Detrimental Effect of Water Soluble Contaminant on Steel/Paint Interface

Ukpaka, C.P.

Department of Chemical/Petrochemical Engineering Rivers State University of Science and Technology Nkpolu, Nigeria

Abstract

It has also been well documented that water soluble particularly chlorides and sulphates, initiate and accelerate corrosion of steel, and become deeply embedded within the iron corrosion products. They are also capable of causing breakdown of the coating by the mechanism of osmotic blistering. The presence of soluble salts at the steel/paint interface is known to have a detrimental effect on the integrity of most paint systems. Though this is a long-standing problem, it has recently come to receive greater attention from the protective coatings industry. In the paper the following points are reviewed: degradation mechanisms of the steel/paint system, the role of the metallic substrate, the nature, origin and detection of water soluble, critical thresholds of soluble salts and risk levels for premature failures, exposure conditions, and prevention measures.

Keywords: Detrimental effect, water, soluble contaminant, steel, paint, interface

1. Introduction

In recent years, many specialists have called attention to the subject of nonviable contaminants on steel, of most concern are water-soluble such as chlorides, sulphates, and nitrates, which are deposited on the steel surface by acid rain, marine spray, and chemical splash and spillage (Morcillo, 1998; Chandler, 1966; Calabrese and Allen, 1978; Johnson, 1983; Hernandez, et al., 1998; Griss, 1983; Funke, 1981; Evans and Taylor, 1972). It was Mayne who brought this topic to light when he published his interesting article on painting rusty steel. He observed premature degradation of paint systems applied over rusty steel when this was withdrawn from the atmosphere in the winter months for laboratory painting (Van and Heertjcs, 1975; West and Jackson, 1982). Mayne demonstrated that this effect was due to the presence of ferrous sulphate in the rust, and that the failure of the paint system occurred only when the ferrous sulphate content reached a certain level (938 mg/rn). During the winter months (at which time the atmosphere reached its highest levels of sulphur dioxide content) the ferrous sulphate content in the rust was higher, while its level was lower when the specimens were taken out in the summer months, (Mayne, 1959; Dasgupta, 1969; Cathcart, 1992; Martin, 1989; Keane et al., 1974; Mckelvie and Whitehouse, 1980; Mungerler, 1990). Though the topic lay dormant for some time, interest in studying this interesting phenomenon has grown over the last 20 years to the point that much of the protective coatings industry currently requires testing for water- soluble (Spence and Hayine, 1985).

The presence of water-soluble contaminants at the metal/paint interface is an accelerating factor of the metallic corrosion process. They also have a negative effect on the behaviour of organic coatings applied over contaminated substrates *West, 1985). The presence of hydrosoluble species, e.g. chlorides and sulphates, at the steel/paint interface promotes osmotic blistering of the coating and underfilm metallic corrosion (Thinklenberg, 1987). Both processes can lead to the deterioration of the paint system in a very short period of time. Painting of rusty steel is prone to suffer this problem Loss of adhesion, cathodic disbondrnent, scribe creep and a decrease in the adhesion/cohesion strength of the coating can be also consequences of the presence of water-soluble . Detrimental Effect — causing harm or injury; "damaging to career and reputation, prejudicious harmful - causing or capable of causing harm. Contamination is defined in different ways by different studies. The following area of studies defines contaminant as follows also. In chemistry, the term usually describes a single constituent, but in specialized fields the term can also mean chemical mixtures, even up to the level of cellular materials. In environmental chemistry the term is in some cases is virtually equivalent to pollution, where the main interest is the harm done on a large scale to humans or to organisms or environments that are important to humans. In radiation protection the radioactive contamination is radioactive substances on surfaces, or within solids, liquids or gases (including the human body), where their presence is unintended or undesirable, or the process giving rise to their presence in such places. Solubility (Water Soluble) is the property of a solid, liquid, or gaseous chemical substance called solute to dissolve in a solid, liquid, or gaseous solvent to form a homogeneous solution of the solute in the solvent. The solubility of a substance fundamentally depends on the used solvent as well as on temperature and pressure. The extent of the solubility of a substance in a specific solvent is measured as the saturation concentration, where adding more solute does not increase the concentration of the solution ,solubility is the analytical composition of a saturated solution expressed as a proportion of a designated solute in a designated solvent. Solubility may be stated in units of concentration, morality, mole fraction, mole ratio, and other units. Solubility occurs under dynamic equilibrium, which means that solubility results from the simultaneous and opposing processes of dissolution and phase joining (e.g., precipitation of solids). The solubility equilibrium occurs when the two processes proceed at a constant rate. Steel/Paint Interface: this involves the concept of applying paint on steel or Iron to protect the steel from corroding.

The aim of this research is to investigate the detrimental effect of water soluble contaminants at steel/paint interface, under the following objectives: to investigate the concept of steel/paint interface, to understand the evidence of the effects and impact of water soluble at steel paint interface, the techniques for detecting and identifying these contaminants, the techniques to remove them or negate their effects and what levels of soluble salts are permissible on steel paint interface?

In the premature failure of paint coatings induced by the presence of water soluble at the steel/paint interface, there are many questions that it would be interesting to clear up, and parallel studies aimed at clearing up these questions are lacking. Considering the metallic surface/soluble salt/paint coating/environment system, This project work presents an overview of the subject, reviewing the different factors which influence the premature deterioration of paint systems due to the existence of water soluble at the steel/paint interface and making reference to the related research.

The purpose of the research work is to determine the detrimental effect of water soluble contaminant at steel 'paint interface, in other to resolve at the following conclusions:

are water soluble contaminants detrimental to steel paint interface, residual levels of the water soluble that can affect steel paint interface, prevention strategies for water soluble contaminant and effective usage of steel paint interface. Though there are many questions to be answered as regards the water soluble contaminate at steel paint interface, but this project work shall be limited to the deterioration of painted steel, which may lead to corroding of the steel been painted.

2. Materials and Methods

Much of the industry now requires testing for soluble salts, and trends show that these requirements are increasing. Laboratory and field methods for sampling and analyzing soluble salts have been developed both laboratory and field testing involves a two-step procedure: (a) extraction and (b) measuring. In research carried out, a comparative study was made of the sensitivity and reliability of different methods for extracting and analyzing soluble contaminants on steel surfaces. Experiments were carried out on clean unalloyed steel specimens contaminated with known amounts of chlorides and sulphates and rusted unalloyed steel specimens. In this work the galvanized carbon steel will be used to carry out the test for the detrimental effect of water soluble at steel paint interface.

2.1 Apparatus

Plastic containers, Wire Brush, Hacksaw, Tape, Weigh Balance, Magnetic Picker

2.2 Material

Salt water, Galvanized Carbon Steel, Coating Paint, Chloride, Accelerator [Sodium Chloride (NaC12)]

2.3 Procurement of Material

20 liters Salt water was collected from Mgbuodohia stream in a plastic can Galvanized carbon steel 'as gotten from Metal Market Port Harcourt. Never Paint Manufacturing Company, Accelerator (Sodium Chloride NaCl2)) was collected from the laboratory.

2.4 **Preparation of Coupon and Material**

Four (4) pieces of galvanized carbon steel pipe (coupon) each having a length of 50mm, a diameter of 6mm and thickness of 3mm, were treated using wire brush to properly clean the surface and after the process all samples were washed with distilled water, alcohol and dried using for fifteen (15) minutes. Tests were carried out on the collected salt water and the following parameters were considered.

Temperature, pH, water soluble contaminant (sulphate and chlorine), Total dissolved solid, Biochemical oxygen demand

2.5 **Procedures**

Collected salt water was poured into four plastic containers, and labeled

A-D, Galvanized carbon steel was painted and kept for three (3) days, Paint Coated Galvanized carbon steel (coupon) was placed in the water sample, Water soluble contaminants (chlorine) was added into the coupon sample. 5mg of sodium chloride (NaC1) was added into the coupon sample to accelerate the deterioration rate. Coupon samples were kept in an environment slightly higher than room temperature, t• Coupon Sample A was withdrawn three (3) weeks later and amount of water soluble contaminants were tested in the laboratory, Coupon sample B was Withdrawn six (6) weeks later and test were also carried out. The third coupon sample C was withdrawn nine (9) weeks.

The fourth coupon sample D was kept for four (4) months and tests were carried out.

Tests that were carried out includes; Chlorine, Sulphate and Level of deterioration of steel/paint interface

2.6   **Method of Testing**

To carry out a proper experiment of the steel/paint interface, three methods will he considered, to test the amount of soluble salt in the steel surface.

Soluble salts were extracted from steel surfaces using 2 different methods: Swabbing method, Mayne methods.

Swabbing Method: The swabbing method relies on surface rinsing. A pure cotton wool swab was soaked in a beaker containing 10 ml of distilled water. The whole metal surface was swabbed with a cotton ball held by tweezers. After swabbing, the cotton was swirled in the water and squeezed. This process was repeated at least 4 times. The cotton ball was subsequently placed in the beaker, and the test area was dried with a fresh cotton ball, which was also then immersed in the beaker. The water and the cotton balls were then swirled and stirred for at least 2 minutes to assure thorough mixing. The total volume of extract thus obtained was 10ml. The test was performed in triplicate at each site of contamination. Mayne Method—this method, also known as the boiling and rinsing method, was first used by Mayne. A volume of 200 ml of distilled water was placed in a beaker; the water was boiled for 10 minutes and cooled in a nitrogen stream. Each specimen was then immersed in the water for 30 minutes, after which it was removed and rinsed with distilled water that was also collected in the beaker. The extract thus obtained was filtered and diluted to 200 ml for subsequent analysis. The test was performed in triplicate at each contamination site.

3. Result and Discussion

3.1   Techniques for Identifying and Detecting water Soluble.

This section reviews the procedures for identifying and detecting water soluble contaminants on steel/paint interface. These materials are normally deposited in quantities too small to be detected with the unaided eye. In order to establish an analytical procedure, it is first necessary to determine precisely what chemical species are of concern. The two substances receiving the most attention have been chlorides and sulfates. There have been major efforts directed at developing both laboratory and field techniques for detecting and quantifying the amount of the following salts on bare steel or on coated surfaces: soluble chlorides, soluble sulphates, soluble ferrous salts, and total soluble salts by conductivityThe question is not simply one of removing or extracting the surface layer, or of cutting out a section of steel and analyzing it. One must also be concerned with the location and distribution of the chemical species within the oxide layer, the pits, and the steel matrix. Thus, how to sample the surface becomes an important question. Sampling procedures will be discussed subsequently.

Soluble Chlorides: Several specific techniques have been developed for analyzing chloride ions, some of which can be accomplished in the field. One technique, which has been used primarily as a laboratory reference method, is the selective ion electrode. The technique also requires a specific ion analyzer and calibration against known standards. This method is capable of measuring chloride concentrations down to about 1 ppm. The equipment is sufficiently portable for field use; however, the delicacy of the equipment, the need for stable conditions, and the expense would tend to limit its use in this area. A semi-quantitative field technique involving use of paper chromatography has also been developed and implemented by several organizations. The chromatography strips are normally dipped into a solution containing the unknown chloride. In Chloride can also be detected using silver nitrate or silver chromate.Soluble Sulphates: As with other chemical species, a number of analytical techniques have been developed for detecting sulfate in the laboratory. These involve measurements of quantities such as scattering or turbidity and would not be very suitable for routine evaluations of field specimens. The South African Bureau of Standards (SABS) has developed a test method for qualitative detection of soluble sulfate. The filter paper is soaked in barium chloride solution and pressed onto the steel surface in the presence of potassium permanganate solution. Pink spots on the barium chloride paper indicate the presence of soluble sulfates.

Soluble Ferrous Salts: As noted previously, sulfates and chlorides not only act as electrolytes, but also react with steel to form ferrous sulfate and ferrous chloride, respectively. These ferrous salts are concentrated at the bottom of pits and become responsible for the localized "rust-back" that occurs on blast cleaned, pitted steel exposed to atmospheric moisture. Thus, it is of great interest and importance to detect the presence of ferrous salts in steel to be painted, as they represent points at which accelerated corrosion and premature coating failures may occur.

Rust-Back Test: Ferrous salts in pits of steel will readily absorb moisture from the atmosphere and cause a localized darkening of a blast-cleaned steel surface. Thus, one indication of these salts is the occurrence of rust-back within a short time after blast cleaning. This criterion is currently used by many specifications, which stipulate that paint must be applied before any rust- back occurs. However, the general remedy applied if there is any rust-back is to re-blast the surface, which may not remove the salts. Consequently, applying the paints before rust-back occurs will not correct the problem if ferrous ions are in the pits. Thus, a more reliable means of detecting these contaminants may be required.

Total Salt Concentration by Conductivity: As an alternative to measuring the concentration of specific ions, several groups have chosen to look at the conductivity of solutions of these species. This approach may be justified as follows:

The presence of any soluble salt is detrimental to paint performance because of the formation of electrolyte and the possibility of osmotic blistering. In many cases, the major contaminating species is known or assumed (e.g., sulphate in industrial environments or chloride in marine environments). The primary question for users is the quantity of these contaminants. A single test is easier and more practical for field use; it may be possible to establish an upper limit based on the conductivity (i.e., go/no-go test). Alternatively, conductivity may be used as a screening test to determine the need for more specific analyses.

Conductivity of solutions can be measured quite reliably with a small, portable conductivity meter.

This section discusses the reliability and sensitivity of field analytical determinations of chloride and sulfate conducted in the laboratory as shown in Tables 1-4

On non-rusted steel, both the Mayne/test strip and the plastic patch/test strip combinations provided excess extraction efficiencies. Again, the plastic patch method gave overestimated values. It should be noted that the extraction of soluble salts in the boiling method was performed using 200m1 of distilled water, so the chloride concentration in the final extract is usually below the detection limit of the test strips (30 ppm). Because of the low chloride concentration, the boiling/test strip method failed to detect the chloride levels applied on fresh steel. This result may have occurred because of the preferential accumulation of chloride ions at the steel/paint interface, which hindered their removal. Even though the boiling method does not ensure complete extraction of soluble contaminants from the steel/paint interface, it is more efficient because dissolved ions are more readily soluble and mobile at high temperature. Also the chlorine concentration on steel contaminated with known level of chlorine increases with different samples as shown in Table 1. The test conducted on soluble contaminant was illustrated in Table 2 with increase in concentration of the contaminants as the period of exposure increases.   The result presented in Table 3 illustrates the different testing method with the period of exposure, increase in concentration data was obtained with increase in the period of exposure. Table 4 illustrate sulphate concentration on steel contaminated with known level of chlorine, increase in contamination influence the system. Similarly, the results obtained were presented in Figures as shown in Figure 1 and 2. From Figure 1 it is seen that increases in component concentration with time was observed among the components under consideration. Figure 2 illustrates the result of different weight loss using different testing approach, increase in weight loss was observed with increase in time. The variation on the weight loss concentration can be attributed to the variation on time as well other environmental factors as shown in the Appendix for all the Figures and Tables.

4. Conclusion

The above data demonstrates the complexity of the task of determining specific effects of water soluble on paint performance. There are a number of important variables, including the method of producing the contamination, the method of detecting the contaminants, the type of contaminant property analyzed, the type and thickness of the coatings applied, the type of exposure environment, and the method of evaluation. The data presented do not allow us to establish any definitive levels for specific contaminants, but they do provide firmer evidence that these materials are detrimental for coating performance. We can derive some conclusions from the above discussions and define areas where additional knowledge must be sought. The principal conclusions are as follows: Atmospheric chlorides, sulphates (or sulphur oxides), and similar gases or particulates will be deposited on exposed steel. All water-soluble salts not removed from steel during surface preparations can produce osmotic blistering of the coating. The extent of blistering depends on the concentration of the salt, the thickness of the coating, and the chemical nature of the coating, as well as the specific exposure environment. Chlorides and sulphates react chemically with steel and form corrosion nests or cells that concentrate in the pits of steel. These corrosion nests can cause accelerated degradation of the coating system. Conventional cleaning techniques, including abrasive blasting, do not remove all these embedded contaminants. There are a number of suitable techniques for detecting the levels of the most important soluble contaminants. Standard methods are expected to be forthcoming within the next year or so. Chloride and sulfate levels of several micrograms per sq centimeter are sufficient to induce blistering in certain types of coatings. These are only very rough. Under certain circumstances much higher levels of those contaminate may be tolerated.

References

Chandler, K.A. (1966). The influence of salts in rusts on the corrosion of the underlying steel, British Corrosion Journal. **1**: 264-266

Calabreses, C. and Allen, J.R. (1978). Surface characterization of atmospherically corroded and blast cleaned steel, corrosion J. **34** : 331-338.

Cathcart, C. (1992), Evaluation of the Bresle method for detecting soluble salts on steel, KTA Tutor Inc personal communication: 72.

Dasgupta, D. (1969). Mechanism of atmospheric corrosion of steel: A review. British Corosion Journal. **20** :119

Evans, U.R. and Taylor, C.H.A. (1972). Mechanism of atmospheric rusting. J. Corrosion science. **12**(3): 227-246

Funke, W. (1981). Blistering of paint films and filiform corrosion, progress in organic coatings, Corrosion J., **9**(11) : 29-46

Frondisotu, Y. (1985). Coatings for non abrasive cleaned highway steel. Report No. FHWA/RD 86-053. SSPC report

Gross, H. (1983). Examination of salt desposits found under German painted steel bridges decks. Materials performance **22** : 28-33

Johnson, W.C. (1983). Detrimental materials at the steel/paint interface. New, concepts for coating protection of steel structures, ASTM STP 841, D.M. Berger and R.F. Wind, editors, report SSPC 83-01.

Keane, J.D., Bruno, J.A. Jr., and Weaver, R.E.F. (1974). Surface profile for anti-corrosion paints. Report No. SSPC 74-01

Mayne, J.E.O., (1959). The problem of painting rusty steel. Journal of applied chemistry, **9** : 673-680

Moreillo, M. Ruiz J.L. and Simanacas, J. (1989). Prot. Coat linings, JPCL, **6** : 11-81

Martin, K. (1971). The spreading of sulfate nests on steel in atmospheric corrosion. Corrosion Science, **11**(12) : 937-942.

Mckelvie, A.N., and whitehouse, N.R. (1980). Quality control procedures when blast cleaning steel: A critical survey of methods of determining profile and surface cleanliness. Paint research association, Waldegrave Road Teddington Middlesex TW 118LH England.

Mungerler, S. (1990). The setting up of an Ibero American map of atmospheric corrosion. MICAT Study – Cyted-D, proceedings of the 11th International Corrosion congress, Florence, Uraly, 2: 235

Spence, J.W. and Haynie, F.H. (1987). Research plan for determining the effects of acid deposition on exterior coating. Report by U.S. Environmental Protection agency ASRL. Research triangle park NC27711

Tinklenberg, G.L., and Allen J.R. (1987). Surface profile. What's best? Published in conference proceedings, improving the field reliability of protective coatings. Editors R.W. Drisko, B.R. Appleman and J. Rex, Report No. SSPC 87-07

Townsend et al (1981). Breakdown of oxide films on steel exposed to chloride solution. Corrosion, J,. **37**: 384

Van der Meer-Lerk, L.A. and Heertjes, P.M. (1975). Blistering of varnish films on substrates induced by salts. J. Oil and Colour Chem. Assoc. **58**:79-84.

West, J. and Jackson, P. C. (1982). Salt contamination of steel surfaces before coating. Prepared for the central council of British shipping . The British ship research Association: 34.

West, J (1985). The relationship between coating thickness and salt contamination on Blistering of coatings. Presented at UK corrosion/85 Harrogate, 4-6. Munger, C.G. corrosion prevention by protective C.: 121

Appendix

Table 1:   Chloride concentrations on steel contaminated with known levels of chloride

Field steel contaminated with chloride:	Mayne method (lab)		Bresle method (field)	
	Chlorides concentration, mg Cl-/m^2	Extraction efficiency, %	Chlorides concentrationmg Cl-/m^2	Extraction efficiency, %
	Chloride ion-selective electrode (laboratory)			
50mg Cl⁻/m^2	59	118%	-	-
150 mg Cl⁻/m^2	148	99%	200	133%
500 mg Cl⁻/m^2 l.000mg Cl⁻	658	125%	828	166%
/m^2	1,123	109%	-	-
Average		113%		150%

Table 2: Test Conducted on Soluble Contaminant

Parameters	Concentration (mg)			
	3 weeks	6 weeks	9 weeks	12 weeks
Chlorine	103	143	169	207
Sulphate	58	71	101	146
Other contaminants	141	152	163	192

Table 3: Level of Deterioration (W1ehgt Loss) Per Week

Test Method	Weight Loss (mg)			
	3 weeks	6 weeks	9 weeks	1 2 weeks
Mayne test	0.036	0.057	0.063	0.071
Bresle test	0.029	0.032	0.042	0.051

Table 4: Sulphate concentrations on steel contaminated with known levels of chloride

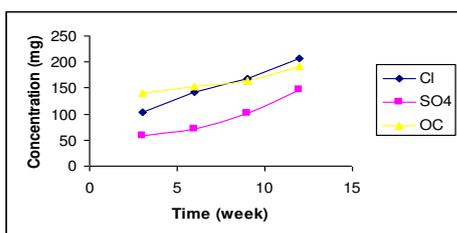| Field steel contaminated with sulphate:	Mayne method (lab)		Bresle method (field)	
	Chlorides con centration, mg Cl-/m^2	Extraction efficiency, %	Chlorides concentration, mg Cl-/m^2	Extraction efficiency, %
	Chloride Ion-selective electrode (laboratory)			
1000mg SO_4^2/m^2 1500 mg so_4^2m^2 2000 mg so_4^2/m^2	1,388	118% 99%		
	1,676	125%	200	128%
1500mg so_4^2/m^2	2,183	109%	828	151%
		198%		162%

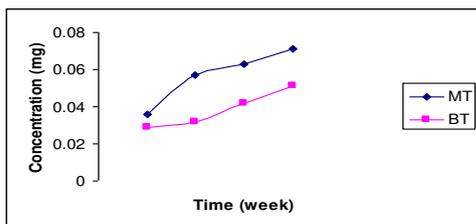Figure 1: Concentration of some component versus time

Figure 2: Level of Deterioration (weight loss) per week using Mayne and Bresle test method