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REDUCING TEST BIAS IN EVALUATING REACH COMPLIANT PAINT SYSTEMS

NIHAD BEN SALAH, R&T MANAGER ADVANCED PROCESSES
BAPTISTE FEDI, R&T ENGINEER ELECTROCHEMICAL PROCESSES
VIRGINIE MATHIVET, STUDENT IN ENGINEERING

SAFRAN TECH (SAFRAN RESEARCH CENTER)

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PRESENTATION OUTLINE

Context

Salt Spray scribe test on Cr VI free corrosion protection systems on steels – Repeatability concerns

Cross hatch dry adhesion tests – Questions on the significance of the test

Conclusions

Concerns during the validation of new REACH Compliant anti-corrosion paint systems

Non-repeatability of the results

Paint systems on Zn-Ni plated steels don't pass corrosion and adhesion tests

Same paint systems on other substrate types not concerned

Note: No paint system brand will be given, paint systems will be labeled paint A or B



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TESTS OF CORROSION RESISTANCE SYSTEM

Salt Spray test on scribed specimens (ASTM B117)

Salt Spray scribe test

Definition of the systems:

4130 Steel substrate + sacrificial (Alkaline Zn-12-15%Nickel + CrIII sealing) + (Primer + Paint)

Test:

Scribed specimen tested per ASTM B117/ ISO9227: Salt Spray Tests

Requirements:

No rust in the scribe, and blistering not permitted

Results:

Some specimens show no rust and no blistering, others failed.



FAIL

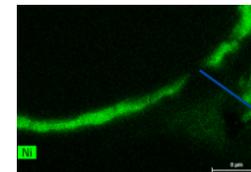
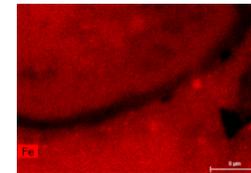


PASS

Salt Spray scribe test



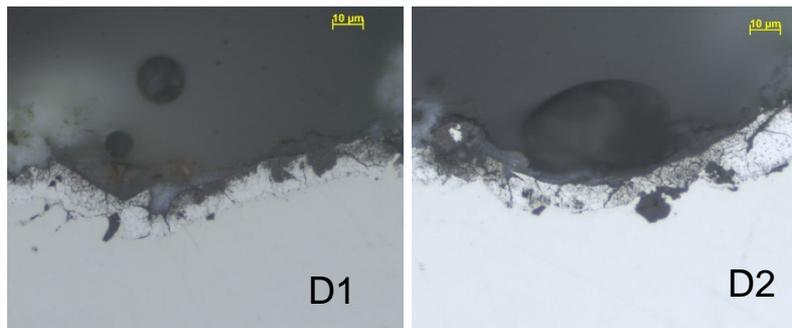
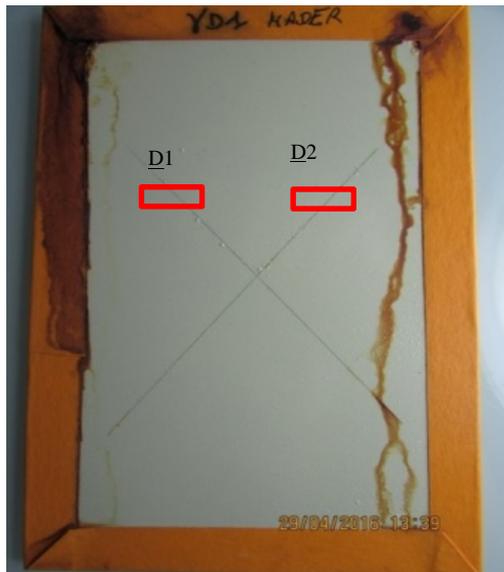
- In the non corroded scribed area, the scribe did not cut the Zn-Ni coating
- In the corroded area the scribe went through the Zn-Ni to the base metal



Scribe

Repeatability of the scribe in the same specimen is in question!

Salt Spray scribe test

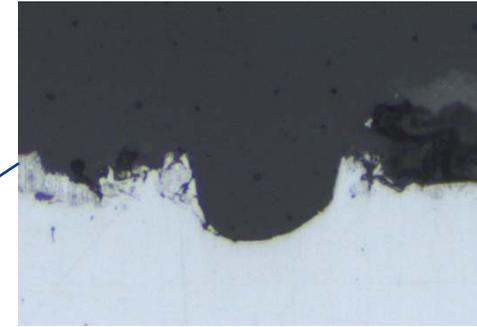
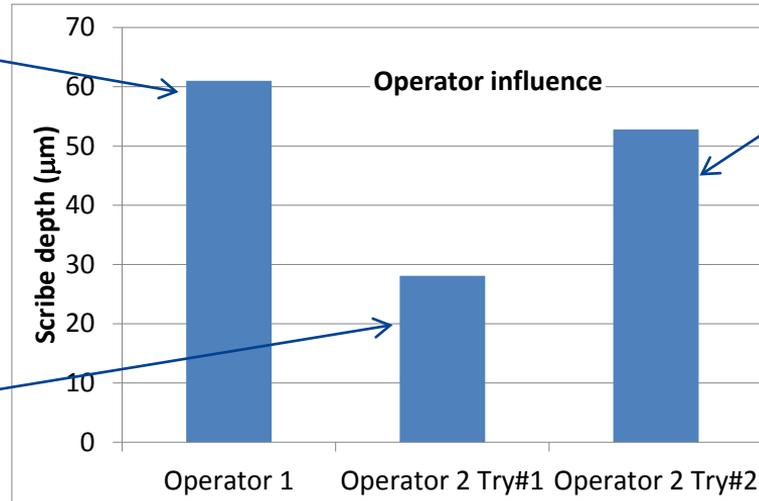
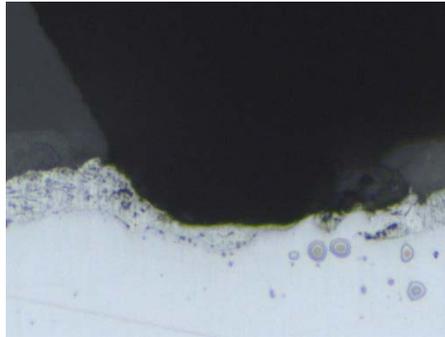
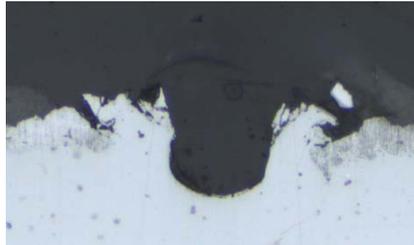


In the non corroded specimens, the scribes did not go through the Zn-Ni to the base metal

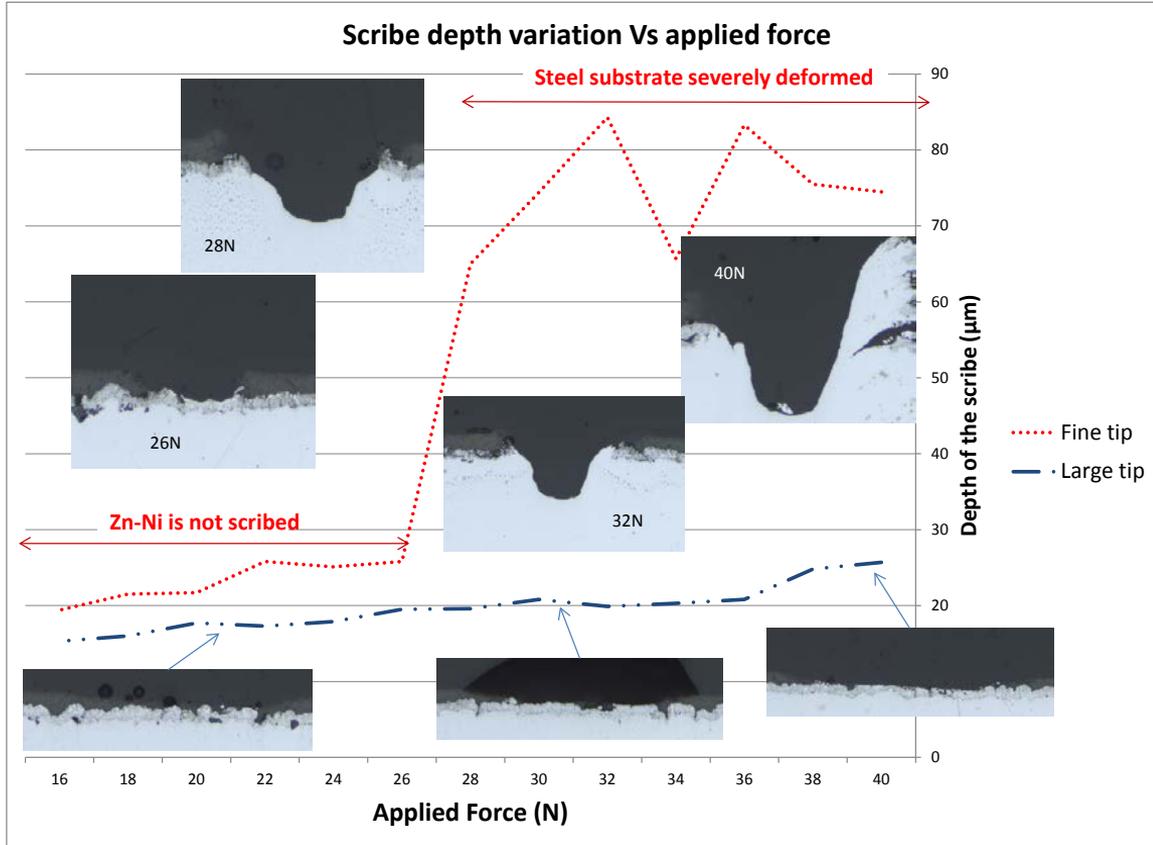
Repeatability of the scribe in the same specimen and from one specimen to another is in question!

Salt Spray scribe test – Scribe repeatability test

Manual procedure is not reliable for scribe repeatability



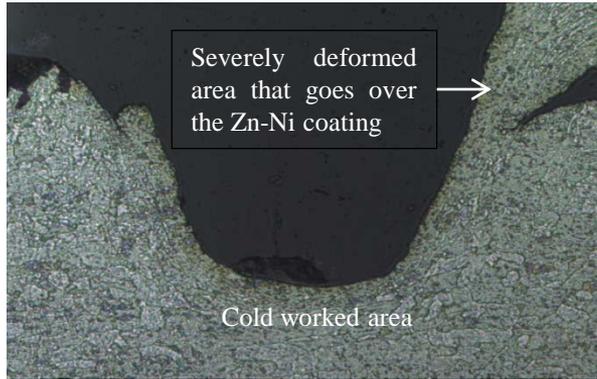
Salt Spray scribe test – Scribe repeatability test



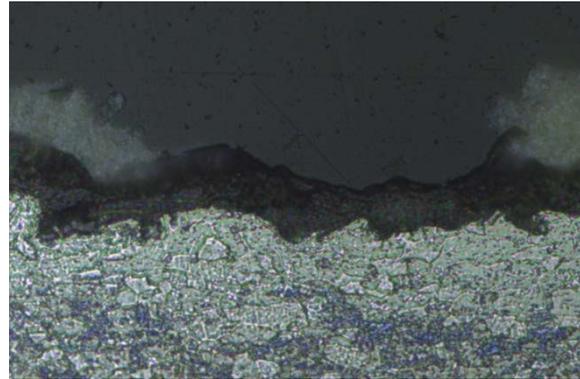
Apparatus used to produce controlled scribes

Whatever the applied force, large indenter tips did not bring enough stress to go through Zn-Ni. Finer tips are needed to bring enough local stress to break the Zn-Ni plating...but it severely deforms the steel substrate

Salt Spray scribe test – Scribe repeatability test



Applied force = 40N → Scribe went through Zn-Ni, but 4130 steel substrate severely deformed

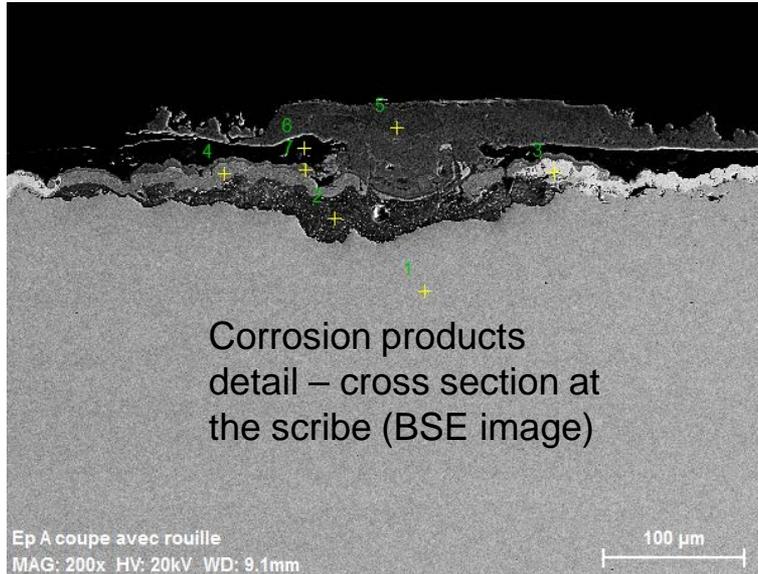


Applied force = 26N → Scribe did not go through Zn-Ni

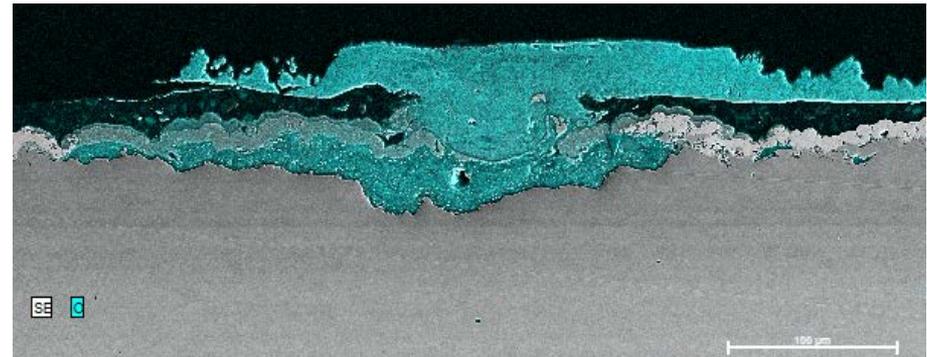
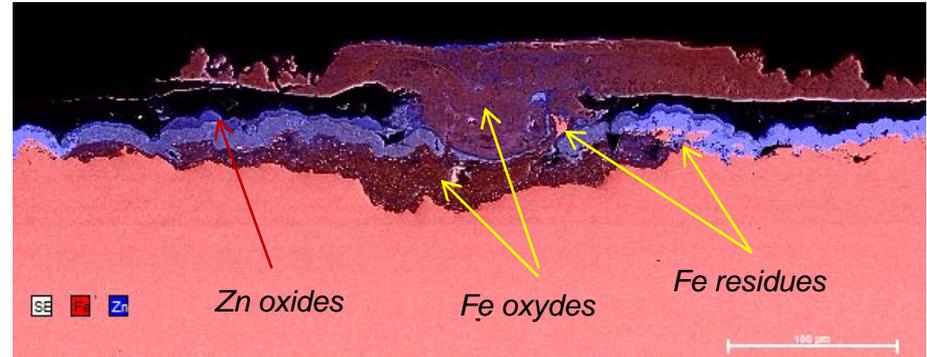
4130 steel hardness:
26-28 HRC
Zn-Ni hardness: 40-45
HRC

The production of scribe on Zn-Ni plated steel that did not affect the substrate is possible in a very narrow range of applied force for a given indenter tip size.

Salt Spray scribe test – Did the Zn-Ni play its sacrificial role?



- ***In the scribe, steel residues are observed above the Zn-Ni coating***
- ***Zn oxide is found at the surface of Zn-Ni at the scribe vicinity***
- ***Steel in the scribe area is severely corroded***



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WET PAINT ADHESION TESTS

Cross Hatch wet adhesion tests (followed by pull off test after immersion in demineralized water (ISO2812))



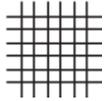
Cross hatch wet adhesion tests

Definition of the systems:

4130 Steel substrate + (Zn-Nickel + CrIII sealing) + (Primer + Paint)

Test:

Immersion in demineralized water ISO2812-2, followed after 24h by 1) Cross hatched panels per ISO2409 + adhesive pull-off test



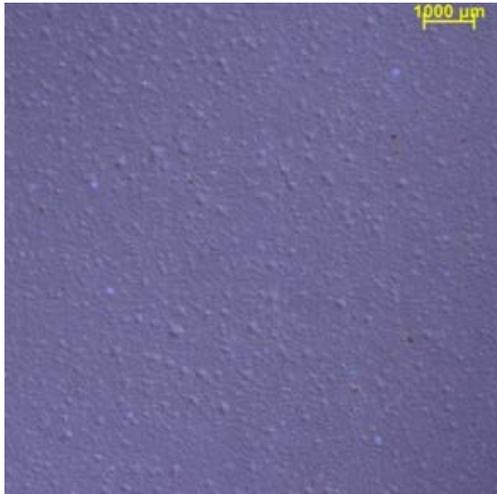
Requirements:

No more than 5% detachment of small flakes at the intersection of the cuts permitted

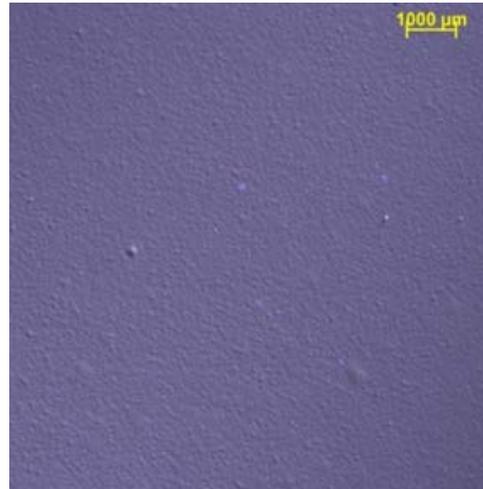
Results:

- Painted Zn-Ni plated panels show micro-blistering after 1000h immersion
- Adhesion tests on cross hatched specimens do not meet the requirement
- Same paints on other coatings do not show this phenomena

Cross hatch adhesion tests – microblistering → Dem Water Vs Salt Spray



Micro-blistering after 1000h immersion in demineralized water for paint A and B

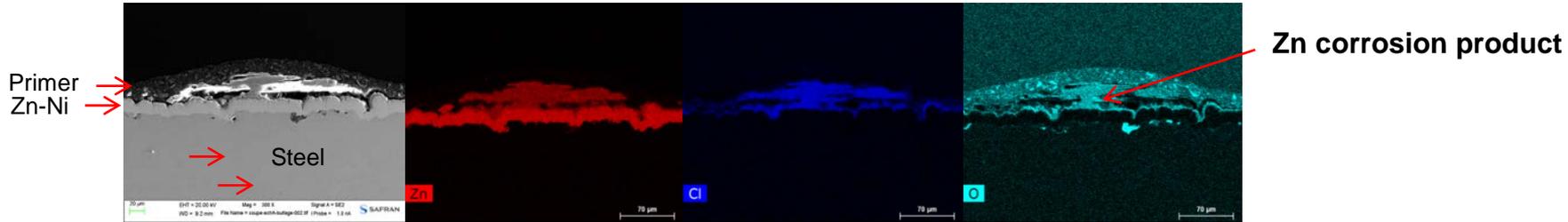


No micro-blistering after 3000h in salt spray for paint A

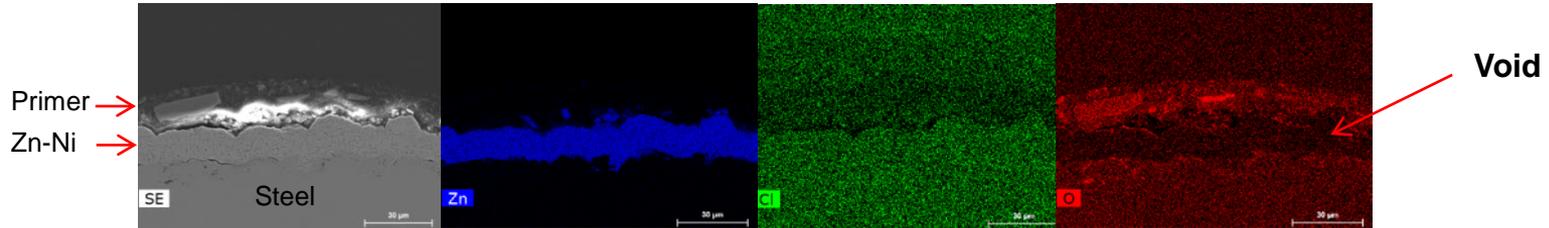


Blistering after 3000h in salt spray for paint B

Cross hatch adhesion tests – microblistering → Dem Water Vs Salt Spray



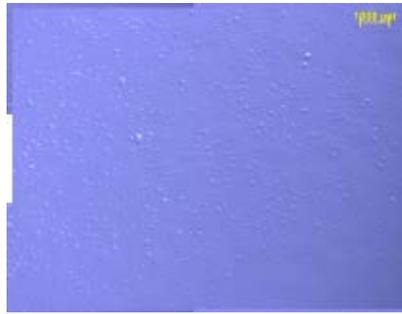
SEM/EDX - Cross section on a blister after **3000h in Salt Spray** – Presence of Zn oxides at the interface between Zn-Ni and the primer (paint B)



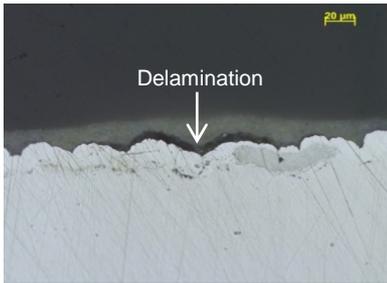
SEM/EDX - Cross section on a blister after **1000h in demineralized water** – Void observed at the interface between Zn-Ni and the primer

Unlike in salt spray, micro-blistering in demineralized water is not due to corrosion

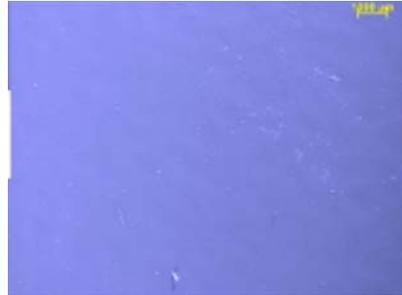
Cross hatch adhesion tests – microblistering



Demineralized water



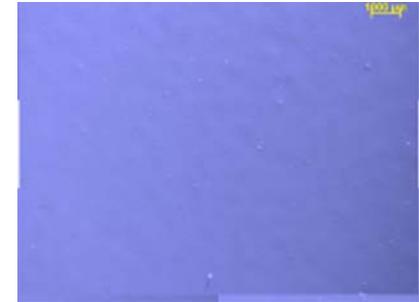
Delamination



Demineralized water +0,1% NaCl



Demineralized water+10% NaCl

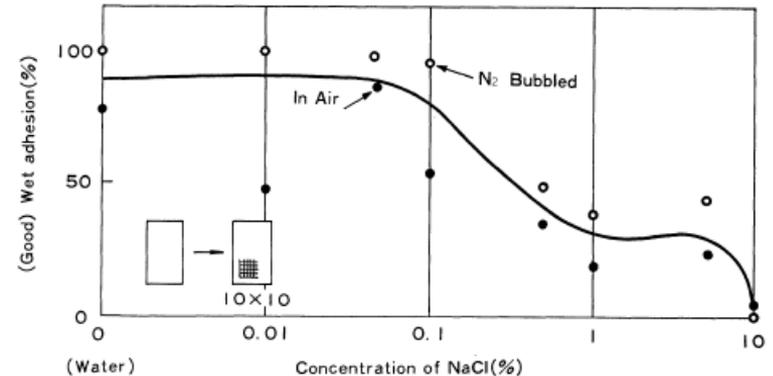


Demineralized water+1% NaCl

Micro-blistering observed in demineralized water disappears when NaCl is added highlighting the osmotic effect

Cross hatch adhesion tests - microblistering

- *Microblistering that appears after demineralized water immersion on the paint system deposited on Zn-Ni plated is not due to corrosion since no corrosion product is observed at the interface primer/Zn-Ni*
- *Delamination of the paint is not due to paint water absorption per se.*
- *This phenomena disappears when NaCl is added to demineralized water*
- *This phenomena is observed on CrIII passivated Zn-Ni only*
- *Interpretation: this local delamination phenomena seems to be due to the osmotic pressure produced by the difference in species concentration at the interface metal/polymer (soluble salt ions at the passivated Zn-Ni surface) and the media (demineralized water → low ions content). This phenomena is widely described in the literature and reported when wet adhesion is affected.*



Y.Miyoshi, Evaluation Technology of Corrosion Behavior for Automotive Steel Sheet, ISIJ International. Vol.31, no.2, pp. 122-123, 1991, pp. 122-123

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CONCLUSIONS



Conclusions

- *Salt spray scribe tests could lead to erroneous conclusions if the scribing is not controlled. This control is hard to achieve for Zn-Ni coated steels (compared with Cd-plated)*
- *Zn-Ni is harder than 4130 steel substrate (that is used for corrosion quality control). Thus scribes that succeed to go through Zn-Ni will deform the steel substrate. Cold working of the substrate would increase its susceptibility to corrosion.*
- *Zn-Ni played his sacrificial role as revealed by extensive Zn oxides presence in the areas where steel corroded.*
- *The scope of the test is biased.*

- *Cross hatched adhesion tests per ISO2812 after immersion in demineralized water is biased due to the occurrence of osmotic delamination linked to the salt ions gradient between the surface of the paint and its interface with CrIII passivated Zn-Ni.*
- *This phenomena disappears when NaCl is added to demineralized water which create an ions equilibrium with the ion-rich interface and eliminate the effect of osmotic pressure.*
- *What are we testing?*



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