Questioning our Assumptions about Primers in Immersion and their Place in the Water Industry

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Abstract
Here we examine a brief history of the engineering of water tank corrosion protection and lining systems. The author also presents a technical review of the two most specified primer types in the modern potable water tank building industry (solvent borne epoxies and moisture cured urethane zinc primers). Engineering, application, and cost considerations area examined in detail. The author seeks to inform the reader with an in-depth holistic approach to immersion primer selection. Here we conclude that in light of these considerations, and despite their prevalence in the specification literature, moisture cured urethane zinc primers do not offer a significant performance, constructability or cost advantage over non-zinc filled epoxy primers.

INTRODUCTION

For all the history of metallic water tanks builders; designers and operators of these tanks have utilized some method to control corrosion in the tank interior. Historical methods have varied from simple cosmoline or "grease" liners to complex multi-coat thermosetting spray or brush applied paint systems. Non-coating-based solutions such as cathodic protection systems, galvanizing or the construction of non-ferrous tanks have been utilized as well.

Coatings, or "paint" based corrosion solutions are typically referred to under the catch all term "linings" or "lining systems" in the case of multi-coat or non-single coat application paint systems.

Lining system installations typically consist of a paint crew abrasive blasting and preparing a steel surface that will go on to receive a "primer coat" and any subsequent topcoats that will comprise the complete lining system. One coat, two coat and three coat lining systems are all frequently encountered as we will detail below. For new tank construction steel is often primed at the fabrication shop with the rest of the lining system installed on site. For rehabilitation and repaint work tanks are often blasted and repainted in plave

These polymer linings systems include but are not limited to amine and polyamide cured two component Diglycidyl ether Bisphenol-A epoxies and isocyanate cured two component aromatic urethanes. Many of these systems are detailed in AWWA D102[1], (*American Water Works Association: Coating Steel Water Storage Tank D102*) the commonly accepted industry standard for the specification of potable water tank linings. A general synopsis of the interior lining systems detailed in AWWA D102-21 is shown in figure 1 with their accompanying dry film thicknesses in parentheses.

The focus of our examination here is that first coat above we referred to as the "primer". The term "primer" brings with it many connotations. What is a primer in the non-colloquial sense? The presence of a primer implies that some layer of paint is being applied to a substrate in anticipation of some additional topcoat. The primer is there to prepare the substrate to receive the topcoat.

For the purpose of consideration it is useful to conceive of an immersion primer as having three functions:

1. To protect the state of the substrate prior to receiving the complete lining system. This is commonly known as "flash rust" prevention.
2. To exist as part of the complete lining system and aid in protecting the substrate after receiving the topcoat
3. Provide strong adhesion between the substrate and the lining topcoat, or not limit the performance of the complete lining with poor adhesion

All immersion primer types in common use satisfy those three requirements to varying degrees.

In the table below "Coat 1" is the current selection of AWWA D102 primers for immersion service.

Lining System	Coat 1 (mils)	Coat 2 (mils)	Coat 3 (mils)
ICS-1	Epoxy (3)	Epoxy (5)	-
ICS-2	Epoxy (3)	Epoxy (4)	Epoxy (5)
ICS-3	Organic Zinc or Epoxy (2.5)	Epoxy (20)	-
ICS-4	Organic Zinc or Epoxy (2.5)	Polyurethane (25)	-
ICS-5	Organic Zinc (2.5)	Epoxy (4)	Epoxy (4)
ICS-6	Organic Zinc (2.5)	Epoxy (10)	-

are the materials that will be in direct contact with the *SSPC SP-10* blasted steel surface. The version of AWWA D201 cited here was written in 2021 however version of AWWA D102 going back to 1953 exist[1]. AWWA D102-1964, the oldest version for which digital copies are available in 2023, details coatings systems including a “two component epoxy paint system”, “Five component vinyl system”, “chlorinated rubber paint system”, “high solids vinyl coatings”, “heavy hot-applied coal tar enamel system”, “cold applied coal tar paint system”, and a “metallic sprayed [molten] zinc system”[2] Only the two component epoxy paint system resembles anything commonly applied today or in AWWA D102 for the last decade.

The contents of AWWA D102-1964 confirm that the space of polymer technologies for which an acceptable primer can be formulated is not limited to those listed in AWWA D-102. Vinyl esters, epoxy-novolacs, and other resin technologies are regularly used in identical or near identical immersion services outside the water industry, however limits on extractable chemicals are often the practical limitation for the selection of drinking water coatings. In the United Sates and Canada these limits are set by the standard know as *ANSI-NSF 61*.

It is not controversial to assert that epoxies and urethanes are among the most commonly specified resin types in the industrial coatings industry. Anecdotal evidence of this is found in AWWA D102, a summary of which is shown above. All product types listed are either of the two-component amine epoxy time, two component aromatic urethane type (AWWA D102 ICS-4), or the single component moisture cured urethane type (referred to as “organic zinc” in the industry and in the table above). For the remainder of this white paper moisture cured urethane zinc primers will often be referred to as “MCU Zinc”.

ZINC PRIMERS

In three of the six cases above from AWWA D102-21 an “organic zinc” primer is listed. Zinc rich coatings are commonly specified in the coatings industry as a form of galvanic protection that operates under the assumption the following standard electrode potentials hold true[3]:

$$1) \qquad 4\mathrm{Fe} + 3\mathrm{O_2} \rightarrow 2\mathrm{Fe_2O_3}$$

$$\mathrm{Fe}^{3+}_{(aq)} + 3e^- \rightarrow \mathrm{Fe}_{(s)}\ ;\ \mathrm{E_0} = \text{-}0.037\ \ \mathrm{V}$$

$$2) \qquad 2\mathrm{Zn} + \mathrm{O_2} \rightarrow 2\mathrm{ZnO}$$

$$\mathrm{Zn}^{2+}_{(aq)} + 2e^- \rightarrow \mathrm{Zn}_{(s)}\ ;\ \mathrm{E_0} = \text{-}0.7618\ \ \mathrm{V}$$

The zinc dust, which is often present in zinc rich primers in large amounts (often more than 70 weigh percent in the dry film) readily sacrifices itself to become zinc oxide, a reaction more thermodynamically favoured (and kinetically favoured due to the fine nature of the zinc pigment) than iron’s oxidation from bulk iron metal to iron oxide, the rusting that such primers are trying to prevent.

Zinc primers do that very effectively under ambient atmospheric conditions. Namely conditions where the zinc primer is continually exposed to a fresh supply of oxygen and an aqueous environment of sufficient ionic strength to continue the oxidative process. The open cell potential for the carbon steel substrate/zinc dust system must remain below about -0.85 V for the zinc to remain galvanically active.[4,5,6]

It has been previously established that galvanic protection of steel by zinc is entirely a surface bound phenomenon [4], being confined almost entirely to the zinc/iron interface. Given this fact it is interesting that zinc primers have become one of the dominant primer types in immersion service over the last decades given the extremely low oxygen permeability of modern thick film and large aggregate epoxies that are often specified over the zinc primer.

Zinc primers come in a variety of formulation types, many of which we will enumerate here though this is not an exhaustive list.

<u>Tetraethyl Orthosilicate Zinc</u> – This class of zinc primers is often referred to colloquially as “inorganic zinc” or “IOZ”. This class of products varies remarkably little from manufacturer to manufacturer in terms of marketable properties. These primers are composed of a tetraethyl ortho-silicate liquid phase that may have ASTM D520 Type II or Type III zinc dust already dispersed in-can or may have that same zinc dust incorporated by the applicator during the mixing process. These resin systems cure by hydrolysis of the silicate ester moiety (Si-O-C linkage) resulting in condensation of an ethanol molecule and chain growth of the silicate network. The resultant cured film is extremely high in zinc composition by weight and volume, often exceeding 85% zinc by weight. The non-zinc portion of the cured film is almost entirely inorganic in nature save the presence of any trapped solvent molecules or additives. These films perform robustly, un-top-coated in immersion but are not commonly used in water tank lining systems for a variety of pragmatic reasons beyond the scope of this work.

<u>Epoxy Zinc</u> – “Epoxy zincs” are typically two component organic formulations, similar in resin composition, to non-zinc filled epoxy primers. These zinc primers contain significantly less zinc than the tetraethyl silicate primers and are not in common use in the water tank lining industry though they do see common use in maintenance painting in atmospheric service.

<u>Moisture Cured Urethane Zinc</u> – MCU Zincs often contain zinc content intermediate between epoxy zincs and inorganic zincs. These products are the main focus of our current analysis of immersion primers as they are by far the most common type of zinc primer used in water tanks.

MCU Zincs are typically one component formulations (though two component formulations are known) where zinc dust is dispersed in-can with a mixture of solvents, one component urethane resins and additives. These formulations cure by ingress of atmospheric into the film resulting in a complex series of steps that ultimately leads to the formation of a urethane polymer network. The curing mechanism inherently involves the action isocyanates as in all urethanes.

EPOXIES

Non-zinc filled amine, polyamide or polyamidoamine-cured epoxy films protect underlying substrates through an entirely different mechanism likely dominated by barrier properties[7]. The film thickness, degree of polymerization, high degree of cross-link density and high solubility resistance of epoxy coatings stands in stark contrast to the porous galvanic thin film strategy employed by moisture cured urethane zincs.

Epoxy coatings typically used in potable water immersion are cured through the reaction of Bisphenol A Diglydicyl Ether with polymeric amines, small molecule amines, polyamides or polyamidoamines (depending on formulation). The cure mechanism a direct reaction between epoxy resin and amine hardener completely decoupled from atmospheric humidity. The resultant cross-linked polymer networks are known in the polymer chemistry literature for being particularly tenacious, low in permeability, and tightly adherent to metal substrates (even in marginal surface preparation conditions).

In AWWA D-102 recommended internal lining systems the penultimate lining coat is composed of a two-component, chemically cross-linked coating, specifically an epoxy in all cases but ICS-4. It is impossible to know the mind of the American Water Works Association at the time of the writing of that document but standard practice throughout other industries may be suggestive as to why the standard has been in a similar state for some time. Epoxies are simply the most impermeable, chemical resistant resin types readily accessible on the market that can be had at a competitive price point. The engineering literature for immersion grade linings in the chemical and petroleum industries is also littered with epoxy recommendations for this same reason.

FORMULATION CHEMISTRY

Both amine cured epoxy primers and moisture cured urethane zinc primers are commonly specified as immersion grade primers in today's water tank coatings as is evidenced by the contents of the current AWWA D102 standard. Both types of coatings perform well in a variety of services but accomplish this through very different technical means.

Modern epoxies have advanced considerably since the advent of moisture cured organic zinc rich primers and today, the two resin types have a fundamentally different mutual performance relationship than they did in decades past.

Moisture cured urethane zinc primers' performance advantage, where it exists, can almost entirely be attributed to the galvanic processes detailed above as has been detailed before[7] and it is well understood that urethanes as a class have higher water permeability than epoxies. *Hare et al* [7] pointed out in his prior JPCL review that the adhesive bond of moisture cured urethanes to the underlying metal was itself likely bolstered by the formation of zinc oxide salts inside the film during the corrosion process.

Moisture cured urethanes are, and in the case of urethane zinc primers designed for, far more permeable to moisture ingress than epoxies. At zinc loadings high enough to induce galvanic protection at the substrate the film itself is quite porous as a result of having zinc pigment present in amount near the *critical pigment/volume concentration* (cPVC). At some point in the lifetime of the zinc primer its zinc load, where exposed begins to become exhausted[8] and galvanic protection ceases or is reduced to a negligible rate.

The porosity of moisture cured urethane zinc films can be understand as a function of the pigment volume concentration of the zinc filler. The *pigment volume concentration* or PVC is given by the following relationship (in its fractional form):

$$PVC = \frac{V_p}{V_p + V_r}$$

Where V_p is the total pigment volume of the formula and V_r is the total resin and liquid additive volume of the formula.

The cPVC is the concentration of pigment within the liquid binder system that results in a cured film containing the maximum amount of pigment that can be fully "wetted" by the resin system. Additional pigmentation beyond the cPVC inherently results in a drastic increase in pigment/pigment contact in the dried film.

cPVC may be derived empirically from the following relationship[9]:

$$cPVC = \phi \left[\sum_{i=1}^{n} \left(\frac{1}{V_i(1 + A_i)} \right) \right]$$

Where φ is the densest random packing for the cured film, V_i is the pigment volume for a given pigment n of particle size i, and A_i is the experimentally determined oil absorption for a pigment particle of a given size.

All zinc primers that are galvanically active contain zinc dust in amounts that necessitate is being at or near the cPVC[4]. This is an inherent property of galvanically active zinc filled coatings. Organic zinc primers must contain enough zinc dust for the individual zinc particles to be in electrical communication with each other in the cured film. That is, there is a certain average maximum distance between zinc particles that will allow sufficient in-film conductivity for the sacrificial galvanic oxidation of zinc to continue.

High solids epoxies (generally considered to be liquid epoxy coatings above about 85% solids by volume) inherently have a higher capacity for barrier pigment incorporation due to their high proportion of resin in the liquid material (lower solvent load) as commercially available moisture cured urethane zinc primers tend to be lower solids products.

Four of six of the above listed AWWA D102 systems allow for the use of an epoxy primer alone. Relying entirely on the barrier properties, low permeability and high cross-link density of non-galvanic epoxies or thick film polyurethane/polyureas to protect the substrate.

In every case where a zinc primer is recommended (ICS 3, 5 and 6) an epoxy topcoat is specified to provide additional barrier protection. To the knowledge of the author no major coatings manufacturer currently recommends the use of a stand-alone moisture cured urethane zinc as a potable water lining system. There are cases where zinc primers are specified as standalone lining systems in the outside the water industry but in these are almost always tetraethyl ortho silicate based zinc primers often referred to as "inorganic zinc"; an entirely different resin class of coatings often erroneously mistaken for moisture cured urethane zinc. Inorganic zincs are typically not specified to receive topcoats in immersion service[10,11]

It has not been well established to what extent zinc dust remains active under film when top-coated with barrier materials likely due to the difficult nature of measuring such phenomena. Work by R. Jagtap *Et al* [12] from 2008 has indicated that addition of zinc oxide to zinc primers can result in both an increase in open circuit potential of a voltaic cell (creating less cathodically protecting conditions) but also a concurrent increase in corrosion protection. This is attributable to the increased barrier protection and "filling of film gaps" with zinc oxide[12]. All zinc rich primers tested in that work (with or without the addition of zinc oxide) showed a marked increase in open circuit potential over the course of 75-day exposure to a 3.5% NaCl salt solution and -1.05 V_{SCE} impressed current; as much as a 300 mV increase over the course of the first 30 days (approximately -1050 to approximately -700 mV_{SCE}). The open circuit potential must remain below approximately -850 mV_{SCE} for the zinc dust to remain galvanically active and cathodically protecting the steel. Given this experiment was conducted in conditions harsher than are encountered in a potable water tank, this experiment does appear to suggest that the supply of zinc dust under film may cease to be galvanically active after some time. Leaving only barrier coat of relatively porous moisture cured urethane and zinc oxide corrosion products behind.

Work by *S. Skale Et al* [13], also from 2008, did not explicitly compare epoxy coatings and zinc rich primer but did use electrochemical impedance spectroscopy (EIS) to demonstrate that additional film thickness, not pigment activity, was the dominant factor in a new coating system resisting change to its electrical impedance properties on exposure to 65 days of wet chamber accelerated ageing in accordance with ISO 6270.[13]

APPLICATION CONSDERATIONS

Potable water tanks are often lined via applicators applying liquid coating material to a blasted steel substrate. The coating is typically applied via hand roller or airless spray unit. An airless spray unit works by discharging a reservoir of liquid paint at high pressure through a small orifice typically 10-50 thousandths of an inch in diameter. Primers for the tank internals are often applied in shop at the site where the steel is fabricated though some tanks are primed on site after construction.

Both epoxy and moisture cured urethane zinc formulations may be applied by either method. However moisture cured urethane zinc has additional limitations imposed on it due to the highly zinc filled nature of the coating. All commonly used moisture cured urethane zinc primers require agitation during application[14,15,16,17]. This is easily accomplished with an airless spray rig and hopper though it requires additional equipment and/or additional personnel to physically agitate the material during application. When it comes to roller application this becomes pragmatically difficult and application of non-agitated zinc may result inhomogeneous distribution of the zinc dust in the dry film, leading to galvanic protection being entirely absent in some areas.

Epoxies may generally be applied via airless spray, roller or even plural airless spray. Plural airless spray reduces the need for manual mixing time required by most zinc and non-plural applied epoxies. Plural spray combines the two components of an epoxy coating inside the spray rig itself resulting in very fast production rates.

A study conducted by J Helsel[18] in conjunction with NACE International attempted to estimate the costs and service lives of various coating types as a function of resin type, application method, service type and variety of other contractor related application factors. In this study it was determined that on average in shop primer application of zinc primers costs a nominal $0.77 per square foot[18]. Likewise, two-component epoxies come in at $0.75 per square foot. Neither of these costs include material costs but to first approximation this these costs are quite comparable.

The study fur4hermosre goes on to detail practical costs per square foot for a given thickness. Moisture cured organic zinc is said to cost $0.499 per square foot for a 3 mil system where "epoxy primer" comes in at $0.171 per square foot for practical spray application for a two mils system. Adjusted on a per mil basis this results in an almost two-fold difference in practical applied spray cost for moisture cured organic zinc rich primers versus epoxies i.e. a one mil application of organic moisture cured zinc rich primer cost approximately 1.9 times what one mil of coverage equivalent epoxy would cost to apply.[18]

The comparison is complicated when attempting to compare the two resin types on a "brush and roll" application basis as many manufacturers do not recommend organic moisture cured urethane zinc be applied by brush or roller due to the potential for inhomogeneous zinc distribution in the dried film. KTA does however cite numbers for both product types with respect to brush and roll and the relative ratios are very similar[18].

It must be considered, in any discussion of application characteristics of a coatings, the difference between shop application on new construction, field application on new construction, and repair or rehabilitation on an existing water tank.

TOTAL COST CONSIDERATIONS

The previously cited survey by Helsel[18] goes on to estimate the service lives of various immersion coating systems in potable water for a given film thickness. The values found there for the relevant systems of interest (in potable water service) are

Coating System for Immersion Service	DFT (mils)	*Service Life (years)
Epoxy/Epoxy (AWWA ICS-1)	6	10
Epoxy/Epoxy/Epoxy (AWWA ICS-2)	12	15
Epoxy 100% Solids (AWWA ICS-3)	20	18
Organic Zinc/Epoxy/Epoxy (AWWA ICS-5)	10	16
Metallizing/Epoxy/Epoxy	13	24

**See reference 18 for thorough explanation of service life calculations*

reproduced below:

Upon even a cursory glance it is apparent that on a per thickness adjusted basis a three-coat epoxy system as per AWWA ICS-2 produces a very comparable service life to an organic zinc/epoxy/epoxy system. This real-life data is congruent with conclusions drawn from the electrochemical experiments cited above, i.e. that the galvanic action of top-coated zinc rich primers in immersion does little to extend the useable service life of the system in practice.

Using the values from the same work we can divide the cost of a given system by its expected service life and readily derive a decent approximation for the cost effectiveness of each system. Those values are reproduced for the above systems below:

Coating System for Immersion Service	Cost (USD / ft^2)	Cost (USD · ft^{-2} · yr^{-1})
Epoxy/Epoxy (AWWA ICS-1)	$0.481	$0.0481
Epoxy/Epoxy/Epoxy (AWWA ICS-2)	$0.791	$0.0527
Epoxy 100% Solids (AWWA ICS-3)	$1.894	$0.1052
Organic Zinc/Epoxy/Epoxy (AWWA ICS-5)	$1.119	$0.0699
Metallizing/Epoxy/Epoxy	N/A	N/A

Values for metallizing here could not be found in the Hensel study. The immediate conclusion one may glean from this meta-analysis is that organic zinc and 100% solids epoxies are disproportionately expensive to apply on a lifetime adjusted basis when compared to the other thin film epoxy systems.

However, one must ask whether these cost numbers factor in less tangible yet still cost significant (or even cost determinative) factors such as return to service time, time elapsed between coats and time spent on re-work. Here we attempt to address a few of these qualitatively.

The ICS-3 100% solids system is inherently applied in one coat. This comes with it a lower cost due to curing delays, bad application conditions or other "between coat" delays. It is not clear the degree to which these numbers reflect the cost associated with having an installation crew on site for multiple days. If these numbers do not reflect those costs then these numbers likely represent a lower bound on the costs of multi-coat systems and an upper bound on the costs of single coat systems.

CONCLUSIONS

Three coat epoxy, organic zinc primed-epoxy, and 100% solids epoxy lining systems represent the bulk of the market for domestic water tank lining in North America.

All three types of systems are viable and produce satisfactory results when specified in the proper service environment. However, among these three types of systems there are two chemical mechanisms of action that work to prevent corrosion to the underlying steel. Galvanic protection from zinc dust in the case of zinc rich primers and barrier properties in the case of epoxies.

Despite there being two mechanisms of action in these commonly used lining systems, experimental data and quantitative surveys/analyses of the field strongly suggest that barrier properties are the dominant mode of action at work in these systems; even in the instances where a zinc rich primer is present.

The academic literature is quite scant on references with respect to moisture cured urethane zinc due to its proprietary and relatively recent development (1980s and 1990s era). Despite an exhaustive search not one citation in the chemical or industry academic literature could be found measuring the barrier effect or permeability of zinc rich primers or their unfilled moisture curing urethane resin systems alone whereas the literature is replete with examples of these properties being measured in epoxies, aromatic thick film urethanes, polyurea sand other commonly used water immersion resin types.

The common understanding about the galvanic mechanism of action in organic urethane zinc primers deserves re-examining at the systemic level. When subject to quantitative cost analysis organic zinc rich primers do not appear to offer any cost advantage or even a measurable performance advantage in real life scenarios when compared to three coat epoxy potable water lining systems. In the introduction of this work the three primary engineering criteria for immersion primers were laid out:

1. To protect the state of the substrate prior to receiving the complete lining system. This is commonly known as "flash rust" prevention.
2. To exist as part of the complete lining system and aid in protecting the substrate after receiving the topcoat
3. Provide strong adhesion between the substrate and the lining topcoat, or not limit the performance of the complete lining with poor adhesion

In an objective comparison with epoxy primed systems MCU Zinc offers no distinct advantage in any of the three.

The author calls on the industry and academic community to examine these questions further to serve our water consuming (and utility paying) communities in a cost effective and efficient manner that is guided by sceptical examination of new technologies and old technologies that may now, or may have considered in the past, the default option.

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