Development of water-based, bio-based paints with high corrosion performance

A.-P. Romano[1], E. Lachery[1], T. Senechal[1], L. Terrien[1], J. Lazko[1], M. Poelman[1], J.-M Raquez[3], M.-G. Olivier[1-2]

[1]Materia Nova Research Center, Avenue N. Copernic, 3, Parc Initialis, 7000 Mons, Belgium
[2]Service de Sciences de Matériaux, Université of Mons, 20, Place du Parc, 7000 Mons, Belgium
[3]Service des Matériaux Polymères et Composites, Université of Mons, 20, Place du Parc, 7000 Mons, Belgium

Interreg France-Wallonie-Vlaanderen
UNION EUROPÉENNE EUROPESE UNIE
WBDuraPaint

VIRTUAL EUROCORR

Context

Evolution of the paint formulation = waterborne resins

Emitting VOC or using toxic isocyanate

Biobased paint formulation use is limited due to their global performance and durability

Aim = developing non-toxic low environmental impact formulation with improved properties such as corrosion resistance and weathering resistant

Strategy

Synthesis of biobased waterborne binder

Selection and functionalization of clays

Existing resins in commercial paint substituted by bio-based waterborne non-isocyanate polyurethane

Incorporation of clays in anti-corrosion paint

Synthesis of biobased binder

Development of NIPU binder

Biobased binder for corrosion protective coatings

In aqueous phase

Lowering VOC emissions
Lowering solvents use

Challenge
Hydrophobic polyurethane must be dispersed into water

Non-isocyanate polyurethane

Avoiding toxic compounds from classic synthesis
~~Isocyanates (+ Phosgene)~~

Challenges
New paths must be explored
Further formulation must be adapted

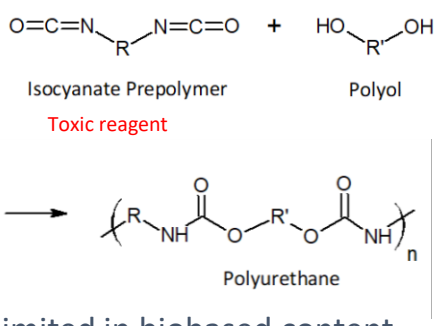
Synthesis of biobased binder

Development of NIPU binder

Chemistry of NIPU

Classical way leading to PU

Diol + Diisocyanate



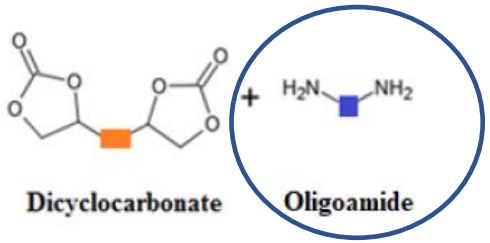
Limited in biobased content

Way leading to NIPU

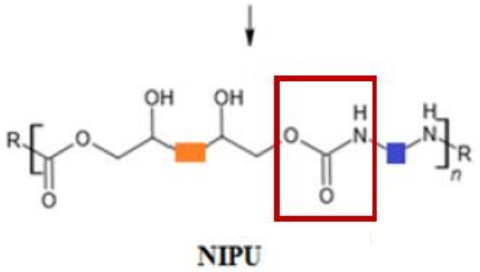
Polyaddition

Low industrial availability

High biobased possibility



High biobased possibility



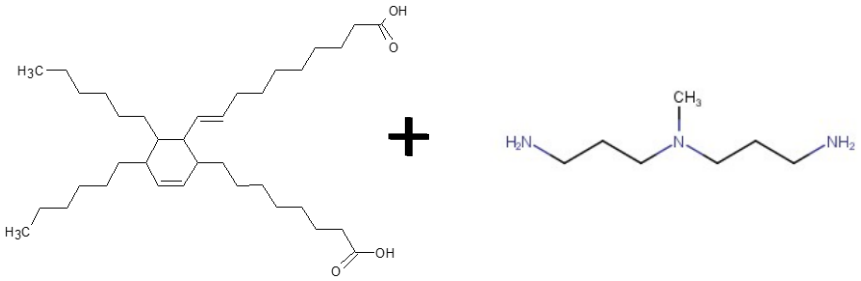
Synthesis of biobased binder

Development of NIPU binder

Chemistry of NIPU

Way leading to NIPU

Step 1
Synthesis of prepolymer oligoamide



From vegetable oil

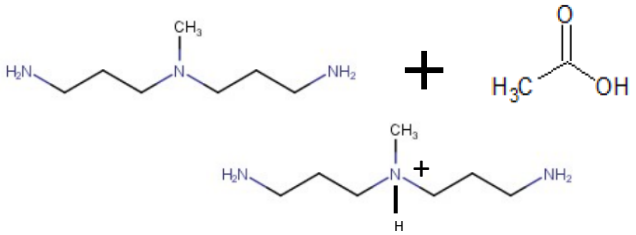
Input of biobased carbonated chain

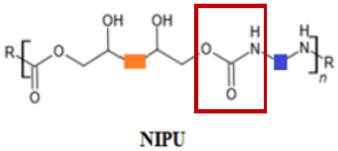
Diamine with tertiary amine

For further water dispersion

Goal → Developing NIPU's amphiphilic nature

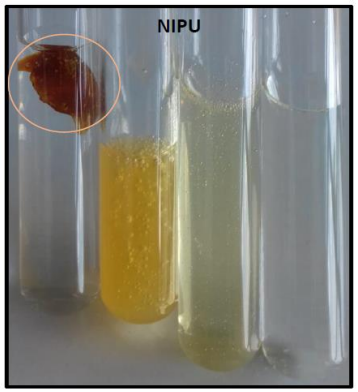
Work focuses on **cationization** of tertiary amine





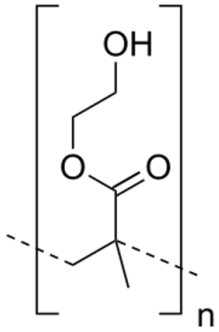
NIPU water dispersion

Increasing cationic parts



Commercial paint

- Definition = high-performance anti-corrosion paint, waterborne, acrylic emulsion, based on acrylic polymers and specific additives, polymerization at room temperature



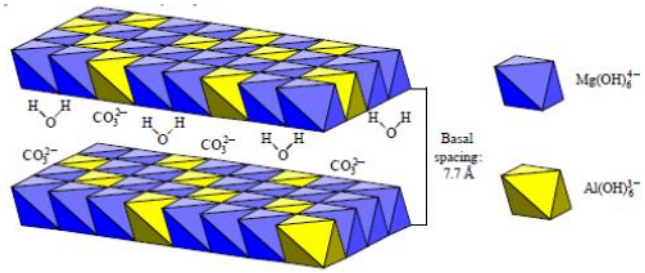
- Substrate : Q-Panel QD36 (mild steel)
- Surface preparation : ethanol degreasing
- Bar coat : 200 µm wet
- Colour : white

Modification of commercial paint by incorporation of (functionalized) clays

- Clays : mechanical and barrier reinforcement
  - Functionalized clays : corrosion inhibitors

Selection of clays

Anionic clays : Pural MG 61
(lamellar)

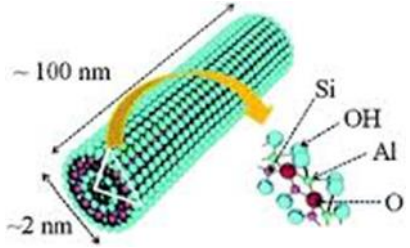


Process:

- Thermal treatment (450°C to eliminate carbonates)
- Restructuration and inhibitor incorporation in *carbonate-free* inhibitor solution (Molybdate Na)

5-10 wt% of Mo in Pural Mg 61

Halloysites/aluminosilicate nanotube
($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$)
(tubular)



Process:

- Incorporation of corrosion inhibitors inside tubular structure of halloysite by direct incorporation

8-10 wt% of benzotriazole (BTA) in halloysite

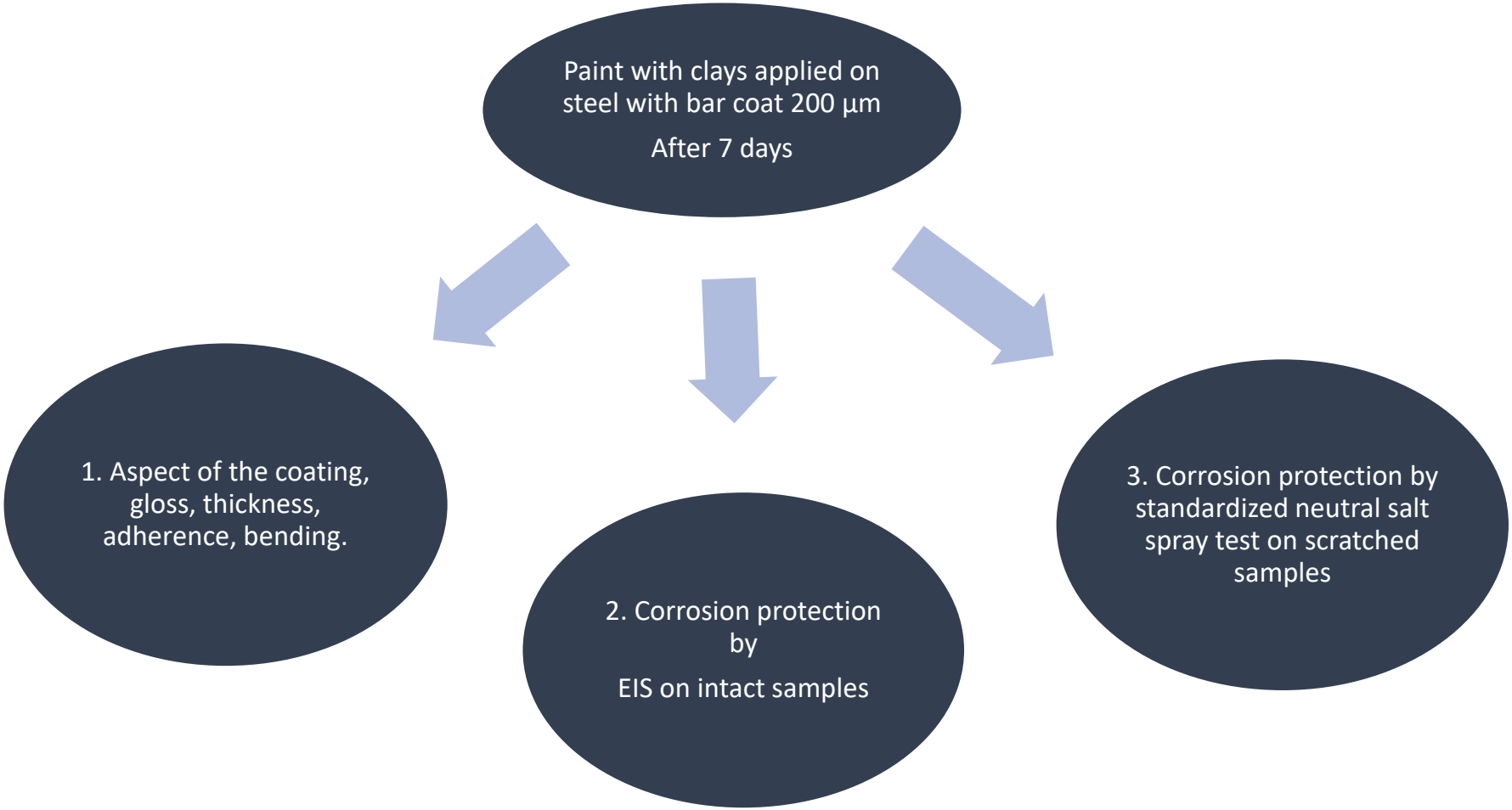
Selection of 4 clays functionalized or not with corrosion inhibitors

Paint modification with clays

PVC = 14,07

Paint formulation	Abbreviation
Commercial Paint	CP
Commercial paint without commercial anti-corrosion	CP without
Commercial Paint without commercial anti-corrosion + 3 % Pural MG61	Pural
Commercial Paint without commercial anti-corrosion + 3 % Pural MG61 Mo	Pural Mo
Commercial Paint without commercial anti-corrosion + 3 % Halloysite	Hal
Commercial Paint without commercial anti-corrosion + 3 % Halloysite BTA	Hal BTA

Characterisation of modified paint with clays



1. Aspect of the coating, Gloss value (ISO 2813)

	Visual observation
CP	Uniform
CP without	Uniform
Pural	Uniform
Pural Mo	Uniform
Hal	Uniform
Hal BTA	Uniform

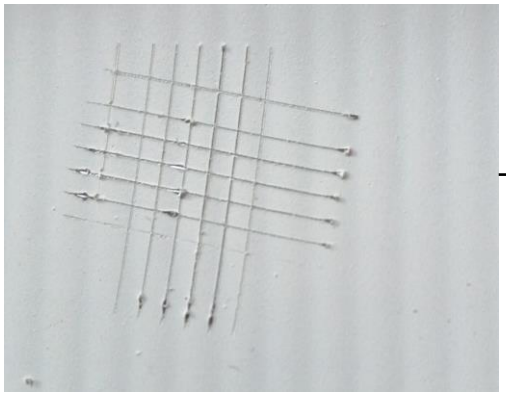
	Determination of gloss value at 20 °	60°	85°
CP	34	60	80
CP without	40	63	87
Pural	8	24	49
Pural Mo	9	32	35
Hal	8	26	33
Hal BTA	10	30	37

Incorporation of clays modified the gloss value

1. Thickness, adherence and bending

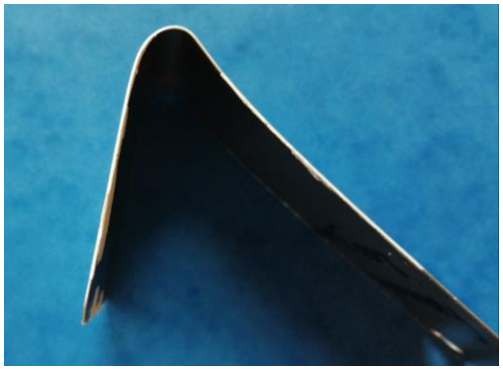
CP
CP without
Pural
Pural Mo
Hal
Hal BTA

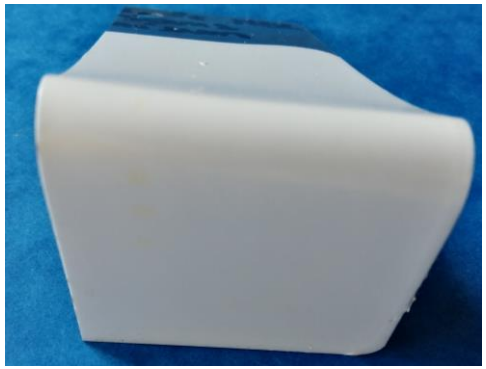
- Thickness : 100 ± 5 µm
- Cross-cut test (ISO 2409)



→ Grade 0 (ok for the 6 systems)

- Bend test (cylindrical mandrel 5 mm) (ISO 1519)

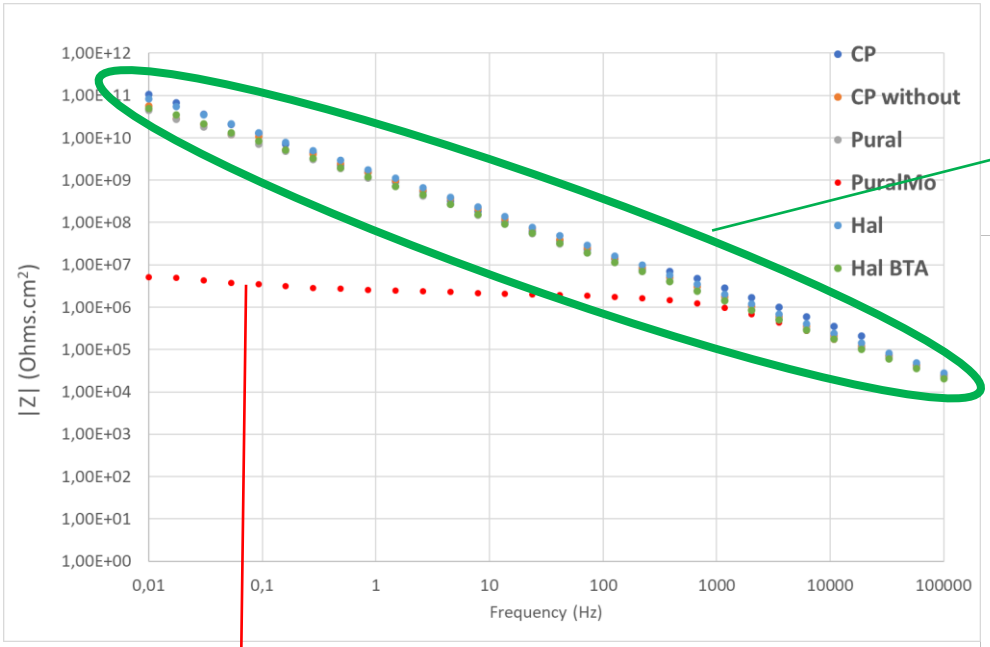




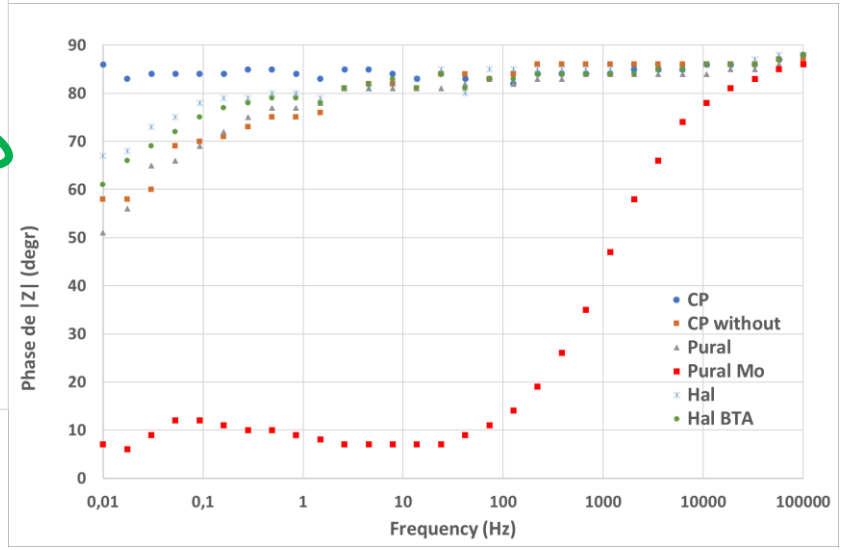
→ ok for all systems

2. Corrosion protection by EIS on intact samples

Immersion 1 day in 0,5 M NaCl



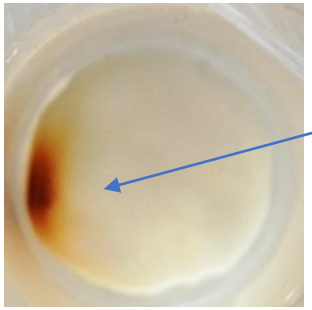
Capacitive behaviour
Intact coating



Coating with defects

2. Corrosion protection by EIS on intact samples

Immersion 32 days in 0,5 M NaCl



Hal BTA – good corrosion protection – same as reference

3. Corrosion protection by standardized neutral salt spray test on scratched samples (ASTM B117)

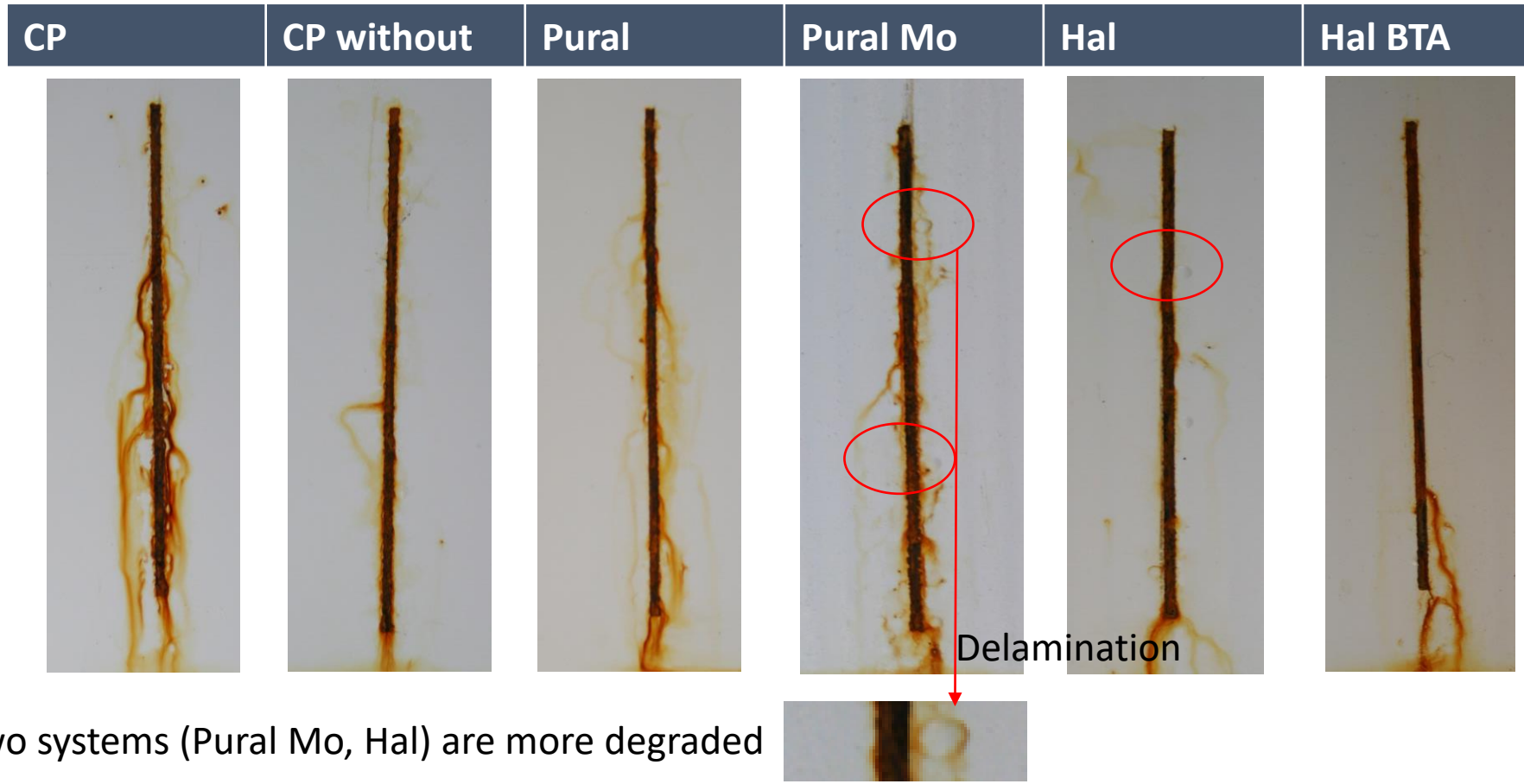
After 1 h of neutral salt spray test

CP	CP without	Pural	Pural Mo	Hal	Hal BTA

The same behaviour is observed for all systems

3. Corrosion protection by standardized neutral salt spray test on scratched samples (ASTM B117)

After 24 h of neutral salt spray test



Two systems (Pural Mo, Hal) are more degraded

Discussion /conclusion

« Clays » = new high efficient anti-corrosion pigments for the water-based paint with high corrosion performance ?

4 clays incorporated with 3 % in anti-corrosive paint

- Uniform film, Gloss value ↘, Good adherence, Good bending
- Corrosion test

  Hal BTA gives the same results as the reference

For the future …of the study

- Modification of the % of inhibitors in the clay, in the paint
- Optimization of the dispersion

Discussion /conclusion

Interreg France-Wallonie-Vlaanderen — UNION EUROPÉENNE EUROPESE UNIE

WBDuraPaint

For the future….of the project

- Modification of the % of inhibitors in the clay, in the paint
- Optimization of the dispersion

flamac a division of SIM

- Mixed systems resins

UMET — Université de Lille

- Flame retardant system

Crepim

- Substitution TiO_2

MATERIA NOVA Materials R&D Center

- Lifecycle analysis / VOC measurements

We thank the INTERREG program for financial support

Interreg France-Wallonie-Vlaanderen
UNION EUROPÉENNE EUROPESE UNIE
WBDuraPaint

Wallonie

Consortium

MATERIA NOVA Materials R&D Center

Crepim

Université de Lille

flamac a division of SIM

UMET

Thanks for your attention

www.materianova.be