Influence of climatic factors (UV, salt concentration, wet-dry cycle) in cyclic corrosion tests used for marine paint systems

Nathalie LEBOZEC, Dominique THIERRY, French Corrosion Institute, Brest, France
Philippe LE CALVE, DCNS, Lorient, France
Jean-Pierre PAUTASSO, Direction Générale de l'Armement, Bagneux, France

Summary

Corrosion resistance is an important property requirement for marine paint systems used in naval industry. This implies to test the coating performance in order to make a good selection of the paint systems. This is generally made by conducting accelerated corrosion tests such as the standard neutral salt spray test (ISO 9227) and particularly cyclic corrosion tests including ISO 20340-Annex A. However, these tests may not be fully representative of real ship environmental conditions. Thus, there is a need to improve and simplify the testing conditions by better understanding the influence of key parameters on marine paint systems. In the present study, a design of experiment was used to study the effect of important climatic parameters such as UV, NaCl concentration and wet-dry cycle on the corrosion resistance of 15 different marine paint systems. From the results, it was shown that NaCl concentration plays an important role in the paint degradation while UV exposure in a cyclic corrosion test has no major influence.

1 Introduction

Testing the corrosion resistance of marine systems is imperative in order to make an appropriate selection of paints, to qualify new protective systems and to validate new surface preparations. The selection of paint systems for marine application is often based on results from accelerated laboratory tests such as the neutral salt spray test (ISO 9227, ASTM B-117) or cyclic corrosion tests such as ISO 20340 annex A. This last test cycle is indeed recommended for the assessment of paint systems for offshore applications. With a total duration of 4200 hours, ISO 20340 annex A alternates UV/condensation (ISO 11507), neutral salt spray (ISO 9227) and a freezing phase (-20°C) as shown in Table 2. This requires the use of three different cabinets (e.g. a QUV, a salt spray chamber and a climatic cabinet) as there are no automatic equipment and the transfer of test panels, which results in a rather costly test. Moreover, the transfer of tests panels several times a week may induce some deviations in the reproducibility and repeatability of the test. In addition, it is well-known that these tests may not be fully representing the environmental conditions under which ships operate. Indeed, a previous study concluded that the ISO 20340 test was not suitable to correctly discriminate between marine paint systems, based on the testing of over 13 different systems [1]. In particular, the test demonstrated poor performance of zinc substrates and zinc pigmented paint, and this was in contradiction to a satisfying performance of those materials when exposed under marine atmospheric conditions, classified as C5M sites. In recent work, Binder observed a good correlation between the results of ISO 20340 tests and tests at the immersion zone of seawater [2]. From another work, the cyclic corrosion tests were found to be more predictive in ranking coating performance, but the authors warned that cautions should be taken when using artificially generated data [3]. Based on such results, outdoor exposures in marine atmospheres of high corrosivity, e.g. C5M class, ought to be performed on long term bases [4]. Thus, there is a need to develop more reliable corrosion tests for C5M environment or improve existing accelerated corrosion tests taking also into consideration economical aspects. The present work aims to study the influence of key parameters on the corrosion resistance of various marine paint systems using a design of experiment based on ISO 20340 annex A test cycle, with the final objective of designing an accelerated corrosion test more reliable and fully automatic. This study is part of on-going research program aiming to develop more reliable accelerated corrosion testing conditions for marine paints in C5M environments where both laboratory tests and field exposure on operating ship are conducted [6].

2 Experimental

2.1 Test panels and evaluation

15 different paint systems namely S1 to S15 applied on abrasive blasted Sa2$^{1/2}$ steel (S355NL) panels (100x175x5mm) were tested. As given in Table 1, the commercial paint systems included one of the three main properties of a coating e.g. barrier effect, galvanic effect and inhibiting effect. Among the 15 organic coatings, one reference paint system (S14) composed of vinyl epoxy primer coat 100µm; vinyl epoxy intermediate layer 80µm and silicone alkyd topcoat 2x30µm was also applied. It should be mentioned that the selection of the paint systems was made in order to cover a large range of expected performance in field from poor to excellent systems, based on previous field studies such as in reference [5]. Prior to exposure, a vertical scribe parallel to the longest side of 100x0.5 mm was applied using an Elcometer 1538 scribing tool equipped with a rectangular blade of 0.5mm in width.

Table 1: Coating category and thickness applied on steel substrates

Paint Label	Category of protection			Dry Film Thickness, µm
	Barrier	Galvanic (Zn)	Inhibiting	
S1	x			350
S2	x			450
S3	x			260
S4		x		250
S5	x			350
S6	x			350
S7	x			400
S8	x			450
S9	x			440
S10	x			500
S11		x		520
S12		x		400
S13		x		340
S14			x	240
S15			x	150

2.2 Testing conditions

ISO 20340 annex A was selected as basic test for C5M environment to assess the corrosion performance of the different paint systems. The test which cycle is described in Table 2 was conducted during 25 weeks, e.g. 4200 hours. In a first stage, as one objective of the work was to automate as much as possible the corrosion test, the influence of UV phase was studied by performing 4 accelerated corrosion tests of 2000 hours (3 months) which are described in Table 3. It is indeed almost impossible to automate tests which involve UV and salt spray phases. It should be underlined that the frequency of UV and condensation phases was modified to allow manipulation of the samples by an operator. Thus, test 1.1 corresponds to ISO20340 annex A cycle with 12 h of UVA followed 12h of condensation instead of 4 h cycles. In the three other test variants, the UVA phase was replaced by a phase at 60°C performed in a climatic chamber (test 1.2) or in a combined salt spray/climatic chamber (test 1.4) or by an ambient phase in the laboratory (test 1.3). Three paint systems were used e.g. S2, S9 and S14.

Table 2: Description of ISO 20340 annex A test cycle

Day 1	**Day 2**	**Day 3**	**Day 4**	**Day 5**	**Day 6**	**Day 7**
UVA60°C 4h / Cond. 50°C 4h ISO 11507			SS NaCl 5% - 35°C ISO 9227			-20°C

Table 3: Description of test cycles of stage 1 (top) and test equipments (bottom)

	Day 1	**Day 2**	**Day 3**	**Day 4**	**Day 5**	**Day 6**	**Day 7**
Test 1.1	UVA60°C 12h / Cond. 50°C 12h			SS NaCl 5% - 35°C			-20°C
Test 1.2	60°C 12h / Cond. 50°C 12h			SS NaCl 5% - 35°C			-20°C
Test 1.3	Ambient 12h / Cond. 50°C 12h			SS NaCl 5% - 35°C			-20°C
Test 1.4	60°C 12 h/ Cond. 50°C 12h			SS NaCl 5% - 35°C			-20°C

	UV or temp. Phase /Condensation	**NSS**	**-20°C**
Test 1.1	QUV (Q Panel) ✋	Weiss SC/KWT 1000 ✋	Climatic chamber Secasi ✋
Test 1.2	60°C : Climatic chamber Binder Condensation : QUV ✋		
Test 1.3	Ambient : Laboratory conditions Condensation : QUV ✋		
Test 1.4	Weiss SC/KWT 1000 ✋		

✋ .... manual transfer of the test panels

In a second stage, a design of experiments (DOE) made of 4 accelerated tests was first used in order to study the influence of the concentration of NaCl (1 and 5 wt%) and the drying phase (0 and 24 h). The variable and set parameters are shown in Table 4 while the resulting test cycles are summarized in Table 5. A drying phase (S) of 24 h was introduced in the test sequence after the 3 days of salt spray which resulted in 2 days of wet/dry cycles instead of 3 when no drying phase is added.

Table 4: Description of variable parameters (top) and set parameters (bottom) for stage 2

A- Variable parameters		
	-	+
NaCl concentration (wt %)- **BS**	1	5
Drying phase in ambient conditions (h) - **S**	0	24

B- Set parameters	
Total duration (weeks)	25 (4200 h)
Duration of 1 cycle (week)	1
Duration of freezing phase (h)	24
Duration of salt spray (h)	72
Salt solution	NaCl / pH 6.5-7.2 / 1-2 mL/h, 80cm² /35°C
Wet phase	50°C , 95% RH
Dry phase	60°C, 40% RH

Table 5: Description test cycles of stage 2 as defined in Table 3.

		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
2.1	BS1/S0/C50	60°C 4h	95%HR 4h		BS NaCl 1% - 35°C			-20°C
2.2	BS5/S0/C50	60°C 4h	95%HR 4h		BS NaCl 5% - 35°C			-20°C
2.3	BS1/S24/C50	60°C 4h	95%HR 4h	BS NaCl 1% - 35°C			Amb.	-20°C
2.4	BS5/S24/C50	60°C 4h	95%HR 4h	BS NaCl 5% - 35°C			Amb.	-20°C

Amb…. ambient lab conditions (23°C, 50%RH)

2.3 Evaluations

The evaluation of the coating degradation was performed according to ISO 4628 standards in particular ISO 4628-2 for blistering and ISO 4628-3 for rusting. Regarding the scribe creep, the maximum value M1 ($M1=(V_{max}$-scribe width)/2) was considered as well as the mean value of 8 segments after coating removal ($M4=\sum(X_n$-scribe width)/8, disregarding 10 mm of each end of the scribe line.

The adhesion pull off strength was determined according to ISO 4624 with a PAT equipment on the test samples before ageing and after completion of the tests.

3 Results

3.2 Influence of UVA phase

In a first stage, the influence of UVA was tested as shown in Figure 1 which presents the corrosion creep from the scribe line measured on three paint systems after 2000 hours of ageing in the different test variants described in Table 3. The data are compared with those from ISO 20340 test at similar exposure duration. The results indicated no differences whatever the test variants including ISO 20340 on the reference system S14. Regarding the other paint systems both involving a barrier protection, more scribe creep was observed than on system S14. System S2 behaved rather similarly whatever the test variants unless in test 1.3 where the UV phase was replaced by an ambient phase. A comparison of test 1.1 and ISO 20340 which only differ by the frequency of UVA/condensation, e.g. 12 h versus 4 h in test 1.1 and ISO 20340 respectively, showed a tendency to form more creep with higher frequency (e.g. Test ISO 20340) for both barrier based paint systems S2 and S9. This is in agreement with a comparable study conducted on electro-coated cold rolled steel in accelerated corrosion tests for automotive application [7]. It may also be observed a tendency to be more aggressive when conducting the wet/dry cycle and the salt spray in the same chamber (test 1.4) for system S9. It should be noted that this last system was among the less performing ones, which may explain more variability upon the testing conditions. From the results, it was concluded that the UVA phase was not a key step regarding corrosion degradation of coated steel and thus could be replaced by a thermal phase at 60°C. This was in agreement with previous work from University of Toulon showing that only a few µm of the top coat was affected by UV radiations [8]. Thus, if it is possible to exclude UVA phase, there is a chance to partly automate the corrosion test and thus reduce the cost and improve the test reproducibility. It should be noted that most of accelerated corrosion tests used by the automotive industry do not include any UV phase and are conducted in fully automatic corrosion cabinets [9].

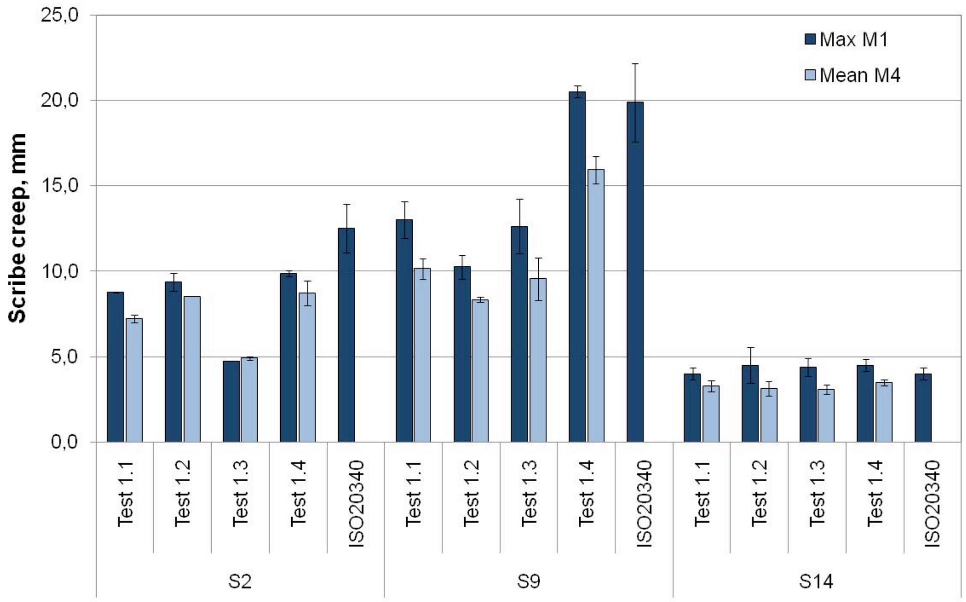

***Figure 1**: Influence of UVA on scribe creep after 2000 hours of ageing in test variants described in Table 3*

3.1 Influence of salt concentration and drying phase

In a second stage of the work, the influence of two parameters e.g. the concentration of NaCl and the drying phase was studied as described in table 4 and 5. None of the coated materials presented defects on the overall surface e.g. no rusting or blistering. The scribe creep is plotted in Figure 2 as a function of the paint system and the ageing conditions including ISO 20340 annex A test. All tests were conducted during 4200 hours with intermediate inspections. The results indicated a rather similar material ranking whatever the testing conditions, systems involving a galvanic protection (zinc) being the most efficient systems (S4, S11, S12 and S13), closely followed by systems S14 and S15 (inhibiting action), while barrier protected systems S7, S8 and S9 showed the largest scribe creep. It is interesting to note that tests involving NaCl 5wt% in the salt spray have an obvious tendency to boost the corrosion from the scribe line. The influence of the variable factors was studied using a statistical method (Modde 7 in PLS fit) and the results are summarized in Table 6. Obviously, changing the concentration of NaCl from 1 to 5 wt% during the salt spray phase will result in an increase of the underpaint corrosion whatever the paint system. The introduction of a drying phase in ambient conditions has an effect which is system dependent, but in all cases, its effect is less significant than the concentration of NaCl which seems to dominate the corrosion from scribe line. This would indicate that the continuous salt spray phase is probably the dominating phase. However, this shall be verified by performing additional test cycles, where it is indeed intended to examine the influence of cycling the salt spray phase.

Simple linear regression analysis was applied to evaluate the linear relationship between two tests and the coefficient of determination R^2 was calculated. A R^2 of 1.0 indicates that the regression line perfectly fits the data. Thus, the best correlations are those with a R^2 close to 1. Two examples of linear regression plots are presented in Figure 3 while R^2 coefficients are summarized in Table 7 for all tests including ISO 20340 test. It is interesting to note that the best correlation was obtained with testing conditions using similar salt concentration e.g. tests 2.1 and 2.3 for NaCl 1wt% and tests 2.4 and 2.4 for NaCl 5wt%. This again supports the observation that the salt spray phase is dominating. An inferior but still reasonable correlation was found when correlating the test variants with ISO 20340 annex A test. These observations indicated that the changes of salt concentration (from 1 to 5 wt%) and the insertion of a ambient drying phase of 24h didn’t significantly modify the material ranking. Nevertheless, the extent of corrosion was noticeably more important in tests involving 5 wt% NaCl in the salt spray phase as shown in Table 8 regarding the total scribe creep of the 15 paint systems.

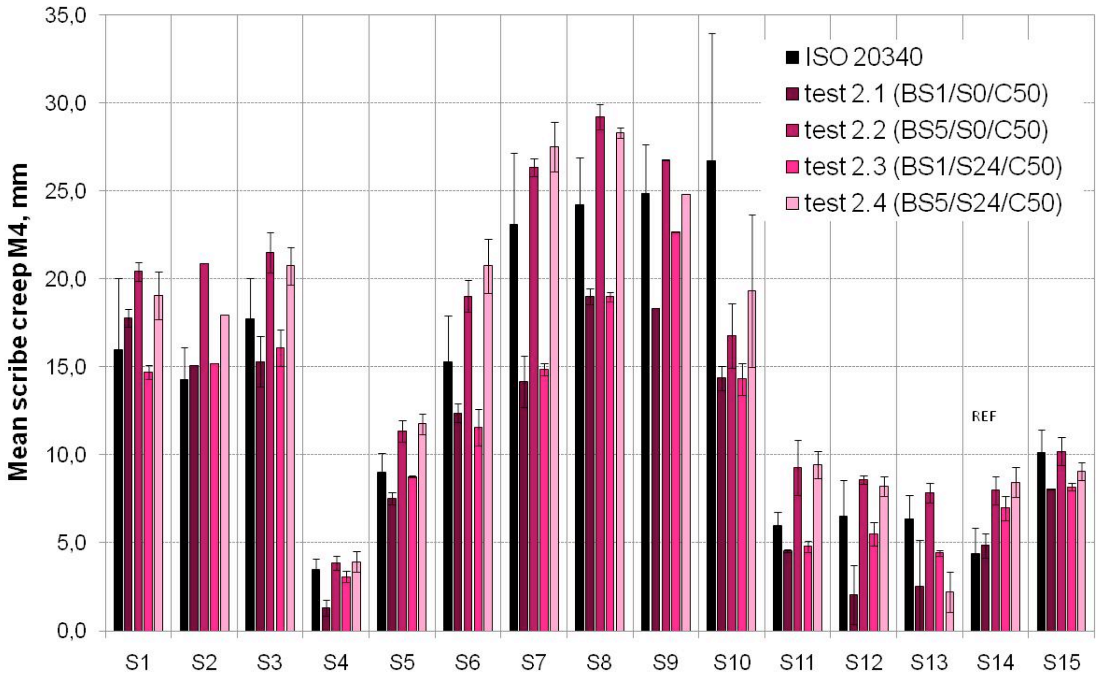

Figure 2: Influence of salt concentration and drying phase on scribe creep after 4200 hours of ageing in test variants described in Table 5. Comparison with ISO 20340.

Table 6: Effect of salt concentration (BS) and drying phase (S) on corrosion from scribe line. ++: positive (major)... +: positive (medium)... 0: no ... -: negative (medium)

Paint Label	Category of protection			Influence of	
	Barrier	Cathodic (Zn)	Inhibiting	NaCl conc. (1-5wt%) - BS	Drying phase (0-24h) - S
S1	x			++	-
S2	x			++	-
S3	x			++	0
S4		x		++	+
S5	x			++	+
S6	x			++	0
S7	x			++	0
S8	x			++	0
S9	x			++	+
S10	x			++	+
S11		x		++	0
S12		x		++	+
S13		x		+	-
S14			x	++	+
S15			x	++	-

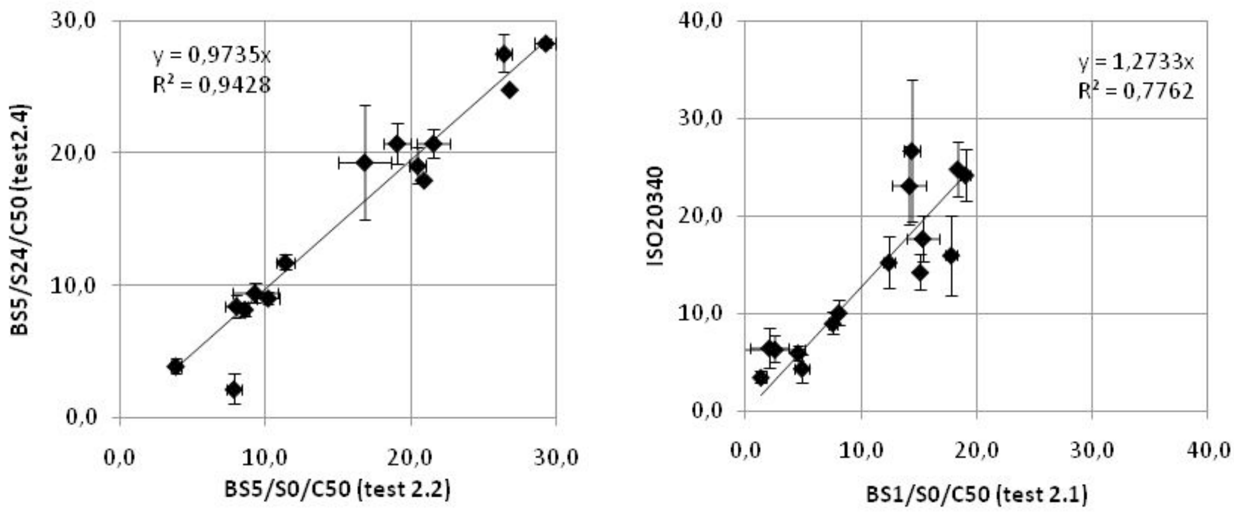

Figure 3: Examples of linear regression plots (mean scribe creep, M4)

Table 7: Test correlation (R^2 value)

R^2		ISO 20340	Test 2.1	Test 2.2	Test 2.3	Test 2.4
			BS1/S0/C50	**BS5/S0/C50**	**BS1/S24/C50**	**BS5/S24/C50**
ISO 20340		**1**	0,77	0,79	0,81	0,82
Test 2.1	**BS1/S0/C50**		1	0,84	**0.91**	0,82
Test 2.2	**BS5/S0/C50**			1	0,89	**0,94**
Test 2.3	**BS1/S24/C50**				1	0,84
Test 2.4	**BS5/S24/C50**					1

Table 8: Total mean scribe creep of 15 systems as a function of testing conditions

	ISO 20340	Test 2.1	Test 2.2	Test 2.3	Test 2.4
		BS1/S0/C50	**BS5/S0/C50**	**BS1/S24/C50**	**BS5/S24/C50**
Total mean scribe creep (15 systems), mm	210	160	240	170	230

Adhesion was investigated by pull-off testing according to ISO 4624. The results are given in Figure 4. All coating systems satisfied the ageing resistance criteria defined in ISO 20340 unless coating systems S4 which lost more than 50% of the initial value whatever the testing conditions. Some adhesive failures were also observed on paint systems 11 and 13, however with a pull-off strength higher than 5 MPa. No significant trend may thus be observed upon the testing conditions.

It should be mentioned that this work is part of on-going research programme aiming to develop more reliable accelerated corrosion testing conditions for marine paints in C5M environments. Additional laboratory tests were on-going when writing the paper as well as field exposure on stationary sites of C5M corrosivity class and on operating ships [6]. The results from laboratory tests will be further compared to data from field exposures.

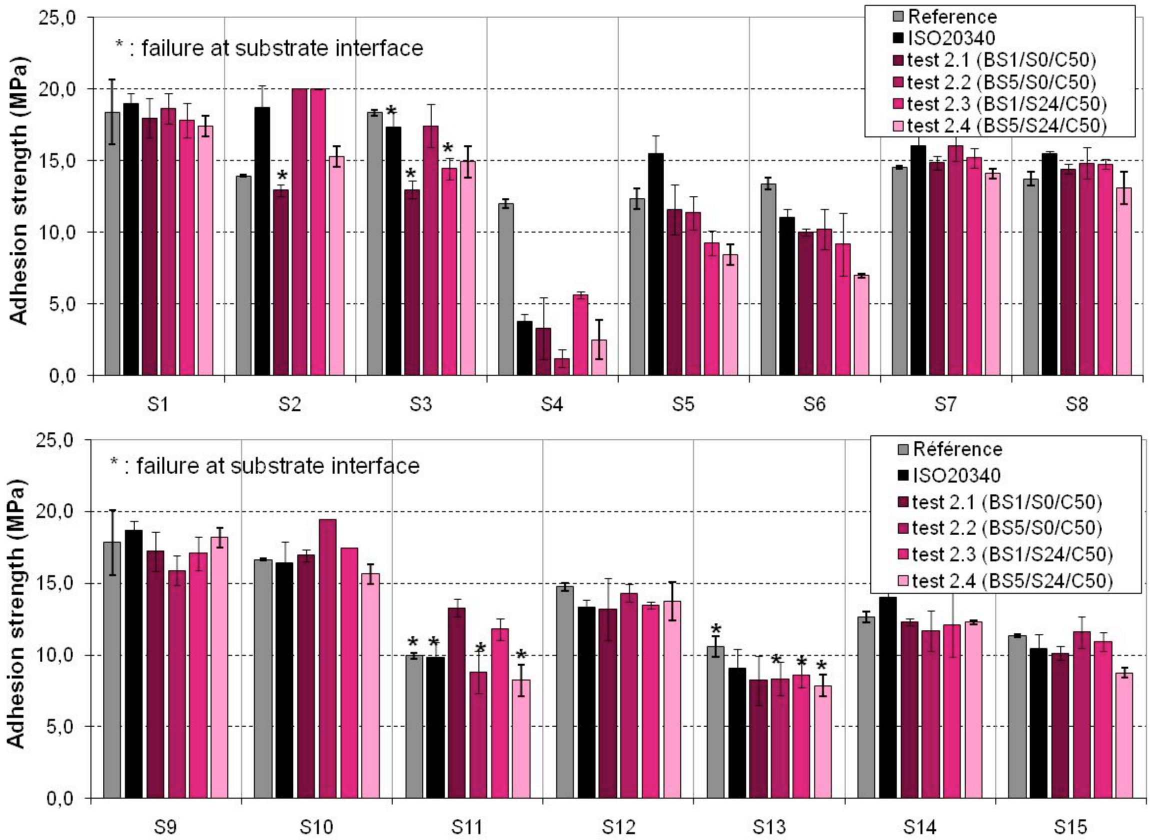

Figure 4: Influence of salt concentration and drying phase on adhesion after 4200 hours of ageing in test variants described in Table 5. Comparison with ISO 20340.

4 Conclusions

The influence of important climatic parameters such as the concentration of NaCl (1 and 5wt%), the drying phase and the UVA phase on the corrosion performance of marine paint applied on steel panels was studied. The accelerated corrosion tests of a duration of 25 weeks were designed on the basis of ISO 20340 annex A using a design of experiment. 15 different paint systems covering a large range of performance were selected and 8 different tests were conducted.

From the results, it was shown that UV exposure in a cyclic corrosion test had no major influence on the corrosion degradation of coated steel which allows a possibility to partly automate the accelerated corrosion tests. NaCl concentration within the range 1 to 5 wt% had an important role in the paint degradation whatever the paint system. The integration of a drying phase in ambient conditions has an effect which is system dependent, but in all cases, its consequence was less significant than the concentration of NaCl which seems to dominate the corrosion from scribe line. This would indicate that the continuous salt spray phase is probably the dominating phase. Hence, the best correlation was obtained with testing conditions using similar salt concentration.

Additional laboratory tests are still on-going aiming to study the influence of the freezing phase as well as the cycling of the salt spray. The results from laboratory tests when fully completed will be then compared to data from field exposures on operating ships as well as on stationary marine sites.

5 References

[1] P. Le Calvé, J.-M. Lacam and N. LeBozec, Protective Coating Europe, **10(7)** (2005) 29.

[2] G.J. Binder, CORROSION/08, **Paper 08001**, New Orleans, NACE (2008).

[3] D. Ward, CORROSION/08, **Paper 08003**, New Orleans, NACE (2008).

[4] J. I. Skar and P.G. Lunde, CORROSION/08, **Paper 08015**, New Orleans, NACE (2008).

[5] P. Le Calvé, J.-P. Pautasso and N. LeBozec, **Paper 4659**, Eurocorr 2011, September 4-8, 2011, Stockholm, Sweden.

[6] N. LeBozec, P. Le Calvé, J.-P. Pautasso and D. Thierry, **Paper 4629**, Eurocorr 2011, September 4-8, 2011, Stockholm, Sweden.

[7] N. LeBozec and D. Thierry, Material and Corrosion, 2010, 61(10), 845.

[8] C. Merlatti, Rapport R15-L2-14-12-06, ISITV, PEA 98 07 23.

[9] N. LeBozec, N. Blandin and D. Thierry, Materials and Corrosion, **2008,** 59, 889.