observed on blast cleaned regions, with the steel manufacturer’s brand clearly apparent (Figure 8). Blasted regions were patch repaired with solvent borne inorganic zinc (Figure 9). Adhesion of repaired regions was excellent (Figure 10) as was adhesion of the new coating to the existing IZS. As the underside of this overpass is not visible or accessible, this scattered treatment was considered acceptable. Patch blasting and painting in this instance is effective and very economical, as the number of square metres treated was minimal and the work was carried out quickly. To have introduced an additional or more widespread cleaning process over the whole area of mostly sound coating, and to apply an additional coating, would significantly add to the cost of the project with little additional durability benefit.
6. OTHER ISSUES REGARDING RECOATING WITH IZS

As well as adhesion, application with IZS has other concerns among specifiers and applicators. Humidity, temperature and ambient conditions during application are important, with solvent borne coatings requiring high humidity and water-borne coatings low humidity and good air flow for proper curing. Application is critical, with storage, mixing, and application requiring skilled operators.

Mudcracking as a result of excessive thickness is one special concern. This arises when IZS is applied to excessive thickness. Application of the zinc to a uniform thickness in corners and other tight spaces between bridge girders is difficult and, as expected, there is often a wide range of film thicknesses in such situations. Where mud cracking and loss of adhesion have been observed in corners and edges (Figure 11) reblasting and recoating is required. However, it is only when the thickness reaches very high levels that this problem arises. Figure 12 shows a region of mudcracking barely visible with some spot thickness test results, indicating that it is only when the thickness reaches the order of 400 microns or so that mudcracking becomes visible. This is with one specific product and it may be that other products have different limits. It must be remembered that IZS is a porous coating and the cracks will fill up with corrosion products. As long as it is properly cured and adherent, mudcracking is far less of a problem with IZS than cracking in a conventional coating.

Another weakness claimed for IZS coatings for maintenance is that it must be sprayed and cannot be brushed. Brushing is often required for difficult regions and small repairs. However, spraying is not necessarily essential, although it is desirable. Small misses, badly mudcracked regions and regions of low thickness can be successfully repaired by brushing after cleaning (Figure 13), saving time and money. The finish is not as good, the DFT is low and brushing cannot be done for large areas, but the occasional use of the brush is acceptable.

Inorganic zinc silicate provides good protection in atmospheric environments, but is not recommended for exposure to flowing water. In the Duncans Road case study discussed above, regions of beams near the expansion joints showed more severe coating breakdown due to exposure to flowing water from the bridge deck. These regions were coated with a single coat of high solids epoxy to the manufacturer’s recommendations after the IZS had cured (Figure 14). Again, an additional coating would be required when aesthetics are important, but for economy and functionality a single coat of epoxy in water-affected areas is all that is required.
7. CONCLUSIONS

A single coat inorganic zinc silicate can provide excellent protection in a range of atmospheric environments. However, repair will be required at some stage. This paper has looked at how such coatings degrade, the results of trials to determine appropriate repair procedures, and successful repair case studies in Victoria and South Australia. These show that repair of single coat inorganic zinc can be carried out successfully and economically.

The key aspects of inorganic zinc silicate coating degradation and its repair are:

(a) The existence of red rust within a degraded inorganic zinc silicate coating does not necessarily indicate significant steel corrosion and the percentage breakdown that can be tolerated before repair is required is greater than for other coatings.

(b) Surface preparation of corroded areas before application of repair coating requires removal of the degraded coating and other contaminants. Brush blasting or power tool cleaning combined with a thorough pressure water wash is ideal. The actual extent of surface preparation and cleaning depends on the degree of coating breakdown.

(c) Either solvent borne or water borne coatings can be applied as repair coats, with selection depending on expected weather conditions and applicator skill.

(d) The initial adhesion of a repair coating is often only moderate, but will increase significantly with ageing and weathering. Adhesion of the repair coat after a year or so will usually be excellent with proper surface preparation and application.

REFERENCES

3. AS/NZS 2312 – Guide to the protection of structural steel against atmospheric corrosion by the use of protective coatings, Standards Australia, Sydney; 2002

(Papers 1, 5 and 6 are available in “Sixty Years of Inorganic Zinc Coatings”, R A Francis (ed), ACA, Melbourne, 1998)
Water-borne Silicates in Coatings and Construction Chemicals

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Keywords: Alkali silicates, Alkali carbonates, Efflorescence, Inorganic zinc silicates, Silicate emulsion paints, Water absorption, Water vapour permeability, Damp proofing.

1. Introduction
Water-borne alkali silicates have a long history in coatings applications but, particularly in overseas markets such as Europe, have gained greater prominence since the 1970s in the form of silicate emulsion coatings (also known as organo-silicate coatings). In this paper the history, production, formulation and applications of water-borne alkali silicates are discussed in areas such as:

- Silicate coatings
- Silicate impregnations
- Silicate emulsion coatings
- Silicate emulsion plasters

End markets for these products include:

- Architectural coatings
- Architectural renders
- Water-borne zinc rich protective coatings
- Masonry impregnation
- Water-borne consolidating primer
- Chemical damp-proofing

Silicate coatings are typically 2-component coatings (sometimes referred to as 2-K coatings) which have been used in Europe for architectural coatings since the late 1870s. Although still being used now, they suffer from the disadvantages of requiring mixing and permitting to mature before application.

Victor Nightingall essentially started the industry of 2-K inorganic zinc coatings in Melbourne during the 1940s. These were initially based on water-borne alkali silicate resins mixed with high proportions of zinc dust (essentially an analogue of the earlier 2-component coatings, although based on different pigments and designed for anti-corrosive applications rather than architectural applications). Subsequently these coatings were replaced by solvent borne ethyl silicates and were adopted in other parts of the World, particularly throughout USA and Europe. During recent times, with the reduction in VOC content of coatings, developments have returned to zinc rich silicate coatings based on water-borne silicates, essentially a case of the wheel of progress turning full circle!

Silicate impregnations may be and are being used in a number of areas including:

- The impregnation of concrete to achieve surface hardening
- The consolidation of weathered natural stone
- The incorporation of a chemical damp-proof course to act as a barrier against damp, particularly rising damp.

Silicate emulsion coatings were first introduced into the market in Europe in the 1960s, coming to prominence in the 1970s. With the experience of long-term stability of exterior coatings based on 2-K silicate paints as well as the benefits of organic emulsion paints with their attractiveness, ease of production and good storage stability, there was a desire for a single pack (1-K) coating system to
exhibit the properties of mineral paints together with ease of production, ease of application and
good storage stability. About 10-15% of the water-based architectural paint market in Europe is
based on silicate emulsion paints. Introduction into other markets including United States of America,
Asia and Australasia is occurring at the present.

Water-borne alkali silicates in coatings are believed to be harmless to the environment and exhibit
no significant health risks during application.

2. Background
In nature, it is understood that more than 95 volume % of the earth’s crust is composed of quartz and
a few rock-forming silicates. These include:
- Plagioclase, Na(AlSi$_3$O$_8$) - Ca(Al$_2$Si$_2$O$_8$) – 42% by volume
- Potassium Feldspars KAlSi$_3$O$_8$ – 22% by volume
- Quartz (or Silica) SiO$_2$ – 18% by volume

Other more complex silicates include Amphibole at 5% by volume and other silicates at 12% by
volume. Silicon compounds are also present in the hydrosphere, mainly as dissolved silica. Also, a
large number of silicates have been identified in extraterrestrial material. It is understood that man
as far back as 600,000 years ago has been using silica in the form of flint (which is a cryptocrystalline
silica called chert). In this form the crystals are so fine as to be indistinguishable except under
powerful magnification.

So it is probably appropriate to suggest that as materials “Silicates are very close to Nature”.
However for our particular discussion we are focused on soluble silicates (in particular on water-
borne alkali silicates) which may be used in applications such as coatings and construction chemicals.

It is understood that alkali silicates were produced by the ancient Egyptians some 6000 years ago,
where sodium (and possibly also potassium) silicates were produced by fusing together quartz sand
and naturally occurring soda ash or possibly potash produced from combustion processes. It is
believed that alkali silicates formed an important part of the frescos or wall paintings found in the
ruins of Pompeii and Herculaneum which were preserved by the eruption of Vesuvius in 79 AD.

The first description of the solubility in water of a fused mixture of flint pebbles with potash was
made by Jean Baptiste van Helmont (1577 – 1644), a Brussels physician in his posthumous work
“Ortus medicinae”, Amsterdam 1648. Independently, Johann Rudolph Glauber (1604 – 1670)
obtained a “thick” solution, which he named “Liquor Silicum” from a fused mixture of sand, flint
pebbles, or crystalline quartz with potash. Glauber recommended its use as a curative agent, for the
production of liquid fluxes in metal smelting, and for glazing earthenware vessels (Furni Novi
Philosophici, Amsterdam 1648 – 1650). Even the famous German poet, Johann Wolfgang von Goethe
became interested in potassium silicate in 1768, during the course of his alchemical studies.

Despite a number of references in the literature, the commencement of water-soluble silicates being
put to practical use occurs at about 1825 when Johann Nepomuk von Fuchs, Professor of Mineralogy
and Academician of Munich, who lived from 1774 to 1856 carried out his pioneering work and
investigated the industrial production of water-soluble potassium and sodium silicates, which he
named “waterglasses” (i.e., water-soluble glasses) He proposed their solutions could be used as
adhesives, cements, fire-proof paints, for sealing porous stone, and as binders for fresco painting. He
also coined the name “stereochromie” which was a technique of painting with silicate solutions
which he studied extensively. He observed the reactions of silicate solutions with various pigments,
and sought to explain in chemical terms such phenomena as precipitation by alcohol, the
efflorescence of sodium carbonate from a silicate solution which contained potash as its major base,
and the preparation of solutions with a high silica ratio by dissolving hydrous precipitated silica in
silicate solutions obtained by dissolving the glassy melts made in the furnace. He proposed silicates
as cleansing agents in the laundry directly and in admixture with soap, as reagents in textile dyeing, for fluxes in soldering and welding, and as fertilizers. By 1855 the year before von Fuchs died, water glass was being made commercially both in Europe and in America.

Meanwhile in Europe, on July 23, 1896, in the last days of the industrial revolution at the end of the 19th century, Eduard Woellner laid the foundations for the Woellner Group. At that time, his company, Woellner Werke in Ludwigshafen, produced a number of products, particularly waterglass, washing soda (hydrated sodium carbonate) and Glauber Salt (hydrated sodium sulfate).

Without dwelling any further on the historical aspects of water-borne alkali silicates, let us now move on to more present-day themes.

3. Properties of the Alkali Silicates
Firstly, looking at the Periodic Table of the Elements (Figure 1), the Alkali Metals are the Group 1A elements on the left hand side of the Periodic Table. Only the first three lithium (Li), sodium (Na) and potassium (K) are of commercial significance for our discussion.

![Figure 1: The Periodic Table](image)

3.1. Production of alkali silicates
As a starting point, it is worth commenting that to the best of my understanding, alkali silicates represent the only inorganic materials which are frequently used as binders in the coatings industry. Water-borne alkali silicates are entirely synthetic materials, generally of indefinite composition, manufactured by melting sand with sodium or potassium carbonate in glass-making furnaces at temperatures of above 1300°C, and the reaction is represented in Equation 1, where M = sodium (Na) or potassium (K):

\[
M_2\text{CO}_3 + n \text{SiO}_2 \rightarrow M_2\text{O} \times n \text{SiO}_2 + \text{CO}_2
\]

Equation 1

The molten glass is run from the furnace onto cooling conveyor belts, and the resulting soluble glass is dissolved in hot water under pressure where any insoluble glass and unreacted sand filtered off.
These are true glasses where they do not have any distinct stoichiometric constitution, but rather that the constitution depends upon the ratio of the raw materials in the above equation. The soluble silicates form clear or opalescent colloidal solutions in water which exhibit non-Newtonian viscosity behaviour at all but the lowest concentrations.

The factor $n$, shown in Equation 1 above is the ratio of silica to alkali-metal oxide, and is called the molar ratio (sometimes designated as $R_M$). Generally, the usual ratio referred to in common practical use is the weight (wt %) ratio sometimes designated as modulus, ($R_W$). However, the molar ratio, $R_M$, can be more useful, particularly when comparing ratios of lithium, sodium and potassium silicates. The conversion factors $R_M/R_W$ are shown in Table 1.

<table>
<thead>
<tr>
<th>Alkali Silicate</th>
<th>Chemical composition</th>
<th>Conversion factor Molar Ratio/Weight Ratio ($R_M/R_W$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>lithium silicate</td>
<td>Li$_2$O $\times$ n SiO$_2$</td>
<td>0.491</td>
</tr>
<tr>
<td>sodium silicate</td>
<td>Na$_2$O $\times$ n SiO$_2$</td>
<td>1.032</td>
</tr>
<tr>
<td>potassium silicate</td>
<td>K$_2$O $\times$ n SiO$_2$</td>
<td>1.568</td>
</tr>
</tbody>
</table>

Normal glasses which contain calcium, magnesium, and aluminium silicates are insoluble in water, whereas glasses which contain sodium ($Na^+$), potassium ($K^+$), can be dissolved in hot water to produce alkaline solutions of various viscosities. The change in viscosity for weight ratio, $R_W$ for the range of sodium silicates is shown in Figure 2.

![Figure 2: Viscosity curves for sodium silicates](image)

In some countries, different expressions of density are used for alkali silicate solutions. Thus, Twaddell was an arbitrary hydrometer scale used in England during the 19th to 20th centuries, and was derived as follows:

$$^*Twaddell = \frac{200 \times (\text{density of liquid at 60°F}) - 1}{\text{density of distilled water liquid at 60°F}}$$

Nowadays, it would be more routinely stated as:

$$^*Twaddell = \frac{200 \times (\text{specific gravity of liquid}) - 1}{\text{density of distilled water liquid at 60°F}}$$

Another scale, sometimes used for alkali silicate solutions is the Baumé Scale, which was derived in France to correlate to the percentage concentrate of a brine solution. Now, considering for liquids heavier than water (which applies to alkali silicate solutions) at a temperature of 20°C, it would be stated as:
specific gravity of liquid = \frac{145}{145 - °\text{Baumé}}

Finally to conclude this area of liquid density scales, Figure 3 shows the relationship between density, degrees Baumé and degrees Twaddell scales.

The change in viscosity for weight ratio, \(R_W\) for the range of potassium silicates is shown in figure 4. It can thus be seen that commercial alkali silicates are characterized by their solids content and the weight ratio \(R_W\) \(SiO_2: M_2O\) (where \(M\) is the alkali), which results in certain densities and viscosities.

The correlation between the alkalinity, expressed by increasing pH values, against concentration of alkali silicate for different weight (or molar) ratios is shown in Figure 5. It should be pointed out that pure caustic soda and caustic potash solutions exhibit linear pH curves which lie above the soluble silicate curves.
The correlation between the molar ratio and alkalinity, expressed by increasing pH values is shown in Figure 6.

![Figure 6: Alkalinity relationships of alkali silicates](image)

4. **Molecular structures of water-borne alkali silicates.**

As discussed above, water-borne alkali silicates are glasses which contain a wide variety of species. Using different physicochemical methods in examination of water-borne alkali silicates, the structures of various molecular species have been identified as anions which are monomers, dimers, trimers, tetramers, as well as branched chains, ring structures and 3-dimensional networks. These structures are shown in Figures 7.

![Figure 7: Molecular structures of alkali silicates](image)

Another way of viewing the silicate structures is shown in Figure 8. The repeating unit represents the tetrahedral Silicate group:
At varying alkali content levels, the oxygen atoms are present either as undissociated silanol (Si-OH) groups or as negatively charged anions (Si-O\(^{-}\)), with the counterion being the positively charged alkali cation (M\(^{+}\)). Dependent on concentration, alkalinity etc the distribution of monomeric, oligomeric and polymeric silicate groups in a solution is not fixed but is in dynamic equilibrium. There are two principal equilibria in the solution, these are:

The acid-base equilibrium:

\[
\text{Si-OH} + \text{K}^{+} \text{OH}^{-} \rightleftharpoons \text{Si-O}^{-} \text{K}^{+} + \text{H}_{2}\text{O} 
\]

Equation 2

The condensation polymerization or dissociation depolymerisation equilibrium:

\[
\text{Si-OH} + \text{HO-Si}^{-} \rightleftharpoons \text{Si-O-Si}^{-} + \text{H}_{2}\text{O} 
\]

Equation 3

Also there is the normally irreversible reaction with polyvalent cations such as Ca\(^{2+}\)

\[
\text{Si-O}^{-} \text{K}^{+} + \text{Ca}^{2+} + \text{K}^{+} \text{O}^{-} \text{Si}^{-} \rightleftharpoons \text{Si-O}^{-} \text{Ca}^{2+} + \text{O-Si}^{-} + 2\text{K}^{+} 
\]

Equation 4

These three reactions influence the physicochemical behaviour of silicate aqueous systems in addition to the curing mechanisms on application.

5. **Ratio of Silica to Alkali Oxide.**

The higher weight (or molar) alkali silicates (which contain relatively lower concentrations of alkali oxide, and in turn proportionately higher concentrations of silica) have understandably lower alkalinity and tend to be the main products used in coating applications. In fact, the ratio of silica to alkali oxide has a significant effect on the coating characteristics, as is shown in Table 2.
Table 2: Effects of different ratios

<table>
<thead>
<tr>
<th>The higher the ratio gives greater:</th>
<th>The lower the ratio gives the higher:</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscosity</td>
<td>specific weight</td>
</tr>
<tr>
<td>drying speed</td>
<td>solubility</td>
</tr>
<tr>
<td>curing speed</td>
<td>pH value</td>
</tr>
<tr>
<td>susceptibility to low temperatures</td>
<td>susceptibility to water influence</td>
</tr>
<tr>
<td>chemical resistance of coatings</td>
<td>tacking and binding power</td>
</tr>
</tbody>
</table>

6. Chemistry of cure of alkali silicates.

The curing process of alkali silicates can involve a number of various basic reactions either with the constituents of the substrate or with the components of air. These can be summarised as follows:

The reaction with burnt lime (calcium hydroxide), where M = sodium (Na), potassium (K) or lithium (Li):

\[
M_2O \times n SiO_2 + Ca(OH)_2 \rightarrow CaO \times SiO_2 + (n-1) SiO_2 + 2 MOH
\]

Equation 5

The alkali hydroxide can then react further with atmospheric carbon dioxide to produce alkali carbonate:

\[
2 MOH + CO_2 \rightarrow M_2CO_3 + H_2O
\]

Equation 6

The curing reaction with quartz sand, particularly on the surfaces of the particles:

\[
M_2O \times n SiO_2 + m SiO_2 \rightarrow M_2O \times (m+n) SiO_2
\]

Equation 7

The chemical curing with carbon dioxide from the air:

\[
2M_2O \times n SiO_2 + CO_2 \rightarrow M_2O \times (2n-1) SiO_2 + M_2CO_3 + SiO_2
\]

Equation 8

Incomplete silicification can occur with raising of the weight ratio (leading to higher viscosity):

\[
M_2O \times n SiO_2 + CO_2 \rightarrow n SiO_2 + M_2CO_3
\]

Equation 9

Observant readers will recognize that this is essentially the reverse of the reaction used to manufacture the alkali silicates in the first place from quartz and alkali carbonate. Complete silification results in insoluble silica gel formation, with physical water elimination by drying or freezing, can be represented as follows:

\[
M_2O \times n SiO_2 + z H_2O \rightarrow M_2O \times n SiO_2 + (z-y) H_2O
\]

Equation 10
As a consequence of this, the higher concentration leads to higher viscosity which leads to gelling. Incidentally, through the use of certain additives, this process can be produced on demand so that we can effectively accelerate the gelling process, if required.

As we can see from the above equations the inorganic alkali silicate binder systems can be cured in a variety of ways. In essence, the desired curing may be brought about by atmospheric carbon dioxide or by reactive constituents contained in the substrate. At the same time hardening of the coating may occur by physical water elimination, which may occur by water abstraction through heating or freezing. However in such situations, this may only be apparent hardening, such that when further contact with water occurs the coating may soften with the possibility of binder migration.

With properly applied and cured silicate coatings the physico-chemical bond between the binder system and the substrate can be very strong, such that these types of coatings are not regarded as film forming coatings but rather as coatings which essentially become the substrate. At the same time this cured binder produces a porous inorganic substrate with very high water vapour (and carbon dioxide) permeability. Such coatings can be of advantage particularly on historic buildings, (which can often be damp) as coatings on incompletely cured concrete. In the case of damp historic buildings, the passage of water vapour permits damp buildings to effectively dry out. For coatings on incompletely cured concrete, the passage of carbon dioxide is permitted to occur thus leading to subsequent carbonation (with consequent hardening of the concrete). Generally film forming coatings based on e.g. pure organic emulsion paints, although considered to be permeable, still hinder the passage of water vapour through the substrate, and have nowhere near as high a gas permeability as coatings based on silicates.

7. Carbonate Formation

7.1. Sodium silicates.

So far, we have been looking at the alkali silicates in order of increasing atomic number (i.e. lithium, sodium, and potassium). However in terms of general commercial importance by far the most important alkali silicates which are used in a wide variety of applications are the sodium silicates. Because they represent the greatest majority of alkali silicates manufactured, they are generally the most economic in production cost and selling price and tend to be the most used wherever possible. It has been suggested that some sodium silicates with particular molar ratios are suitable for coating purposes, and on first considering this it might be surprising that sodium silicates are not more commonly used in coating applications.

During curing of alkali silicates alkali carbonates are produced. Sodium carbonate exists in a number of forms with degrees of hydration (water of crystallization) as shown in Table 3.

<table>
<thead>
<tr>
<th>Degree of hydration</th>
<th>Other names</th>
<th>Molecular Formula</th>
<th>Solubility in Water (g/100 g) @ 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous</td>
<td>Soda Ash</td>
<td>Na₂CO₃</td>
<td>30.7</td>
</tr>
<tr>
<td>Monohydrate</td>
<td>Crystal carbonate; Thermonatrite</td>
<td>Na₂CO₃·H₂O</td>
<td>30.7</td>
</tr>
<tr>
<td>Decahydrate</td>
<td>Washing Soda; Natron; Natrite</td>
<td>Na₂CO₃·10H₂O</td>
<td>30.7</td>
</tr>
</tbody>
</table>

Note (1): Solubility in water is expressed as the grams of Sodium Carbonate (excluding water of hydration) which dissolve in 100 grams of water at 25°C.

As can be seen from the above table these carbonates existing in various degrees of hydration. The anhydrous product is hygroscopic to absorb water to form the decahydrate which tends to recrystallize to form a white efflorescence on the surface of the cured silicate coating. At the same time sodium silicate paints are mainly post-curing in nature and either require stoving at 175°C or the
use of a suitable catalyst to assist room temperature curing. In particular, this concern with efflorescence generally precludes the use of sodium silicate in most coating applications.

### 7.2. Potassium silicates.

In common with its sodium analogue, potassium carbonate exists in at least two forms with degrees of hydration (water of crystallization) as shown in Table 4.

**Table 4: Properties of potassium carbonate**

<table>
<thead>
<tr>
<th>Degree of hydration</th>
<th>Other names</th>
<th>Molecular Formula</th>
<th>Solubility in Water (1) (g/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous</td>
<td>Potash</td>
<td>$K_2CO_3$</td>
<td>111 @ 25°C</td>
</tr>
<tr>
<td>Sesquihydrate</td>
<td></td>
<td>$2K_2CO_3\cdot3H_2O$</td>
<td>111 @ 25°C</td>
</tr>
</tbody>
</table>

*Note (1): Solubility in water is expressed as the grams of Potassium Carbonate (excluding water of hydration) which dissolve in 100 grams of water at 25°C.*

However, as can be seen from the table, these potassium carbonates are not so water rich as the sodium carbonates. The anhydrous product is hygroscopic to absorb water to form the sesquihydrate, which is not hygroscopic, with a much lower tendency to crystallize, and generally does not produce white efflorescence because small amounts of potassium carbonate formed at the surface are relatively easily removed by rain when used particularly on exterior coating applications. At the same time, coatings based on potassium silicates are self curing and do not require the use of any added curing agent. However, when used as sole binders without any modification they tend to be relatively slow curing and can be susceptible to leaching out from the coating during the first 24 hours or so. One of the ways to overcome this has been the use of “High Ratio” potassium silicates, with molar ratios of $SiO_2:K_2O$ of 4.8:1 to 5.3:1, and there is an interesting NASA patent (now expired) which refers to the use of such “High Ratio” potassium silicates in 2-K inorganic zinc silicate coatings for anticorrosion protection coatings.

Because of this lack of efflorescence discussed above, we tend to see a significant use of potassium silicates in coating applications whether as 1-K silicate emulsion coatings or as 2-K inorganic silicate coatings.

### 7.3. Lithium silicates.

In contrast with its sodium and potassium analogues, lithium carbonate only exists as the anhydrous form with relatively low water solubility (which decreases with rising temperature), as shown in Table 5.

**Table 5: Properties of lithium carbonate**

<table>
<thead>
<tr>
<th>Degree of hydration</th>
<th>Molecular Formula</th>
<th>Solubility in Water (1) (g/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous</td>
<td>$Li_2CO_3$</td>
<td>1.30 @ 25°C</td>
</tr>
</tbody>
</table>

*Note (1): Solubility in water is expressed as the grams of Lithium Carbonate (excluding water of hydration) which dissolve in 100 grams of water at 25°C.*

Because lithium silicates have high molar ratios (i.e. they have a low alkali content) as well as the consequential lithium carbonate having such a low water solubility, lithium silicate finds uses in applications where the production of water-soluble by-products or any form of efflorescence is undesirable, including 2-K inorganic zinc silicate coatings as well as the strengthening or consolidation of masonry such as natural stone or concrete. It should be pointed out that lithium silicates are stable at and around room temperature, but precipitate on heating to >ca. 60°C. This effect is reversible upon cooling. Thus, they should not be used in heat accelerated systems.
8. Pure Silicate Architectural Coatings

The range of applications of alkali silicates is very wide, including adhesives, detergents etc., but for this discussion we will concentrate on coatings and related areas, in particular the 2-K silicates and the 1-K silicates in architectural coatings.

As discussed earlier, a number of workers experimented with alkali silicates and in 1879 Adolf Keim of Augsburg in Bavaria was granted German patent number 4315 for silicate-based mineral wall paints, as shown in Figure 10.

![Adolf Keim's 1879 Patent](image)

Figure 10: Adolf Keim’s 1879 Patent

To this day, the company known as Keim Farbe still bears his name, and is one of the best known companies worldwide involved in manufacturing and supplying of mineral-based paints. Such coatings have the following advantages:

- Silicate based masonry paints are suitable for indoor and outdoor applications.
- They can be supplied at an acceptable cost level.
- Their adhesion on to the siliceous masonry substrate is very high because of the chemical reactions between the binder and the masonry substrate.
- Silicate based masonry paints have excellent resistance to industrial gaseous pollutants.
- Silicate based masonry paints can provide the most superior exposure durability to weathering of all coatings.

A typical starting point formula is shown in Table 6. Mix Components A and B in a 3:1 ratio and allow to mature before application.

So if these coatings are so durable why are they not used more often nowadays? As can be seen from the formulation this is a 2-component (often referred to as 2-K) coating. It requires mixing on site, and needs to be left to ripen or mature for some time before they can be used on the substrate.

Also it would appear that these paints are unable to cure when the relative humidity drops below 20%. Whilst on the face of it, it would appear that this restriction of low relative humidity could be a barrier against the use of these coatings (and possibly also the 2-K zinc silicate coatings discussed in the next section), further examination suggest that this may not be such a concern. Australian Bureau of Meteorology data collected over a 30 year period (from 1961 to 1990) suggests that
conditions of relative humidity below 20% only typically occur in the afternoon in isolated locations such as Marble Bar and the Western Desert usually during the months around October. Looking at the Australian Bureau of Meteorology data, no Australian capital cities show average relative humidity below 20% at any time during the year.

Table 6: Formula for silicate masonry paint

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component A (Powder)</td>
<td></td>
</tr>
<tr>
<td>Marble filler with optimal storage</td>
<td>30.0</td>
</tr>
<tr>
<td>Silicate earth</td>
<td>20.0</td>
</tr>
<tr>
<td>Thicking agent</td>
<td>0.2</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>3.0</td>
</tr>
<tr>
<td>Zinc oxide pigment</td>
<td>11.5</td>
</tr>
<tr>
<td>Lithopone</td>
<td>6.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>10.0</td>
</tr>
<tr>
<td>Marble filler</td>
<td>9.1</td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>10.0</td>
</tr>
<tr>
<td><strong>Sub-total Component A</strong></td>
<td>99.8</td>
</tr>
<tr>
<td>Component B (Liquid)</td>
<td></td>
</tr>
<tr>
<td>Potassium silicate (e.g. Woellner Betolin™ type)</td>
<td>71.3</td>
</tr>
<tr>
<td>Water</td>
<td>28.4</td>
</tr>
<tr>
<td>Glycerine</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Sub-total Component B</strong></td>
<td>100.0</td>
</tr>
</tbody>
</table>

2-K coatings are still used nowadays, but apparently only in relatively special situations, and even then predominately by Master Painters who with appropriate care and attention can accommodate their disadvantages in mixing and application. The mechanism of cure of such coatings would be expected to follow the equations discussed in the earlier section on Chemistry of Cure.

9. Inorganic Zinc Silicate Coatings

Here it would be remiss to ignore the pioneering work carried out by Victor Nightingall, who essentially started the industry of inorganic zinc coatings in Melbourne during the 1940s. There is an excellent publication available from the Australasian Corrosion Association Inc, which reviews 60 years of this industry and it is recommended to anyone who are interested in this topic, although they are becoming scarcer daily! What I find of great personal interest in this topic is the fact that the industry started by Victor Nightingall has now become a worldwide industry, and yet outside of those involved in the specialised area of Anti-Corrosion Protective Coatings I am not sure that his contribution to the paint industry is well recognized. In fairness to the Australasian Corrosion Association, since 1997 (50 years after his passing) they have made an annual award known as the "Victor Nightingall Award" to honour a coatings specialist who has made an outstanding contribution to the protective coatings industry in Australia and New Zealand. A number of recipients of this award are and have been members of our association.

Victor Nightingall’s formal training was in the area of electrical engineering, (where he gained his only academic qualification), although he later carried out further studies in chemistry and chemical engineering. Possibly his first area of training encouraged him to look at the area of the prevention of corrosion, where he was most successful, despite carrying out other work in other relatively unrelated technical areas.

In the area of anticorrosion protection, he recognized the potential of silicate based coatings loaded with high levels of zinc. The silicate binders on which he carried out his work initially were the sodium silicates, presumably on the basis of cost and availability. The original product (referred to in
Australian patent number 104,231, lodged in 1937, with the title of “Improvements in and connected with silicated compositions” and shown in Figure 11) was composed of zinc dust which was mixed on site with a solution of sodium silicate to which a small amount of sodium carbonate (to produce carbon dioxide on heating to a temperature of nearly 100°C), and sometimes other pigments were incorporated. The cross linking and polymerization of the silicate ions formed polysilicic acid, and this silicate matrix reacted with the zinc to form a silica zinc polymer.

Such coatings were formulated to be typically applied onto steel surfaces such that the reaction which occurs between the steel, zinc particles and the silicate binder produced a complex chemical structure which effectively becomes part of the steel surface. Over the ensuing life of the coating further reactions occur with any residual alkaline silicate being neutralized (particularly by reaction with atmospheric carbon dioxide) producing a dense metal-like coating. Even zinc corrosion products which may be formed assist in filling the pores of the coating. Although other zinc rich coatings such as e.g. 2-K zinc rich epoxy coatings have also gained significant usage, it appears that inorganic zinc rich coatings can improve in durability with age in contrast with organic coatings.

As a postscript to the story of Victor Nightingall, the company which he was involved in founding was called Dimet Pty Ltd. In 1974 it was sold to PGH Industries, and after being owned by a number of companies it was acquired by Jotun of Norway in 1992 with its name disappearing in Australia in 1995. Its name however still lives on in various companies that were founded in a variety of countries, particularly in South-East Asia.

Subsequent developments in water-borne inorganic zinc silicate based coatings have focused more on potassium silicate as a binder. Potassium silicate coatings are self curing at ambient temperatures and do not require the addition of any curing catalyst, and on atmospheric exposure, they do not develop white carbonate efflorescent films, unlike those based on sodium silicates.
Unfortunately, under conditions of high humidity and low ambient temperature such coatings can cure relatively slowly with a water insolubility ranging from 1 hour to 24 hours or longer. Nevertheless from the early 1960’s to the late 1970s such inorganic zinc silicate coatings based on potassium silicate were the most generally used primers. Because in these coatings we are considering alkali silicates being used with a high loading of zinc dust and typically coated onto steel, then we do not expect to see the same types of reactions as we discussed earlier which were primarily on siliceous substrates such as masonry, where the presence of calcium ions is frequently encountered.

Initially, as the water evaporates from the alkali silicate/zinc coating, there is a concentration of binder with initial drying and primary deposition of the coating on the substrate. After evaporation of water, silicate prepolymer is formed as shown in the equation below:

\[
\begin{align*}
\text{Equation 11} \\
\end{align*}
\]

Insolubilization of the silicate matrix by reaction with zinc ions from the surface of the zinc particles, together with possibly ferrous (Fe$^{2+}$) from the steel substrate to form iron zinc silicate polymer as shown in the equation below:

\[
\begin{align*}
\text{Equation 12} \\
\end{align*}
\]

Subsequent to this, the silicate undergoes a hydrolysis reaction in the presence of carbonic acid (present in the atmosphere and formed from carbon dioxide and water) to produce polysilicic acid which then reacts further with the zinc ions present in the zinc dust to form a zinc silicate polymer which gives a 3-dimensional inorganic matrix structure. This final reaction, shown below, which takes many months to complete, is expected to occur at the surface of the coating with the atmosphere, and gradually moves through the depth of the coating down to the steel substrate. Over this period the cross-link density of the coating is increased such that a very hard, durable and dense coating is achieved.
Although this is not a central theme of this presentation, we should just mention that since the late 1970s the dominant binder used has been that of solvent-borne ethyl silicates, which after air drying for 20 to 30 minutes produce a coating which does not suffer from damage through exposure to early rain. Essentially the silicate binder produced from the tetra ethyl silicate reacting with water is similar to the silicate binder produced from water-borne alkali silicates, with ethanol being produced as a by-product rather than alkali carbonates, as shown below:

\[
\text{Si(OC}_2\text{H}_5\text{)}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH}
\]

Equation 13

Here we have simplified the situation, by ignoring the formation of the iron zinc silicate polymer as described above. Nevertheless, with the formation of the silica, through production of polysilicic acid, it can be considered to produce a similar zinc silicate polymer giving way to a 3-dimensional inorganic matrix structure essentially similar to that produced using the water-borne alkali silicate.

The above tetra ethyl silicate systems are normally 2-K, in other words one pack normally contains binder while the other contains the other ingredients (generally powder) including pigments. Usually these systems are mixed on-site just prior to applications in accordance with the manufacturer’s specification. It is appropriate to point out that 1-K tetra ethyl zinc rich silicate systems do exist where free water (as opposed to chemically bound water) has been excluded to avoid gassing problems. However whilst these have the attractiveness of not requiring mixing on-site, they are extremely difficult to formulate successfully such that an acceptable shelf life of such a 1-K system is guaranteed. It is believed that such 1-K systems only form a very small proportion of the commercial market.

With the emphasis on environmental acceptability, and reducing the use of solvents in coatings, as well as simplifying cleanup (using water instead of solvent), it is significant to see that one of the major anticorrosion paint manufacturers has recently relaunched a water-borne inorganic zinc silicate coating for corrosion protection. Other companies appear to have had such products on their product range for a number of years. Possibly there is an increased emphasis on water-borne alkali zinc silicate coatings, which seems to be fulfilling a forecast made a number of years ago that with the changes in environmental requirements of coatings, the emphasis on such coatings was expected to grow in the future. Looking back at the original work carried out by Victor Nightingall, perhaps one might say this is an example of the wheel somewhat turning full circle!

Lithium silicates with a silica ratio of up to 8.5:1 are generally used to formulate water-borne inorganic zinc coatings. They have the advantages of also being self curing at ambient temperatures, having long pot lives and can develop good water resistance within an hour of application. They have
the best performance in anticorrosion protection of any water-borne inorganic zinc silicate coating, because they have the lowest alkali content, producing higher binding power and less efflorescence. Also, as discussed earlier, any lithium carbonate that is produced during curing is water insoluble and should therefore not provide any path of weakness of the coating. Cured films are regarded as being similar to those of baked sodium silicate binders and are characterized by great hardness, durability and abrasion resistance. I recall a colleague involved in the protective coatings industry who was involved in the supply of anti-corrosion protective coatings telling me that such coatings were used in the marine industry on decks of ships (as well as on the insides of tanks) where their abrasive resistance would certainly be tested and were found to be superior. A typical starting formulation is supplied as Table 7. Mix Components A and B in a 1:1 ratio and mix homogeneously. Unfortunately lithium silicate is a somewhat more expensive binder than potassium silicate, and on the basis of achieving an appropriate economic level of protection and durability it would appear that blends of potassium and lithium silicates are more commonly used.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component A (Powder)</td>
<td></td>
</tr>
<tr>
<td>Zinc dust, ca. 7µ</td>
<td>75.0</td>
</tr>
<tr>
<td>Chromium (III) oxide green</td>
<td>5.0</td>
</tr>
<tr>
<td>Muscovite mica MU – M 2/1</td>
<td>18.0</td>
</tr>
<tr>
<td>Natural bentonite – NA (Wyoming)</td>
<td>1.0</td>
</tr>
<tr>
<td>Woellner Betolin™ V 30, thickener</td>
<td>0.2</td>
</tr>
<tr>
<td>Sub-total Component A</td>
<td>99.2</td>
</tr>
<tr>
<td>Component B (Liquid)</td>
<td></td>
</tr>
<tr>
<td>Lithium silicate (e.g. Woellner Betolin™ Li 24)</td>
<td>99.4</td>
</tr>
<tr>
<td>Dispersant (e.g. Woellner Sapetin ™ D 20)</td>
<td>0.4</td>
</tr>
<tr>
<td>Alkali stable wetting agent</td>
<td>0.2</td>
</tr>
<tr>
<td>Sub-total Component B</td>
<td>100.0</td>
</tr>
</tbody>
</table>

10. Silicate emulsion coatings

With the experience of long-term stability of exterior coatings based on 2-K silicate paints as well as the benefits of organic emulsion paints with their attractiveness, ease of production and good storage stability, there was a desire for a single pack (1-K) coating system to exhibit the properties of mineral paints together with ease of production, ease of application and good storage stability. Requirements of such a 1-K coating system were to include the following:

- Ready-to-use products
- Easy and fairly quick production
- Proper rheological behaviour
- Stabilization of binder — filler/pigment system against reagglomeration
- Good storage stability (shelf life at least one year)
- Small degree of syneresis and sedimentation
- Good redispersibility on stirring
- Good application properties
- Sufficient diffusion into substrate for strong adhesion and surface hardening
- Reinforcement of substrate
- Good and equal colour retention on the substrate
- Perfect curing without chalking
- Good weathering stability
- Maintenance of easy water vapour permeation

1-K Silicate emulsion systems were created to satisfy these criteria in the areas of paints and plasters.
10.1. Main constituents of silicate emulsion coatings
The main constituents of silicate emulsion paints and plasters are:
- Water
- Inorganic binder (typically potassium silicate such as Betolin™)
- Organic binder (typically styrene acrylic dispersions or other alkali-stable organic dispersions)
- Fillers
- Pigments
- Additives

In order to maintain the essentially inorganic nature of the coating on the masonry substrate (typically a wall) and the water vapour permeability, the total level of organic content must be restricted. The German standard DIN 18 363 which refers to painting and coating defines silicate emulsion paints as those containing no greater than 5% w/w of organic content based on the total mass of formulated product as determined by the loss on ignition at 450°C/2h of a material pre-dried at 200°C/2h.

The formulation of a silicate emulsion paint is an easy process, although it should be pointed out that the individual components can cause complex interactions. Understandably, the choice of raw materials and the process of addition is important for the quality of silicate emulsion paints and plasters.

10.2. Selection of organic polymer emulsion for silicate emulsion coatings.
A point in question is the selection of the organic polymer emulsion which is suitable for mixing with the potassium silicate. Here a compatibility test is carried out between the potassium silicate and the organic polymer emulsion using the starting point formula in Table 8.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>70</td>
</tr>
<tr>
<td>Organic polymer emulsion</td>
<td>10</td>
</tr>
<tr>
<td>Potassium silicate (e.g. Woellner Betolin™ P35)</td>
<td>20</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100</td>
</tr>
</tbody>
</table>

The procedure followed is:
1. Dilute organic polymer emulsion with water.
2. Slowly add potassium silicate under stirring.
3. Give the system a little time to defoam (according to requirement, maximum time is approx. 1-2 hours).
4. Pour the mixture over a glass plate and examine the resulting film.
5. The film should be clear without any spots, particles or irregularities.
6. Repeat the test after one week storage of the mixture in an oven at 60°C.

10.3. Production of silicate emulsion coatings and plasters
Normally after preparation, silicate emulsion paints and plasters are permitted to stand for up to a week. During this period the viscosity performs thickening such that the final viscosity is achieved.

The nature of the thickener is critical as well as the interaction with the binder, the temperature and choice and purity of raw materials. It is therefore recommended that stock mixtures be prepared and sufficient quantities of these to be kept in store. In particular this applies to textured finishes, because grain size distribution can be obtained for the individual qualities. The physico-chemical interaction of the components is directed by certain hydration and swelling processes and by:
Forces of repulsion
- Horn approximation (collision diameter)
- Coulomb repulsion (electrostatic forces)
- repulsion by adsorbed polymer particles

Forces of attraction
- Van der Waals forces (dispersion and induction forces)
- dipole-dipole orientation
- hydrogen bridging bonds
- electrostatic attraction by interfacial charges
- formation of polymer bridges

10.4. Formulation, assessment and production of silicate emulsions

Typically the formulation components which are involved are as follows:

**Binders**
- inorganic
  - potassium silicate solutions
  - pre-stabilized potassium silicate solutions
    (mostly recommended)
- organic
  - polyacrylates
  - styrene acrylates
  - terpolymers

**Fillers**
- quartz
- calcite
- clay
- talc
- barytes
- Neuburg chalk
- fibrous materials
- plasterite
- Na-Al-silicates

**Pigments**
- titanium dioxide
- lithopone
- inorganic unreactive pigments (e.g. inert iron oxides, BaSO$_4$ etc)

Without trying to single out any particular area of concern, the choice of suitable fillers and pigments is very important, and they should not contain any reactive polyvalent cations (Ca$^{2+}$, Mg$^{2+}$, Al$^{3+}$, Fe$^{3+}$), since the presence of these can cause thickening and possibly gelling of formulations. As an example for this reason, the use of dolomite fillers should be avoided.

**Additives**
Additives which may be used in silicate emulsion systems include:
- Dispersants: polyphosphates, polyacrylates, phosphonates, naphthene and lignin sulfonates
- Wetting agents: anionic, cationic, amphoteric and non-ionic surfactants
- Defoamers: silicon emulsions, hydrocarbons, long chain alcohols etc.
- Stabilizers: special polyfunctional, mostly cationic compounds
- Coalescents (if needed): alkali-stable esters, glycols, hydrocarbons
- Rheological additives: cellulose derivatives (CMC, HEC), xanthan gums, polyurethane, polyacrylate, modified starch, bentone and other lamellar silicates
- Water repellents: alkyl silicones, siloxanes, wax emulsions, fatty acid Li salts
- Biocides: (Generally, due to their alkalinity silicate emulsion paints and plasters do not need special in-can preservatives, but it may be necessary to incorporate special algacides or fungicides for film preservation).

The pH of the final silicate emulsion paint or plaster is expected to be typically in the area of 10.0 to 10.5, and so any additives should be resistant to saponification at that level of alkalinity.
As discussed earlier, to screen test for good long term stability of the products (aiming for a shelf life of at least 1-2 years), it is recommended that each raw material be tested in a standard testing formula, as shown in Table 9 for a silicate emulsion paint. The silicate emulsion paint/plaster is produced according to the standard testing formula, and samples are stored in closed containers:
- at room temperature (about 20°C)
- at elevated temperature of say 60°C (for accelerated stress testing)

### Table 9: Silicate Emulsion Paint

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>17.2</td>
<td></td>
</tr>
<tr>
<td>Dispersing agent (e.g. Woellner Sapetin™ type)</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Thickening agent</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Stabilizer (e.g. Woellner Betolin™ Q type)</td>
<td>0.5</td>
<td>dissolve</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>Defoamer</td>
<td>0.2</td>
<td>dissolve</td>
</tr>
<tr>
<td>Filler (carbonate type)</td>
<td>30.0</td>
<td>add with stirring</td>
</tr>
<tr>
<td>Filler (silicate type)</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Polymer dispersion</td>
<td>8.0</td>
<td>add and stir for about</td>
</tr>
<tr>
<td>Butyl diglycol</td>
<td>0.5</td>
<td>10 minutes</td>
</tr>
<tr>
<td>White spirit</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Potassium silicate (e.g. Woellner Betolin™ type)</td>
<td>24.6</td>
<td>add and stir to</td>
</tr>
<tr>
<td>Rheological additive/viscosity regulator (e.g. Woellner Betolin™ type)</td>
<td>0.5</td>
<td>homogeneity</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.4</td>
<td></td>
</tr>
</tbody>
</table>

After being stored for one day and then at defined intervals of up to at least 30 days the quality is assessed with regard to the following parameters:

**Silicate emulsion paint/plaster properties, including:**
- Syneresis (water on top of system)
- Deposition of solids
- Stirrability
- Viscosity development
- Thixotropy
- Agglomeration or coagulation

**Silicate emulsion paint/plaster application properties, including:**
- Hiding power
- Wash and scrub resistance
- Very low chalking

It should be possible to formulate and produce stable products using strictly quality controlled pure potassium silicate solutions, however the use of pre-stabilized potassium silicate products can provide a much easier path to develop a suitable formula with consistent quality over the life of the product.

In Figures 12 and 13 below, we can see the different behaviour of silicate emulsion paints based on unstabilized and pre-stabilized potassium silicates in regard to the shear stress ($\tau$, in units of tau/Pa) against shear rate ($\dot{D}$, in units of rotations per second). These graphs compare measurements in the upwards curve (signified as + on the graphs) against the downwards curves (signified as x on the graphs) with the development of thixotropy expressed by the areas under the curves. It is quite apparent, particularly with the testing at 60°C, that there is an undesirably much greater increase in
viscosity and development of thixotropy in the silicate emulsion paint based on the unstabilized potassium silicate than with the one based on the pre-stabilized potassium silicate.

Figure 12: Rheology of silicate emulsion paint with unstabilized potassium silicate

Figure 13: Rheology of silicate emulsion paint with pre-stabilized potassium silicate

**Silicate binder contents**
The paint in the testing formula described above contained about 6.9% of potassium silicate, based on the use of 24.6% w/w of 28% w/w solids of potassium silicate solution. We recommend that the effective amount of potassium silicate in the finished formulated product should be as in Table 10.

**Table 10: Recommended Levels of Potassium Silicate**

<table>
<thead>
<tr>
<th>Application</th>
<th>Recommended Potassium Silicate solid content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exterior paints</td>
<td>Ca 4.5-7.0%</td>
</tr>
<tr>
<td>Interior paints</td>
<td>Ca 3.5-5.0%</td>
</tr>
<tr>
<td>Plasters</td>
<td>Ca 2.0-4.0%</td>
</tr>
<tr>
<td>Brush or spray plasters</td>
<td>Ca 3.0-5.0%</td>
</tr>
<tr>
<td>Primers</td>
<td>Ca 5.5-8.5%</td>
</tr>
</tbody>
</table>
As the silicate binder content increases, generally the following will be observed:

- Higher viscosity
- Less tendency to thicken on storage
- Significantly larger thixotropy areas
- Slight increase in spreading resistance on application
- Less easy levelling
- Higher tendency of 'burning up', especially on warm and dry substrates
- Slightly higher tendency for white efflorescence
- Higher tendency for colour variation on different substrate surfaces
- Slightly lower water resistance at the beginning of the curing period

**Polymer dispersion content**

As the organic polymer dispersion content increases, generally the following will be observed:

- Slight increase in viscosity
- Slightly smaller thixotropy areas
- Sometimes less tendency of colour variations on different substrates
- Earlier water resistance

### 10.5. Performance of silicate emulsion paints

Below, we provide our recommendations regarding the suitability of various substrates for coating with silicate emulsion paints and plasters. Silicate emulsion paints can be applied on most mineral and also various other substrates, such as:

- Fresh or set high calcium lime-sand mortar (interior)
- Fresh or set lime-cement-sand rendering
- Fresh or set cement rendering
- Concrete surfaces (after removal of formwork and release agent residues)
- Sand-lime-brick masonry
- Brick masonry
- Fibre cement (e.g. cellulose fibre cement) boards
- Metal surfaces, especially aluminium and galvanized iron

Silicate emulsion paints can be fairly suitably applied (after pretreatment or where necessary with specially formulated products) on:

- Natural stone (depending also on stone type)
- Kiln fired brick
- Aerated cellular concrete (very porous, causing high absorption)
- Inorganic foamed insulation materials
- Iron surfaces (e.g. interior fire proofing coatings)
- Fresh limewash coatings
- Old limewash coatings
- Old strongly adherent emulsion paint coatings (water vapour permeation will not be obtained)

Silicate emulsion paints are unsuitable for application (or only after special pretreatment with specially formulated products) on:

- Gypsum finish (pretreatment strictly required)
- Particle boards
- Existing oil paint coatings
- Fatty or oily or strongly soiled surfaces
- Plastic surfaces
All substrate surfaces should be of such condition that good but not unnecessarily high penetration of the paint into the pores and capillaries can be achieved. For example, cement or lime sinter surfaces on concrete or plaster are pretreated only if really necessary with a fluorosilicate etching liquid to reduce absorption. Where highly absorbent or an evenly absorbed substrates are encountered, it is recommended that a diluted silicate emulsion paint or a special silicate emulsion primer as shown in Table 11 should be used:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>69.5</td>
</tr>
<tr>
<td>Styrene acrylate emulsion (e.g. BASF Acronal™ S 559 or S620; Alberdingk SC 4400 or AS 6800; Celanese Mowilith™ DM 6119 or DM 765A)</td>
<td>0.5</td>
</tr>
<tr>
<td>Stabilizer (e.g. Woellner Betolin™ A11)</td>
<td>0.5</td>
</tr>
<tr>
<td>Potassium silicate (e.g. Woellner Betolin™ K28, P35 or P50)</td>
<td>20.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Depending on substrate conditions, a 1:1 dilution with water, or a mixture 1 part water/ 1 part primer / 1 part silicate emulsion paint may also be applied. It should be applied preferably using a brush. Generally, one coat of silicate emulsion paint is applied by brush or paint roller, waiting at least 12 hours after application of the silicate primer.

Whilst silicate emulsion paints have a very high gas permeability, they also have a very high water absorption. To therefore minimize/prevent absorption of water onto the cured silicate emulsion coating, the addition of a water repellent is recommended, or an additional impregnation with water repellent is applied as the last coat. The water repellent should only be included in the final coat, or else this may give rise to adhesion problems when subsequent coats are applied.

The most suitable weather conditions for the application of 1-K silicate emulsion paints and plasters are:

- Temperatures between +5 and +25°C (during and at least 48 hours after application)
- Moderately high relative humidity (but no rain)
- No strong sunshine heat on the walls
- No dry warm wind

Where for reasons of geography or other reasons it is impossible to ensure such situations as the above, certain application methods or adjustments to the formulations may be required to overcome any difficulties.

The properties of appropriately applied and cured silicate emulsion paint coatings compared with other systems are shown in Tables 12 and 13.
Table 12: Selection Criteria for the Application of Various Coating Systems (Part 1):

<table>
<thead>
<tr>
<th>Property</th>
<th>Area</th>
<th>Emulsion Paints (A)</th>
<th>Limewashes (B)</th>
<th>1-K Silicate Emulsion Paints (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>Commercial</td>
<td>Inexpensive</td>
<td>Inexpensive</td>
<td>Inexpensive</td>
</tr>
<tr>
<td>Binder</td>
<td>Coating property</td>
<td>Polymer Dispersion</td>
<td>Lime</td>
<td>Potassium Silicate + Polymer Dispersion</td>
</tr>
<tr>
<td>Manufacturing</td>
<td>Coating formulation</td>
<td>Easy, possible without experience</td>
<td>Easy, possible without experience</td>
<td>Easy for expert, take note of high alkalinity</td>
</tr>
<tr>
<td>Pigment Types</td>
<td>Almost unlimited</td>
<td>Inorganic pigments</td>
<td>Inorganic pigments</td>
<td>Inorganic pigments</td>
</tr>
<tr>
<td>Coating Property</td>
<td>Thermoplastic to elastic</td>
<td>Rigid</td>
<td>Rigid</td>
<td>Rigid</td>
</tr>
<tr>
<td>Odour</td>
<td>Nil to high odour, dependent on dispersion type and formulation</td>
<td>Nil odour</td>
<td>Nil to low odour</td>
<td>Nil to low odour</td>
</tr>
<tr>
<td>Hiding Power</td>
<td>Good hiding power, dependent on formulation</td>
<td>Low hiding power</td>
<td>Good hiding power, dependent on formulation</td>
<td>Good hiding power, dependent on formulation</td>
</tr>
<tr>
<td>Suitable substrates</td>
<td>Coating application</td>
<td>All surfaces except lime plaster</td>
<td>Primarily mineral substrate</td>
<td>Primarily mineral substrate (but with appropriate formulation)</td>
</tr>
<tr>
<td>Suitability on Concrete</td>
<td>Set concrete surfaces (not until after 28 days curing)</td>
<td>Not known</td>
<td>Fresh or set concrete surfaces</td>
<td>Fresh or set concrete surfaces</td>
</tr>
<tr>
<td>Unsuitable substrates</td>
<td>All surfaces except lime plaster</td>
<td>Exposed and aerated concrete, brickwork, and sand-lime bricks</td>
<td>Particle boards, existing oil paintings, fatty or oily or strongly soiled surfaces</td>
<td>Particle boards, existing oil paintings, fatty or oily or strongly soiled surfaces</td>
</tr>
<tr>
<td>Water release</td>
<td>Very slow</td>
<td>Fast</td>
<td>Fast</td>
<td>Fast</td>
</tr>
<tr>
<td>Temperature Restrictions</td>
<td>Best applied at temperatures between 5-30°C</td>
<td>Not known</td>
<td>Best applied at temperatures between 5-30°C</td>
<td>Best applied at temperatures between 5-30°C</td>
</tr>
<tr>
<td>Penetration of binder into mineral substrate</td>
<td>Uncured coating property</td>
<td>Almost none</td>
<td>Almost none</td>
<td>Up to 6-7 mm</td>
</tr>
<tr>
<td>Fixing and Reinforcing Capacity for structure</td>
<td>None to low</td>
<td>None</td>
<td>Moderate to good</td>
<td>Moderate to good</td>
</tr>
</tbody>
</table>
Table 13: Selection Criteria for the Application of Various Coating Systems (Part 2):

<table>
<thead>
<tr>
<th>Property</th>
<th>Area</th>
<th>Emulsion Paints (A)</th>
<th>Limewashes (B)</th>
<th>1-K Silicate Emulsion Paints (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding Type</td>
<td>Cured Coating Property</td>
<td>Adherent film on substrate</td>
<td>Cohesive weak physicochemical bonding to substrate</td>
<td>Cohesive strong physicochemical bonding to substrate</td>
</tr>
<tr>
<td>Coating Property</td>
<td></td>
<td>Thermostatic to elastic</td>
<td>Rigid</td>
<td>Rigid</td>
</tr>
<tr>
<td>Flexibility</td>
<td></td>
<td>Good flexibility, dependent on dispersion type and formulation</td>
<td>None</td>
<td>Slight flexibility, can be regulated within certain limits</td>
</tr>
<tr>
<td>Covering of Capillary cracks</td>
<td></td>
<td>Fairly good</td>
<td>No elastic covering, but filling of fine cracks</td>
<td>No elastic covering, but filling of fine cracks</td>
</tr>
<tr>
<td>Water and Driving Rain Resistance</td>
<td></td>
<td>Good to very good</td>
<td>Low</td>
<td>Good</td>
</tr>
<tr>
<td>Capillary Water Absorption</td>
<td></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Water Vapour Permeability</td>
<td></td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Carbon Dioxide Permeability</td>
<td></td>
<td>Dependent on dispersion type and formulation</td>
<td>Poor</td>
<td>Good weathering resistance depends on silicate type</td>
</tr>
<tr>
<td>Weathering Resistance</td>
<td></td>
<td>Dependent on dispersion type and formulation</td>
<td>Good UV resistance</td>
<td>Good UV resistance</td>
</tr>
<tr>
<td>Ultra Violet Resistance</td>
<td></td>
<td>Good fading resistance, dependent on dispersion type and formulation</td>
<td>Very good fading resistance</td>
<td>Very good fading resistance</td>
</tr>
<tr>
<td>Fading resistance</td>
<td></td>
<td>Poor to good solvent resistance, dependent on dispersion type and formulation</td>
<td>Good solvent resistance</td>
<td>Good solvent resistance</td>
</tr>
<tr>
<td>Solvent Resistance</td>
<td>Cured Coating Property</td>
<td>Poor to good solvent resistance, dependent on dispersion type and formulation</td>
<td>Good solvent resistance</td>
<td>Good solvent resistance</td>
</tr>
<tr>
<td>Acid Rain Resistance</td>
<td></td>
<td>Good acid rain resistance, dependent on dispersion type and formulation</td>
<td>Poor acid rain resistance</td>
<td>Good acid rain resistance</td>
</tr>
<tr>
<td>Dirt pickup</td>
<td></td>
<td>Low to high, according to recipe respectively binder</td>
<td>Low to high, according to recipe</td>
<td>Low</td>
</tr>
<tr>
<td>Chalking resistance</td>
<td></td>
<td>Good to very good</td>
<td>Excellent</td>
<td>Good to excellent, depends on silicate type</td>
</tr>
<tr>
<td>Scrub resistance</td>
<td></td>
<td>Good to very good</td>
<td>Poor</td>
<td>Good to very good</td>
</tr>
<tr>
<td>Angle of brightness/Appearance</td>
<td></td>
<td>Adjustable across formulation</td>
<td>Matt finish “naturally” shaded</td>
<td>Matt finish “naturally” shaded</td>
</tr>
<tr>
<td>Overpaintability</td>
<td></td>
<td>Can be overpainted with (C)</td>
<td>Can be overpainted with (C)</td>
<td>Can be overpainted with (C)</td>
</tr>
</tbody>
</table>

In addition to the properties of cured paint coatings such as appearance and mechanical strength etc, which allow focus on the area of water absorption and water vapour permeability. These are relevant to the heat insulation properties and heat exchange behaviour of the wall system. To prevent build up of humidity in the exposed exterior wall, it is necessary that any moisture absorbed during a rain period is quickly and totally released again during dry periods. The German standard DIN 18 558 defines that the product of the water absorption coefficient, \(w\) (kg/m²h⁰.⁵) and the water vapour diffusion resistance coefficient \(s_d\) (m) should be lower than 0.2 (kg/mh⁰.⁵⁻¹). Thus, \(w \times s_d < 0.2\) (kg/mh⁰.⁵⁻¹), \(w < 0.5\) (kg/m²h⁻⁰.⁵) and \(s_d < 2\) m. This applies to polymer improved plasters claiming good rain resistance. For external walls which are exposed to severe driving rain, to provide good protection, \(w \times s_d < 0.1\) (kg/mh⁰.⁵⁻¹).

In order to meet both of these conditions both properties must be well adapted to each other. Generally, the water absorption coefficient, \(w\) of silicate emulsion paints in category II (water repellent) range from 0.1-0.5 kg/m²h⁻⁰.⁵. Where additional water repellent has been applied then they will come in category I (water impermeable) with water absorption coefficient, \(w < 0.1\) kg/m²h⁻⁰.⁵. 
As regards water vapour diffusion resistance coefficient $s_d$, this is typically for silicate emulsion paints in category II (water vapour permeable) and range from 0.1-0.5 m. Suitable formulation and application of silicate emulsion paints can meet the above conditions.

Finally, it is appropriate to comment that the water absorption coefficient is deeply influenced by the type and amount of:
- Inorganic binder (potassium silicate)
- Organic polymer dispersion
- Water repellent

The above are demonstrated in Figures 14, 15 and 16.

As can be seen, an increase in potassium silicate concentration results in increases in water absorption of the 1-K silicate coating system.

As can be seen, an increase in organic polymer emulsion concentration results in decreases in water absorption of the 1-K silicate coating system.
The last graph in Figure 16 shows the reduction in water absorption when water repellent is included in the silicate emulsion paint formulation (the lower curve showing the effect of incorporation of water repellent).

10.6. Ignition and fire resistance behaviour of silicate emulsion coatings and plasters.
Generally, according to German standards, coatings with thicknesses below 0.5 mm are not subject to classification in different classes of flammability. So, the flammability of silicate emulsion paints usually do not have to be considered. However silicate emulsion plasters, particularly where used for interior applications, need to be considered because their thickness is typically greater than this. Depending on the total content of organic materials, silicate emulsion plasters are either classified in:
- class A2: non-flammable construction materials (lower contents of organic additives), or in
- class B1: hardly flammable construction materials (somewhat higher contents of organic additives).

No indication exists that silicate emulsion plasters have in any case aggravated an outbreak of fire or that serious quantities of noxious gases have been evolved. Because the proportion of organic materials in silicate emulsion paints and plasters are significantly lower than that in standard emulsion paints or plasters the potential hazard is significantly lower, and might even be considered as negligible.

10.7. Main advantages, preconditions and restrictions of silicate emulsion paints and plasters.
The main advantages of 1-K silicate emulsion paints and plasters are:
- Ready-to-use products
- Good storage stability with long shelf life
- Fairly easy application with good workability
- No significant health risk during application
- No allergenic potential from silicate binders
- Zero VOC systems may be formulated using zero VOC organic emulsions
- Applicable to a wide range of substrates (Sometimes pretreatment may be necessary)
- Also compatible with relatively fresh plasterings containing active alkalinity
- Appropriate for interior and exterior application on new and old buildings
• Adequate technical properties of the cured coatings
• Fixing and reinforcement of mineral substrate structure
• “Natural” looking matt surface appearance with good colour stability
• Open pore character of cured coating with excellent water vapour permeability
• Low tendency of dirt pickup, self-cleaning behaviour
• Good heat insulation properties of wall systems
• Long term stability also under varying humidity of the substrate leading to a good economic lifetime
• High resistance against atmospheric influences
• No special hazard in case of fire
• Acceptable cost level
• High eco-compatibility

The main preconditions and restrictions of 1-K silicate emulsion paints and plasters, which should be observed are:
• Scrupulous selection and examination of raw materials
• Careful formulation and testing
• Appropriate instruction concerning application
• Critical selection, inspection and if necessary pre-treatment of substrates
• Protection of alkali susceptible areas (glass, lacquered surfaces, anodized aluminium etc.)
• Conditions for correct curing must be attainable
• Coatings are not flexible and so therefore should not be applied on flexible substrates

10.8. Silicate emulsion primer

We discussed earlier the use of silicate emulsion primers on highly absorbent substrates or substrates with varying absorption. Another application for appropriately formulated silicate emulsion primers is for the consolidation of friable or weakly bound substrates, which may be encountered under a variety of circumstances, especially with old, weathered substrates. In such situations, a silicate emulsion primer with its high depth of penetration may be used to consolidate the substrate prior to overcoating with a silicate emulsion paint or plaster or even an organic emulsion paint or plaster. Where appropriately formulated silicate emulsion paints or plasters are used as the coating systems, then water vapour permeability would normally be maintained. However if the top coats are organic emulsion paints or plasters, then because of the closing of the pores in the coating during film formation it would be expected that water vapour permeability would be significantly reduced.

Nevertheless, the use of silicate emulsion primers could present an interesting concept to solving the problem of application of many coatings (both film forming and non-film forming) on to friable or weak substrates, since generally with film forming coatings such as organic emulsion paints they do not penetrate to anywhere near the same extent as silicate emulsion systems. Although other consolidants may be used for friable substrates, such consolidants are generally solvent borne systems or systems which have such low flashpoints that they fall within Dangerous Goods classification. A significant advantage of silicate emulsion primers in this regard is that they provide the consolidating effect, but are water-borne with the advantages of water cleanup and no flashpoint concerns. In addition, they probably represent the only choice for a relatively inexpensive water-borne consolidating system which can be factory prepared and have an extended shelf life in comparison with other water miscible consolidants. In general, we would recommend the use of potassium silicates as the inorganic binder of preference in silicate emulsion primers, since as discussed earlier the use of sodium silicates in this application could lead to high levels of efflorescence with implications for the performance of the top coats.
Finally, for those who are looking for further reading on the subject of silicate emulsion paints and plasters, there is an excellent 569 page German book by Schultze on this area.

10.9. Impregnation of stone substrates
Alkali silicates may be used for impregnation of a variety of siliceous masonry substrates including stone and concrete. Natural stone, by its very occurrence has a longevity spanning millennia; otherwise we would not be able to find it in its natural state. However, over periods of time, environmental effects can cause weathering of the stone. This can be of particular concern where natural stone has been used to build carved items such as monuments etc. since if they go unheeded the environmental effects can cause such destruction of the stone carving that its appearance is impaired or even completely destroyed. In some natural stones the binder is calcium carbonate (which is relatively insoluble in water) and which under exposure to acid rain is converted to gypsum or calcium sulfate (which although still being relatively insoluble in water is more soluble than calcium carbonate) and can be leached out from the stone.

As a result of this loss of binder (which tends to be particularly prevalent just below the surface), the stone gradually loses its strength over time and the outside crust can spall off. This is chemically represented as follows:

\[
\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2
\]

Equation 15

The water and carbon dioxide (both freely available in the atmosphere) combine to form carbonic acid, \(\text{H}_2\text{CO}_3\). The carbonic acid can also react with the calcium carbonate binder as follows to produce calcium bicarbonate (which is soluble in water) and can be leached out from the stone:

\[
\text{CaCO}_3 + \text{H}_2\text{CO}_3 \leftrightarrow \text{Ca(HCO}_3)_2
\]

Equation 16

To replace the leached out binder with silica, silicates may be used. Over many years, stone consolidants based on organic silicates such as tetra ethyl silicate have been used. As described earlier, the silicate binder is produced by the tetra ethyl silicate reacting with water, with ethanol being produced as a by-product, as shown below:

\[
\text{Si(OC}_2\text{H}_5)_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{C}_2\text{H}_5\text{OH}
\]

Equation 17

In former times, these products were typically solvent borne systems, but a major global manufacturer of stone consolidants has produced a solventless system. Nevertheless even this solventless system has sufficiently low a flashpoint that it is deemed to be a Dangerous Good, according to the Australian Dangerous Goods Code.

Here, yet again we can see an application for water-borne alkali silicates, and because we are trying to achieve good consolidation of the natural stone substrate, but without the appearance of any efflorescence, in such applications Lithium Silicates are recommended with their advantages of
ambient cure, water wash up, not being regulated as Dangerous Goods as well as the formation of no water soluble by-products.

Again we see, as shown earlier the typical cure being the following reactions shown in Equation 18 and Equation 19 below:

\[
M_2O \times n SiO_2 + Ca(OH)_2 \rightarrow CaO \times SiO_2 + (n-1) SiO_2 + 2 MOH
\]

Alkali Silicate  Calcium Hydroxide  Calcium Silicate  Silicon Dioxide  Alkali Hydroxide

Equation 18

\[
2 MOH + CO_2 \rightarrow M_2CO_3 + H_2O
\]

Alkali Hydroxide  Carbon Dioxide  Alkali Carbonate  Water

Equation 19

10.10. Impregnation of concrete

Concrete is yet again another siliceous substrate, but in this situation, consolidation of the concrete may be used to increase the hardness of the concrete above what has already been achieved through the appropriate water/cement ratio. Typically, it would appear that a number of impregnations with the water-borne alkali silicate are carried out, followed by mechanical surface finishing such as diamond grinding to achieve the desired surface finish.

Sodium silicates have been used for many years and are believed to form the basis of a number of well-known products in the marketplace. Potassium silicates with their particular advantages of less efflorescence also have a significant presence in this market. In particular in the USA, lithium silicates appear to be enjoying a high growth rate in this market, and it would appear that a number of such American developed products are being imported into Australia.

In some formulations it is understood that silica sols are added to water-borne alkali silicates, although high ratio soluble alkali silicates are much more reactive and are preferred because they are generally expected to lead to better results in concrete hardening. Silica sols (also known as colloidal silica solutions) are solutions of colloidal silica with typical particle sizes ranging from 8 to 125 nm, (somewhat larger than the size of the silicate particles in water-borne alkali silicates, which are of the order of 2 to 3 nm). Silica sol colloidal solutions may appear nearly clear and almost colourless at the lowest particle size, and with increasing particle size and concentration may range in appearance from opalescent (say around 40 nm particle size) to milky at larger particle sizes. Their stability reduces with increased particle size.

One method of manufacture of silica sols developed by Iler and Wolter described in a 1953 patent and mentioned in Iler’s textbook involves the reduction of the sodium content of sodium silicate solutions by ion exchange with H⁺ ions.

Silica sols may be stabilized through the addition of alkali (such as ammonia, if no increase in sodium ions is desired). The addition of an unstabilized silica sol to a water-borne alkali silicate is expected to result in generally undesirable premature gellation, and only appropriately stabilized silica sols should be used in such applications.

Although as discussed above, formulations based on sodium silicates (with their price advantage) have been well-known for many years, it appears that potassium and lithium silicates are generally used in the area of blends with silica sols because of stability issues with formulations based on sodium silicates.
Although the particle sizes of the components of formulations of potassium and/or lithium silicates mixed with silica sols are very small, the active ingredients are only expected to penetrate concrete to depths of say 1-2 mm because the silica particles are retained on the surface and are really only effectively surface hardeners. Nevertheless, such surface hardening of concrete is desirable in a number of applications and has produced a sizeable industry for formulators and applicators alike.

Where hydrophobicity of such formulations is desired, the addition of water miscible hydrophobizing agents (e.g. water-borne alkali siliconates such as potassium methyl siliconate) is carried out.

**10.11. Damp Proofing**

Typically in rising damp situations, the rising damp carries dissolved salts upwards. Due to lateral evaporation the water content reduces and the salt level increases with greater distance from the ground as shown in Figure 17.

![Figure 17: Rising damp (4) carries dissolved salts upwards](image)

Referring to Figure 17, the external sources of water can be as follows:

1. Driving rain, climatic condensation water or dampness from defective maintenance conditions and disposal lines
2. Hose water or surface water
3. Seepage water
4. Rising damp

With increasing salt concentration efflorescence results from crystallisation of the dissolved water soluble salts. At the same time pressure builds up due to crystallisation of these salts with spalling of masonry near the surface.

Typically, such rising damp may be prevented by the use of insertion of a physical damp-course, or more recently through the use of injection of a chemical to produce a horizontal damp-course. Potassium silicate solutions may be used in the impregnation of masonry substrates for chemical damp-proofing, normally against rising damp. Here, potassium silicate solutions (also known as potassium water glass) are used to seal the capillaries of the dry absorbent masonry substrate consequently providing a chemical damp course barrier against water from rising damp.
Where water repellency is sought to enhance the effectiveness of the chemical damp course, water miscible hydrophobizing agents such as potassium methyl siliconate are added (as an example in a ratio of potassium methyl siliconate to potassium silicate ranging from 1:4 to 1:11 w/w). The concentration of active substance in chemical damp-proofing formulations based on potassium silicate solutions typically ranges from 5-10%. Typically, sloping holes (at angles of 30 to 45° below horizontal) about 12-15 cm apart are drilled into the masonry and the chemical damp course is injected, typically under the effect of gravity as shown in Figure 18.

![Figure 18: Drilling Holes Arrangement for Impregnation of Masonry with Chemical Damp-proofing Liquid by Gravity Feed.](image)

However, because the curing of the alkali silicates/siliconates requires atmospheric carbon dioxide, the formation of active ingredients is relatively slow and may even be unsuccessful where the masonry is saturated with more than 50% water content.

Other chemical damp-proofing formulations are available such as those based on silanes, siloxanes, acrylic resins and metal stearates are available, but these contain solvents which suffer from the disadvantages of being Dangerous Goods on the basis of flammability. At the same time the solvents in such solvent-borne chemical damp-proofing systems have a residence time in the treated masonry substrate such that human occupancy of the treated building should be delayed until all traces of residual solvent have disappeared. There is no such restriction with potassium silicate solutions (with or without water miscible hydrophobizing agents) since the only carrier used is water.

11. Ecotoxicity.
We would suggest that water-borne alkali silicates are harmless to the environment on the basis that:

- Essentially, the finished cured products produced are silicate based; and as we said at the beginning of this paper, in nature it is understood that more than 95 volume % of the earth’s crust is composed of quartz and a few rock-forming silicates. So, on that basis, it is as if we producing cured systems which are effectively very close to what already exists in nature.
- According to the criteria of the Australian NOHSC (National Occupational Health & Safety Commission), now absorbed into the ASCC (Australian Safety and Compensation Council), water-borne alkali silicates are not hazardous substances.
- According to the criteria of the ADG-7 (Australian Dangerous Goods Code, 7th edition) water-borne alkali silicates are not Dangerous Goods.

As we also outlined earlier:

- No significant health risk during application
- No allergenic potential from silicate binders
- Alkali silicates are zero VOC products
- Zero VOC systems may be formulated using zero VOC organic emulsions
- A good economic lifetime of the coating (leading to less requirement to reapply the coating) due to long term stability.
12. Summary.
In this paper we have endeavoured to provide information about the production of alkali silicates, their properties, chemistry of cure and applications in a variety of coating and construction chemical systems including silicate coatings, silicate impregnations, silicate emulsion coatings and silicate emulsion plasters.

End markets for these products include architectural coatings, architectural renders, water-borne zinc rich protective coatings, masonry impregnation, water-borne consolidating primers, and chemical damp-proofing.

Silicate emulsion coatings were first introduced into the market in Europe in the 1960s, coming to prominence in the 1970s. About 10-15% of the waterbased architectural paint market in Europe is based on silicate emulsion paints. Introduction into other markets including United States of America, Asia and Australasia is occurring at the present.

With greater emphasis on reduction of VOC levels in coatings and construction chemicals, as well as their enhanced long-term durability compared with organic resin based systems, water-borne alkali silicates represent an environmentally friendly way of coating and consolidating masonry surfaces.

13. Acknowledgments.
We would like to acknowledge the assistance of Dr Joachim Krakehl of Woellner GmbH & Co. KG in Ludwigshafen, Germany in the preparation of this paper.


AUTHOR PROFILE
Adrian Thomas was born in England and graduated with B.Sc (Hons) from the University of Southampton in 1969 prior to transferring to Australia. In Australia he has had extensive experience with a number of multinational companies (including Unilever, Shell and Wacker Chemicals) in a range of manufacturing, sales and marketing positions at management levels. His professional memberships include: American Chemical Society, Royal Australian Chemical Institute; Royal Society of Chemistry, United Kingdom; Australian Marketing Institute; Australasian Corrosion Association; Australian Society of Cosmetic Chemists and Surface Coatings Association Australia (SCAA). His commercial activities include consulting in areas including technical consulting and regulatory affairs consulting as well as trading in a range of raw material chemicals for industries including the surface coatings industry. Chemicalia is the distributor in Australia and New Zealand of water-borne silicates from Woellner GmbH & Co. KG in Germany.
**Potential Re-coating Treatment for Inorganic Zinc Silicate Coatings**

June Zhang and Andrew Walker  
VicRoads, Burwood East, Victoria.

**Abstract:** Inorganic zinc silicate coatings have been an attractive coating for steel bridges due to their excellent long-term corrosion protection extending for up to 40 years. The re-coating of inorganic zinc silicate coatings has been regarded as a difficult process, due to the strict steel surface preparation requirements. In order to establish cost effective re-coating treatments for inorganic zinc silicate, a field trial was conducted by VicRoads, which involved the treatment of a sample of bridge girders using several simple surface preparations and the application of different types of zinc-rich coatings. The effects of both surface preparation method and coating system type were evaluated.

**Introduction**

Inorganic zinc silicate (IZS) coatings have been used for many years to provide a very high level of corrosion protection for steel bridges and other steel structures.

The estimated service life, before first maintenance, for IZS - Water borne coatings, applied at 75 microns dry film thickness in environments of medium corrosivity, is 25 or more years, according to AS/NZS 2312 [1].

It has been generally considered that steel structures coated with IZS coatings cannot be patch-painted with IZS coating to restore the coating system as part of a maintenance or re-coat program. The *Coatings Guide for New Steel Bridges* [2], published by BHP, provides specific recommendations for recoating of old, existing IZS paints. The Guide indicates IZS "should never need complete removal provided that adequate maintenance is carried out to ensure that coating breakdown and rusting does not exceed 5% of the total surface area at any stage."

In this paper, an attempt has been made to investigate effective re-coating treatments for IZS coated bridges and provide some support to the above views. The effects of both the surface preparation method and the coating system type were examined through a trial of controlled application and re-assessment after a lengthy monitoring period.

The surface preparation methods used in the trial were sweep abrasive blast cleaning, pressure water cleaning, power tool cleaning, and pressurized water cleaning with abrasive injection. The coating systems selected for this study were: Inorganic Zinc Silicate - Solvent borne, Inorganic Zinc Silicate - Water borne, Organic Zinc-Rich primer (Zinc-rich epoxy), and Moisture-Cure Urethane (MCU) - zinc-rich primer.

**Background**

VicRoads has management responsibility for over 400 steel bridges on the Victorian road network. About one third of these bridges are protected from corrosion with a single coat of either water-borne or solvent-borne inorganic zinc silicate paint. This coating system was first
applied to bridge steelwork in 1965 on the Ovens River Bridge at Wangaratta, and to the Boggy Creek Bridge at Nowa Nowa in 1967. A single coat of IZS paint has been the first choice for corrosion protection of structural steelwork since 1968 and has been in general use since that time.

Conventional advice has been that steel bridges with IZS coatings cannot be patch-painted or overcoated with the same coating to restore the coating system as part of a maintenance or re-coat program. One reason for this is the porous nature of an existing IZS coating, which absorbs some of the binder from the new application, resulting in the new IZS being under-bound and powdery with possible loss of adhesion. However, as the original IZS ages, the voids fill with zinc corrosion product making an effective barrier coating and the existing IZS may be less likely to absorb binder from an overcoat treatment. Coating consultants and paint manufacturers do indicate that re-coat treatments can be carried out with appropriate surface preparation, where all loose zinc corrosion products and debris are removed prior to re-coating.

A project was established to assess the proposal that by early intervention on IZS coatings in generally good condition, with less than 5% surface area rusted, simple and inexpensive surface preparation and followed by the application of zinc rich paints could be used [3].

To achieve this purpose, a number of surface preparation methods and re-coating systems were applied to an existing bridge that had originally been coated with an inorganic zinc silicate coating typical of the early use period around 1970. Bridges of this vintage are at the highest need for re-coat.

Field Trial

Selection of Structure
The Graham Street bridge located in Melbourne was selected for this study based on the following considerations.

- Age of IZS paint of more than 30 years;
- Complete coverage by zinc with minimal areas of rust breakout (less than 5% surface rust);
- No waterway influence; and
- Favourable influence of access, minimal traffic management.

The Graham Street bridge, at the Bay Street end, consists of eleven spans of sixteen 24 x 9 universal beams. These girders were originally coated offsite with an IZS paint when the bridge was constructed in 1968. The span selected for the re-coating trial had only minimal surface rusting and the zinc coating was intact over the sixteen girders.

Surface Preparation Treatments
The field trial was designed to determine the influence of various surface preparation treatments. Each girder was divided into four sections, and each section was prepared so that the surface for re-coat was cleaned to a matte finish with area free of all previously existing visible residues and loose material, using one of the following four surface preparation methods:

(a) Sweep abrasive blast cleaning
(b) Low pressure water cleaning
(c) Power tool cleaning
(d) Low pressure water cleaning with abrasive injection

These methods were chosen because they are generally recommended by paint manufacturers for the preparation of an existing IZS coating prior to recoat or topcoat.

The details of each preparation method are as follows:

(a) Sweep abrasive blast cleaning
The sweep blasting was carried out using a blast nozzle with a 12 mm minimum diameter venturi, at a maximum blast nozzle pressure of 350 KPa (50 psi), with clean garnet of size 0.2 to 0.5 mm, distance of nozzle to surface of 400 to 500 mm, with blasting angle to surface of 45 degrees. Simple containment of ground covers and free hanging dropsheets were effective containment for the dust, debris and spent abrasive media. After the covers were removed, minimal spillage of abrasive had occurred.

(b) Low pressure water cleaning
Low pressure water cleaning was carried out to remove soluble salts and contaminants. Water was applied at a nozzle pressure within the range 20 to 34 MPa (3000 to 5000 lb/in²), using a maximum nozzle-to-surface distance of 400mm. All debris and water was collected so that no material was discharged directly to ground. Waste water was either lost by evaporation, retention on the ground sheeting, or discharge through a filter sock. The pressure water cleaned surface was allowed to dry naturally.

(c) Power tool cleaning
The surfaces with existing IZS coating were prepared by power abrading with an orbital sander. These surfaces had been cleaned previously by pressure water cleaning.

(d) Pressure water cleaning with abrasive injection
This method uses low pressure water cleaning with an injection of abrasive into the water stream. This method removes salts and contaminants, and applies a surface texturing or roughening. Garnet was used as the injected abrasive. Ground cover and drop sheets were provided to limit abrasive and debris contamination of the site, including other parts of the bridge structure. The spent blast media was collected and removed from the site and disposed of in accordance with the relevant regulations.

Surface Profile
The surface profile was measured in each surface preparation area using Testex Press-o-Film tape and a Mitutoyo model 7326 spring-loaded micrometer, following the method described in AS/NZS 3894.5 [4]. The results are given below.

<table>
<thead>
<tr>
<th>Process</th>
<th>Surface Profile (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweep abrasive blast</td>
<td>0.107</td>
</tr>
<tr>
<td>Low pressure water clean</td>
<td>0.097</td>
</tr>
<tr>
<td>Power tool abrading</td>
<td>0.075 to 0.080</td>
</tr>
<tr>
<td>Low pressure water clean with abrasive injection</td>
<td>0.097</td>
</tr>
</tbody>
</table>

These measurements are higher than the expected range 0.035 to 0.065 mm that is specified for the surface of bare steel prior to the application of zinc-rich coatings. The consistency of the results between the different areas masks the unreliability normally associated with a
small number of results. The major effect of a high profile is to cause a higher demand for paint to achieve the wet film thickness requirements.

The surface profile of the sweep abrasive blast areas is slightly higher than for the water-cleaned areas. It is unclear why this difference has occurred; it may be that the abrasive blast has been more aggressive at the high points, causing a small net profile reduction. The values obtained are consistent with profiles measured on other projects.

The low pressure water cleaning did not change the surface profile. The value of 0.097 mm was indicative of the original profile of the existing IZS coating.

Power tool abrasion and low pressure water cleaning with abrasive injection are aggressive to the surface and are capable of altering the surface profile. The results for these methods indicate that a high surface profile can be expected.

Recoat Systems
Four generic coating systems were selected, with a total of fourteen coatings available for application to the bridge for the field trial. The generic coating and number of available coating supplied were as follows:

- IZS - Solvent borne (five coatings available);
- IZS - Water borne (two coatings available);
- Organic Zinc-rich primer (five coatings available); and
- Moisture-Cure Urethane – Zinc-rich primer (one coating available).

These fourteen different coatings, supplied by six paint manufacturers who had gained approval for their products against the relevant Australian Paint Approval Scheme specification criteria, were used in the trial; one coating applied to each girder, at the coating manufacturer’s recommended wet film thickness.

The binders used in IZS coatings are more ultraviolet light resistant than are the binders used for the organic epoxy and urethane coatings. IZS coatings are preferred for single coat systems as used on VicRoads bridges. The other coatings were used in the trial to confirm this and to demonstrate differences in performance.

Application of Coatings
The application of the fourteen coatings for the field trial was carried out over three days in April 2003. The surface preparation was completed on the first day and the coatings were applied on the second and third days. During the trial, each coating was applied to an individual girder at the coating manufacturer’s recommended wet film thickness. The coatings were applied in suitable weather conditions with the lowest temperature of 13.1°C, the highest dew point of 13.4°C, and the lowest difference between ambient and dewpoint of 3.0°C. The weather conditions for the trial were considered to be suitable for surface preparation and application of the trial coatings. The conditions during the delay between surface preparation and coating application were not considered detrimental to the purpose of the trial. If the overnight delay between preparation and coating was to have detrimental influence, then this might accelerate deterioration of some coatings and provide one indicator of performance.

The application of the coating for the field trial has been reported elsewhere [3].
Field Monitoring and Testing

Visual inspection and field testing were performed in April, 2011, eight years after the field trial, with the results shown below.

**Visual Inspection**

Photographic records for the web and the bottom flange of one girder, which was not re-coated in this trial and still had the original IZS coating exposed, are shown in Table 1. The photographic records for a typical coating of each generic coating system on girders which were re-coated in this trial are shown in Table 2. The observations of the conditions of the re-coating paints are described in Table 3. In these tables, W represents the web, and F represents the underside of the bottom flange of the girders.

**Table 1: Current condition of IZS paint originally applied in 1970**

<table>
<thead>
<tr>
<th>Components ¹</th>
<th>W</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original IZS coating, from 1970</td>
<td>![Image of W surface]</td>
<td>![Image of F surface]</td>
</tr>
</tbody>
</table>

¹ W - web of girder, F - underside of the bottom flange of the girder.
Table 2: Condition of typical re-coating paints, applied on the prepared surface, after 8 years exposure.

<table>
<thead>
<tr>
<th>Process area</th>
<th>IZS - Solvent borne</th>
<th>IZS - Water borne</th>
<th>Zinc rich epoxy</th>
<th>MCU - zinc-rich primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweep abrasive blast</td>
<td>W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure water clean</td>
<td>W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power tool clean</td>
<td>W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure water clean, with abrasive injection</td>
<td>W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 W - web of girder, F - underside of the bottom flange of the girder
Table 3: Typical observations of paints applied on treated surface

<table>
<thead>
<tr>
<th>Process</th>
<th>Area</th>
<th>IZS - Solvent borne</th>
<th>IZS - Water borne</th>
<th>Zinc rich epoxy</th>
<th>MCU - zinc-rich primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweep Abrasive blast</td>
<td>W</td>
<td>Excellent condition, no deterioration</td>
<td>Excellent condition, no deterioration</td>
<td>Dispersed, patchy array of faint, fine red rust bloom and blistering</td>
<td>Excellent condition, no deterioration</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>Excellent condition, flange edges with minor white rust and presence of dirt</td>
<td>Excellent condition, no deterioration</td>
<td>Good condition interspersed with minor blistering, flange edges with minor white rust and loss of coating</td>
<td>Good condition, moderate white rust and presence of dirt</td>
</tr>
<tr>
<td>Low pressure water clean</td>
<td>W</td>
<td>Excellent condition, no deterioration</td>
<td>Excellent condition, no deterioration</td>
<td>Dispersed, patchy array of small, fine red rust bloom and blistering</td>
<td>Excellent condition, no deterioration</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>Excellent condition, flange edges with very minor presence of dirt</td>
<td>Excellent condition, no deterioration</td>
<td>Good condition, flange edges with moderate white rust and loss of coating.</td>
<td>Good condition, flange edges with minor white rust and dirt.</td>
</tr>
<tr>
<td>Power tool clean</td>
<td>W</td>
<td>Excellent condition, no deterioration</td>
<td>Excellent condition, no deterioration</td>
<td>Upper web with dispersed, patchy array of faint, fine, red rust bloom. Lower web intact, no rust bloom.</td>
<td>Excellent condition, no deterioration</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>Excellent condition, flange edges with very minor presence of dirt</td>
<td>Excellent condition, no deterioration</td>
<td>Central area good condition, flange edge with significant white rust and loss of coating.</td>
<td>Good condition, flange edges with moderate white rust and presence of dirt.</td>
</tr>
<tr>
<td>Low pressure water clean with abrasive injection</td>
<td>W</td>
<td>Excellent condition, no deterioration</td>
<td>Excellent condition, no deterioration</td>
<td>Dispersed array or small, fine red rust bloom and blistering.</td>
<td>Excellent condition, no deterioration</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>Excellent condition, flange edges with very minor presence of dirt</td>
<td>Excellent condition, no deterioration</td>
<td>Good condition, flange edge with significant white rust and loss of coating.</td>
<td>Good condition, flange edges with moderate white rust and presence of dirt.</td>
</tr>
</tbody>
</table>

W - web of girder, F - underside of the bottom flange of the girder

**DFT testing**
The dry film thickness (DFT) of the re-coated system was measured using a coating thickness meter in each surface preparation area of the web and the bottom flange of each girder.

Typical DFT readings are given in Table 4 for specific girders and for each category of re-coat paint. Note that the specified DFT for the original application in 1970 was 80 micrometres, with average DFT prior to recoat of 167 micrometres, with a range of 110 to 236 micrometres, and a variation between girders. The intended DFT for the re-coat was within the manufacturers target range for the specific paint, as assessed using the wet film thickness values at application.
Table 4: DFT readings (in micrometres) for girders of Table 2.

<table>
<thead>
<tr>
<th>Cleaning process</th>
<th>Area 1</th>
<th>IZS - Solvent borne Girder 15</th>
<th>IZS - Water borne Girder 9</th>
<th>Zinc rich epoxy Girder 3</th>
<th>MCU - zinc-rich primer Girder 13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average DFT for the girder prior to re-coat</td>
<td>All</td>
<td>161</td>
<td>174</td>
<td>143</td>
<td>167</td>
</tr>
<tr>
<td>Sweep abrasive blast</td>
<td>W</td>
<td>210</td>
<td>150</td>
<td>250</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>264</td>
<td>204</td>
<td>236</td>
<td>244</td>
</tr>
<tr>
<td>Pressure water clean</td>
<td>W</td>
<td>192</td>
<td>204</td>
<td>180</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>214</td>
<td>234</td>
<td>194</td>
<td>214</td>
</tr>
<tr>
<td>Power tool abrading</td>
<td>W</td>
<td>220</td>
<td>188</td>
<td>192</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>185</td>
<td>176</td>
<td>252</td>
<td>172</td>
</tr>
<tr>
<td>Pressure water clean with abrasive injection</td>
<td>W</td>
<td>186</td>
<td>188</td>
<td>210</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>218</td>
<td>206</td>
<td>214</td>
<td>192</td>
</tr>
<tr>
<td>Average DFT re-coated (all coatings of type)</td>
<td>All</td>
<td>250</td>
<td>278</td>
<td>250</td>
<td>256</td>
</tr>
<tr>
<td>90% of DFT in range</td>
<td>All</td>
<td>176 to 349</td>
<td>193 to 363</td>
<td>168 to 302</td>
<td>190 to 324</td>
</tr>
</tbody>
</table>

1 W - web of girder, F - underside of the bottom flange of the girder

Adhesion Tests

The coating adhesion test was performed using the parallel cut method following AS/NZS 1580.408.4 method A [5] in the areas prepared using sweep abrasive blast cleaning. Typical test results are shown in Table 5. Adhesion was very good to excellent in all cases.

Table 5: Adhesion testing results

<table>
<thead>
<tr>
<th>IZS - Solvent borne</th>
<th>IZS - Water borne</th>
<th>Zinc rich epoxy</th>
<th>MCU - Zinc rich primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>G15-A</td>
<td>G9-A</td>
<td>G3-A</td>
<td>G13-A</td>
</tr>
</tbody>
</table>

Surface Treatment Influence

The condition of re-coating paints applied to the variously treated steel surfaces are shown in Table 2. It is interesting to note the trends in the condition of paints which were observed. In general, the best paint condition was found for the areas prepared using sweep abrasive blasting, followed in order by power tool cleaning, low pressure water cleaning with abrasive injection and low pressure water cleaning.

The influence of surface preparation method was most evident for zinc-rich epoxy paint. White rust on the bottom flange edge and a dispersed array of fine red rust bloom were observed to only a minor degree on the surface prepared by sweep abrasive blasting. The white rust and the rust bloom became more evident on areas prepared by power tool cleaning and low pressure water cleaning with abrasive injection. On areas prepared by low pressure
water cleaning the most severe coating deterioration, with loss of coating and white rust, was observed.

On the other hand, the surface treatments had a very minor effect for IZS-coated girders. IZS Solvent borne paint developed only minor dirt staining at the edges of the bottom flange of girders, with all other areas still in as-painted condition. No obvious visual defects were identified for surfaces repaired with IZS Water borne paint regardless of the surface preparation treatment.

**Coating Systems Effects**

The dry film thicknesses measurements provided in Table 4 are for the original coating plus the trial coating. These values are greater than 150 micrometres, often by a considerable margin. The only areas tested for adhesion, by the parallel cut method, were those areas where surface preparation was by sweep blasting, Adhesion of all coatings was considered similar and adequate across all prepared areas.

IZS paints generally performed well. IZS - Solvent borne paint showed only minor brown colour at the bottom flange edge, and IZS - Water borne developed no obvious visual coating deterioration. Over the eight years exposure in the trial, the IZS coatings performed very well as a re-coat treatment over an original IZS primer and are recommended for maintenance treatments of these original coatings.

Zinc-rich moisture-cure urethane showed minor coating deterioration on the web, and some degree of coating deterioration on the bottom flanges, such as white rust on the bottom flange edges of girders. Based on the acceptable performance of the MCU zinc-rich primer in the trial, this coating type could be used for re-coat treatments, particularly where its application attributes regarding dew point conditions and restricted working times make this coating type attractive.

By comparison, zinc rich epoxy coatings did not perform as well as the IZS coatings for any of the surface preparation methods, and they developed more heavy coating deterioration. On the webs, dispersed, patchy arrays of small, fine, red rust bloom were noticed. On the bottom flange, white rust appeared on the bottom flange edges, and some flanges even developed significant rust and had loss of coating. The amount and type of coating deterioration depended on the type of surface preparation treatments applied. The exposure trial period was sufficiently long to demonstrate that the zinc rich epoxy coatings, without further coatings, were collectively not able to deliver service life that would meet the requirements of a robust asset management system.

The trial demonstrated that a single coat inorganic zinc silicate coating system can be effectively maintained by intervening before surface rusting becomes significant, using an appropriate preparation and re-coat system.

It should be noted that this trial was to demonstrate that early intervention with a re-coat system prior to significant surface rusting was an effective treatment by minimizing the cost and effort for surface preparation. The girders to which the coatings were applied had only minimal surface rusting and the existing IZS coating was intact over the entire surface. Care would be required to extend the trial results to steel structures where the level of surface rusting is higher, and more invasive surface preparation may be required for minor portions of
such structures, while the majority of the surface area may only need one of the treatments of this trial. For example, other spans of the Graham Street bridge currently have more severe deterioration and heavier levels of surface rusting than was on the trial span, potentially requiring power tool cleaning and even full abrasive blasting prior to coating. In that case, the window of opportunity for a simple re-coat system may eventually pass. The management of the structure would change to maximizing value from the existing coating by leaving deterioration to continue until at some future time the remaining coating and accumulated rust is removed and a new coating applied, with increased cost and complex effort.

Conclusions

- The trial demonstrated that a single coat inorganic zinc silicate coating system can be effectively maintained by intervening before surface rusting becomes significant, using an appropriate preparation and re-coat system.
- Of the four surface preparation methods trialled, sweep abrasive blast cleaning resulted in the best coating performance, followed in order by power tool cleaning, low pressure water cleaning with abrasive injection, and low pressure water cleaning.
- The surface preparation treatments had only minor influence on the performance of IZS paints.
- Inorganic zinc silicate paints, both water-borne and solvent-borne, demonstrated very good general performance for re-coating structures originally coated with IZS paints.
- The zinc rich moisture-cure urethane coating showed some degree of coating deterioration, but could be used to meet specific operational needs.
- The zinc rich epoxy coatings developed severe coating deterioration following some types of surface preparation, e.g. pressure water cleaning, and were generally not able to deliver adequate service life.

Acknowledgements

The authors thank VicRoads for permission to publish this paper. The views expressed in this paper are those of the authors and do not necessarily reflect the views of VicRoads. The authors also wish to acknowledge and thank Mr. Stewart Martin for his excellent assistance during the field monitoring and testing. The authors acknowledge the cooperation both of the major industrial coating companies and of Mattioli Bros, the contractor who performed the work of the trial.

References

1 AS/NZS 2312 — Guide to the protection of structural steel against atmospheric corrosion by the use of protective coatings, Standards Australia, Sydney.
5 AS/NZS 1580.408.4 Paints and related materials - Methods of test- Adhesion (crosscut).
Field Test for Water Insolubility of Water Borne Inorganic Zinc Coatings

Ted Riding, Jotun Australia, PO Box 105 Brooklyn, Vic. 3025

SCOPE:
This method describes the technique used to determine the water resistance of Zinc Rich coatings. [This test may be modified to approximate ASTM D4752 which uses MEK (Methyl Ethyl Ketone) to assess the solvent resistance of ethyl silicate based inorganic zinc coatings. Simple substitution of MEK for water is made and the rest of the process remains unchanged.]

APPARATUS:
1) Clean cotton cloth approximately 300 mm square. Preferably light in colour.
2) Clean Tap water.

PROCEDURE:
3) Apply by Spray to specified WFT/DFT as per specification. Allow to dry under the prevailing conditions.
4) Allow sufficient time to dry/cure according to the indicated times on data sheet appropriate to prevailing conditions. Typically the first test is conducted after the indicated “Hard Dry” time on the Product Data Sheet – allowing 25% longer.
5) Place a water saturated cloth on the surface for 5 minutes and remove before proceeding with the test. Remove excess surface water before proceeding.
6) Rub a moistened cloth over the water soaked area for 80 rubs. Each rub = 1 forward and 1 backwards direction hard rub of panel, using maximum pressure of index finger.
7) Should cloth wear or become dry - alter position of finger in cloth and continue with test.
8) Rubs should be conducted over a longitudinal direction, for a distance of approximately 70 mm, within the area which has been water soaked.
9) **Optional** The moistened area may be scribed first to expose the substrate and the direction of rubs should be perpendicular to the scribe mark. This is a severe test and is only necessary in critical determinations of water borne coatings where the dry film thickness is above 150 µm.

ACCEPTANCE CRITERIA:
Material shall be deemed to have achieved satisfactory water insolubility if 80 rubs (or 50 for MEK test) do not remove sufficient coating to discolour the cloth. In most cases the surface of the material is “polished” by the process and results in a burnished area where rubbed. The photographs on the following page give visual examples of the various states of the coating.
The “burnishing” effect of the cloth alone should also be established by rubbing with a “dry” cloth to see the effect without the solvent present. The result of this should be between Figure 3 and Figure 4 above with only very minor discolouration of the cloth.

This method of testing the solvent resistance of an inorganic zinc coating for suitability for overcoating is much more reliable than simple hardness tests which should not be used for assessing this situation.

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