



TECHNICAL NOTE

Subject: **Salts 101 – An Overview**

Salts 101 - An Overview

Presented Courtesy of CHLOR*RID International, Inc. Introduction

Soluble salts are very much at the forefront of discussion in the coatings industry. There is much information available on the topic, but often is provided in small segments so a complete comprehension is not easy to grasp. It is the purpose of the following to provide an overview to assist in bringing those pieces together.

How are specifications changing?

As few as 4 or 5 years ago, specifications and surface preparation instructions rarely called for testing of salts or for limiting them. Today, testing and allowable limits are included in a large percentage of specifications. In a few short years, it is probable that most all specifications will address salts in some manner. Facility owners are beginning to understand how salts are causing coating life spans to fall short of their intentions and coating manufacturers are finding salts the cause of increasing warranty claims. Consequently, coating professionals throughout the industry are making changes in specifications.

For decades the coatings industry has worked with visual standards and visual comparators. As we begin to deal with soluble salts, which are corrosive even at very low levels, we enter the realm of non-visible contamination. As has been said many times, "Old habits die hard", especially in an industry steeped in perpetuation of established practices. Engineers, specifiers and coating manufacturers are now requiring testing and are setting allowable limits; however there is resistance to change, so such efforts are not always successful. To provide a sound specification for surface preparation, the specification writer must understand the significance of these salts, the problems caused by salts and the appropriate methods of testing evaluating and removing salts. Some specifications without a good understanding of the interaction of salts on metallic surfaces and, consequently, many specifications still do not capture the essence of testing and decontamination that would effectively provide for maximum coating performance.

Surface contamination by soluble salts has long been an issue for the corrosion industry, however, it was the discontinuance of lead-based paints that caused a renewed look at salts with regard to coating service life and their involvement with premature coating failures. A unique property of lead compounds is that they are capable of binding up soluble salts, thereby preventing salts from causing or increasing the corrosivity of the immediate environment. The widespread use of lead-based paints gave us a sense of security but the discontinuance of such products requires that we re-evaluate surface preparation requirements.

What are soluble salts?

An explanation voiced in a NACE (National Association of Corrosion Engineers, International) committee meeting some years ago stated that anything conductive should be considered a salt. Coating professionals had long realized that salts were detrimental to the substrate and to coatings. Though they did not have the means for testing that we do today, they realize that if a clean uncontaminated surface were washed with DI (de-ionized) water, that the water remained relatively non-conductive, but when contaminants were present an increase in conductivity was observed. Since they did not have the means to identify specific ions, especially in the field, estimates were used to determine percentages of chlorides and other ions based on assumptions. Since then, it has been found that these estimates are highly unreliable, but today we do have the means to identify and measure specific ions that are of primary concern. Everything conductive is still considered a salt; however, this conductivity could be comprised of hundreds of different chemicals and not all salts are detrimental to coatings.

Soluble salts are described in the Society for Protective Coatings SSPC, Protective Coatings Glossary as - "*An ionic chemical compound that dissolves in water to form a solution of positive and negative ions*". Clearly, the cleaner the surface, the better the coating performance, but some conductive materials have little effect on corrosion or coating performance, while other conductive materials can effect it to a great degree.

The prime detrimental salts most commonly encountered are chlorides, sulfates and nitrates, though specific industries may encounter others. These salts can be so detrimental that they can cause premature coating failure in as little as weeks in the right environment. These salts definitely can affect the overall life spans of coatings, even if the coating system survives beyond the warranty period.

The question industry is asking today is "How much of what salt can be left on a surface and not significantly affect coating life spans?" There are so many different coating systems available and so many different operating environments that a consensus number will probably never be developed or standardized. As time progresses we are continually gathering more information as to what has and has not worked. NASA engineers identified chlorides for their extreme corrosion effect in the late 70's and they established a chloride threshold limit of 5 micrograms per square centimeter (mg/cm²) as the acceptable limit on surfaces prior to coating. Although there was no adequate, reliable and accurate nondestructive test method for metallic surfaces, NASA held firm with their specification (KSC-STD-0001-D). Until recently they had to allow contractors variances to specifications because of the inability of contractors to meet the specification limits.

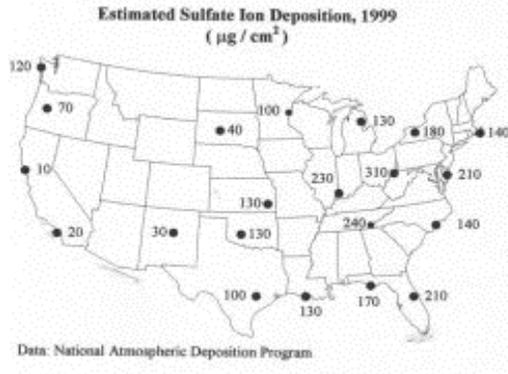


Figure 1

The US Navy started limiting chlorides in the early 90's, setting limits of 10 mg/cm² for non-immersion service and 5 mg/cm² for immersion service. For various reasons, including premature failure, these limits were reduced to 5 mg/cm² for non-immersion service and 3 mg/cm² for immersion service. These lowered limits appear to be providing satisfactory results. Many of the State DOT's have used a limit of 10 mg/cm² but many are also still encountering unacceptable premature failures. Today, at least one state has adopted the US Navy standard as they find it is an achievable level and that coatings are performing as desired. The more knowledgeable the coatings and surface preparation industry is about the direct relationship between salts and corrosion, the more they are beginning to realize how damaging salts are.

Where do salts come from?

Our environment is filled with sources of salt contaminants, both natural and man-made. Chlorides from marine environments, water treatment, paper bleaching and deicing products are only a few of the many sources of chloride contamination to which steel surfaces and uncoated rebar in concrete become exposed. Sulfates are produced by natural sources and are generated from stack gas and diesel emissions (oxidized from sulfur dioxide) (See Figure 1) and nitrates from diesel and auto emissions (oxidized from nitrous oxide). Converted to weak sulfuric and nitric acid in the atmosphere, when in contact with moisture, these are deposited on surfaces as acid rain. Chlorine and sulfuric acid are the two most widely produced and used chemicals in the world. Nitrogen fertilizers, in their manufacture, transport, use and runoff, result in oxidized nitrates, another salt, which is corrosive on metallic surfaces. Even without human intervention, nitrogen is in a constant cycle, alternating between soil and atmosphere. Nitrogen is constantly available in the atmosphere for deposition, and lightning readily converts atmospheric nitrogen to nitrogen oxides, which can form nitric acid.

A common practice is to acid etch concrete surfaces prior to applying coatings. If this is performed with hydrochloric acid, chlorides are left behind; etching with sulfuric acid leaves a sulfate residue. It is important to remember that surface contaminating salts are not localized to coastal areas or locales where de-icing salts are used. Industrial and automotive emissions transform to acids, which can convert to surface salts. Salts are all around us and in so many products that we do not even realize their presence. Salts are so widely spread from so many diverse sources that virtually every surface is subject to salt contamination at some level.

How do salts impact coating performance?

Salts left on a surface prior to the application of coatings can be the cause of several occurrences. Salts, as encountered in the coatings industry, are hygroscopic in nature, meaning they draw moisture. In this form, they achieve their highest level of chemical stability. As an example, in many households around the world, there are grains of rice or pieces of cracker in the saltshaker to absorb moisture. If these are not used, the salt will draw moisture from the air and cake. Salts, such as chlorides, sulfates and nitrates, do the same thing when left on a metallic surface. An active corrosion cell requires an anode, a cathode, a metallic pathway and an electrolyte (See Figure 2).

Corrosion Cell Elements

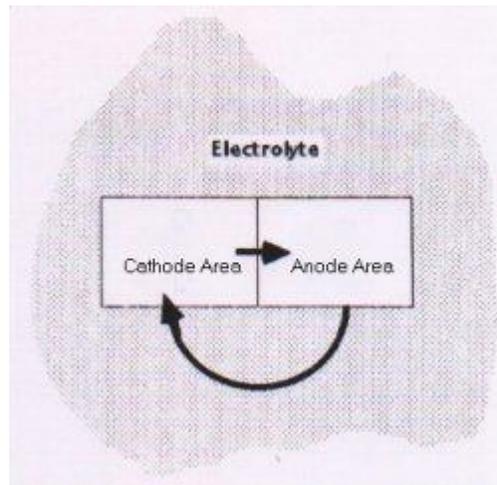


Figure 2

The surface of a piece of steel consists of many thousands of minute areas that are either anodic or cathodic to each other. The steel itself provides the metallic pathway. Introduce a chloride ion into the equation, which will draw moisture from the air and become the electrolyte, and there are now all the components of an active corrosion cell. All liquid applied coatings are permeable, thereby allowing the salt on a substrate to "pull" moisture through the coating, causing active corrosion of the substrate long before the protective coating fails. The coating is applied, the salt ion draws moisture through the coating and forms an electrolyte behind the coating and an active corrosion cell is formed. The products of the corrosion cell activity are acidic and will corrode the metallic surface around the cell. We have all seen blistered paint which, when the blister is broken, exhibits rust on the backside (See Figure 3). In nearly all cases, that paint was applied over salts. In immersion service and atmospheric service, other than very dry environments, this same hygroscopic action will cause osmotic blisters.

The scenario is much the same with coatings applied to concrete. Salts left on the surface will absorb moisture through the coating, producing weak acids. The weak acids, such as hydrochloric and sulfuric acids, will react with the concrete and cause it to deteriorate beneath the coating. These same salts, in immersion or damp service, can also cause osmotic blistering of concrete coatings. These salt contaminants can also be introduced onto a concrete surface when etched by or exposed to hydrochloric or sulfuric acid.

Salts also can interfere with adhesion or bonding between coats. For example, at a lighthouse in the Florida Keys, the specifier was aware of the probable contamination from the marine environment, so the specification required the surface to be washed with potable water and a salt remover added to the water. The surface was washed, the prime coat applied and left to dry overnight. The next day, an intermediate coat was applied. The third day, a finish coat was applied. In a few weeks time the coating began blistering and peeling. It was not blistering from the surface, but from between coats. Subsequent investigation determined that in the time period between coats the surface had become recontaminated with salts.



Typical Chloride Induced Coating Failure

Figure 3

What about flash rust?

Virtually all rust on metallic surfaces is caused or induced by salt contamination. We have been taught to believe that whenever there is bare steel and humidity that there will be rust. This is so ingrained into our thinking that some have a hard time believing that bare steel can be wetted and not rust. Take a clean uncontaminated steel coupon, abrasive blast it to a White Metal finish, hold it at a 45 degree angle, and pour DI (de-ionized) water over it. Even though it will be thoroughly wetted, it will not rust! Take the same piece of steel and pour tap water over it, and light flash rust will form, caused by the salt in the tap water. Pour salt water over the same panel and it will flash rust much more heavily (See Figure 4). As stated by Dr. Gerald Soltz in his research work for the National Shipbuilding Research Program, in the executive summary, "Clean uncontaminated steel will not rust, even in 100% humidity, for thousands of hours." The old habit of "Blast it and paint it quick before it flashes" now has been found to often be inappropriate. If flash rust occurs to any great degree, contamination should be tested for, because the rust is the result of non-visible soluble salt contamination. Without some form of contamination, there will not be rust.

Salt Contaminated Steel Panels-Left to Right:

Abrasive Blasted-Blasted & Watered Washed-Blasted & Water Washed with Salt Remover



Figure 4

How do you identify and test for salts?

There are several common field methods to test for contamination and to determine contamination levels. None of the field test methods can measure the contaminants directly on the surface. The contaminants first must be extracted from the surface into a solution where they can be measured in parts per million (ppm). The ability of a certain method to perform this extraction is called the extraction efficiency, typically stated in the percentage of contaminants extracted from the surface versus the total on the surface. No method provides 100% extraction and the efficiency differs greatly from method to method. Once the contaminant is in solution, a variety of methods can be used to measure the ppm of a particular ion. This also varies from method to method, with different degrees of difficulty, accuracy and other limitations, such as the minimum detection limit. The chosen test method is, therefore, a combination of two separate critical steps blended in a single methodology. Whichever methodology is chosen, in order to have useful information, the ppm must be converted to micrograms per square centimeter (mg/cm^2), meaning a specific amount of salt over a specific area, a prime concern to adequate surface preparation. To perform this conversion, multiply the concentration of salts in solution (ppm) by the volume of extract liquid (milliliters) and divide that by the surface area sampled (square centimeters). The result is micrograms per square centimeter, expressed as mg/cm^2 .

The Society for Protective Coatings SSPC-TU-4, Field Methods for Retrieval and Analysis of Soluble Salts on Substrates, notes two of the more common methods, the swab method and the adhesive cell method. Another choice is the **CHLOR*TEST™**, which has been introduced since TU-4 was published. The primary differences between the test methods are the degree of accuracy, lower limit of detection, ease of use and the degree of potential operator error. Errors usually occur because of complexity of procedures, operator accuracy in measuring and cross-contamination from reuse of components. Several things should be considered when choosing a test method. No matter how cautious an operator is or how accurately he measures, he cannot overcome the accuracy, efficiency, limit of detection or other limitations of the test method.

According to SSPC-TU-4, retrieval efficiency of swab method is between 25 and 35%, as determined under controlled laboratory conditions. The same document reports the retrieval efficiency of the adhesive cell as 45 to 60%. The manufacturer of the **CHLOR*TEST** reports retrieval efficiency as 65 to 75%, as tested by an independent laboratory.

The swab method is extremely hard to perform on a vertical surface and all but impossible overhead. The other two methods can be performed in any direction. It is easy to see when critical areas are vertical or overhead surfaces, good quality assurance requires the appropriate method be used.

Another important variable that must be considered is the test limit of the kit, more specifically the lower limit of the method used to determine the concentration of salts in solution. This has typically been measured by titration strip or tube. One common titration strip has a lower limit of ~ 30 ppm, while a common titration tube has a lower limit of ~1 ppm. Since concern for soluble salts is generally in the lower concentrations, this lower limit comes into the equation, therefore, using certain kits can cause false negatives.



CHLOR*TEST
all test materials included and pre-measured
Figure 5

Just as important, is that the specifier be aware of both extraction efficiencies and possible operator error from things such as cross contamination from test to test, inaccurate measurement of liquids and area, and overall complexity of the test procedures. Directions for performing these tests are included in SSPC document TU-4 and at www.chlor-rid.com. Those two references will provide the necessary information for an owner or specifier to determine which test method to require. Those same references can be very helpful and informative to the inspector or contractor so they would fully understand the requirements. The **CHLOR*TEST** kit is the only test method in which all required materials are supplied and are pre-measured for accuracy, with all components designed for one-time use to avoid cross contamination (See Figure 5). This test is also the only method which does not require mathematical calculation to convert parts per million to micrograms per square centimeter.

In view of the variables involved in testing for soluble salts, it is reasonable to say that a correctly written specification should require that a specific test method be used and it should indicate the maximum test result allowable by that method. A specification could also be written to allow other methods to be used by specifying a multiplier for each of the various allowed methods, respective to the extraction efficiencies. A specification that simply says, for example, "chlorides are not to exceed 5 micrograms per square centimeter" leaves much to be interpreted. Does the specifier intend the test result to be a maximum of 5 micrograms? Can any method be used? It is easy to see how an inspector or contractor could be left in controversy by the

specification. A specification should stipulate a particular test method, an acceptable test result and/or a factor (multiplier) to be used for different test methods. The real life situation is that it has been determined that any amount of salt, particularly chlorides, sulfates or nitrates, is detrimental to the overall lifespan of the coating. The cleaner the surface, the more successful a coating is going to be. Since salts are a relatively new subject to many people, it is easy to understand that people are also not aware of the costs or methods of salt removal. Many specifiers fail to specify low allowable concentrations of soluble salts for fear of cost; others simply do not want to spend any additional funds whatsoever. When all costs of asset downtime, surface preparation, and coating application are factored into a cost analysis, the cost of a premature failure is exorbitant when compared to the costs of taking reasonable steps to identify the existence of and to remove soluble salts. Costs of surface preparation and coating application are generally estimated in dollars per square foot, while reasonable costs of soluble salts testing and removal are generally estimated at only cents per square foot.

How do you remove salts?

Removal of soluble salts can range from very easy to extremely difficult, depending on actual conditions, which can vary greatly. Consider just one very common salt, sodium chloride. The chloride ion is never found by itself. As it is commonly encountered in the coatings industry, the chloride ion is always coupled with something else. For chemical stability, the chloride (also applies to sulfate and nitrate ions) ion wants to attach to something, forming compounds such as sodium chloride, zinc chloride, lead chloride or ferrous chloride or any of several other combinations. When a coated surface becomes contaminated with sodium chloride, the salt lies on the surface. Due to the chloride ion's strong affinity for metals and its extremely small size (1 mg of $\text{FeCl}_3 = \sim 3,686,600,000,000,000$ molecules), even very small imperfections in the coating allow the ion to migrate to the metal surface. At the metal surface, with the chloride ion having its affinity for metals, it leaves the sodium and bonds with the metal surface for greater stability. The chloride ion forms an electro-chemical bond to the metal and that bond becomes extremely strong. That is why it cannot be simply washed off with a garden hose. Where the sodium chloride would have been relatively easy to remove from the surface of the coating, the chloride ion now has bonded with the metal surface and is far harder to remove. For example, most of the salts on the surface of a coating can be removed with low pressure water blasting, but salts that have attached and complexed with the metal substrate often cannot be removed with 40,000 psi Ultra High Pressure Waterjetting (UHP-WJ).

Once these chloride ions form an attachment to the metal substrate, a very high level of energy is necessary to break that electro-chemical bond and remove them. That energy can be in the form of mechanical energy or chemical energy, or both. The properties of mechanical energy are widely known, but many coating professionals are unaware of the chemical requirements of a salt remover. For maximum effectiveness, a salt remover should have several distinct properties, as follows: 1) The pH should be below 7 to facilitate disbonding, but not cause a hydroxide layer to form which can mask remaining salts, as occurs with a high pH material; 2) It should be capable of being used with water that contains a fairly high level of salts, such as 600 ppm of chlorides, as is common with many water sources; 3) It should not leave any type of residue that will interfere with adhesion of coatings; 4) Nor should it leave an inhibitor film that requires rinsing or removal prior to coating application. As has been stated, the mechanical energy of 40,000 psi alone often cannot do the work, but when combined with the chemical energy of a salt

remover, such as **CHLOR*RID®**, a patented one-of-a-kind technology, the work becomes much easier. One form of energy assists the other, thereby providing the needed energy to complete the task. On an abrasive blast cleaned surface, chlorides can usually be adequately removed with the mechanical energy of a 3,000 psi pressure washer with the salt remover added, providing the chemical energy needed to perform the task. The mechanical action of water pressure is important for penetrating the crevices of the surface profile that exists on abrasive blasted metal surfaces. The action of a chemically balanced salt remover will take on the challenge of disbonding the chloride ion from the metal ion.

When discussing water on bare steel, the subject of flash rust invariably arises. Reviewing what was stated earlier, contaminants cause flash rust, so when the contaminants are removed the cause of flash rust is removed. Note: Since it is uncommon to totally remove all contaminants from all surfaces, there usually are some very low levels of salt contaminants remaining after decontamination. This is because of the irregular structure of the metal surface after abrasive blasting. When an abrasive blasted surface is viewed under magnification, it can be seen that the abrasive has impinged onto the surface, forming the valleys and peaks of the profile. Also visible at the same time is that succeeding abrasive grit has burred over the peaks and even created cave-like formations where one peak burrs over and meets another (See Figure 6). To remove 100% of these incredibly small ions from such locations can be almost impossible. Even a very small amount of contamination can cause some flash rust, but it is typically very minimal and in most cases reblasting is not necessary. Some manufacturers of coatings, primarily for immersion service, do require a full white metal surface with no flash rust. In this case, it is usually necessary to perform a light sweep blast to remove any small amount of flash rust.

There are several methods available to remove salts; only one of which is a dry method, the others all include the use of water. The dry method involves repeated abrasive blasting. A fine grit abrasive blast media is more effective at removing salts than coarse grit, so an engineered abrasive mix is sometimes specified (coarse abrasive to provide the necessary profile and fine abrasive for cleaning) but seldom can an effective job of removal be accomplished in a single abrasive blast. Typically a surface has to be abrasive blasted, allowed to rust back and then reblasted. In the corrosion or rust back cycle, a small amount of the salt ions get caught in the rust formed and, when the surface is reblasted, the small amount of salts in the rust is removed. It is not unusual to have to reblast a highly contaminated surface four to eight times to reach an acceptable level of cleanliness, particularly on highly contaminated surfaces such as those found in marine environments, pump bodies and water inlets. The rust back process can be actuated by atmospheric humidity or hastened by a water wash; simply add moisture and the salts will do the rest.

Magnified Blasted Surface
Photo Courtesy Dr. Lydia Frenzel

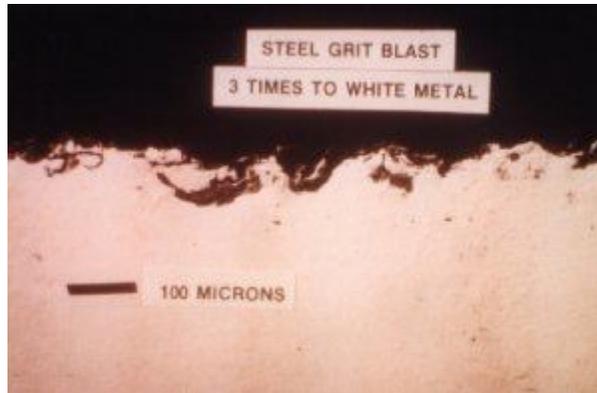


Figure 6

Of the wet methods, there are several choices, such as UHP-WJ, wet abrasive or slurry blasting, and dry blasting in conjunction with a water wash with a salt remover added, which sometimes requires a reblast as stated above. Other less common methods exist, such as specialty abrasives, but a particular type of abrasive alone will probably not remove all salts, though some abrasives do "scrub" the surface better than others. Reviewing the various options available, it can be determined which method will work best for a particular job.

UHP-WJ will usually, but not always, result in the desired level of cleanliness. If you want to be assured of attaining the desired cleanliness levels on a first time basis, add **CHLOR*RID**, a chemical salt remover to the water. This combines both mechanical and chemical energies, each assisting the other. This also allows the operator to proceed as fast as the visual work can be performed while being assured the non-visible contaminants will be removed. Maximum production can be achieved in this manner.

Wet Abrasive blasting, or slurry blasting, can remove chlorides, but may not attain the desired result in a single blast. A chemical salt remover, such as **CHLOR*RID**, can be added to the water, thereby combining chemical energy with mechanical energy. In every reported case, this method has resulted in chlorides being reduced to a non-detectable level with a single blast. A brush blast may be required to remove very light flash rust, usually quickly and easily accomplished. Wet abrasive blasting is not used frequently because "old habits die hard" and contractors are accustomed to dry abrasive blasting. Many contractors say that they do not want to make major equipment investments, not knowing the task can be accomplished with something as simple as a water ring, usually costing under \$100.00, or an injector type nozzle, costing just slightly more, installed on their existing blast equipment. There are cleanup considerations, such as, wet abrasive does not sweep easily, but it can be vacuumed or shoveled much the same as dry. This method does offer greatly increased visibility which is a major consideration. Because wet abrasive blasting is almost dust free, environmental compliance is far less an issue. Since operators have better visibility, additional blast nozzles can be operated to complete a job more quickly. Because dust is not generated, it does not have to be removed, which results in a time and labor savings with a cleaner surface for coating adhesion.

The technique most commonly used is a dry abrasive blast of any rusted areas, sufficient to remove rust to an exposed bare steel substrate, such as would be provided by an Industrial Blast Standard. Depending on the extent of rusting, this could be either a spot blast or a blast over the

entire surface. This blast is merely to remove any barrier materials, such as rust or damaged coating and to provide access to the chlorides so they may be removed. A pressure wash is then performed, usually a minimum of 3000 psi, with **CHLOR*RID** salt remover added to the water, again providing a combination of mechanical and chemical energy for removal. A final blast is then performed to the standard required by the specification. This same technique can also be performed by dry abrasive blasting to the standard required, then performing the pressure wash, with **CHLOR*RID** salt remover, followed by a brush blast to remove any excessive flash rust. Either method works well and can be relied on to achieve the desired result. These methods are very cost effective and cause no problems to cleanup, workers, or the environment. Each of the above is uniquely different and as each job is different, the option should be chosen that will provide the best result for each specific project.

In conclusion, our industry is changing. We, as a group and as individuals, are faced with change and challenge in order to keep up with technology. While we have relied on visible standards for surface preparation, we need to recognize that we must also be concerned about non-visible contaminants. This requires specific testing and to avoid premature failure of coatings, excessive soluble salt contaminants must be removed. There are numerous methods of removing soluble salts, most of which require the use of water and, when a wet method is allowed or used, removal is enhanced by the use of **CHLOR*RID** salt remover. It is possible to achieve a "non-detectable" level with the use of our product and in most cases it is economically viable. In almost all cases it is practical and cost effective to limit salts to levels such as are stipulated by the US Navy. A coating professional should also bear in mind that any amount of soluble salt contamination will have some adverse impact on the life span of any liquid applied coating.

The information provided above is a synopsis of the materials presented at **CHLOR*RID** International, Inc.'s Soluble Salt Training Sessions. We believe that education is beneficial to all coating professionals. Consequently our firm provides these sessions without charge. Anyone desiring to attend a full session, wanting to sponsor a session for their workgroup or for further information, please contact our office or visit our website. Additional educational and informational materials are also available on our website at www.chlor-rid.com

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