Measuring Salt, NaCl, and Soluble Contaminants with Bresle Patches—Part 1

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The presence of salts on a substrate can have serious effects on coating performance. This two-part article discusses understandings and misunderstandings about salt contamination, describes the Bresle test and the complexities involved in obtaining accurate data, and explains the importance of correct data interpretation. Part 2 will be published in the December 2009 issue of MP.

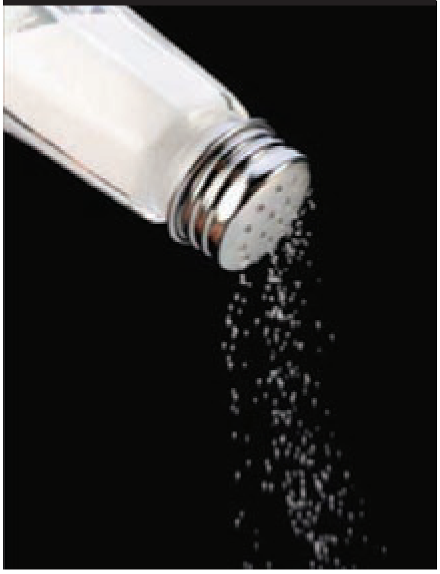
The coating industry understands that salt contamination underneath a coating can cause serious problems in future years. This is because of the hygroscopic nature of salt. This tendency to attract water, in combination with the permeability of a coating, creates an accumulation of water molecules between the substrate and coating. The presence of these water molecules, together with the entrapment and migration of oxidation agents, is ideal for creating an electrochemical shift that causes corrosion in conjunction with the salt molecules present.

Blasting or mechanical cleaning will not remove these salt molecules completely and often causes chloride inclusion into the substrate, making the situation even worse. Washing the surface with deionized water is the most-used solution. A substrate free of soluble salts is critical in today's protective coating work and is an issue in each paint specification, which nowadays can include limits for soluble salts. Some regulations set the maximum concentration of soluble salts, measured as sodium chloride (NaCl), on a surface to 20 mg/m^2.

The Principle of a Bresle Test

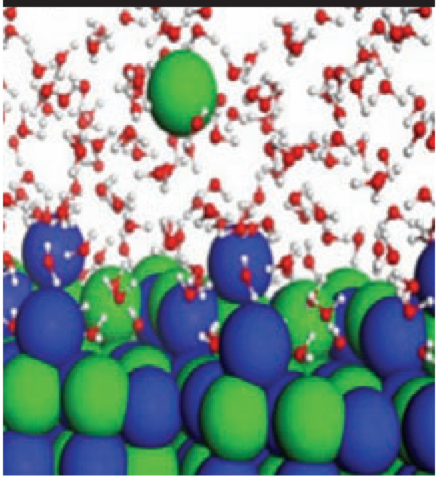
When performing the soluble salt test, water is injected in a patch that is placed on the surface. The injected water dissolves the salt present at the surface. The salt solubility in water depends on the type of salt. Common salt, NaCl, can be dissolved in cold water to a concentration of 357 g/L. Not only does solubility differ among salts, but conductivity also differs. Thus, when taking a measurement, common salt and all other salts present on the surface are dissolved. This mixture of salts is eventually measured with a conductivity meter or by other means.

FIGURE 1



Typical layman's understanding of salt.

FIGURE 2



An illustration of the difference in size and solubility of salt molecules.

Misunderstanding of What is Actually Measured

Because it is impossible to predict which salts are present at the surface, an assumption is made in the Bresle method. The term "measured as sodium chloride" indicates that this mixture of salts is interpreted as being only NaCl. Clearly indicating how the conductivity is interpreted is essential when creating a report. At present, there are several interpretations in use. Some speak about NaCl while others mention mixed salts or just chlorides, and each has a different calculation factor.

Salt, Sodium Chloride, and Soluble Contaminants

Our vocabulary is full of words that have a double meaning. If you ask people what salt is, they virtually always reply by referring to the stuff we put on our French fries (Figure 1). If you ask, what is "sodium chloride?" they say it is salt. This statement is true, but, the other way around is not. Think of it as follows: a cow is an animal; however, an animal does not have to be a cow. The same is true for NaCl (common salt). NaCl is a salt; however, salt does not have to be NaCl. Here the extensive meaning of the word "salt" starts to cause a problem.

The chemical meaning of the word salt is a lot broader than the common word. Salt is a neutral product formed by a neutralization reaction between acids and bases. The reaction product is an ionic compound. This means that when the product is dissolved in water, it splits into an anion (negatively charged particle) and a cation (positively charged particle). Both the anion and the cation can be inorganic or organic, as well as mono- or polyatomic (one or multiple atoms combined). The breakdown into a cation and anion produces an electrolyte in water. Only the products that dissolve in water and not those that disperse will create this electrolyte. Within a solution, NaCl is no longer present as such; it has split into sodium and chloride ions. This also indicates that it is not possible to have just chloride ions on a surface.

Solubility

The nominal volume in the test chamber of the original Bresle patch is 2.5 cm^3. Considering the volume and solubility of salt, it is possible to dissolve 892.5 mg of common salt in the patch. This correlates to 7.29×10^5 mg/m^2 NaCl. Comparing this to the IMO regulation of 20 mg/m^2, there is a factor of ~36,000 between these concentrations. Thus, the solubility of salt is not an issue when conducting the test. A level of 20 mg/m^2 NaCl is actually only 0.025 mg NaCl in the patch. Even salts that are harder to dissolve will be present in such concentrations that should not provide any solubility problems.

Not all salts are equally soluble in water; there is a great difference in solubility. While NaCl can be dissolved to 357 g/L, its chemical brother silver chloride (AgCl) can be dissolved only for 0.00089 g/L. This is stated as the solubility product K_{sp}. At these concentrations, the solution is saturated and equilibrium is reached between dissolved and non-dissolved. A dissolved salt produces ions and with it forms an electrolyte. The non-dissolved salt does not produce ions and does not produce an electrolyte. This means there is no significant increase in conductivity. Even calcium carbonate ($CaCO_3$) is a salt, a very insoluble salt, but nevertheless a salt. It has a solubility of 0.014 g/L. Figure 2 is an illustration of the difference in size and solubility of salt molecules.

Determining Solubility

To determine if a salt is soluble, there is a chemical rule. In chemistry, a concentration in mg/L is not interesting, because of the difference in weight between different molecules. The amount of molecules is what is of interest to a chemist. Look at it as bolts and nuts. A bolt is heavier than a nut; to have as many bolts as nuts means that you need 1 kg of nuts to screw onto 2 kg of bolts. A chemist looks at a concentration in mol/L. The term moles can best be compared to the definition, reactive, or working units. In chemistry, the solubility is stated in three groups:

A salt is soluble if it dissolves in water to give a solution with a concentration of at least 0.1 mol/L at room temperature. A salt is insoluble if the concentration of an aqueous solution is <0.001 mol/L at room temperature. Slightly soluble salts give solutions that fall between these extremes.

Conductivity

The method of measuring the conductivity of an electrolyte is not the same as the procedure used to measure conductivity of copper wire. Conductivity is measured with a sine wave potential across two defined plates set at a defined distance from each other. Between these plates, the ions in the electrolyte conduct the current backward and forward. The size and distance between the plates determine the cell constant. This constant is also the factor that is adjusted during calibration.

When taking a conductivity reading of the solution acquired with the Bresle method, all dissolved salts are measured, even the small dissolved portion of the insoluble salts.

This electrolyte is what can be measured by a conductivity gauge. The higher the concentration, the higher the conductivity. The conductivity of an electrolyte not only changes by concentration, but also by variation in the ions present. The same concentrations of NaCl or potassium chloride (KCl) produce electrolytes with a different electric conductivity. Conductivity is thus quantitative and qualitative dependent. Temperature and pressure also influence the measurement. With higher temperature comes a higher enthalpy. Enthalpy is a measure of the heat content at subatomic level. Very simply stated, this means that the hotter a subatomic particle gets, the more active it gets, as does its reactivity and interactivity. A microwave oven does not put heat in your food; it imparts more energy/activity, which in turn produces heat. The higher the temperature in a solution, the higher the conductivity. Modern conductivity gauges are compensated for this temperature influence. To determine conductivity, reference salts are used. This is done by having a solution with a fixed concentration of a pure reference salt, usually KCl.

Conductivity is a nonspecific measurement method; it detects all soluble salts, with all different varieties. The salt mixture that is found in the measurement cell usually is not made up of one type of salt. This multi-ion electrolyte requires an interpretation when the conductivity has to be reported as a concentration. This interpretation is one of the biggest misunderstandings when measuring. The results, according to ISO 8502-6[1] and ISO 8502-9,[2] have to be reported as mg/m^2 soluble salts measured as NaCl. The statement "measured as sodium chloride," means that not only NaCl is measured but also all other dissolved salts.

To have a traceable result, an easy reference salt has to be selected. NaCl is chemically a reference salt. Not only is it suitable as a reference salt, but also it is the biggest cause of problems and has the highest share in concentration, making it the ideal salt to report. At present, there are multiple interpretations in use. The most common used is the reference to NaCl. Some others are mixed salts and chloride. With the Bresle method, this relates to the respective factors 6, 5, and 3.6. Here, factor 6 calculates as NaCl, factor 5 as mixed salts, and factor 3.6 to an industry-fantasized possibility of having only chloride ions present. Even when test methods are specified, it would still be very helpful if all involved parties stated the salt concentration the correct way. Not stating the answer with the right interpretation can cause serious differences in the result. If the specifications are in chloride and the measurement is made as NaCl, there is a significant difference that can lead to extreme costs caused by unnecessary cleaning.

What is the Correct Interpretation of Data?

Referring to the total salt mixture on a surface as NaCl is an interpretation. Let us, however, compare it to measuring traffic jams. The length of a traffic jam is not measured, but calculated. It is a multiplication of the amount of cars times their length. You never know, however, which cars are in the traffic jam, so you don't know the exact length of each car. You can look at sales figures in the car industry and calculate an average car length from this, but what about the old cars? Second, cars are just like salt deposits—region specific. Americans drive Hummers, Europeans drive Mercedes, and Asians drive the Tata Nano. There is no real comparison and uniformity. The traffic controllers for the coating industry, in this case ISO, gave the solution. A traffic jam stated in length is calculated by the length of just one car, a 1949 Cadillac Deville, the length of which is known worldwide. This means that the amount of cars in any traffic jam worldwide can thus be multiplied by a standard value and all traffic jams are then comparable. The same goes with salt measurement—soluble salts in g/m^2 are measured as NaCl.

Conclusions

Part1 has presented a general understanding of salts and also explained many misunderstandings. The Bresle test has been introduced, along with many aspects of salt solubility and solution conductivity. Part 2, to be published in the December 2009 issue of *MP*, will cover sampling procedures, measurement techniques, the effect of climate on test results, and comment on commercially available test kits.

References

1 ISO 8502-6, "Preparation of steel substrates before application of paints and related products—Tests for the assessment of surface cleanliness—Part 6: Extraction of soluble contaminants for analysis—The Brestle method" (Geneva, Switzerland: ISO).

2 ISO 8502-9, "Preparation of steel substrates before application of paints and related products—Tests for the assessment of surface cleanliness—Part 9: Field method for the conductometric determination of water-soluble salts" (Geneva, Switzerland: ISO).

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