NANORELEASE FROM AUTOMOTIVE COATINGS HIGHLIGHTS SIMILARITY OF (NANO) PIGMENT EMISSION DESPITE THEIR DIFFERENT CHARACTERISTICS

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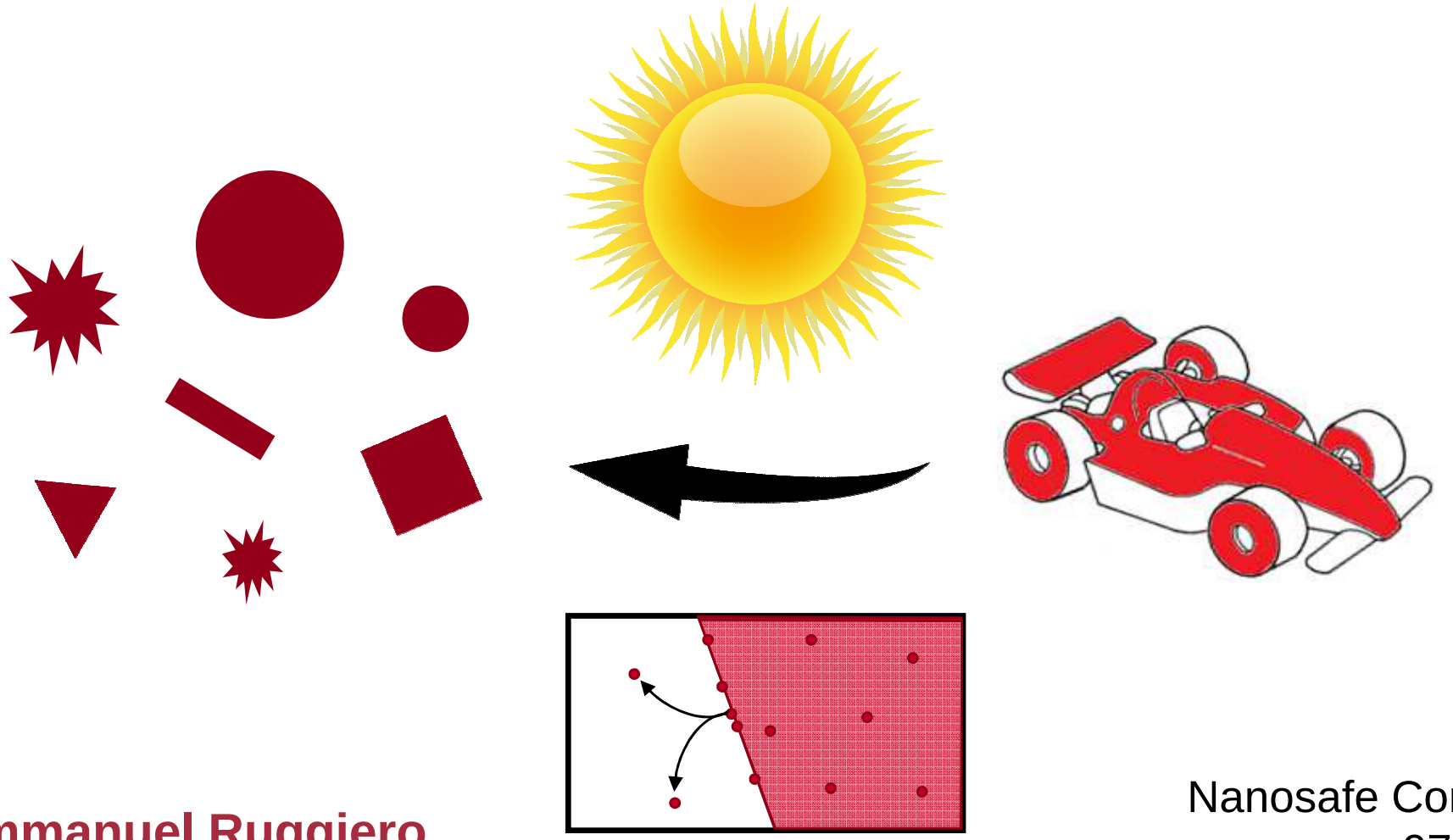
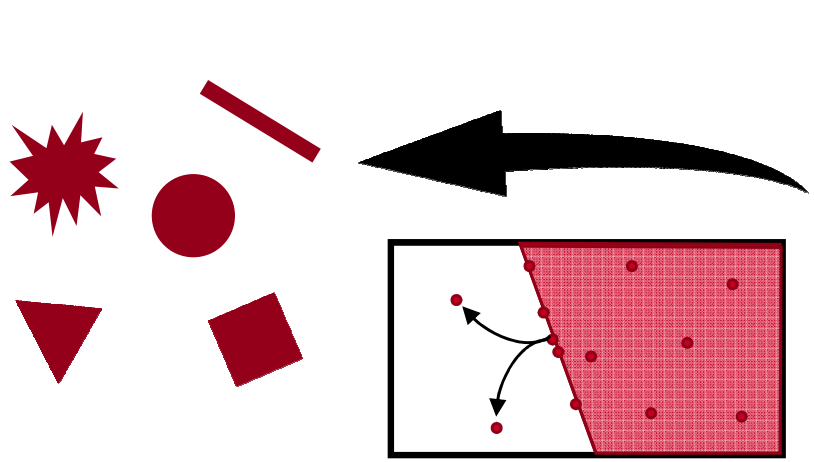
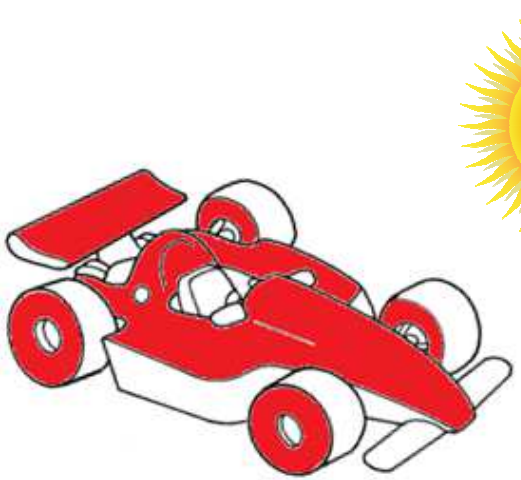


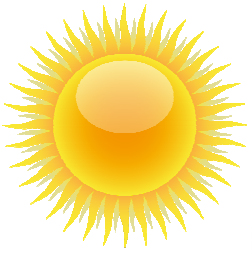
Emmanuel Ruggiero

Nanosafe Conference
07.11.2018

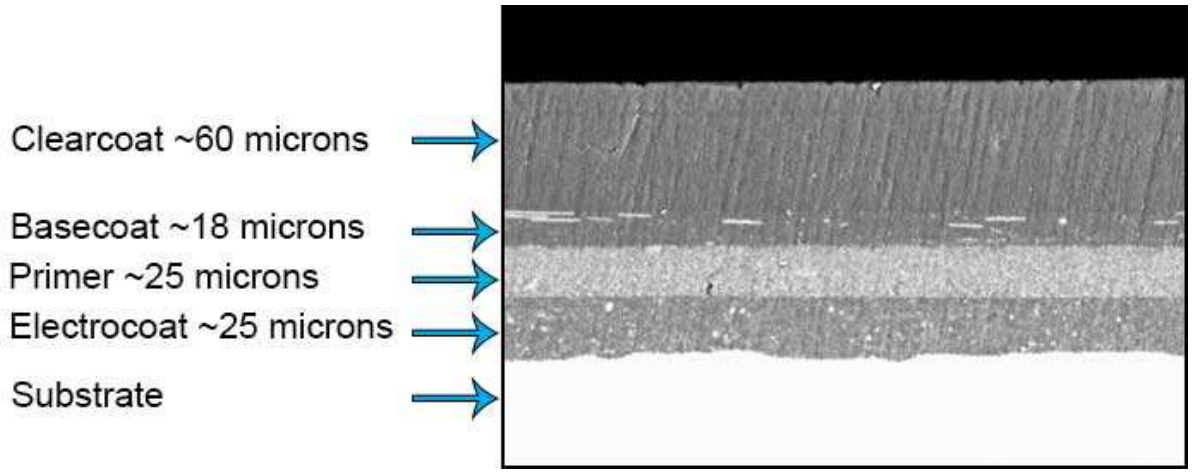
Release from nano-enabled coatings: How NM characteristics modulate the emission?







DPP Fe_2O_3 CuPhtalo

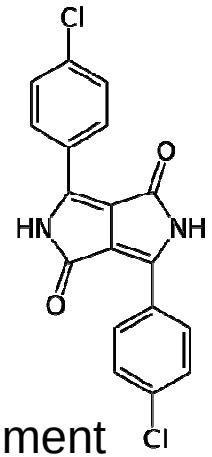


Organic Nano Pigment: DPP

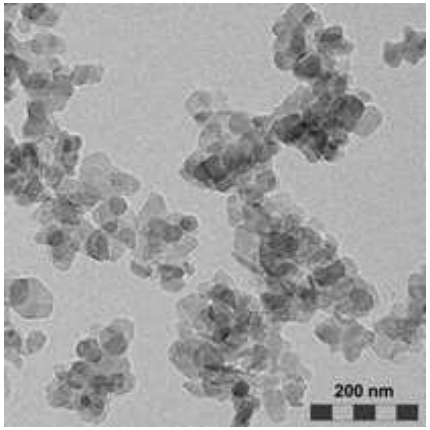
Diketo**p**yrrolo**p**yrrole dye

In acrylic-polyester coating (A)

DPP



Pigment content: 3%



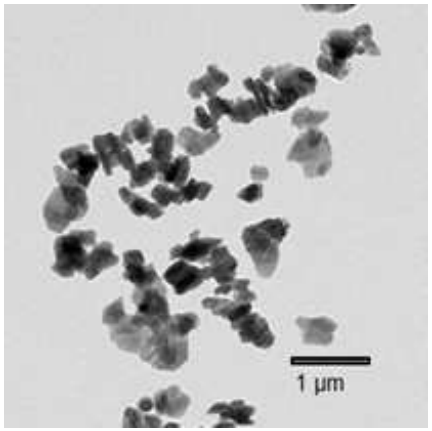
DPP nano
(size ~ 40nm)

On white

On black

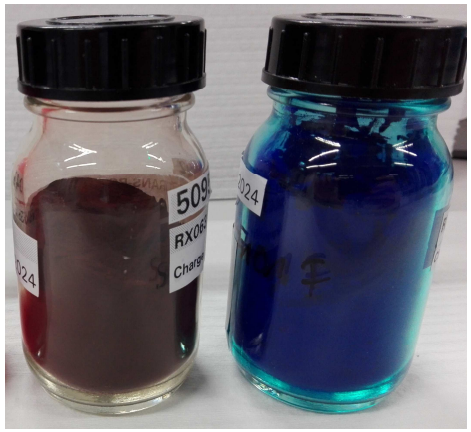
In alkyd-melamine coating (B)

Different forms of DPP influence the final chromatic properties

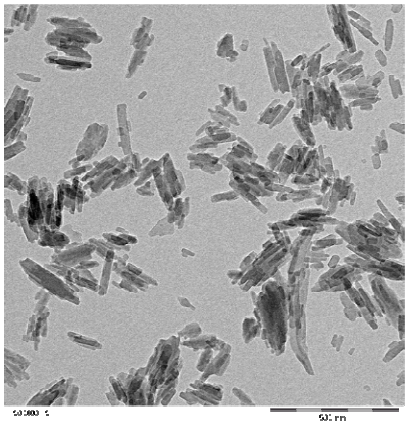


DPP non-nano and DPP coated
(size ~ 230nm)

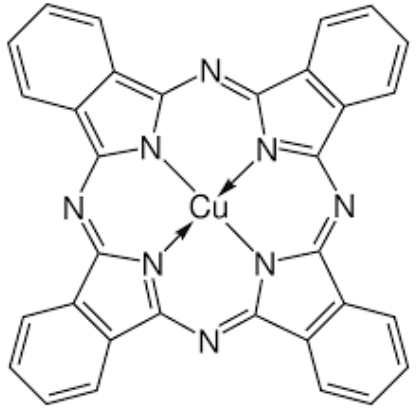
Inorganic Pigments: CuPhtalo & Fe_2O_3



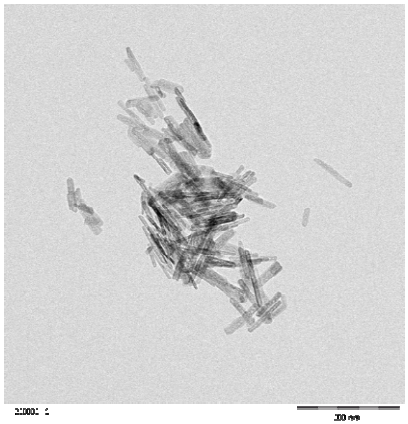
Pigment content 3% in acrylic-polyester coating (A)



(size ~ 17 nm)



Cu-Phtalocyanine



(size ~ 9 nm)

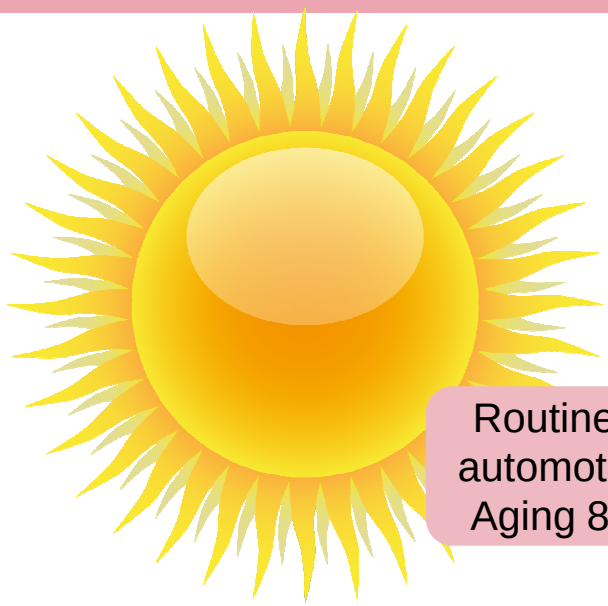
Fe_2O_3

Control plate: no pigment

Reference plate:
acrylic-polyester coating (A)

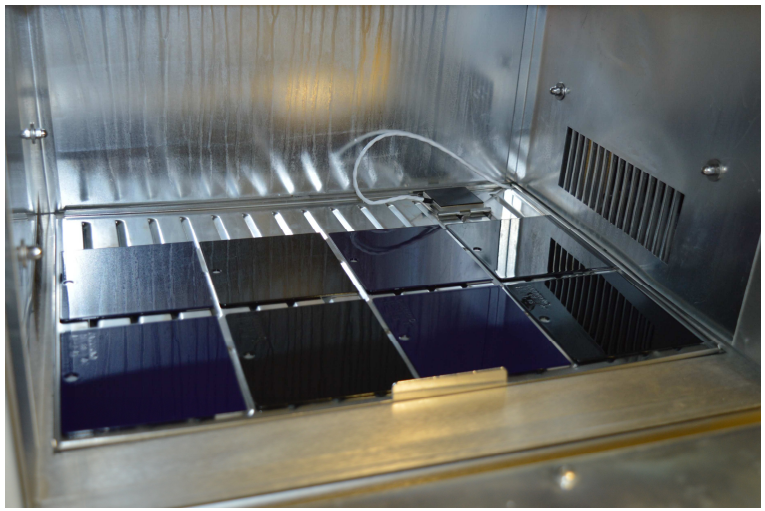
Artificial aging: Kalahari protocol

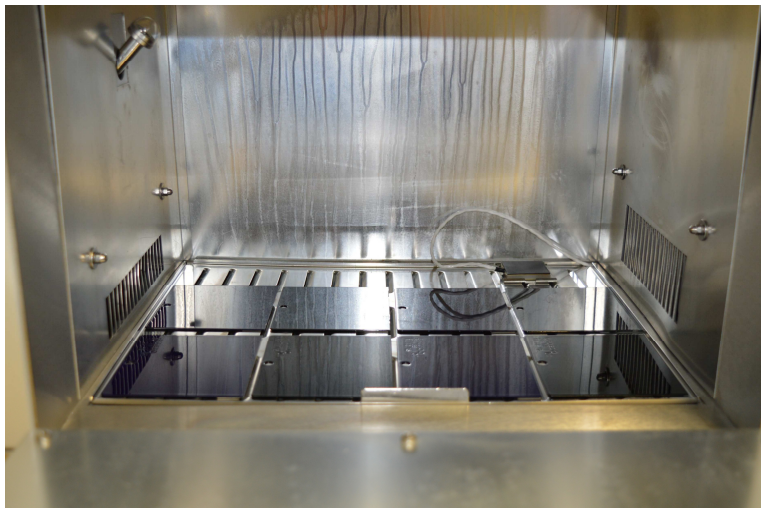
Kalahari desert



Conditions:
UV 65 W/m^2 within 300-400 nm
Temperature 90°C
3 months

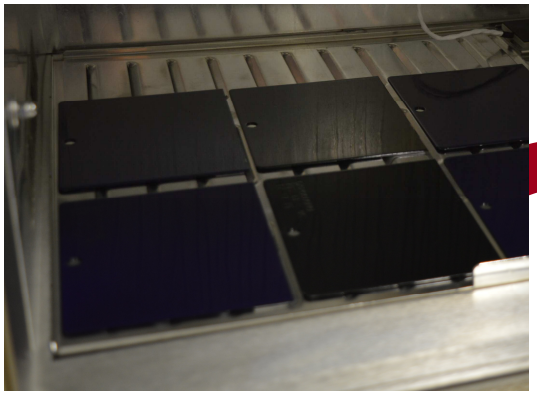
Routine protocol for automotive industries
Aging 8 times faster



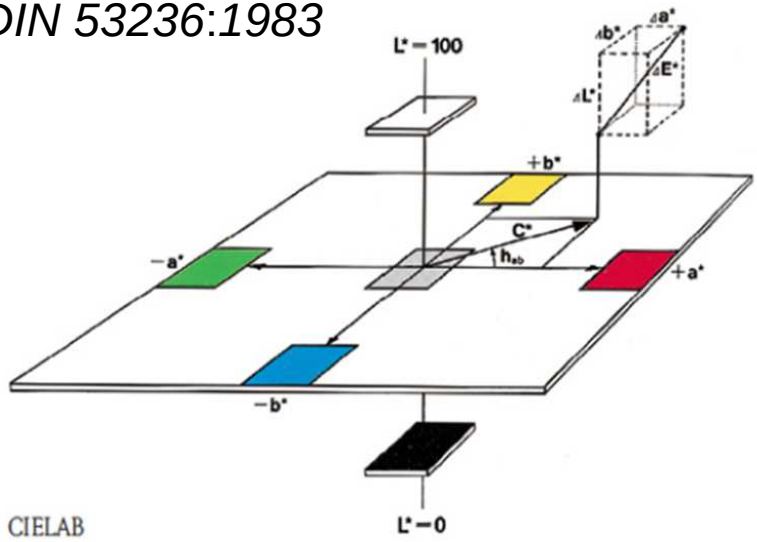


Suntest XLS+ climate chamber

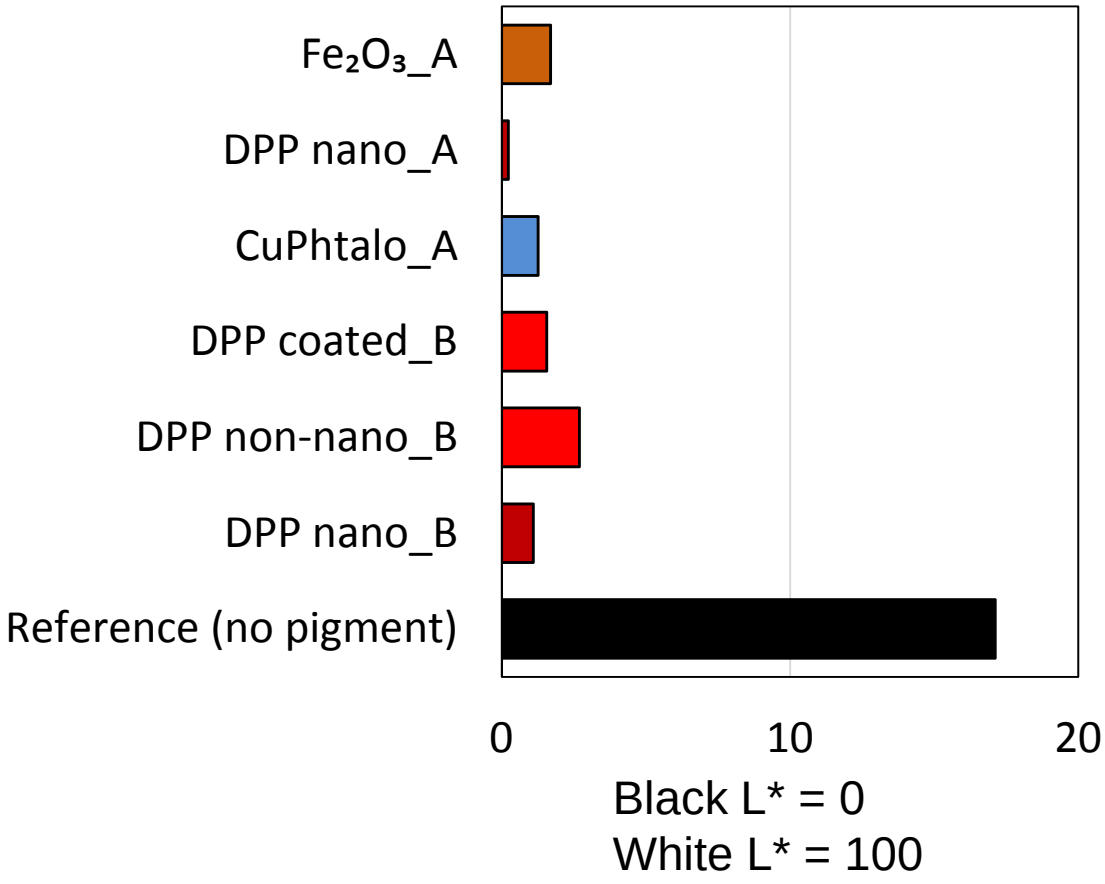
Colorimetric evaluation



L*a*b* color space method
DIN 53236:1983



2 Month Change in Lightness (dL*)



Black L* = 0
White L* = 100

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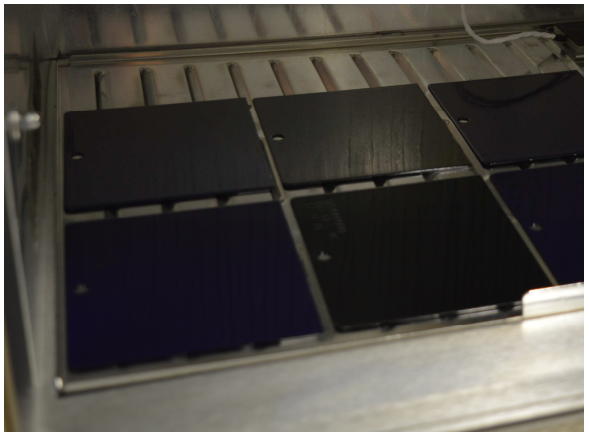
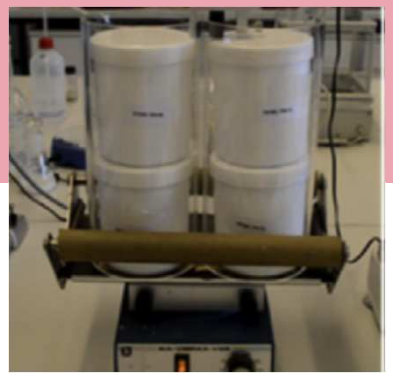
NanoRelease



Plates were immersed in water and subjected to **shaking** (12h) or bath **sonication** (1h)

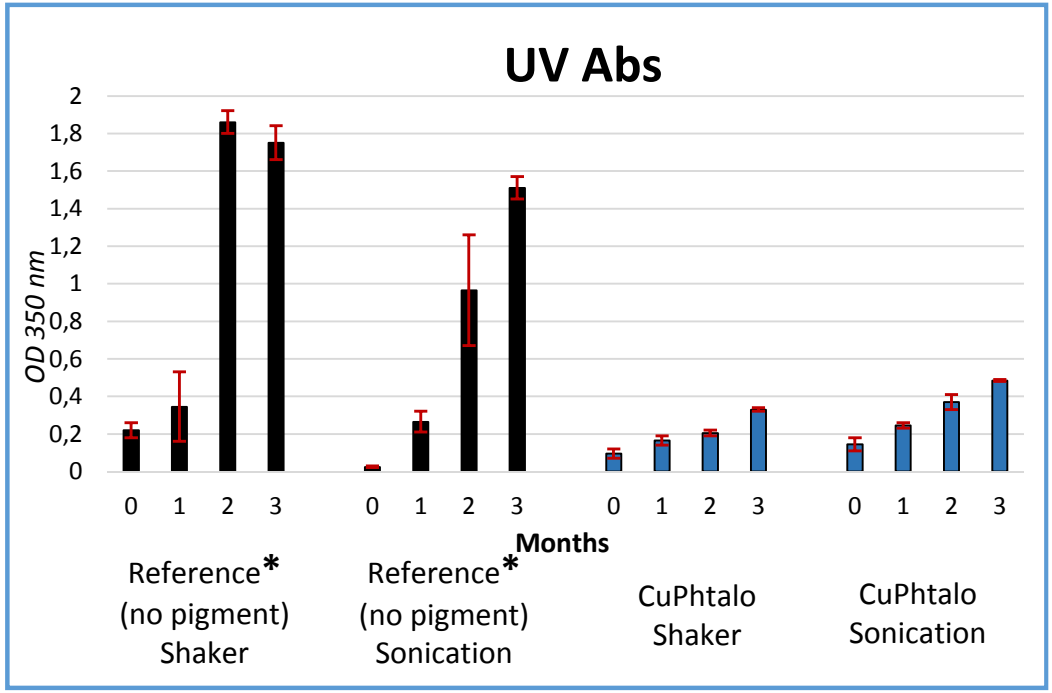


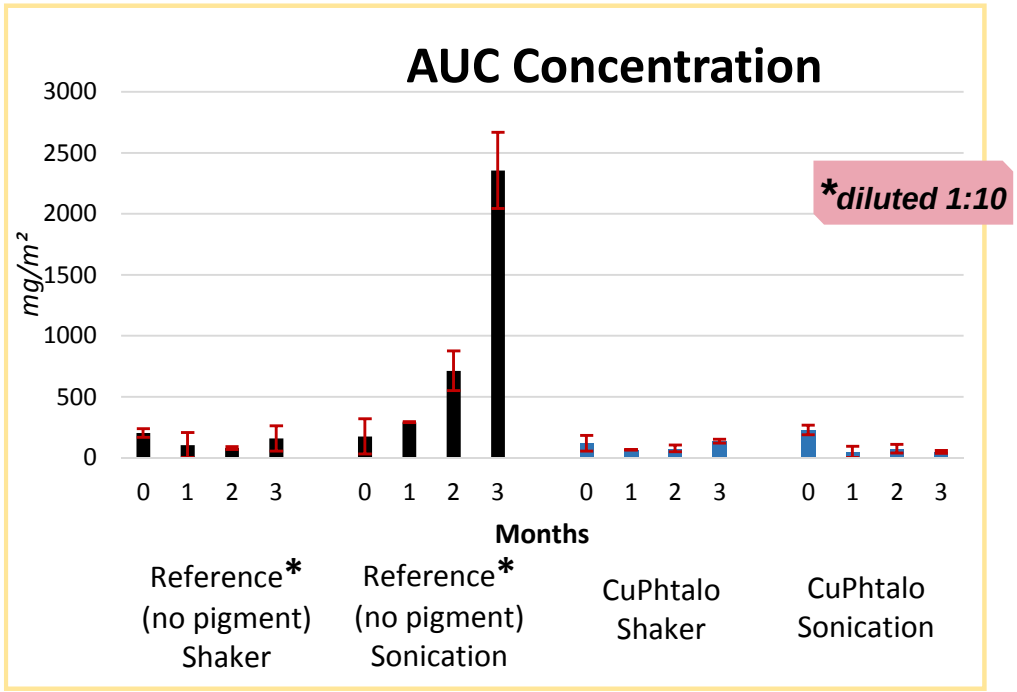
For each 12-mL aliquot apply the following analyses:

- **TEM** “check which structures are observed”
  - place drop on TEM grid, evaporate water.
- **ICP-MS** “tracer elements of embedded NMs”.
  - with acid digestion of any released fragments
- de-agglomeration by addition of SDS to 0.5g/L.
- **UV-Vis** “absorption/turbidity of leaching medium”
- **Analytical UltraCentrifuge** “absorption in size range 10nm – 20µm”

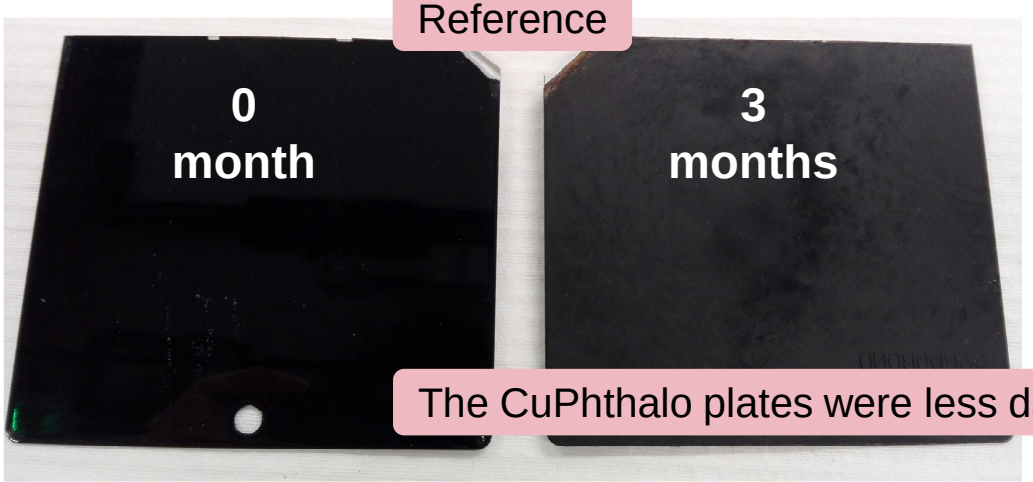
NanoRelease protocol: Wohlleben, Kingston, Zepp et al., Carbon (**2017**) 113:346-360

CuPhthalo and reference plates release in Coating-A

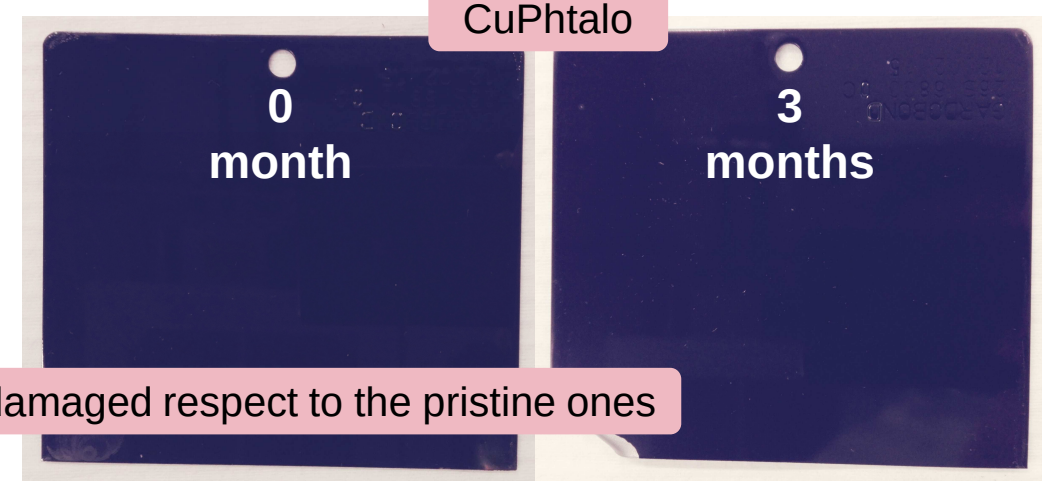




Reference



CuPhtalo



The CuPhthalo plates were less damaged respect to the pristine ones

Reference plate evolution over months

After 2 month the topcoat was completely detached from the steel plate

0 month

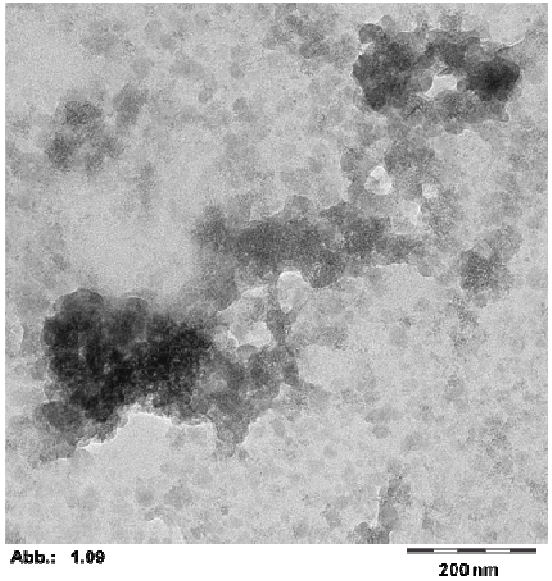
1 month

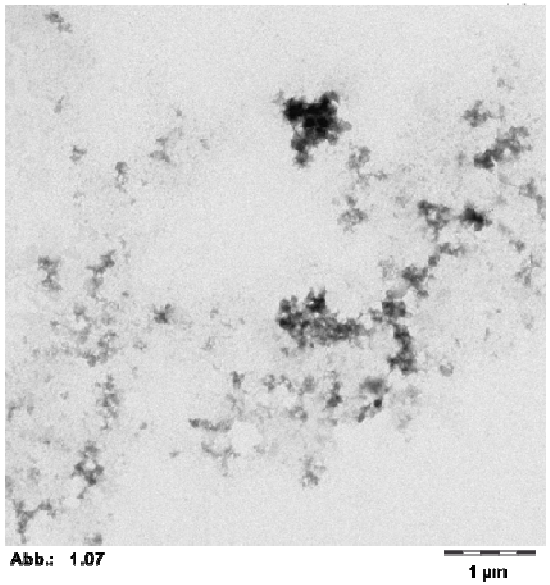
2 months

3 months

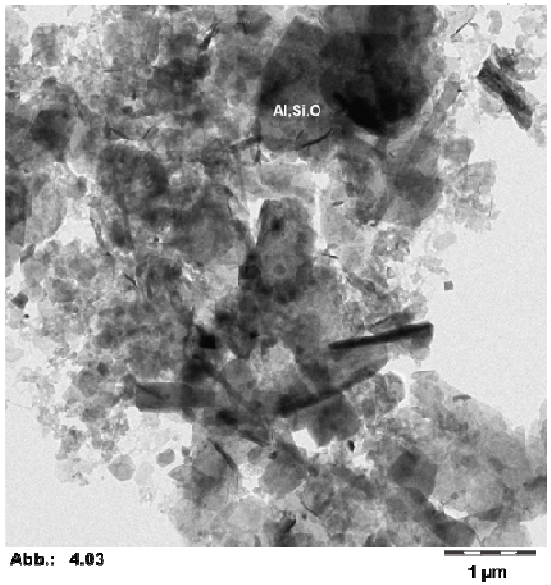
TEM: reference plate release (Coating-A)

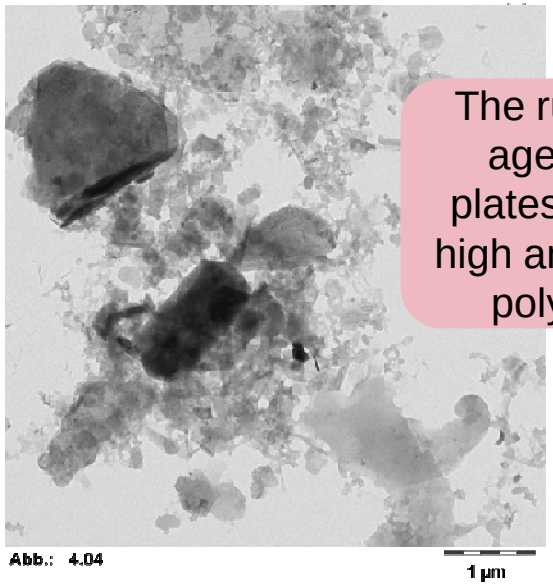
0 month weathering + 1h sonication





3 months weathering + 1h sonication

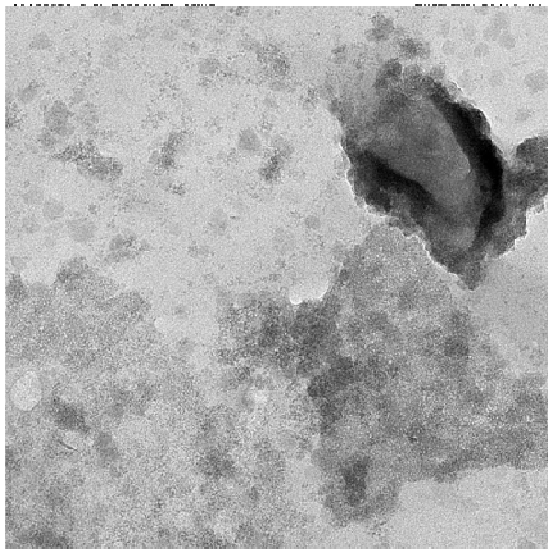


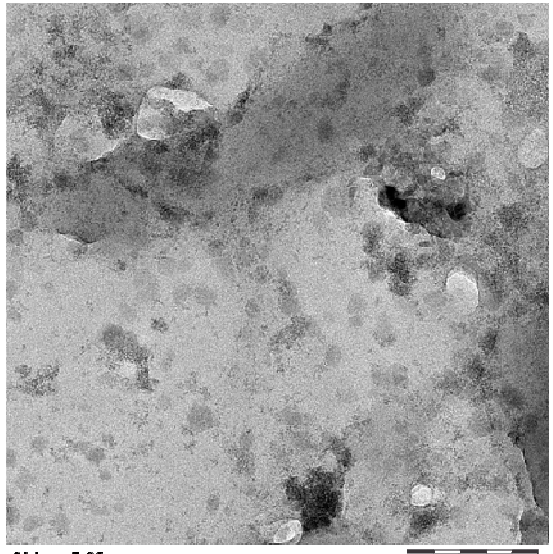


The runoff water of aged reference plates displayed an high amount of micro polymer debris

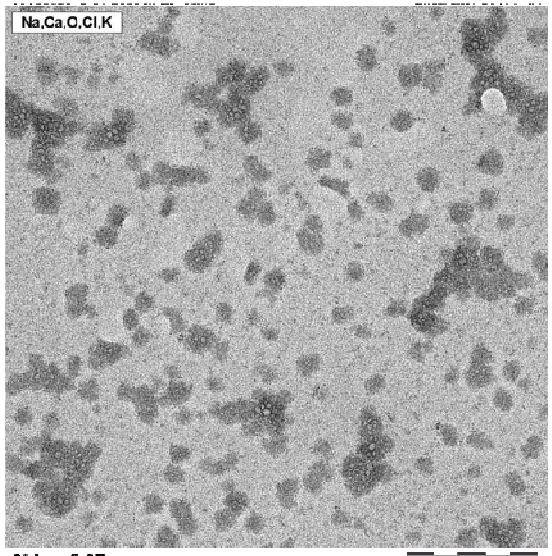
TEM: CuPhtalo plate release (Coating-A)

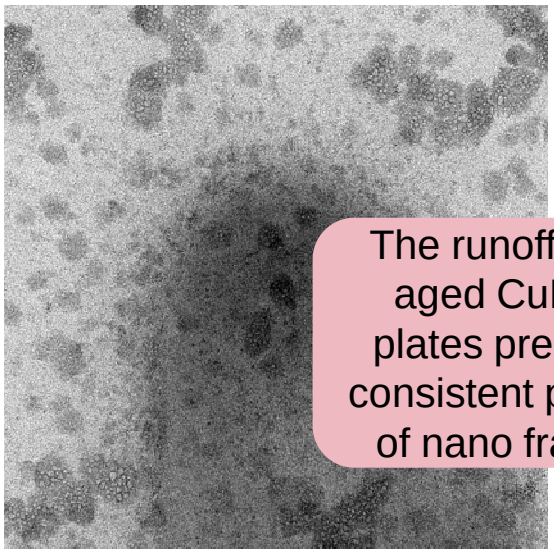
0 month weathering + 1h sonication





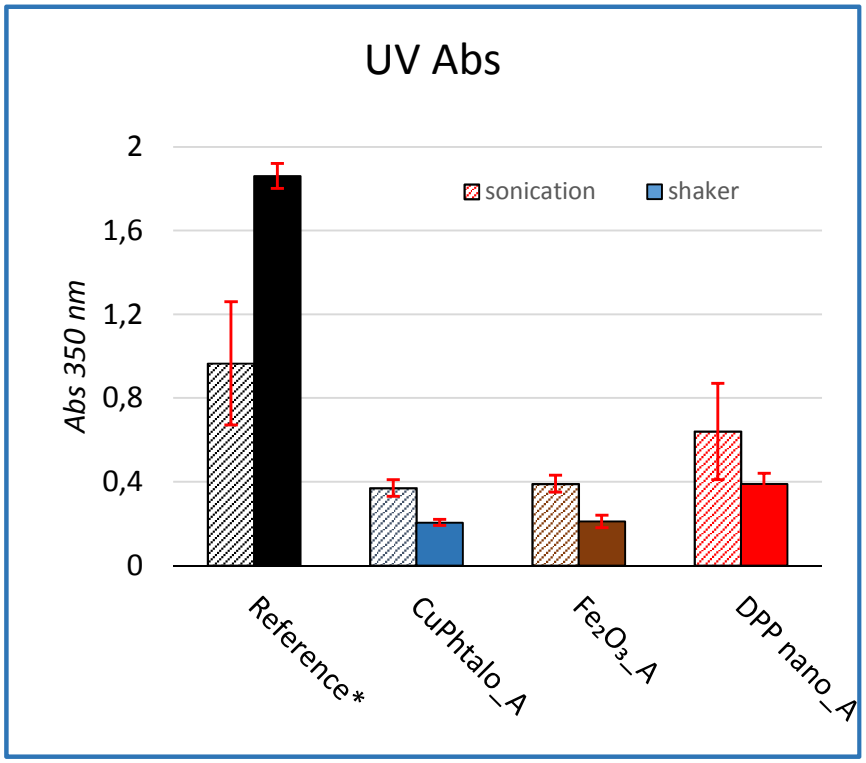
3 months weathering + 1h sonication

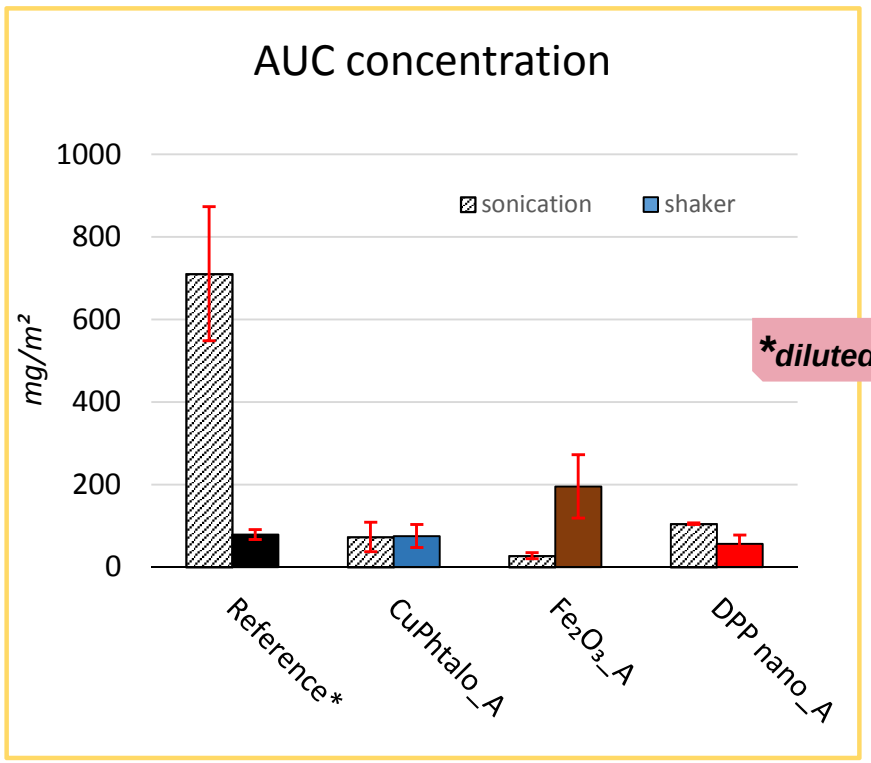




The runoff water of aged CuPhthalo plates presented a consistent population of nano fragments

Nano Pigments release in Coating-A after 2 month aging

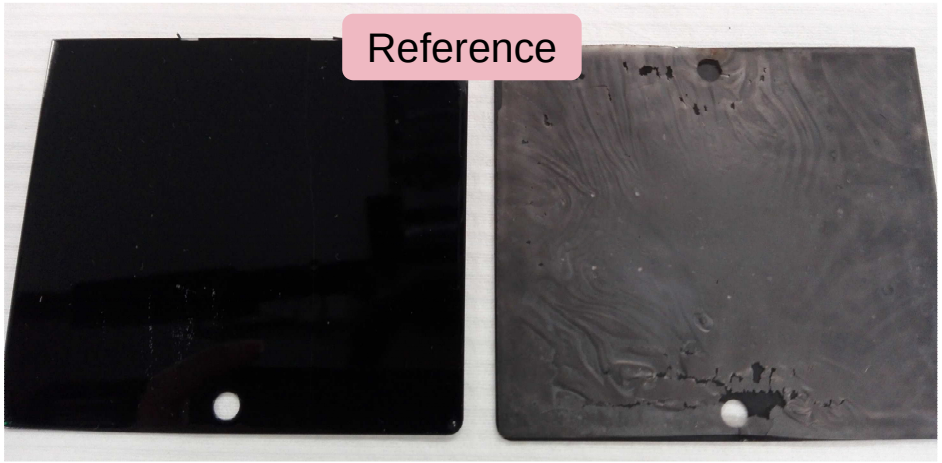


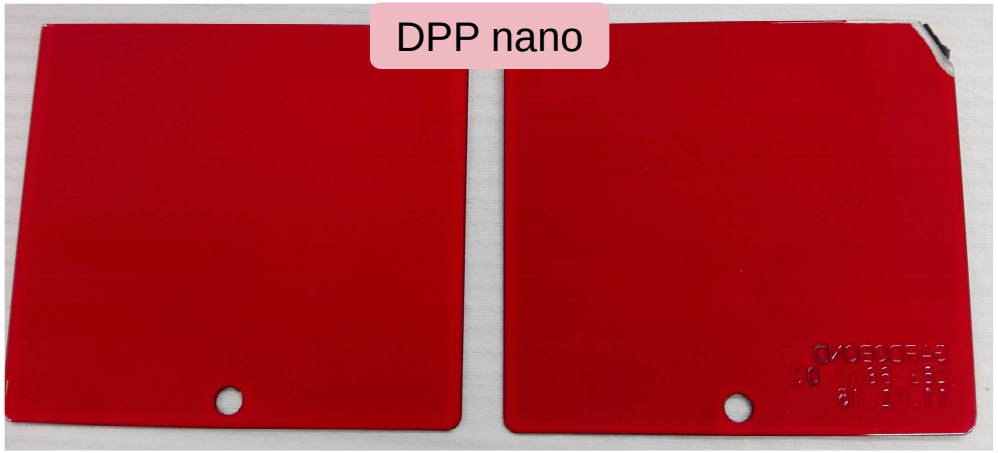


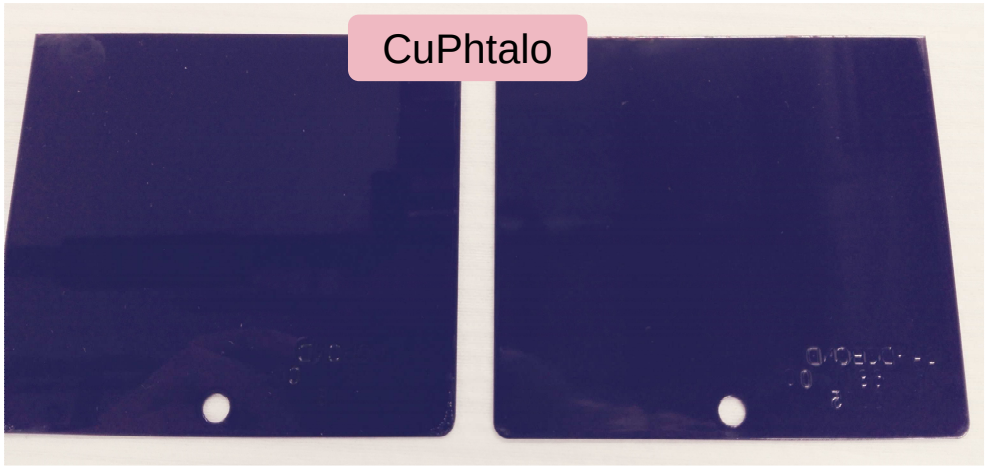
*diluted 1:10

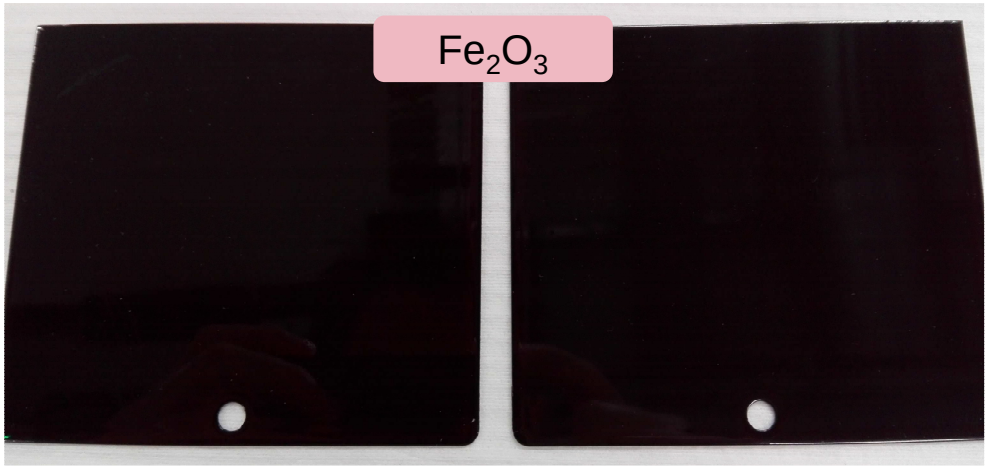
Plate evolution over months

0 month	2 months	0 month	2 months





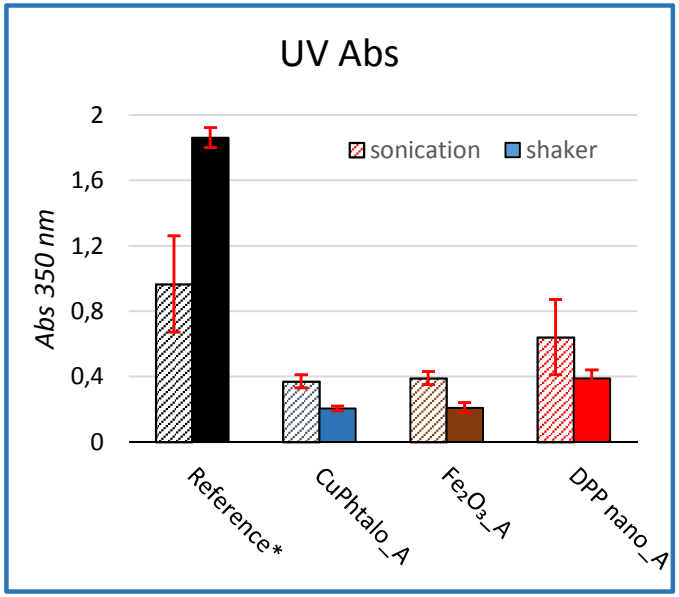


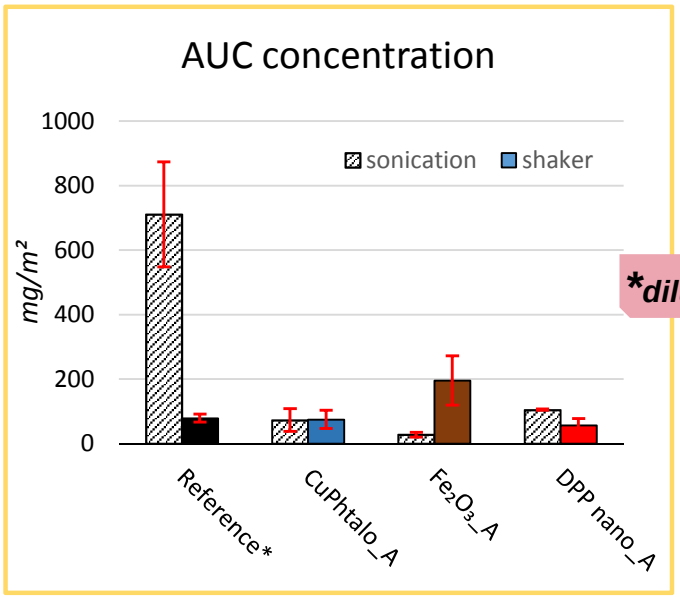


0 month	2 months	0 month	2 months

Nano Pigments release in Coating-A and –B after 2 month aging

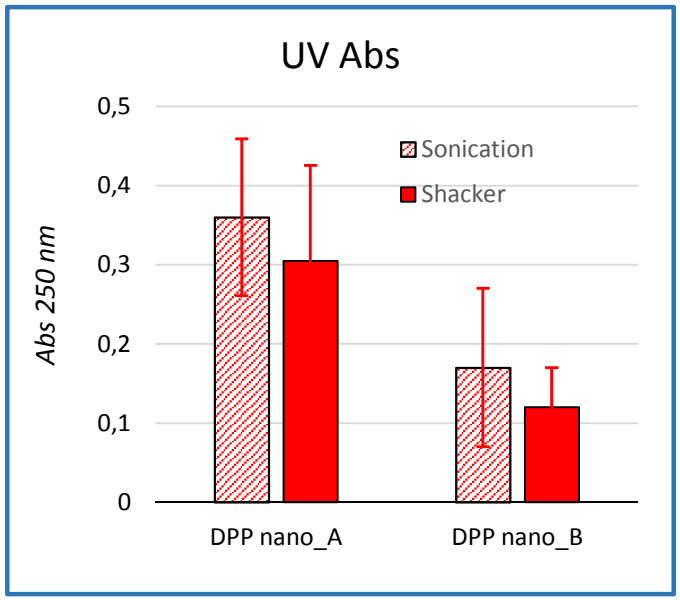
Only in *acrylic-polyester* coating (A)

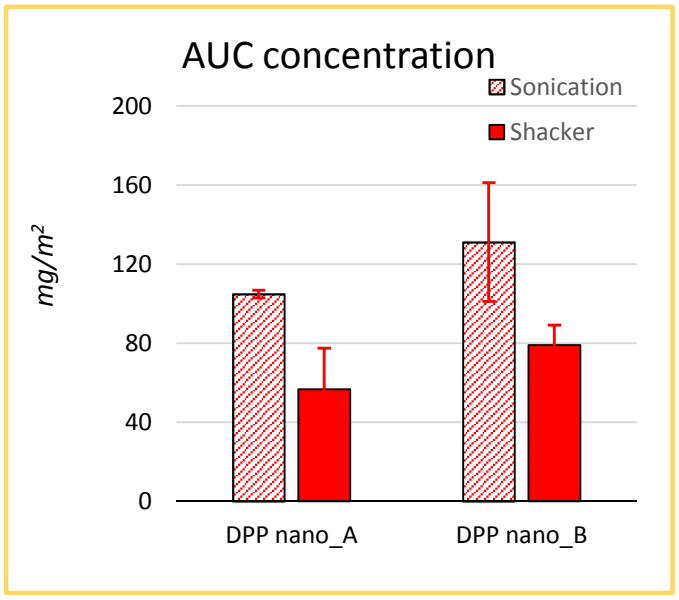




*diluted 1:10

In *acrylic-polyester* coating (A) and *alkyd-melamine* coating (B)

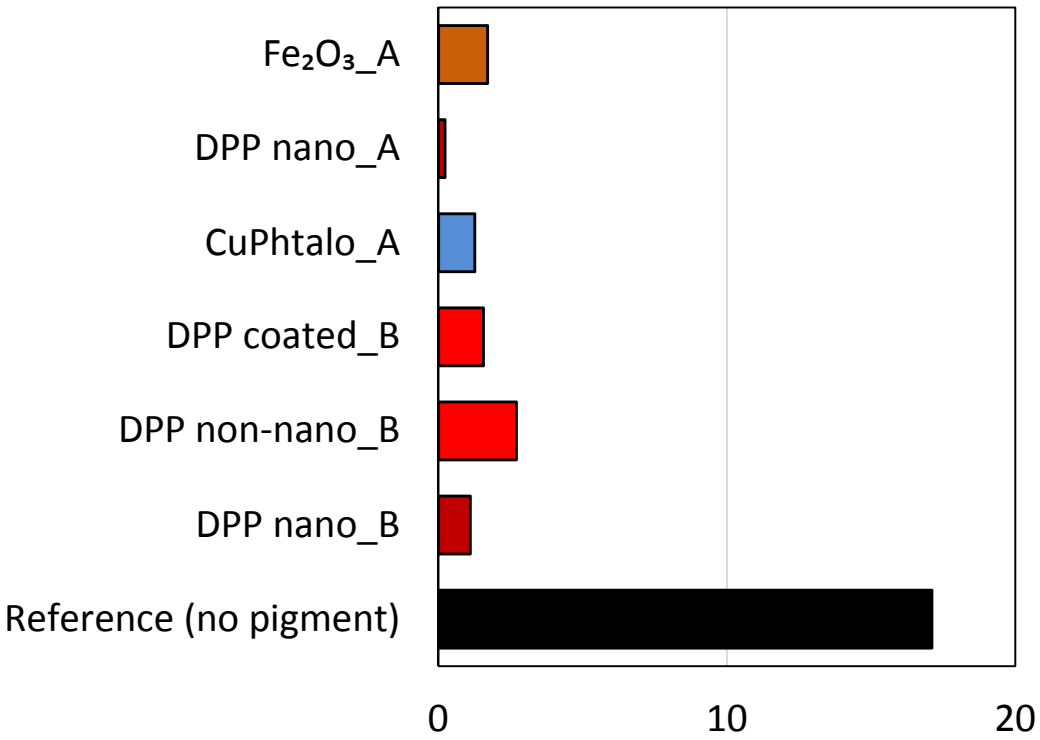




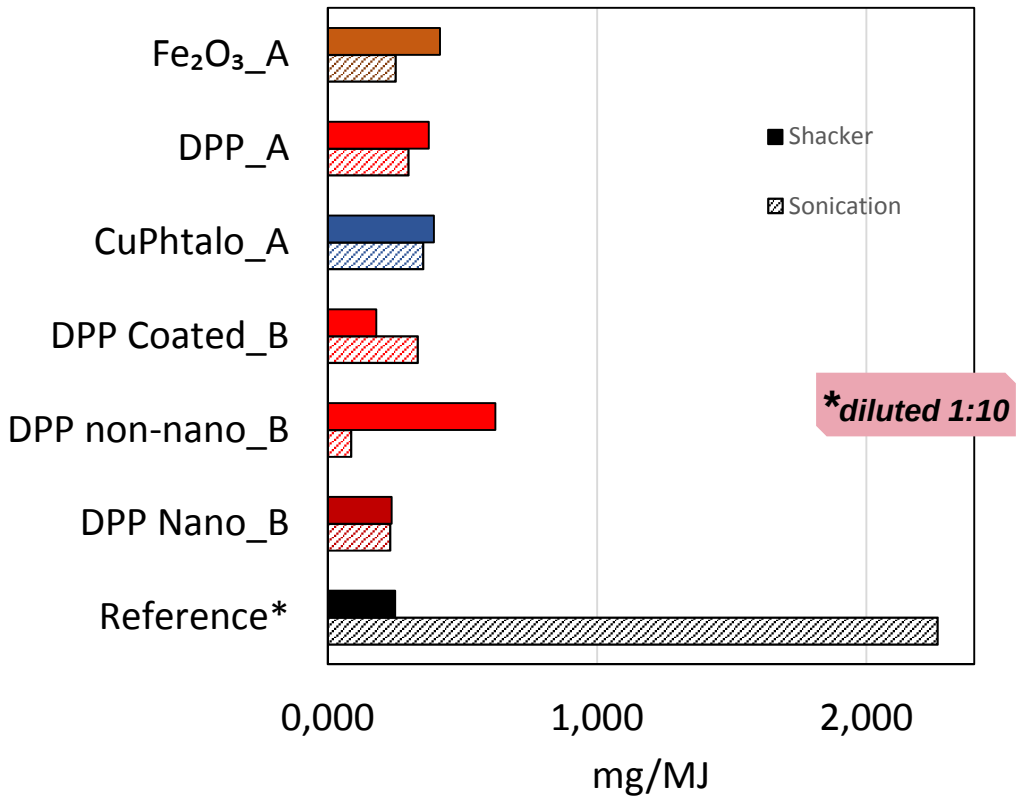
*diluted 1:10

Nano Pigments release in Coating-A and -B

2 Month Change in Lightness (dL*)



Release rates of the 2 months aged plates

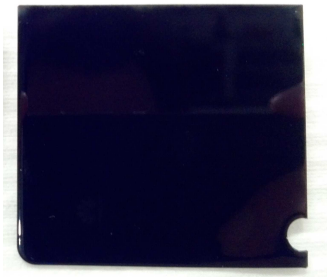


Combination of different fillers and matrixes show the same release profile

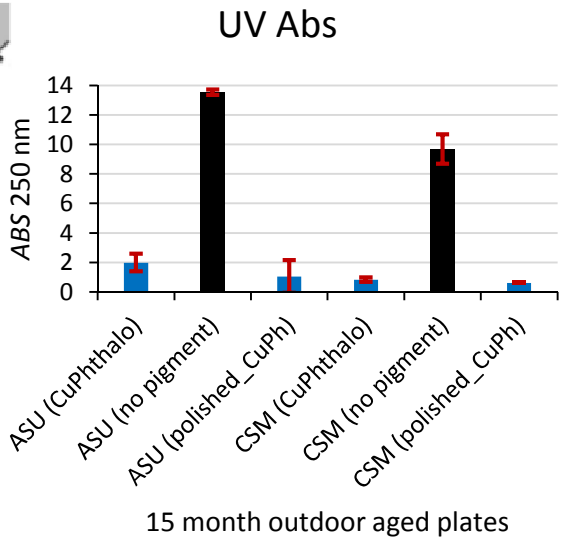
*diluted 1:10

Collaboration with US universities: Natural aging

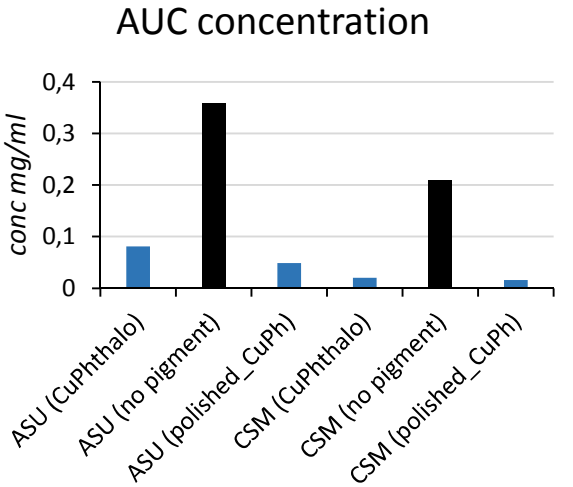
Reference
15 months



CuPhtalo
15 months



15 month outdoor aged plates



15 month outdoor aged plates

Short summary and Conclusion

- NanoRelease protocol is a successful method to quantify particle emission (10 nm - 20 µm). The results were in agreement with the colorimetric analysis (L*a*b* color space) and with visual degradation of the plate.

- All the nano fillers displays a photoprotection effect, increasing the aging resistance of the coatings and improving their performance.

- For grouping prospective, the three different nanoforms (organic, inorganic, metallo-organic) can be grouped together. The different NM characteristics only slightly influence the fragment release. The release is mostly modulate by the nature of the matrix.

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Thank you for your attention!

LC nano

nanoGRAVUR

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NIST National Institute of Standards and Technology U.S. Department of Commerce

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Releases from transparent blue automobile coatings containing nanoscale copper phthalocyanine and their effects on J774 A1 macrophages

NanoImpact 7 (2017) 75–83

Chengfang Pang[a], Nicole Neubauer[b], Matthew Boyles[c], David Brown[c], Nilesh Kanase[c], Danail Hristozov[a], Teresa Fernandes[c], Vicki Stone[c], Wendel Wohlleben[b], Antonio Marcomini[a]

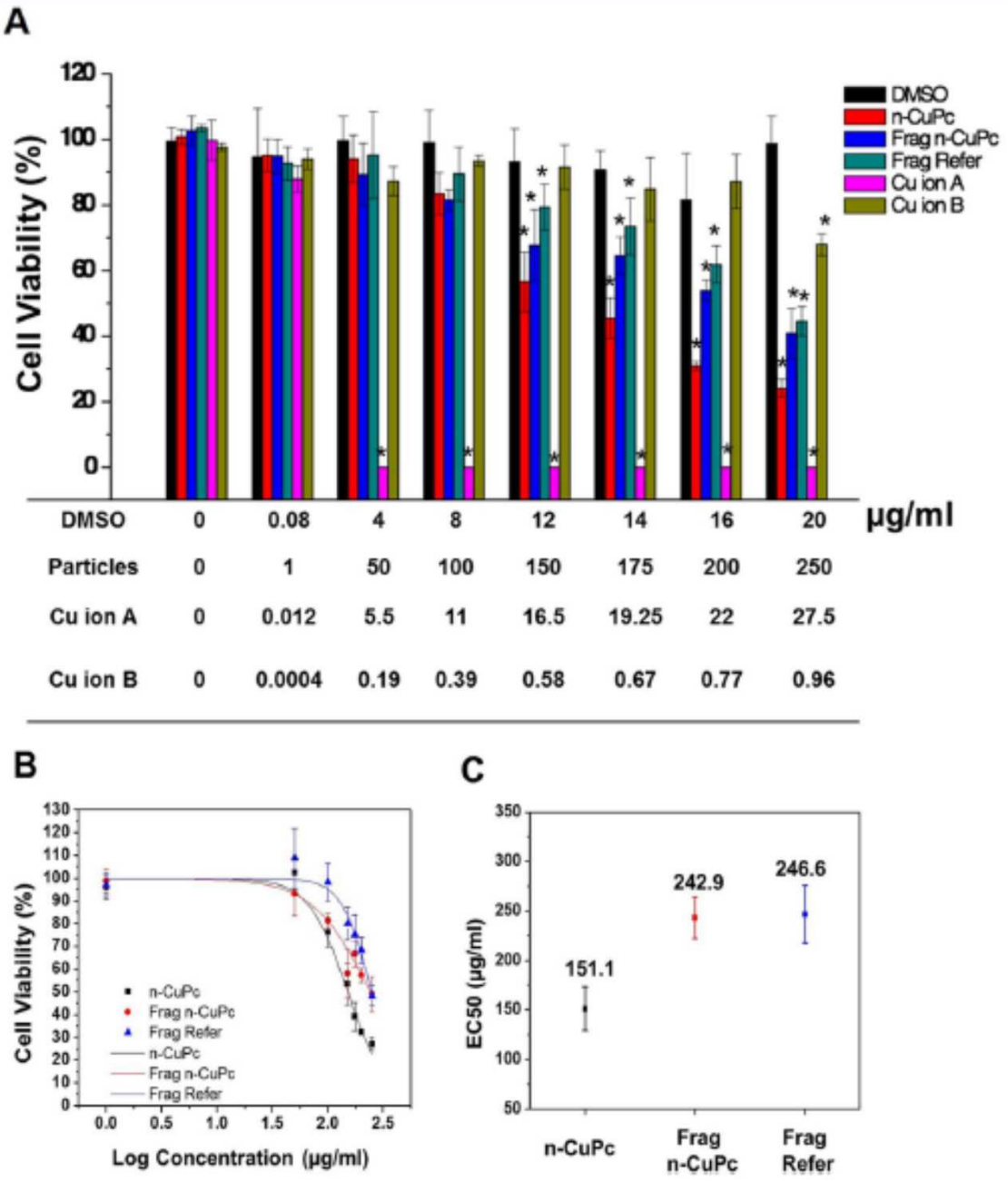

Fig. 4. (A) WST-1 assay of cell viability of n-CuPc, Frag n-CuPc, and Frag Refer to J774 A1 after 24 h exposure. The y axis represents the percent of cell viability compared to control. The x axis represents the concentrations of particles or copper ion or DMSO. The value represents the mean ± standard deviation of three replicates. (B) Cell viability of J774 A1 cells treated with n-CuPc, Frag n-CuPc, and Frag Refer for 24 h. (C) The EC50 values were determined using the software Origin 8. Data are shown as plots of the EC50 of n-CuPc, Frag n-CuPc, and Frag Refer to J774 A1 for 24 h. The value represents the mean ± standard deviation of three replicates.