UPDATE

Measuring Surface Salt Contamination with Bresle Patches

In the last issue of PCE, the subject of measurement of surface salt contamination was raised in relation to equivalence of testing equipment for the IMO PSPC standard, and the recognition of errors with different sources of Bresle patches introduced (New Standard Development by NACE for use with the IMO Protective Coatings Performance Standard for Ballast Tank Coatings, PCE, April-June, 2009).
In the following article, Nico Frankhuizen of TQC bv, Zevenhuizen, The Netherlands, and Chairman of NEN NC 342.035, the Dutch Committee within ISO, TC 35 discusses the results of a study into the soluble salt measurement with the use of Bresle patches. This study indicates there is a lot of confusion about interpretation of test results, and identifies many possible errors in the procedures and equipment used, factors which could cause serious quality problems.

Basics

Everybody in the coating industry knows that salt contamination underneath a coating can cause serious problems in future years. This is due to the hygroscopic nature of salt. The tendency to attract water in combination with the permeability of a coating creates a accumulation of water molecules between the substrate and coating. The presence of these water molecules together with the entrapment and migration of oxidation agents, are ideal to create an electrochemical shift causing 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 deionised 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 professional paint specification, which nowadays can include limits for soluble salts. For example, the IMO PSPC regulations set the maximum concentration of soluble salts, measured as sodium chloride, on a surface to 20 mg/m^2.

All photos courtesy of TQC bv.

Quality of salt which can be dissolved in 2.5cm3 (2.5ml) deionised water

The Principle of a Bresle Test

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

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 sodium chloride. Clearly indicating how the conductivity is interpreted is essential when creating a report. At present there are several interpretations in use. Some speak about sodium chloride, others mention mixed salts or just chlorides, each having a different calculation factor.

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 x10^5 mg/m^2 sodium chloride. Comparing this to the IMO regulation of 20 mg/m^2 there is a factor of approximately 36000 between these concentrations. Thus the solubility of salt is not an issue when conducting the test. A level of 20 mg/m^2

sodium chloride results actually only in 0.025 mg sodium chloride in the patch. Even salts that are harder to dissolve will be present in such concentrations that should not provide any solubility problems.

Dilution

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

Affect of dilution on the test results

The average residue of 0.15 ml testing liquid remaining in the patch after removing the sample for test 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 15ml cup. Good analytical practice shows that the number of steps required to

Typical Bresle patch

obtain a final test result has to be limited as much as possible. Dilution to 15ml 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 easiest explained as the echo of the measuring signal. Usually disturbance is caused by the "insulation" due to the use of a plastic cup. In analytical laboratories, measurements are always carried out in glass apparatus and at a volume preferably greater than 100ml). All conductivity gauges on the market are influenced by this static disturbance. This can lead up to a difference of 5 μS/cm per conductivity measurement. Diluting the sample liquid by a factor 6 implies automatically that the test result has to be multiplied by a factor 6 as well. In practice this means that each deviation or error will by multiplied by 6. The 5 μS/cm mentioned above could end-up in a 30 μS/cm error! However, new techniques make it possible to measure in smaller samples using the Direct Sample Procedure or 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 μS/cm, with an accuracy of 1 μS/cm. Calculation according to 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.) means that the final result has a resolution of 6 mg/m^2, with also an inaccuracy of 6 mg/m^2. Therefore, when a measurement result is 18 mg/m^2 soluble salts

measured as sodium chloride, the actual value fluctuates between 12 and 24 mg/m^2 , giving a 33% chance that the actual soluble salt concentration is above the limit of 20 mg/m^2 (as in the PSPC standard) . Increasing the gauge's resolution to 0.1 µS/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 15ml diluted solution. When this dilution is not applied and the measurement is made directly on the pure solution from the patch the 0.15ml residue will not affect the final result. New gauges can already measure in 2 ml solution with a resolution of 0.1 µS/cm. When measuring in a volume of 2.5ml, the same as the nominal volume of the patch, there is a significant change in calculation factor. Use of a 2.5ml sample leads to the elimination of the normal calculation factor 6. The concentration of soluble salts measured as sodium chloride is equal to the conductivity in µS/cm. This not only makes the determination easier but also more reliable. Results can now be given with a 1 mg/m^2 uncertainty and resolution of 0.1 mg/m^2. Increasing the accuracy 60 fold.

Direct Sampling Procedure

The new Direct Sample Procedure eliminates the use of the 15ml measurement solution. At present, only one testing kit/measuring instrument is available on the market as other instruments don't have the large measuring cell or the required resolution. Measurements can now directly be made in the solution that is extracted from the patch, eliminating the dilution step. This not only increases efficiency but also eliminates the most error sensitive part of the old procedure. To achieve this there is only 2.5 ml of deionised water injected in the patch. This also reduces the calculation factor to 1. The reading from the gauge therefore doesn't have to be multiplied anymore to get the soluble salt measured as sodium chloride concentration in mg/m^2. Due to the measurement in the gauge's own measuring cell all static disturbance is also eliminated. Increasing the reliability of the analyses even further.

Quality materials

There is a large difference between the soluble salt tests 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 influences the test significantly. The original Bresle patch was square and some of the alternatively shaped patches, which can be found in the market, contribute significantly to the final measurement. During tests these patches contribute on average, 0.7 mg/m^2. soluble salts measured as sodium chloride per patch. High quality patches such as the latex membrane square patches, don't contain any salt residue. These patches pass multiple wash cycles in a clean room-quality production plant to ensure that 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 twelve 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%, only one third of the required volume can be injected in the patch, before leakage starts. When measurements are taken during arbitration using non certified patches, all acquired value's 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 due to the fact the water creeps under the edges of the patch. This value is not corrected and causes even bigger errors in the final results. All errors caused by using inferior patches lead to higher results, which added together usually generate a significant higher and erroneous result.

Climate

Each report produced on soluble salts levels should include climatic conditions and substrate temperature. The ISO 8502-6 standard demands that the test be done at 23°C and 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. During arbitration the lack of these recorded values will also render the acquired results invalid.

Conclusions

Although the above shows there is a lot of "science" behind proper testing for salt contamination, inspectors can benefit from ready made test-kits, which are available on the market, making these kind of tests quite simple. Up-dated Bresle kits are now available on the market with Direct Sampling Procedure, which enables inspectors not only to work faster but also produce more accurate results. The combination of the new technique, high quality gauges and patches, makes these kits the ultimate inspection set for arbitration. ■

Direct Sampling Meter