

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

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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 ions from salt 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 with a controlled amount 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<sup>2</sup>.

## 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.

*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.*

## 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.

## NaCl, Salt, 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

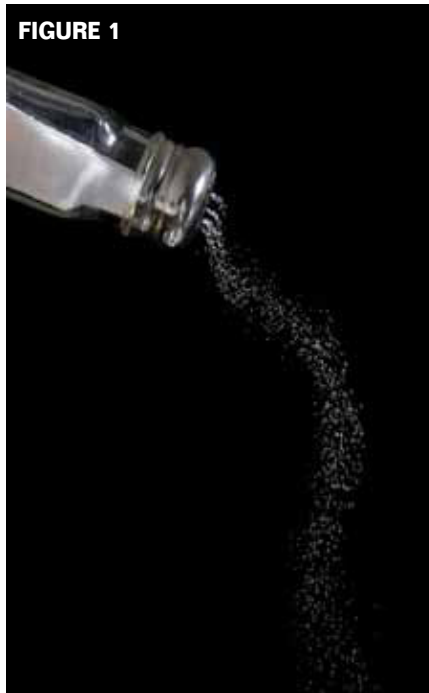


FIGURE 1  
Typical layman's understanding of salt. iStock photo.

create this electrolyte by splitting into ions. 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<sup>3</sup>. Considering the volume and solubility of salt, it is possible to dissolve 892.5 mg of common salt in the patch. This correlates to  $7.29 \times 10^5$  mg/m<sup>2</sup> NaCl. Comparing this to the IMO regulation of 20 mg/m<sup>2</sup>, 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<sup>2</sup> 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 cousin 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

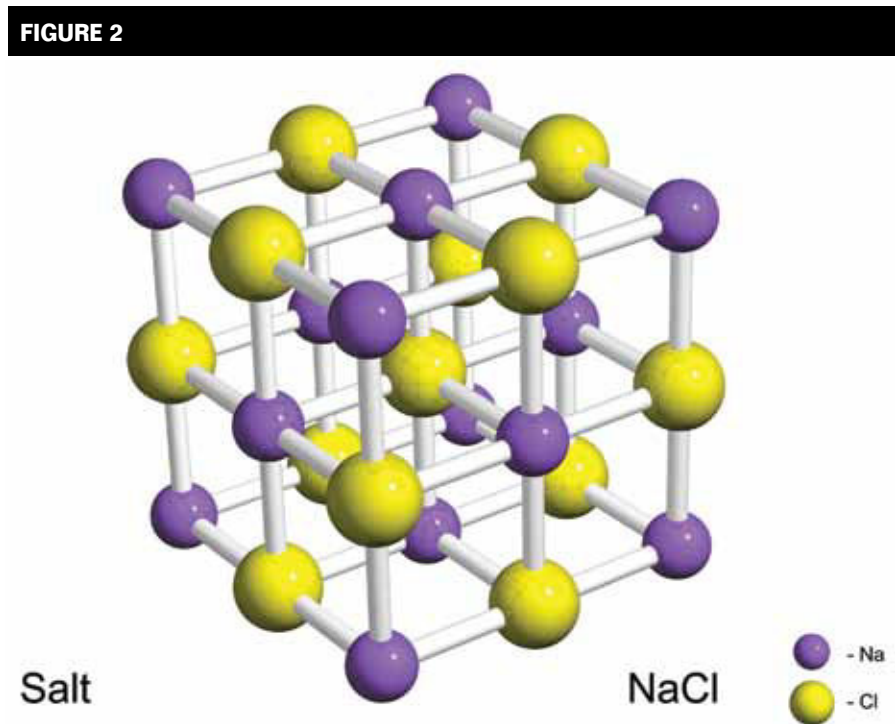


FIGURE 2  
NaCl in crystal structure as present on surfaces. Fotolia photo.

dissolved and non-dissolved. A dissolved salt produces ions and 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 ( $\text{CaCO}_3$ ) 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 NaCl in its crystal structure as present on surfaces.

### **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 atoms and 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<sup>1</sup> and ISO 8502-9,<sup>2</sup> have to be reported as mg/m<sup>2</sup> soluble salts mea-

sured 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 it also 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  $\text{g}/\text{m}^2$  are measured as NaCl.

## Conclusions

Part 1 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 Bresle 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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# Measuring NaCl, Salt, and Soluble Contaminants with Bresle Patches—Part 2

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*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 1 was published in the November 2009 issue of MP.*

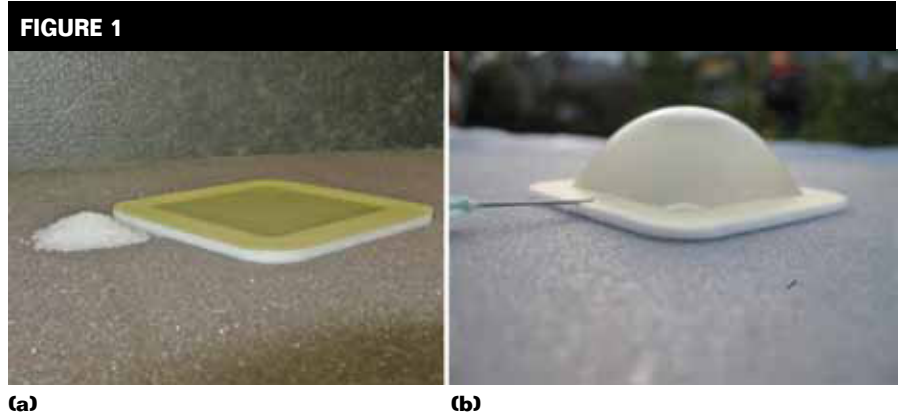
Part 1 of this article<sup>1</sup> presented a general understanding of salts and also explained many misunderstandings. The Bresle test was introduced, along with many aspects of salt solubility and conductivity. Part 2 covers sampling procedures, measurement techniques, the effect of climate on test results, and comments on commercially available test kits.

## Dilution

Contrary to solubility, dilution is a major cause for possible errors. To make it possible to measure the soluble salts with an electronic conductivity meter, usually 15 mL of the sample liquid is required to fully submerge the instrument's probe (Figure 1). Since the actual volume of sample liquid in the Bresle patch is only 2.5 mL, it means that the result has to be multiplied by a factor of 6. Any errors that were made during certain stages of the test will be multiplied by a factor of 6 as well.

## Effect of Dilution on the Test Results

The average residue of 0.15-mL testing liquid remaining in the patch after removing the test sample, and the inaccuracy and improper use of syringes are some causes for errors, but the majority of the problems are caused by diluting the sample liquid as it is often done in a separate 15-mL cup. Good analytical practice shows that the number of steps required to obtain an accurate test result has to be limited as much as possible. Dilution to 15 mL was required in the past to create sufficient quantity of sample solution to submerge a conductivity probe and to prevent extreme static disturbance from the plastic measuring beaker. Static disturbance is caused by the "insulation" from the use of a plastic cup. The disturbance is best explained as the echo of the measuring signal. Usually,



**FIGURE 1**  
The Bresle Patch: (a) 0.9-mg NaCl—2.5-mL water and (b) patch inflated with 15-mL water.

in analytical laboratories, measurements are carried out in a glass apparatus and at a volume preferably >100 mL. All conductivity gauges on the market are influenced by this static disturbance. This can lead to a difference of up to 5  $\mu\text{S}/\text{cm}$  per conductivity measurement. Diluting the sample liquid by a factor of 6 automatically implies that the test result has to be multiplied by a factor of 6 as well. In practice, this means that each deviation or error will be multiplied by 6. The 5  $\mu\text{S}/\text{cm}$  mentioned above could end up in a 30  $\mu\text{S}/\text{cm}$  error! New techniques, however, make it possible to measure in smaller samples using the direct sample procedure (DSP).

### Gauge Accuracy

During the evaluation of our study results, the need for a higher accuracy proved to be a hot issue. The accuracy can be increased in two ways, first by taking a closer look at the gauge. Previous available handheld or mobile conductivity gauges had a resolution of 1  $\mu\text{S}/\text{cm}$ , with an accuracy of 1%. Calculation according to ISO 8502-6<sup>2</sup> means that the final result has a resolution of 6  $\text{mg}/\text{m}^2$ , with an inaccuracy of 6  $\text{mg}/\text{m}^2$ . Therefore, when a measurement result is 18  $\text{mg}/\text{m}^2$  of soluble salts measured as sodium chloride (NaCl), the actual value fluctuates between 12 and 24  $\text{mg}/\text{m}^2$ , giving a 33% chance that the actual soluble salt concentration is above the limit of 20  $\text{mg}/\text{m}^2$ . (Standards such as Norsok already use these concentrations.) Increasing the gauge's resolution to 0.1  $\mu\text{S}/\text{cm}$  contributes to a higher accuracy when determining the soluble salt concentration. This, however, is only one part of the analysis.

Besides gauge resolution, dilution also influences the measurement. The earlier mentioned 0.15 mL of residue remaining in the patch causes an error up to 5% in the 15-mL diluted solution. When this

dilution is not applied and the measurement is made directly on the pure solution from the patch, the 0.15 mL residue will not affect the result. New gauges can already measure in 2 mL solution with a resolution of 0.1  $\mu\text{S}/\text{cm}$ . When measuring in a volume of 2.5 mL, the same as the nominal volume of the patch, there is a significant change in calculation factor. Use of a 2.5 mL sample leads to the elimination of the normal calculation factor 6. The concentration of soluble salts measured as NaCl is equal to the conductivity in  $\mu\text{S}/\text{cm}$ . This not only makes the determination easier but is also more reliable. Results can now be given with a 1  $\text{mg}/\text{m}^2$  uncertainty and resolution of 0.1  $\text{mg}/\text{m}^2$ , increasing the accuracy 60-fold.

### Reporting of Results

The stakes are high when looking at surface cleanliness, but most specifications never state how the result should be reported. Just stating according to ISO 8502-6 and -9<sup>3</sup> is not sufficient. Different test kits give different factors; carefully reading the test kit's manual is essential. Even making a small change in volumes or patches, without correcting the factor, can make entire measurements useless.

The acquired results of any soluble salt measurement have to be clearly formulated. When the concentration is given as  $\text{mg}/\text{m}^2$  soluble salts measured as NaCl, it does not imply that there actually is this amount of NaCl present. The actual

concentration is lower than the measured concentration, because there are also other salts present that are interpreted as NaCl. The same is true for the two other commonly used interpretations. None say exactly what is at the surface, but state what would be present when assuming only NaCl is present. This assumption is what makes the Bresle method so usable. NaCl is the same worldwide, but the preset salt mixture varies by location. Interpreting the result as one type of salt gives a reproducible method. One must consider the fact that it is the presence of a soluble salt that creates the possibility to form an electrolyte, which in turn causes corrosion. Nonsoluble salts are not a significant factor in the formation of corrosion.

### Alternative Methods of Measurement

There are different options in measuring, for example, derivatives from the Bresle method that are ion specific. These measurements don't look at the sum of contamination but at one specific ion, for instance chloride. Determining chloride can be done in multiple ways. Many methods, however, require either large equipment or multiple handlings, but some of them can easily be used. Ion selective electrodes and spectrophotometric determinations are examples of tests used in the field. Spectrophotometric determinations are not new. Swimming pools have been checked by this method for many years,

FIGURE 2



A direct sampling kit.

although the measured concentrations are much higher in these applications. A concentration of 50 mg/m<sup>2</sup> NaCl equals a concentration of ~4.2 mg/L NaCl in the patches test solution, depending on the used volume and patch. The chloride concentration is ~2.5 mg/m<sup>2</sup>, which is much lower than normally measured with these alternative methods. Measuring at low concentrations brings a few problems along. The composition of a sample varies in multiple and mostly unknown ways—this sample composition is called the matrix. Ion specific detection methods are matrix sensitive. Acidity, the presence of similar ions, and many other factors influence the accuracy of these methods.

### Direct Sampling Procedure

The new direct sampling procedure eliminates the use of the 15-mL measurement solution. Measurements can now be directly made in the solution that is extracted from the patch, eliminating the dilution step. This not only increases ef-

iciency but also eliminates the most error-sensitive part of the old procedure. To achieve this, only 2.5 mL of deionized water are injected into the patch. This also reduces the calculation factor to 1. The reading from the gauge therefore doesn't have to be multiplied to get the soluble salt measured as NaCl concentration in mg/m<sup>2</sup>. Because the measurement is made in the gauge's own measuring cell, all static disturbance is also eliminated, increasing the reliability of the analyses even further. Figure 2 illustrates a direct sampling kit.

### Quality Materials

There is a large difference among the soluble salt test kits on the market. Not only the gauge but also the patches differ in shape and quality. A test patch should be as clean as possible. Any salts that remain on the patch during its production process influence the test significantly. The original Bresle patch is square and some of the alternatively shaped patches contribute significantly to the final mea-

surement. During tests, these patches contribute, on average, 0.7 mg/m<sup>2</sup> soluble salts measured as NaCl per patch. High-quality patches such as the latex membrane square patches contain less salt residue. These patches pass multiple wash cycles in a clean room-quality production plant to ensure that almost no contaminants are present.

The ISO 8502-6 standard states in Annex A that only certified patches may be used. This annex describes a stress test to ensure patch adhesion and wash ability. In ratio to the nominal volume of the patch, it has to be injected with an excess of water. Time to leakage has to be determined and eight out of 12 patches must pass in order for the type of patch to be approved. This test must be carried out by an accredited laboratory and the producer must be able to provide a certificate of the test. The high-quality patches have passed these tests. Most of the non-square patches fail this test by 100%, as only one third of the required volume can be injected into the patch before leakage starts.

When measurements are taken using noncertified patches, all acquired values will be useless. Only certified patches may be used. Some patches also face problems with poor and irreproducible adhesion making the test surface irregular. Often 20% extra surface area is exposed because the water creeps under the edges of the patch. This value is not corrected and causes even bigger errors in the results. All errors caused by using inferior patches lead to higher results, which added together usually generate a significantly higher and erroneous result.

### Climate

Each report produced on soluble salt levels should include climatic conditions and substrate temperature. The ISO 8502-6 standard stipulates that the test be done at 23 °C and at a relative humidity of 50%. Any deviation from the defined

parameters has to be reported and agreed upon by both inspector and customer. Surface temperature also influences the test, meaning that this parameter also needs to be recorded. The lack of these recorded values will also render the acquired results invalid.

## Conclusions

This article has shown that there is a lot of science behind proper testing for salt contamination. Inspectors can benefit from ready-made test kits that make these tests quite simple. Updated Bresle kits are now available with the DSP, enabling inspectors not only to work faster but also to produce more accurate results.

The combination of the new technique and high-quality gauges and patches makes these kits especially useful for establishing salt contamination. But, whatever procedures are used, it is essential to perform the test properly and to ensure that accurate data are obtained.

## References

- 1 N. Frankhuizen, "Measuring NaCl, Salt, and Soluble Contaminants with Bresle Patches—Part 1," *MP* 48, 11 (2004): pp. 36-39.
- 2 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 Bresle method" (Geneva, Switzerland: ISO).
- 3 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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