norganic (IOZ) and organic zinc-rich (OZ) primers have served a broad range of industries satisfactorily for many years. However, in recent years, because of the advances in the coating industry, there may now be new ways for protecting the substrates at equal or even better protection levels by using less zinc. This change can be attributed to a better understanding of protection mechanisms, resulting in coating materials with superior barrier characteristics or anticorrosive features.

This article summarizes problems manufacturers and end users encounter when relying on the available standards for materials and performance tests for zinc-rich coatings in today’s industry, particularly newer zinc-rich coatings with lower zinc loadings than earlier versions, and it presents some suggestions for improving the specifications. The reasons for developing new and purely performance-based specifications because of the new, lower content zinc coatings are also explained.

**Background**

One of the challenges of introducing new zinc-rich materials into the market place is the absence of appropriate specifications to accommodate these new materials. Zinc-rich paints are covered by SSPC specifications (Paint 20: “Zinc-Rich Coating—Type I—Inorganic and Type II—Organic,” and Paint 29: “Zinc Dust Sacrificial Primer, Performance Based”), which have been in existence for approximately 29 and 20 years, respectively. Both were most recently revised in 2002 and are now undergoing further revision. Even with the 2002 revisions, there are some misconceptions about the existing SSPC standards. The misconcep-

*Editor’s note: Drafts of SSPC standards undergoing revision are not available to the public, and, until they are approved, they do not replace the existing versions.
tions strengthen the need for new specifications to accommodate new coating materials. Paint 20 is often incorrectly considered a composition-based standard only, because it contains requirements for zinc loading. Paint 29, on the other hand, is often incorrectly considered to be only performance-based. However, as SSPC's “Commentary on Paint Specifications” clearly states, both specifications contain requirements for composition as well as performance.

SSPC Paint 20, for example, classifies zinc-rich coatings as Type I (OZ) and Type II (Organic), and defines three levels of zinc dust loading in the dry film.

- Level 1 — equal to or greater than 85%
- Level 2 — equal to or greater than 77% and less than 85%
- Level 3 — equal to or greater than 65% and less than 77%

It does not account for newer zinc coatings that can be made with zinc dust loadings below 65% by weight.

Paint 20 also classifies the vehicle types used in the coatings, such as Type IA, inorganic post-curing vehicles (water-soluble); Type IB, inorganic self-curing vehicles (water-reducible); and Type IC, inorganic self-curing vehicles (solvent-reducible). Type II vehicles covered by this specification are organic and are chemically cured or dried by solvent evaporation.

Furthermore, because Paint 20 also requires the zinc dust used as the major pigment to comply with ASTM D-520 (which defines the purity of zinc dust), one can easily conclude, incorrectly, that SSPC Paint 20 is purely a composition-based specification.

However, Paint 20 has performance requirements as well. In addition to certain physical property requirements, it requires a minimum of 5 mils’ thickness for mud cracking resistance (when examined under 30x magnification by optical microscope) and a minimum of 4B for adhesion performance when measured by ASTM D3359, Method B. Paint 20 also requires certain rust, blister, and scribe evaluations after exposure of the test panels to ASTM B117 salt fog conditions (3,000 hours for IOZ and 1,000 hours for OZ).

It is very important to note that all of these performance tests are conducted on the primer applied as a single coat directly to steel without topcoating.

Similarly, SSPC Paint 29 is often misunderstood as an entirely performance-based specification. It is true that...
Paint 29 has more detailed performance requirements than those of Paint 20. More importantly, in addition to 3,000 and 1,000 hours of salt fog tests required for IOZ and OZ coatings, respectively, Paint 29 requires two levels of exterior exposure performance for both Type I (IOZ) and Type II (OZ) primers. Blister rating, rust rating, and scribe undercutting evaluations are all required in addition to adhesion performance for both un-aged and salt fog-aged primers along with the mud cracking performance.

Once again, all of these tests are conducted on the primer applied as single coat directly to steel without topcoating. However, Paint 29 does contain a compositional requirement as well: a minimum level of 65% zinc dust in the dry film. Like Paint 20, Paint 29 does not account for new zinc coatings with less than 65% zinc dust loading.

In summary, both Paint 20 and Paint 29 contain requirements for a single-coat zinc-rich primer. However, single-coat zinc-rich systems are rarely used these days. The bulk of zinc-rich primers are applied as the first coat in a two- or three-coat paint system. On the other hand, laboratory testing according to ASTM 5894 and ISO 20340 accelerated corrosion methods has shown that the performance characteristics of zinc-rich primers as a single coat are very different than the performance of a three-coat system when exposed to similar conditions (Figs. 1, 2, 3, and 4).

As seen very clearly from these figures, the topcoated zinc-rich systems usually show more rust creep (undercutting) than single coat systems. In Fig. 1 (p. 41), it is hard to notice any difference on the scribe when a single-coat zinc-rich epoxy primer system is tested alone. Fig. 2 shows that if a three coat zinc-rich epoxy/epoxy/polyurethane system is evaluated using ASTM B117, there is still not much difference, indicating the inferiority of ASTM B117. ASTM D5894 is at least capable of showing the difference between paints A and B. In Fig. 3 (p. 43), the single-coat IOZ shows no noticeable difference with ASTM B117 Salt Spray. In Fig. 4 (p. 44), using ISO 20340 to compare a single-coat IOZ and a multi-coat IOZ/epoxy/polyurethane system, the topcoated IOZ scribe width is always greater than that of the primer alone.

The obvious question in this case is: “What good do the performance tests required by Paint 20 and 29 make if they are solely based on evaluating the performance of the primer alone, which is obviously very different than that of the multi-coat system?”

Another important weakness of these specifications is related to the application properties of zinc silicate systems. Experience shows that problems such as dry spray and inadequate cure may result from variations in humidity levels during application and cure. These variations can have a major impact on the performance of zinc silicates. These points are not taken into account in the presently existing specifications of Paint 20 and Paint 29. Some coatings have been developed in recent years that meet the performance requirements of Paint 20 or Paint 29 but contain less than the minimum specified amount of zinc dust, and, as such, they do not meet the compositional requirements of either standard.

Thus, there are shortcomings in the existing specifications simply because they were written before the advances made on these potential zinc-rich coatings. As a result, the industry needs to develop new specifications for these new coatings—purely performance-based standards that do not restrict coating compositions based on their zinc content. These new specifications must also take into account the real-life application and curing conditions of inorganic zinc coatings.

**The Corrosion Process and Zinc**

Corrosion is an electrochemical process. The standard reduction potential \( E_{\text{red}} \) for the reduction of \( \text{Fe}^{2+} \) (aq) is less positive than that of the reduction potential of \( \text{O}_2 \); therefore, \( \text{Fe}(s) \) can be oxidized by \( \text{O}_2 \) (g).
Cathodic reaction: \[ \text{O}_2 (g) + 4\text{H}^+ (aq) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} (l) \]

\[ E_{\text{red}}^0 = 1.23 \text{V} \]

Anodic reaction: \[ \text{Fe}(s) \rightarrow \text{Fe}^{2+} + 2\text{e}^- \]

\[ E_{\text{red}}^0 = -0.44 \text{V} \]

So the \( \text{Fe}^{2+} \) formed at the anode is eventually oxidized further to \( \text{Fe}^{3+} \), which forms the hydrate iron (III) oxide—the rust. However, everything starts by the oxidation of metallic iron to \( \text{Fe}^{2+} \). For this reason, the idea of using a second metal that is in contact with steel that can be oxidized relatively easily and preferentially—the principle of using sacrificial anodes to prevent corrosion—is really a bright one.

The standard reduction potential of iron as stated above is \(-0.44 \text{ V}\), whereas the standard reduction potential for zinc is \(-0.76 \text{ V}\). Since \(-0.44 \text{ V}\), in relative terms, is more positive than \(-0.76 \text{ V}\), \( \text{Fe}^{2+} \) is easier to reduce than \( \text{Zn}^{2+} \). Conversely, it follows that \( \text{Zn}(s) \) is easier to oxidize than \( \text{Fe}(s) \) is. For this reason, when steel is coated with zinc, it becomes an anode and provided that the area of the anode is large enough, even if it gets damaged and the steel is exposed to oxygen and water, the zinc serves as a sacrificial metal and corrodes instead of the steel, due to the following equations:

\[ \text{Fe}^{2+} (aq) + 2\text{e}^- \rightarrow \text{Fe} (s) \quad E_{\text{red}}^0 = -0.44 \text{V} \]

\[ \text{Zn}^{2+} (aq) + 2\text{e}^- \rightarrow \text{Zn} (s) \quad E_{\text{red}}^0 = -0.76 \text{V} \]

There is no denying that the above principle, which has been the foundation of the sacrificial protection mechanism for preventing the corrosion of steel, has been very successfully used over the years. But this doesn't necessarily mean that we shouldn't be looking into the subject from another perspective, perhaps with a pair of skeptical eyeglasses.

**Another Perspective on Zinc Coatings**

First of all, as seen from the above equations, at least in theory, to protect approximately 56 grams of steel (1 mole of iron) it is necessary to use approximately 63.5 grams of zinc (1 mole of zinc). Considering the fact that zinc is much more expensive than steel, it doesn’t look like a smart idea to use more of the expensive material to protect less of the cheaper one in the first place.

Second, as illustrated in Figs. 1–4, the topcoated versions of IOZ primers perform worse than the primers alone. In other words, the zinc used in the primer of a multi-coat system does not get used the same way as it does in a single-coat system.

Third, zinc is a heavy metal. It may have been serving the industry for many years, and it may still have to be used in the future. But wouldn’t it be more appropriate to use less zinc at least for environmental reasons, had we have some other alternatives?

While the immediate common sense answer to this question is “Yes,” unfortunately, regardless of whether or not the zinc is a heavy metal, and/or by also ignoring the obvious performance discrepancy between the single- and multi-coat systems, the present specifications of the industry do not
allow the use of those alternatives effectively.

In addition to the need for evaluating the performance of the “coating systems” rather than the individual primers alone, there is also a need for addressing some important application- and curing related issues of the inorganic zinc primers. Since the curing of inorganic zinc primers depends on the environment (humidity and temperature), there is a need for guidance in specifications to address this issue. If IOZ primers do not cure properly yet get topcoated, the cohesively weaker IOZ primer cannot accommodate the stresses exerted on it by either the contraction of the topcoat or dimensional changes of the substrate due to sudden temperature changes. As a result, the primers prematurely fail and sometimes split (Fig. 5). Some of the IOZ primers have dry spray application problems that need to be addressed as well.

Another well-known fact about the IOZ primers is their porous nature (Fig. 6 on p. 45). While their porosity is one of the reasons for their weaker cohesive strength, the same is also responsible for the bubbling of topcoats and for their blisters and pinholes (Fig. 7 on p. 47) upon application onto a porous inorganic zinc primer.

While the porosity of the IOZ primers is a disadvantage, particularly when they are topcoated prematurely (with insufficient cure), it can be an advantage when and if they are used without any topcoat. The reason is that, upon corrosion of the zinc, the pores of the IOZ primers are plugged with a variety of corrosion products (oxides, hydroxides, chlorides). Furthermore, the silicate binders generate acid, which...
then reacts with both zinc and iron to form zinc and/or iron silicate salts. All of this happens in a relatively short period of time—such as approximately 3 months. Even with the IOZ primer alone, there is still enough of an electrical conductivity path, due to the large open anode area, to protect the steel underneath. For these reasons, the protection mechanism governed by the use of IOZ primers alone is quite different than that of the multi-coat systems.

Thus, while there is always a possibility for electrical conductivity through which a galvanic protection mechanism exists when and if the IOZ primers are used alone (which may justify the use of a certain amount of zinc for such situations), this is not the case for topcoated systems. This is a very important difference between the topcoated systems and the single-coat primers used alone (without being topcoated), and the specifications must take this into account in their classifications and/or performance evaluation methodologies.

Another interesting laboratory observation from comparing the performance of the topcoated and untopcoated IOZ silicates is already illustrated in Figs. 3 and 4 (pp. 43 and 44). Once again, zinc levels are the same for the single-coated and topcoated IOZ coatings.

The conclusions one may deduce from the first group of tests (ASTM B117 on only primers) could be completely different than the second group of tests (ISO 20340 primer, intermediate, and topcoat). For this reason, it is imperative that the coatings be tested with methods most relevant to
the conditions to which the coatings will be exposed in service.

Another observation made in our labs indicating the importance of testing the complete system instead of only the primer is illustrated in Figs. 8 and 9, which compare the performance of a wide range of zinc silicate formulations.

As seen from Fig. 8, there seems to be no correlation between the width of scribe creep values and the percentage of zinc (in the dry film) when the primer is tested alone according to ISO 20340 test, even when comparing similar formula types where the percentage of zinc dust loading was the only variable.

On the other hand, the observation is completely different if a similar evaluation is conducted with the same test method, ISO 20340, but using the same primers as part of a three-coat system. It is interesting to observe a trend of reducing scribe creep width with increasing zinc content in this case, as seen in the Fig. 9, for the similar formula types. But there is no overall correlation when considering just the percentage of zinc content versus scribe creep. This suggests that while the percentage of zinc in the dry film is a factor in the performance of these primers, the percentage of zinc content by itself is not the sole factor defining performance.

A similar observation could be seen on the panels in Fig. 10 (p. 48), where essentially the same coating system with and without enhanced barrier features is compared. As seen from the first set of panels in Fig. 10, a 65% zinc-containing system couldn’t meet the performance requirement of ISO 20340 test, while the second set of panels indicates that essentially the same material with enhanced barrier features could be made to pass the test. The comparison emphasizes the need for accommodating the use of new materials in specifications, particularly at lower zinc-containing systems. Improved impermeability of barrier coatings does make a difference.

Summary

In summary, to answer the needs of today’s coatings, the coating industry must develop new standards and specifications that are based solely on performance and in accord with the service conditions. This is true not only to avoid imperfections arising from weak and/or insufficient points of the SSPC Paint 20 and 29 standards, but also for ISO 12944.

According to the requirements set out in ISO 12944 and ISO 20340, a zinc-rich primer is expected to have more than 80% zinc in the dry film. While there is still a compositional aspect to ISO 20340, it is one of the most difficult performance tests of the industry, and is required for offshore and highly corrosive C5M environments. The test protocols of ISO 20340 involve employment of 25 cycles of UV/Condensation, Salt Spray, and Low-Temperature (-20°C) testing.
C) exposure steps. Each cycle is composed of $3 + 3 + 1$ day of consecutive exposure of the samples to the conditions described. In this regard, it is our experience that it is harder for a coating system to satisfy the scribe creep performance requirements of a maximum of 3 mm under these testing conditions.

The nature of the ISO 20340 test protocol and the fact it is conducted on the complete coating system rather than on the primer alone make it a better method for comparing the performance of different coatings. However, the test data pre-
presented in the figures above have shown that performance varies significantly among coatings with the same zinc level and that coatings formulated at 65% zinc can outperform coatings with zinc loadings of 80% and higher when used as a primer in a three-coat system. These results and subsequent testing have indicated that achieving the creep below 3 mm, as required for a zinc-rich primer in ISO 20340, may be achieved at significantly lower levels of zinc than the 80% zinc level that ISO 20340 requires.

Barrier protection is an effective mechanism against corrosion. Advances made in recent years have provided the formulators with new and effective anticorrosive pigments too. As a result, by combining both of these features, it is possible to develop superior performing coatings with either lower amounts of zinc or, perhaps, with no zinc. Therefore, new and purely performance-based specifications must be developed and used regardless of the zinc content or type of the coatings because the zinc content is not the only controlling factor in corrosion protection.

Conclusions

- The current versions of SSPC-Paints 20 and 29 include performance tests that are about the evaluation of the primers alone and not relevant to most uses of zinc rich primers.
- New and solely performance based specifications need to be developed to accommodate new coating raw materials, especially for coatings that require lower levels of zinc than traditionally used quantities.
- ISO 20340 performance requirements are more severe than those of the other presently available performance specifications. For this reason, the ISO method needs to be utilized in evaluating the performance of the coatings for offshore applications.
- New specifications need to translate the real life issues of the IOZ primers during their application, curing, and topcoating. They should also include requirements for mechanical properties of the IOZ primers and the multi-coat systems prepared by their use.

Ilhan Ulkem is a senior technology manager at the Worldwide Protective Coatings Group of International Paint, LLC/AkzoNobel, Inc. He is based in Houston, TX, USA, and is responsible with his fellow colleagues for development of a broad range of newer protective coating technologies and products. During his coatings career since 1991, he has worked in a broad range of industrial and protective coatings.

Mike Winter is a technical manager (Development) at the Worldwide Protective Coatings Group of International Paint, LLC/AkzoNobel, Inc. He is based in Houston, TX, USA, and is responsible for the development of chemical-resistant coatings. During his coatings career since 1986, he has worked in protective and marine coatings.
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