

Myths About Salts, chlorides, and Coatings

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Over the years, there has been much written about salts and chlorides. Much of it is true, some of it is misleading, and some of it is downright wrong. The purpose of this article is to try to cut through the marketing hype and sort out myth vs. fact. Four common myths are presented and analyzed for factual truth and understanding. The reader is cautioned to review articles and other presentations carefully to separate myth from fact.

Many specifiers intermix the term “salt” and “chloride.” While most of the salts on metal or concrete surfaces are generally chloride salts, not all salts contain chloride. The only way to determine “salt” in the field is to measure conductivity and make some assumptions to calculate total salts or total dissolved solids (TDS). The only way to measure the chloride anion is to use a test specific for chlorides. To determine which test is best for a specific project, we need to understand the specific concern of “invisible surface contaminants.”

Salts

The first step is to understand what constitutes a salt. Often, salts are referred to as molecules. The fact is, salts are not molecules but should be more properly referred to as “formula units.” This is easy to explain if we look at the lattice structure of a salt crystal. Let’s examine a sodium chloride (NaCl) crystal (Figure 1). Figure 1 shows that each chloride ion is bound to four (six for face-centered cube lattice) sodium ions by strong electrostatic charges called ionic bonds, and each sodium ion is in turn bound to four other chloride ions by ionic bonds. Since no single ion is attached to any other ion, this is not a molecule but a lattice of 1 chloride anion (Cl^-) to 1 sodium cation (Na^+) or NaCl. Salts are typically composed of a metal atom (cation) and a non-metal atom (anion) joined by ionic bonds. Other salts contain two nonmetal atoms

(ammonium chloride [NH₄ Cl])
 or two metal atoms
 (calcium plumbate [Ca(PbO₂)₂]).

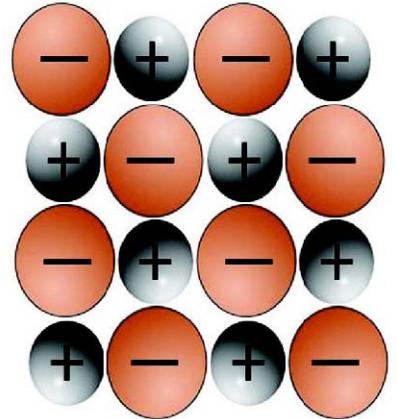
An accepted definition is that a salt is an ionic compound formed by the reaction of an acid with a base.

Bad Salt vs. Good Salt

The industry has been deluged with articles on chloride and salts that imply or state that some salts are worse than others (e.g., chloride, sulfate, and nitrate are bad). The following terms need to be understood:

- **Solution**—A solution is composed of a solvent *and* a solute. For this article, the solvent is water and the solute is the substance on the surface under the paint that is water soluble.
- **Osmosis**—This is a colligative property of solutions that depends on the number of molecules in a given volume of solvent and not on the mass or type of the molecules. Osmosis is independent of the chemical nature of the solute, but it very definitely depends on the solvent. What is dissolved can be ions, solvents, or organics such as sugar.
- **Osmotic pressure**—Osmotic pressure depends on the number of dissolved molecules, not the chemical nature of the solute. So, what the solute is doesn't matter. But what the solvent is does matter. This will be described in greater detail below.

FIGURE 1



NaCl crystal.

Myths

Chlorides Pull Water Through Membranes

Many articles state some salts containing chloride anions are hygroscopic, making these salts worse than other salts. This myth further states that the hygroscopic chloride anion, generally in the form of NaCl, pulls the water through the coating and causes an osmotic cell to grow.

Chloride salts don't pull water through the coating. The air or solution on one side of the coating cannot directly detect what is on the other side unless there is a hole in the coating. In addition, the salt normally cited as the problem, NaCl, is not particularly hygroscopic when compared to many other salts.

A coating is semipermeable, which means it will let small molecules pass through (water) but not larger molecules (anions and cations). When water is on the surface of the coating, small amounts of water migrate through the coating as individual molecules. When the water molecules reach the substrate under the coating, the water dissolves any soluble salts or other water-soluble materials to form a solution. The dissolved particles lower the vapor pressure of the solution, which prevents the liquid from leaving the solution and creates a driving force (osmotic pressure) from the higher vapor pressure side (the liquid outside the coating) to the lower vapor pressure side (the solution beneath the coating). Osmotic pressure is determined by the relationship of two solutions separated by a semipermeable membrane. The number of molecules (molar concentration) in the solution, not the composition of the molecules, determines what the osmotic pressure is. Molecules can be soluble salt ions such as Na⁺ and Cl⁻ or soluble organics such as sugars or solvents.¹⁻³ The important thing to note is this: the solute that is dissolved has no bearing on osmosis. It does not even have to be a salt. What matters is the number of molecules that are dissolved. The theory that treats the concentration of solute molecules in accordance with the "Gas to all solutes and is true

only at extreme dilution, but the theory is valid for this discussion.

While the nature of the solute has no bearing on osmosis, it does have a bearing on the creation of a corrosion cell. If the solute is ionic, the liquid under the coating is now an electrolyte and will form a corrosion cell. The solute that is dissolved will affect the strength of the corrosion cell. If salts present in the solution render the pH acidic, the corrosion cell will be more corrosive than if the solution is basic.

Chemical Additives are Necessary to Remove Water-Soluble Salts

This leads into the discussion of using chemicals to reduce water-soluble salts or chloride contamination. In most situations, the use of high-pressure water is sufficient to remove salts to a level low enough to meet the extraction criterion. It is important to use good-quality water to prevent further contamination of the surface. The objective is to have the surface meet the extraction criterion.

Pressurized water cleans a surface better than just pouring a bucket of water on it. The energy imparted to pressurized water helps break the surface tension of the water to make it more effectively wet the surface. Typically, higher purity water will dissolve more salts. As the wash water quality decreases, or the surface is corroded or pitted, surface cleaners can help remove salts. If the wash water is too contaminated, not even cleaners will help clean the surface. They may even increase the contamination. After washing, the surface should be tested to measure the amounts of salts on it.

All cleaners work in generally the same way. To remove the salts, the solvent (water) needs to reach the solute (salts). It is necessary for the cleaner to reduce the surface tension of the water to better access the salts. The surfactant in the cleaners, along with the high pressure of the water, pull the salts into solution, which also helps to remove insoluble particles and dissolve any soluble salts. This is why most salt removal products require the use of high-pressure water. Generally, the higher the pressure, the more efficient the wash.

Only Acid-Based Cleaners will Remove Chloride, Sulfate, or Nitrate

Many articles state that the only effective way to remove chloride-, sulfate-, or nitrate-containing salts is to use acid-based cleaners. This is a myth. There are several products on the market to remove salts from steel. Acidic, neutral, and basic cleaners can all be used effectively.

The only way to be certain the surface is salt free, even after cleaning, is to run a conductivity test.

A two-year study conducted at Kennedy Space Center compared four cleaners formulated to remove chloride ions.⁴ The cleaners, all off-the-shelf products generically called chemical rinse aids (CRAs), were already in use for washing down aircraft. These CRAs included acidic (initial pH = 3.5), neutral, and basic (initial pH = 9.0) cleaners.

The researchers rinsed various metal coupons and let them dry in a beach exposure. Comparisons were made for coupons rinsed with demineralized water, seawater, and unrinsed. They found that the pH of the cleaner had no effect on how well it removed salts on steel to stop atmospheric corrosion.

Acid-based cleaners are ionic. Once they are used to remove the salts, the cleaners themselves must be removed since they are salts. If the cleaner is still present when the surface is painted, it will form a corrosive solution.

Basic cleaners are generally based on amines; they are nonionic and contribute little or no conductivity to wash water. Some are 100% volatile, meaning they will evaporate from the surface with the water. Should any residue

remain, a corrosion cell will form, but as the solution becomes more basic, and thus inhibits or reduces corrosion.

Testing for Chloride, Sulfate, and Nitrate Ions Ensures a Salt-Free Surface

Since chloride, sulfate, and nitrate ions are in the majority of salts present, they are usually a good indicator of salts left on the surface, and many specifications require testing for one or more of these ions. If the prime concern is chloride-containing road salts, testing for chloride will probably find the majority of these ions still present. It also may not.

For example, acid-based cleaners contain other salts, which may contaminate the surface during cleaning; however, they do not contain Cl^+ , SO^- , or NO ions.

With nonionic cleaners, this is not a concern.

The only way to be certain the surface is salt free, even after cleaning, is to run a conductivity test. If there is no conductivity, there are no chloride, sulfate, nitrate, or any other ions present in solution. European standards and the new International Marine Organization (IMO) standards require conductivity testing for this reason.

Amine Based Cleaners Do Not Remove Salts, They Mask Salts

It is often stated that some cleaners may mask salts so they are not detected during testing. This could be either a myth or fact depending on the chemistry of the cleaner. A few inhibitors work by forming a barrier layer on the surface so that oxygen and water cannot easily migrate through the barrier. A common example is the use of phosphoric acid (H_3PO_4) or phosphates to form iron phosphate on the surface. Phosphatizing steel is a very accepted practice. In the most general terms, an acid is used to react with or etch the steel to create a water-insoluble salt coating. Other very basic inhibitors could form barriers of iron oxide or iron hydroxide [$\text{Fe}(\text{OH})_2$] by reacting with a water-soluble iron salt to form a water-insoluble salt coating. The barrier would mask salts if they were present on the steel under the barrier.

Amines, which are derivatives of ammonia (NH_3), are weak bases and often cited as a film-forming product that can mask salts. Stating it this way is misleading. Some amines are formulated to create a stable hydrophobic film on the metal surface to repel water. These types of amines are often used in the water treatment industry to inhibit corrosion. Again, the amine barrier would mask salts under the barrier if they were present on the steel.

Amines can be formulated to have many different properties, however, including being aromatic. Because they are non-ionic, aromatic amines used in cleaners will not leave a film that masks salts on surfaces, add any salts to the cleaned surface, or form any impenetrable hydroxyl layer on the steel.

Conclusions

Just because it is in print does not make it true. Many coatings and corrosion articles are not based on original research, but rather on previous articles. Often, parts of articles or technical papers are quoted out of context, which alters the meaning of the original text. Errors from one article get passed down to the next article. Some coatings and linings articles are often a mix of personal opinion, practical observation, marketing hype, and little professional peer review. If we say it often enough, myth is perceived as truth.

This excursion from the factual base can be very devious. But knowledge is power. Dust off that old chemistry book, when references are given, take the time to check out the reference to see if it was properly cited, and do not believe something just because someone said it in a lecture or printed it in an article.

References

- 1 C. Hare, *JPCL* 10 (2007): p. 77.
- 2 C. Hare, *JPCL* 2 (1998): pp. 45-63.
- 3 C. Hare, *JPCL* 3 (1998): pp. 17-34.
- 4 J.J. Curran, J.P. Curran, L. MacDowell,

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