

NOTE: These comments were made by Mark Schilling dealing with Salts, Chloride, Osmosis and corrosion. Mark passed away several years ago but I believe Mark knew more about soluble salts than anyone in our industry. He was a paint and corrosion expert and worked for Unical, ExxonMobil and KTA as well as others. I think it is worth passing along some of Marks thoughts on the subject..

General Remarks by Mark Shilling 03-27=2009

When talking about paint application over soluble salt contamination, there are two concerns, osmosis and corrosion. Almost no one in the coatings industry understands that these are two very different phenomena that can be - and should be--discussed separately.

When painting over salt contaminated steel, the first concern is osmosis (osmotic blistering), not corrosion.

## OSMOSIS

Osmosis is physical chemistry. Osmosis is one of the colligative properties of solutions.

Osmosis has absolutely nothing to do with electron transfer or corrosion.

Osmosis is independent of the chemical nature of the dissolved stuff.

Osmosis is really all about the solvent (e.g., water) and not the solute (salt - anions & cations). The colligative properties of solutions (e.g., freezing point depression, boiling point elevation) are due to the **number** of dissolved particles. Most solution properties are due to the chemical nature of the dissolved stuff. For example, sugars are sweet. Organic acids (e.g., vinegar) are bitter. Acetates are fruity. Salts are salty. That can be some very complex stuff. The good news is that by contrast, the colligative properties are simple. It's the **number** rather than the nature of the dissolved stuff.

OK - so what does that mean??

First and foremost - it means that chloride ion is nothing special. Sodium chloride gives sodium and chloride ions in solution. The sodium ions are present in equal number. The sodium ions are of equal importance.

Please read the prior paragraph aloud several times.

With regard to osmotic blistering, chloride ion is nothing special.

However, testing specifically for chloride ion can make good sense because chloride ion is prevalent and it is quick and easy to test for. Chloride ion is often the dominant ion.

For example, the composition of seawater is variable but it is typically about 3.5% TDS. And of that 35,000 ppm, chloride ion registers as number one, at about 19,000 ppm (more than half of the total on a ppm basis). Chloride ion can be a good yardstick.

With regard to osmosis, chloride ion is nothing special. Test for conductivity, which "sees" all the ions in solution. Conductivity gives you a feel for the total number of ions in solution. Conductivity is far and away the proper way to go without any requirement of trying to get a chloride salt equivalent. Conductivity won't tell you anything about non-ionic soluble material. If there were, for example, soluble sugar on the surface, it would also affect the osmosis.

Everything that dissolves in the water affects osmosis.

## Corrosion

Chloride ion is a little something special, but the coating industry professionals often doesn't have a clue as to why and/or how. They aren't chemists.

Osmosis is comparatively simple. Electrochemical corrosion can at times, be exceedingly complex. That's why it is good to address osmosis first and then set it aside.

There are many forms of corrosion. When it comes to paint the thing we focus on is electrochemical corrosion. Electrochemical corrosion is about oxidation and reduction reactions. The iron in steel is thermodynamically unstable. It would like very much to oxidize to ferrous ion ( $\text{Fe}^{2+}$ ) and slip off into the electrolyte. But every atom of iron that does so leaves 2 electrons behind in the steel matrix. That starts to build up a negative potential on the steel so that the steel literally holds onto itself stronger.

The steel needs to find a way to dump electrons in order to continue corroding. That's where the corrodent comes into play. By definition, the corrodent is the cathodic reductant, the chemical species which steals electrons from the steel and in so doing, is itself reduced.

Electrochemical corrosion is all about redox chemistry. The term "redox" reflects **re**duction and **ox**idation reactions. That "game" so to speak is governed by electron accounting. The two reactions (anodic and cathodic) are coupled by way of the electrons. We can do that accounting down to a single atom.

With regard to salts and electrochemical corrosion, let us start with the basics. Pure water is a weak electrolyte. Under ambient conditions, the auto ionization constant of water is ten to the minus 14. That means we have equal numbers of hydroxide and hydronium ions floating around, both at ten to the minus 7 molar concentration. That puts neutrality at pH 7.0.

Let's be careful and clear here. If we start to play games with temperature and pressure, such as water in a boiler, then things change.

The only thing we need to focus on first is this - the word "salt" means anions and cations. If we have "salt" we have both anions and cations.

Returning to electrochemical corrosion - the electrochemical corrosion circuit is completed by the migration of ions in the electrolyte. The electrons in the steel matrix are relatively free to move about. The limiting factor is the migration of ions in the electrolyte. That's where the resistance is. Pure water is not a very good conductor. Adding salt improves the conductivity of the water, or in other words - it decreases the resistance.

OK - fine - it sounds mundane but it's not really because too many people forget the details. Salts consist of anions and cations. Use conductivity to measure all of the ions in solution.

There are many articles written in Material Performance and JPCL that would have us believe that the only thing that matters is the anions - with chloride being the most nefarious and deleterious of them all. No!!

The electrochemical corrosion circuit is completed by the migration of ions in the electrolyte. The salt anions (e.g., chloride ion) migrate toward anodic areas and the cations (e.g., sodium ion) migrate toward cathodic areas.

We need to have **both** anions and cations to complete the circuit. Chloride ion is really nothing special in this regard either.

And so, chloride ion is nothing special when it comes to osmosis (osmotic blistering of coatings) –

And chloride ion is really nothing special when it comes to our first and most fundamental look at electrochemical corrosion.

Now, after that one might choose to talk about how chloride ion may adsorb on the surface of metals and disrupt passivity. We shouldn't start the discussion there. Depassivation is incredibly important for stainless steels. It isn't very important for carbon steel. It's even less important for painted carbon steel.

In conclusion

When painting over salt contaminated steel, the first concern is osmosis, not corrosion.

No matter how one looks at it, osmosis or corrosion, chloride ion is not some super-powered boogey-man.