

# The Short Happy Life of Waterborne Zinc

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## Abstract

*This note briefly reviews the history of zinc silicate coatings in tankers, and then discusses one owner's experience with high ratio waterborne zinc-silicate. Ultimately, this coating proved to be far superior to conventional organic coatings for tanker decks; and, after an unnecessarily difficult learning process, at least as easy to apply.*

## Keywords

Tanker; Coating; Corrosion; Protection; Zinc-Silicate; Waterborne zinc

## 1 A Brief History of Waterborne Zinc

Shop primers aside, nearly all coatings used on tankers today are based on organic polymers. These coatings have several things in common.

1. They are porous to water. If the water molecules that reach the steel encounter contaminants, they blister.
2. They are mechanically weak, easily damaged by wires, fenders and the like.
3. They are poor at resisting damage. When they are damaged, the edges are subject to undercutting and accelerated corrosion.
4. They are sensitive to temperature. Many of these coatings have a Glass Transition Temperature (GTT) less than 50C. Such temperatures are often exceeded on tanker decks and in the top of tanks. If an organic coating is cycled through its GTT, it quickly loses strength and elasticity.

There have been several attempts to avoid these problems by using inorganic coatings. For tankers, the most interesting such effort is based on zinc-silicate.

Zinc silicate coatings originated in Australia in the late 1930's where Victor Nightingall experimented with combinations of zinc and sodium silicates in an attempt to emulate zinc-iron silicate ores. He finally came up with a combination of zinc dust, alkaline sodium silicate, and a little lead which was applied to a 250 mile pipeline in 1942.<sup>1</sup>

<sup>1</sup> To get this job, Nightingall offered a 20 year guarantee. The guarantee was never called in.

<sup>2</sup> On the down side, zinc-silicate is sensitive to PH. If the PH is less than 5 or greater than 10.5, the zinc becomes very reactive and the coating can disappear almost overnight. This has important implications for over-coating as we shall see,

The process involves laying down a sodium silicate-zinc mixture and then heating it to over 350F. This coating was still in "excellent condition" fifty years later.<sup>[2]</sup>[page 134]

The next step was the post-cured zinc silicates developed in the 1950's. In these coatings the heat treatment step was replaced by painting over the coating with a solution which slowly releases a weak phosphoric acid which causes the formation of silicic acid which then polymerizes in the presence of zinc to form a tough zinc-silicate matrix, consisting only of zinc, silicon and oxygen. The curing solution must be washed off at the correct time. Zinc concentrations in the final matrix are over 92% zinc by weight.

By 1960 vendors had developed self-curing versions. This process is still totally inorganic starting with potassium silicate. In the presence of water and air, the potassium is replaced by zinc resulting in a polymer, consisting of zinc, silicon, oxygen and some hydroxyl groups. Zinc concentrations are approximately 90%. This polymer is not quite as tough as the pure zinc-silicate polymer, primarily because hydroxyl groups left over from the potassium silicate get in the way of complete cross-linking. But it is still a remarkable product. Some of the silicon bonds with the underlying iron. These valence bonds are far stronger than the covalent bonds by which organic coating stick to steel. Properly applied zinc simply will not blister. Mechanically the stuff is far tougher than any organic coating, doing a much better job resisting wire damage on decks and fender damage on topsides. And if the coating is damaged, it sacrifices itself to protect the exposed steel. Zinc-silicate does not undercut. In particular, this prevents or at least vastly delays any undercutting or lifting of the topcoat. The coating also has far better temperature resistance than epoxy which become semi-plastic at temperatures as low as 50C. Zinc-silicate can handle 300C without difficulty. It does not support combustion. And has nil VOC with its attendant health hazards for the applicators.<sup>2</sup>

This process was largely an American phenomenon. Chuck Munger, then technical director of Ameron, joined forces with Nightingall's company Di-met to produce Dimetcote. Exxon developed a similar product called Rustban. There were many success stories, especially on offshore rigs and platforms. American tanker owners jumped on the zinc

silicate bandwagon. Exxon USA sped waterborne zinc for its tanker decks. Ludwig used waterborne zinc just about everywhere on his ships. The entire external hull of his tanker was waterborne zinc, top-coated with vinyl with outstanding results.[2][page 164] Most of the zinc coated tankers were built in Japan.

Adoption of waterborne zinc was far slower in Europe. There were a number of reasons for this:

**Weather** Waterborne zinc cures by evaporation of the water. It requires low humidity, and temperatures well above freezing. European yards are faced with long stretches of rainy, low temperature weather, which would badly disrupt their production schedules. By the same token, one must be careful not to overcoat until the Zn-Si is properly cured. In the case of waterborne zinc, this process takes days if not weeks, and is weather dependent. Shipyards like to measure re-coat intervals in hours.

**Sprayer Productivity** During this period, airless spray technology had been developed. Waterborne zinc is best applied by conventional spraying. The zinc clogs up and abrades the airless equipment. Airless equipment is faster and easier for the sprayer to use. The European yards were under extreme economic pressure from the Japanese, productivity was essential to their survival.

**Coating thickness** Coating thickness is limited and must be carefully controlled, Coats must be between 50 and 75 microns. Under-thickness will result in bleed through. Over-thickness will result in mud-cracking. Controlling thickness to this tolerance requires special training and care.

**Failures are obvious** Waterborne zinc is unforgiving. It must be applied on an excellently prepared surface. It must be carefully and continuously mixed. Pot life is short. Weather must be right. Thickness must be right. And most importantly for the yards, errors are almost always immediately apparent. If you do a poor job applying an organic coating, there's a good change it will still pass inspection. This will be a big problem for the owner down the road, but the yard is off the hook. Waterborne zinc on the other hand is self-inspecting.

The paint vendors attempted to address some of these problems by developing solvent borne zinc silicate. Despite being called inorganic zinc by most paint vendors, this is an organic process which starts with ethyl-silicate, a compound in which each silicon atom is surrounded by four ethyl groups. In the

presence of acid, the zinc replaces some of the ethyl groups. Under good conditions, a zinc ratio of 85% is obtainable. The big plus is that this coating requires high humidity to cure. It is much less weather dependent. The hydrolysis of the ethyl groups is dependent on a number of things and results in a structure which is never as good as that theoretically obtainable from properly applied waterborne, and which can be a disaster, especially if it is overcoated too soon. If anything, solvent borne zinc is even more sensitive to coating thickness than waterborne. Touch up is another issue. The bond between the coating and itself is so poor that most vendors say it can't be done, although our own experience indicates that this is not completely true.

In any event, by the 1970's the zinc silicate world had bifurcated, with the Americans and Australians mostly using waterborne, and the Europeans mostly using solvent borne, when they used zinc at all.

In 1970, there was a development that should have shaken up the coating world. NASA was awarded a patent for "high ratio" waterborne zinc silicate. This is basically the same chemistry as normal waterborne zinc, but the potassium silicate is preprocessed to increase the ratio of silicon to potassium from 3.2:1 to 5:1 or higher. This increases the number of reactive silicon groups which means (a) curing is faster, (b) the resulting matrix has fewer hydroxyl groups than ordinary self-cured, producing a matrix that is very close to the original post-cured. Most importantly, this product can be applied in thicknesses up to 200 microns without mud-cracking. Finally, our experience is that with just a little care, **high ratio bonds to itself, and thus can easily be touched up.** You still need excellent surface prep to get the steel and silicon to bond, and you still need reasonably low RH and a decent temperature to get a proper cure.

However, scaling up the NASA process proved to be a problem. For one thing NASA jealously guarded the patent and only allowed a couple of firms to attempt it. It was not until 1985, that **a start-up called Inorganic Coatings (IC) was able to offer a high ratio product commercially. The all important binder was produced by an outfit called Polyset.** The process starts with ordinary 3.2:1 silica/potassium dispersed in water to which ultrapure silicon and some silicone is added. The trick is to keep the high ratio salt soluble in water.

IC ended up with a 5.3:1 silicon/potassium ratio, and called its product IC 531. The product quickly developed a market in the United States, especially among bridge builders. It was also used extensively in Australia on offshore structures, As we shall see, we used it very successfully on tankers. Properly applied it was magic. We sprayed it on badly pitted topsides and ballast tanks with no problem.<sup>3</sup>

<sup>3</sup> Unlike solvent borne organics, zn-si does not shrink during curing. When first laid down the coating has no strength, it just lies there. Any reduction in volume by water evaporation is in depth. This avoids bridging in pits and much of the pullback on edges.

We used in chain lockers, going to thickness well above 200 microns without mudcracking. The coating was so strong and anodic that it actually protected the chain lockers, something no organic coating could have done. Our crews became so proficient at laying down 531 that they made it quite clear that they would not go back to organic coatings, if we had been silly enough to try and make them. The decks we laid down in the early 1990's were still in near perfect conditions ten years later when we had to scrap these ships because of age restrictions.

But in 1992/1993, things began to change. Given our successes, we decided to go all IC 531 for topsides, ballast tanks and decks on the Hellespont Capitol. But when we sprayed the coating on it was extremely rough, like sand paper. This surface was quite different from what we had been getting. A couple of ships reported that IC 531 applied on decks had "disappeared" in the first rain. This had never happened before. IC was not responsive, so it took us a while to figure out what had happened.

In late 1991, IC had started switching from the Polyset binder to a simpler process. This process started with a glass that already had a 5.3:1 silicon/potassium ratio. The idea was to simply grind this glass up very finely and disperse it in water, eliminating the costly, hard to scale, blending step. IC made the switch without telling any of its customers. It turned out to be a terrible mistake. In many cases, the coating simply didn't cure, and washed off in the first rain. In other cases, usually involving salt water, the coating cured; but the surface was so rough that, if it got contaminated before topcoating, it could not be cleaned. IC refused to admit any responsibility, putting all the blame on its customers' poor application. The result was a series of law suits, and a massive black eye for waterborne zinc from which it has not recovered.<sup>4</sup>

In 1996, the NASA patent finally ran out, and a number of major paint manufacturers are now offering a high ratio, waterborne zinc. But they would much prefer to sell you a conventional organic coating. High ratio waterborne zinc is a lose/lose/lose proposition for a major paint vendor.

1. 100 microns of zinc will outperform 300 or more microns of epoxy. The customer needs a lot less paint.
2. High ratio is still relatively unforgiving, so the risk of immediate failure is higher than with conventional coatings in which case the vendor takes a hit.
3. If the coating is properly applied, then it will last far longer than an organic coating, so the vendor sells a lot less paint in the future.<sup>5</sup>

<sup>4</sup> During the same period, Ameron reformulated Dimetcote, the pre-high ratio standard in waterborne zinc, removing the lead for environmental (read legal) reasons. The product was never the same.

<sup>5</sup> In my experience, major company paint salesmen are often unaware that their company has such a product. The supervision teams are unfamiliar with it. And top management would just as soon keep it that way. They keep the product around only because a few of their customers demand it.

And given the 1992/1993 failures, it is fairly easy for paint vendors to steer their customers away from a coating with such a checkered past.

Currently, I am unaware of any tanker owner who is using waterborne zinc.

## 2 Our Own Experience

This is a shame. For it turns out that the somewhat quirky nature of waterborne zinc as far as the yards are concerned makes it an ideal coating for us on-board tankers. But I must say it took us quite a while to figure this out.

Between 1983 and 1987, my firm bought seven very large tankers which had been built in the 1975 thru 1977 period. Five of these ships had decks that had been coated with waterborne zinc. These five decks were in far better shape than the other two ships which has been protected with organic coatings. After three plus years in lay-up, the decks on the latter two ships were a total mess. The decks on the zinc silicate coated ships had at most localized breakdown in way of fittings, nuts, etc. Almost all the area on these five decks was near-perfect.

At the time, we knew absolutely nothing about zinc coatings. But the obvious difference caught our attention. Our operating arm was based in London and Athens. When we approached the European paint vendors about zinc, the initial response is that it is too difficult to apply, and they recommended we use conventional coatings. When we persisted, they told us we could use their solvent borne zinc silicate.

In 1989 we blasted one of the non-zinc decks in a repair yard and coated it with a solvent borne zinc. The yard and the vendor (International Paint) were very concerned about mud-cracking and the coating was definitely on the thin side. The spec was 50 to 75 microns, but the actual thickness was less than this in many areas. International flat out refused to put another coat of solvent borne zinc on top, saying it would not stick. The workaround was to add a coat of zinc rich epoxy primer on top of the zinc, and then topcoat with an epoxy.

This coating held up reasonably well for about six years. But it never looked like the deck coating on the five ships that had been coated with waterborne zinc. It was more sensitive to wire damage, and there was little sign that the coating was sacrificing itself in way of the damage.

In 1991, the waterborne zinc on the Hellespont Capitol disappeared in a matter of months, leaving a horrible mess. This zinc had been overcoated with chlorinated rubber. The chlorinated rubber failed in manner which trapped salt under the topcoat creating a highly alkaline environment. The zinc turned

to zinc chloride and washed away. The lesson is, if you topcoat zinc, you must maintain the topcoating in good enough condition, so that it blocks salt from penetrating through to the zinc. Salt is a big molecule, and just about any organic coating will do this with enough thickness. We settled on top coating with two coats of epoxy, at least 150 microns each.

In the period 1991 through 1995, we reblasted and coated all seven decks at sea with our own crews, using high ratio waterborne zinc. The Capitol zinc was gone. The other original waterborne zinc decks were now 15 to 20 years old and, while still effective, were showing a lot of age, especially in way of fittings. The 1989 solvent borne zinc deck was in the same condition or worse.

By this time our crews had learned to blast to SA 2.5 or better at yard rates ( $8\text{ m}^2/h$ ) or better. This was a painful process requiring two or three years, mainly because initially neither our management nor our crews thought this was possible. The first problem was under-specing compressors. To save money we bought used compressors with a nameplate rating of 8 or 9 bar. These machines proved incapable of delivering 7.5 bar at the nozzle. In many cases, we were getting 5 bar or less. Blasting rates were abysmally low. The old compressors also proved to be maintenance nightmares. Maintenance was further complicated by the fact that the engine side did not regard the deck compressors as essential equipment. So when the machine went down, they were very slow to fix it. The deck crew did not push for the repair, since they now had an excuse to turn their attention to other jobs with which they were more comfortable.

But we persisted. We bought all the ships new 750 CFM, 12 bar compressors. and installed sizable receivers. We ran an air line into the deck steam main, so the crew could tap into air just about anywhere on deck with reasonably low pressure drop. We put pressure gauges on the pots and made sure we had at least 7.5 bar there. We taught the crews how to measure nozzle abrasion and gave them lots of spares.

Thanks largely to the efforts of one stubborn, dedicated, indefatigable port captain, Kostas Lipiris, productivity climbed and continued climbing, Ships that had barely managed to blast  $8\text{ m}^2$  in a working day ended up doing  $10\text{ m}^2$  per hour, sometimes more. This meant we could full blast a 20,000  $\text{m}^2$  ULCC deck to SA2.5+ in about 250 working days. On some ships, we installed two compressors and doubled the productivity.

Of course, we could only blast and coat in good weather. But big tankers spend a lot of time in sunny, hot weather. On sunny days the decks are almost always warmer than ambient. This meant that coating cured from the steel out. We rarely encountered mud-cracking, even in deep pits. We had

no trouble getting the high ratio to bond to itself.<sup>6</sup> If the weather was not suitable for laying down zinc, the deck crew did something else.

And unlike the yards we did not have to worry about recoat times. We simply let the zinc cure, sometimes for several weeks. We then did a quick flashblast, then a mist coat of epoxy, and then two coats of epoxy. There were a couple of isolated cases where the topcoat did not stick, but these were traced to incompletely cleaned oil contamination. We never had a Capitol like failure.

The point is that waterborne zinc's sensitivity to weather and the lengthy and sometimes variable recoat intervals are not nearly the problem for a crew at sea, as they are for a yard with a tight production schedule.

There are three reasons for topcoating zinc in order of increasing importance,

1. It makes the deck easier to clean. Eventually, waterborne zinc will become quite smooth, even slippery, but this can take as long as several years. Before that happens, cleaning zinc decks is nearly impossible.
2. To protect the zinc against acid. This is especially important aft, where stray cinders from sootblowing or engine exhaust can land on the deck. These acidic particles will eat through the zinc.
3. To keep the temperature in the top of the tanks below the tank coating's GTT. To do this we need, a pure white deck. See [1], Appendix A.

Our experience is that top coating waterborne zinc is not particularly difficult. Nor did we have any real problem in touching up the zinc. We simply spot blasted the damaged areas with some feathering at the edges, laid down some new zinc, and topcoated at our convenience. I know of no case where the new high ratio zinc did not stick to the old.

All seven of these ships were scrapped in the period 2002 to 2004. When these ships went to the breakers, all the 8 to 10 year old deck coatings were in near-perfect condition and were requiring very little maintenance.

### 3 The Future at Sea

In 1999, my firm placed orders for four VLCC's and four ULCC's in Korean yards. The four VLCC's were sold prior to delivery. I thought briefly about trying to get the yards to use waterborne zinc a la Ludwig. But the Koreans had no experience with zinc silicate other than shop priming, and their whole coating system would have had to be revised. We ended up going with a white polyurethane over white epoxy topsides and deck.

I expected this organic coating to hold up maybe five years on the deck. The ULCC's were fitted with a permanently installed Ultra High Pressure (UHP)

<sup>6</sup> If we did get mud-cracking, we simply reblasted and recoated.

water blast system. This system uses a 3000 bar jet of water to strip paint. Our tests indicated that we could achieve blasting rates close to that of grit blasting without all the mess and expense of grit. Moreover, we discovered that with distilled water — the only water available on board — the resulting surface was so free of salt that even on a tanker deck the hydro-blasted steel would not turn for 48 hours or more. Piping was fitted along the main deck centerline, so the crew could tap into the UHP water where ever it was needed. UHP blast will not produce a profile; but, since this steel had already been reblasted in the yard to 75 microns or more, this was not an issue.

When the organic system broke down, the plan was to strip the deck using the UHP system, lay down a 125 micron coat of high ratio zinc, and top coat with polyurethane to get the desired pure white color. I think it would have worked fine. But we will never know. In 2004, these ships were sold. But by that time the crew was already making good use of the UHP system for all sorts of touch up jobs.

## 4 The Future in Newbuilding

Despite the yards' antipathy to change, they would do well to think seriously about waterborne zinc.

## References

- [1] J. Devanney. *The Tankship Tromedy*. Center for Tankship Excellence, 2006.
- [2] C. G. Munger. *Corrosion Prevention by Protective Coatings*. NACE, 1999.

Zinc has a number of compelling features for a new-building yard including

1. Nil volatile organics.
2. Low profile. To get really good adhesion with an epoxy coating, you need at least a 75 micron profile, preferably 100. Since zinc uses valence bonding, it is perfectly happy with a 40 or 50 micron profile which can be achieved with minor modifications to existing shop blasting procedures.
3. Much less paint. One 100 micron coat of zinc is worth two or three 150 micron coats of epoxy.
4. Fast drying. Under controlled conditions, waterborne zinc will dry in a matter of minutes, while epoxy takes the better part of day.

The key is adjusting the production system to take advantage of these characteristics. For example, we could have a computer controlled "priming" system that puts a full 100 micron coat of zinc on those areas of plate which will not be welded and a normal 20 micron coat on those areas which will be. After this step only the weld seams would need to be reblasted and recoated. The only other painting would be the final exterior coat for cosmetics. One can imagine a yard with no paint sheds.

Of course, imagining and doing are two different things. For now the short, happy life of waterborne zinc on tankers is over.