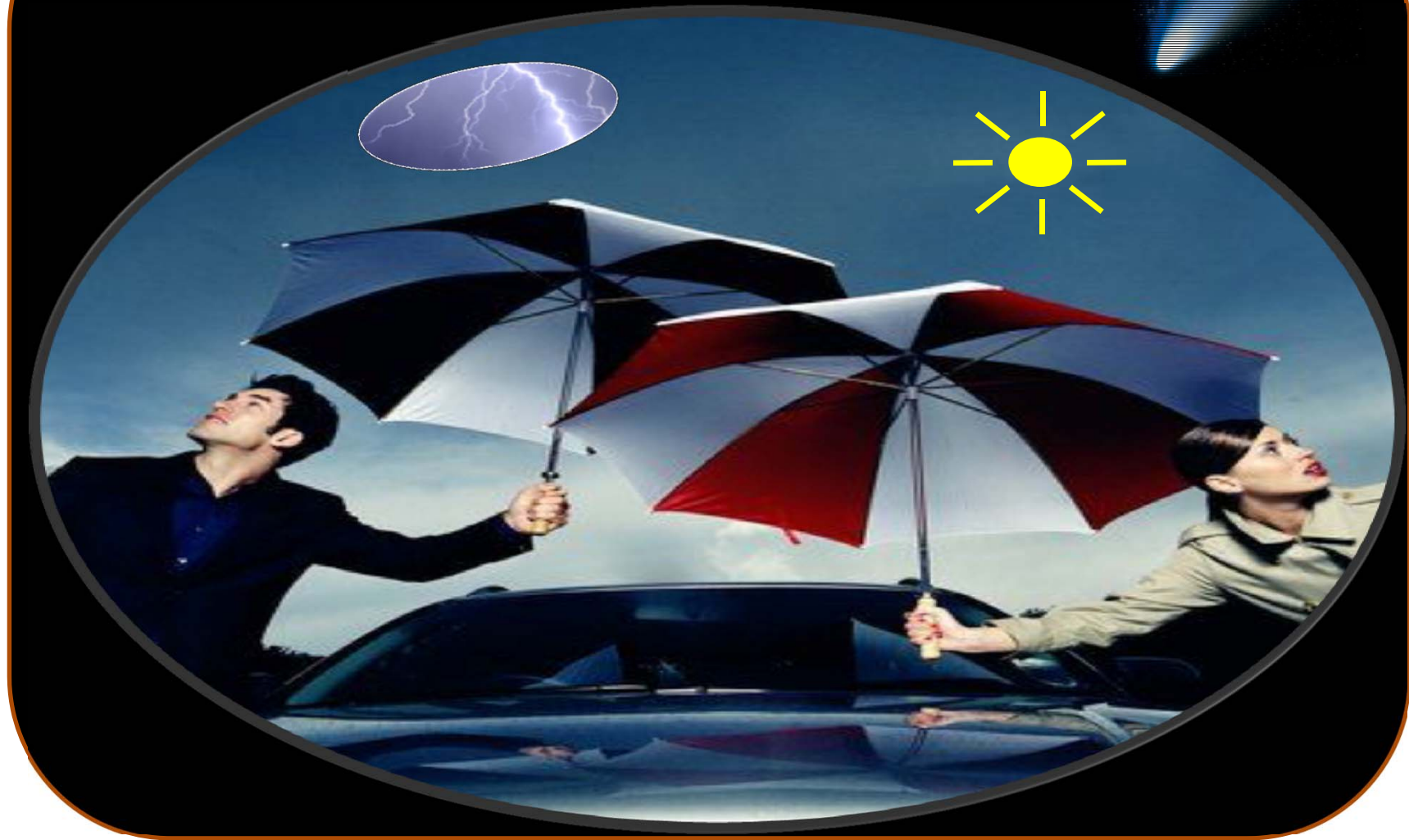

Sustainable UV-protection of coating layers using nanoscale organic and inorganic components

Heinz Greisiger, Dennis Koch, Marc Entenmann

Fraunhofer IPA, Stuttgart, Germany

Sometimes it's impossible to protect your car against environmental aspects



General aspects to be considered regarding the sustainability of multilayer protective coatings

- It is generally accepted, that photochemical degradation processes in coating layers are initiated by the absorption of UV light.
- In multilayer protective coatings, for automotive and general protective coatings on metal, it is mostly the primer or the e-coat layer, directly applied on the metallic substrate, which shows the most serious photochemical degradation effects, when the multilayer coating system is exposed to atmospheric weathering.
- Therefore, a strong need for UV-protective coatings with a high sustainability exists.
- In the presented study, a combination of inorganic and organic nanoscale components was used in clear coat formulations in order to enhance the sustainability of the UV-protection in multilayer coating systems.

Experimental aspects

- For the degradation experiments, OEM-formulations of e-coat, basecoat and clear coat starter formulations were applied onto metal substrates. For the clearcoat and basecoat pneumatic application (air-only), was performed.
- 1.0 wt % Tinuvin 292 and 1.5 wt % Tinuvin 384-2 was used as organic UV-protection.
- To evaluate the transmittance and absorbance properties, free coating films were characterized using the UV-VIS-NIR spectrometer Lambda 900 from Perkin Elmer.
- The degradation experiments were performed by artificial weathering of the coated samples using a Weather-O-Meter equipment (Ci 4000, Atlas Material Testing GmbH).
- For the characterization of the obtained degradation effects a confocal Raman microscope and a FT-IR microscope were used.
- The photooxidative degradation of e-coats in different automotive multilayer coating systems was investigated by evaluation of the photooxidation index (POI). For the POI measurements special flat cross sections of coatings were prepared and the IR-measurements were performed on the original and on the corresponding weathered systems.

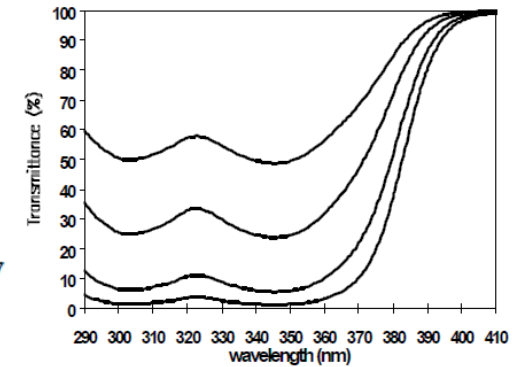
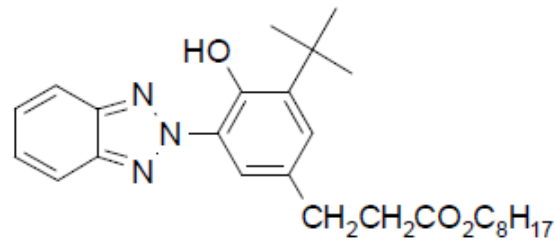
Composition of the clear coat starting formulation

Component	Wt %
Desmophen A665 BA/X (Bayer MS)	50.31
Baysilone OL 17, 10 wt % solution	0.50
Modaflow, 1 wt % solution	0.50
Tinuvin 292, 10 wt % solution	4.97
Tinuvin 384-2, 10 wt % solution	7.46
Methoxypropyl acetate (MPA) / solvent naphtha (1:1)	17.38
Desmodur N 3390 BA (Bayer MS)	18.89
	100.00

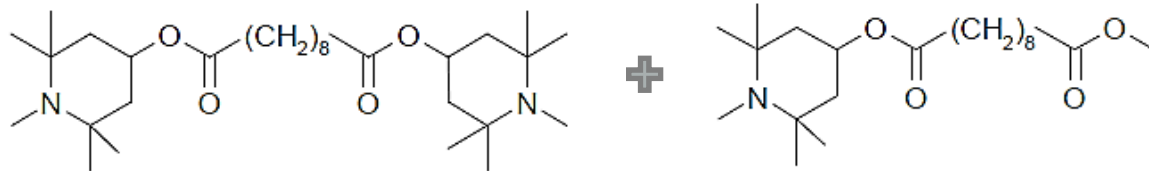
After spray application, the formulation was evaporated for 10 min at room temperature, followed by 25 min. heating at 140°C.

Selected organic UV-protection components

- **Tinuvin 384-2 (UV-absorber)**
(Hydroxyphenyl-benzotriazole)

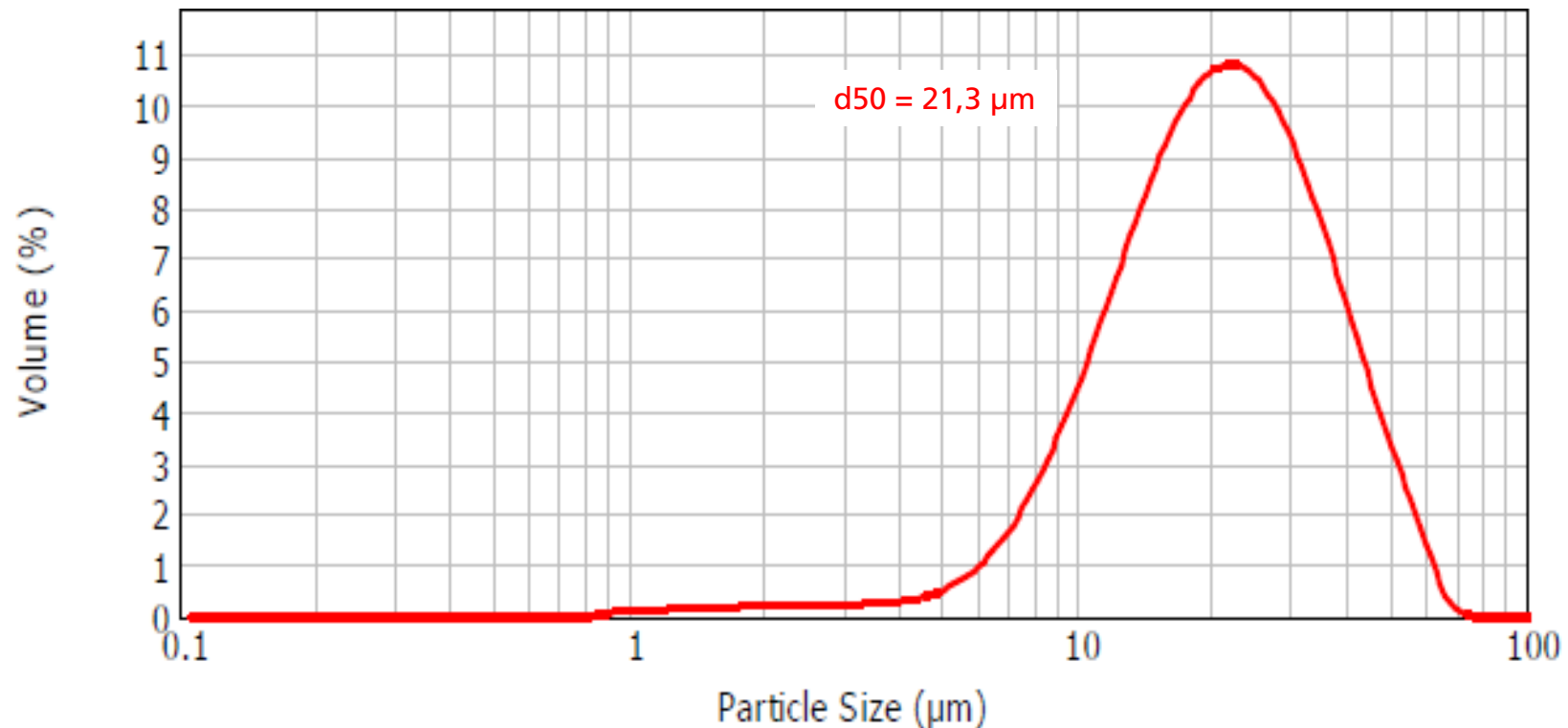


- **Tinuvin 292 (HALS)**
**(Pentamethyl-4-piperidinyln-
sebacate)**



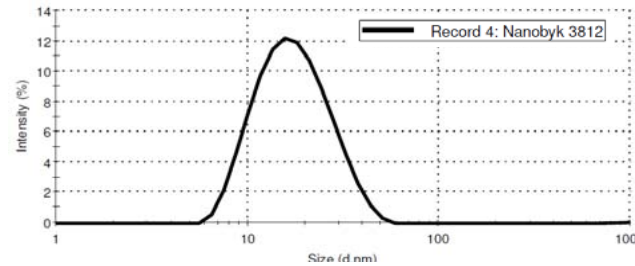
Selected mica as example for a flake-shaped barrier-pigment

- **Iriotech 8800, Merck (Muskovite)**



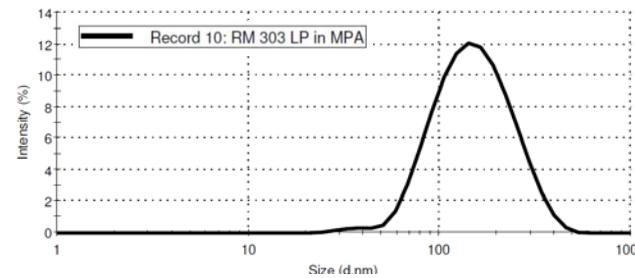
Examples for inorganic (nanoscale) UV-absorber: CeO₂, TiO₂, ZnO, CNT

■ **Nanobyk 3812, Byk Chemie (CeO₂)**



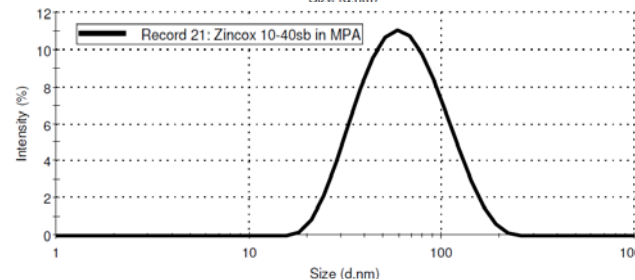
d50 = 18 nm

■ **RM 303 LP, Sachtleben (TiO₂)**



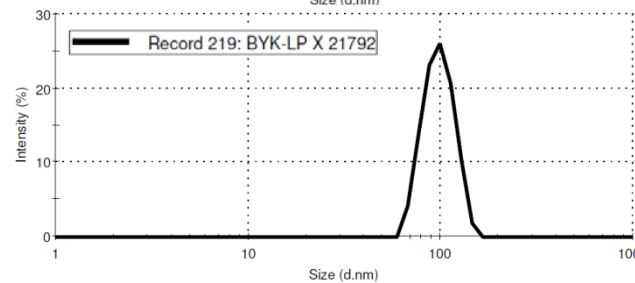
d50 = 162 nm

■ **Zincox 10-40 SB, IBU-tec (ZnO)**



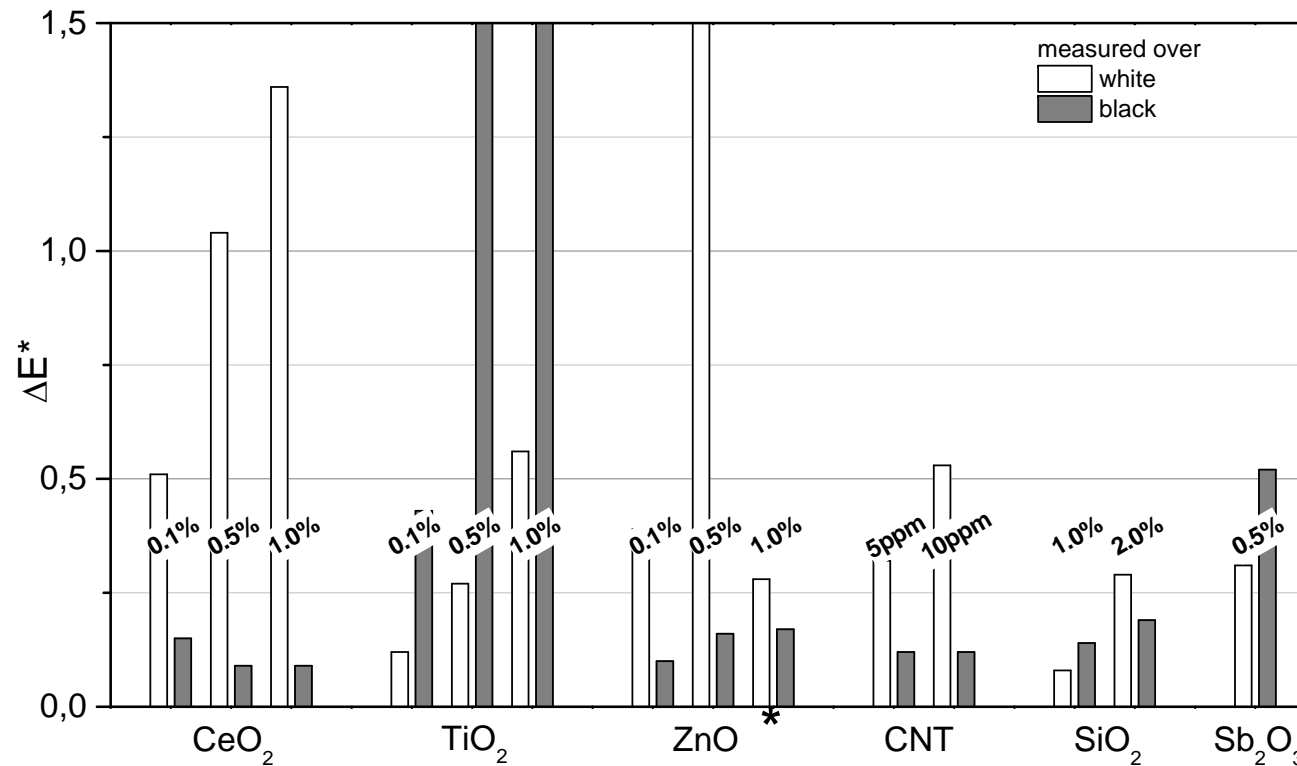
d50 = 68 nm

■ **LP X 21792, Byk Chemie (MWCNT)**



d50 = 89 nm

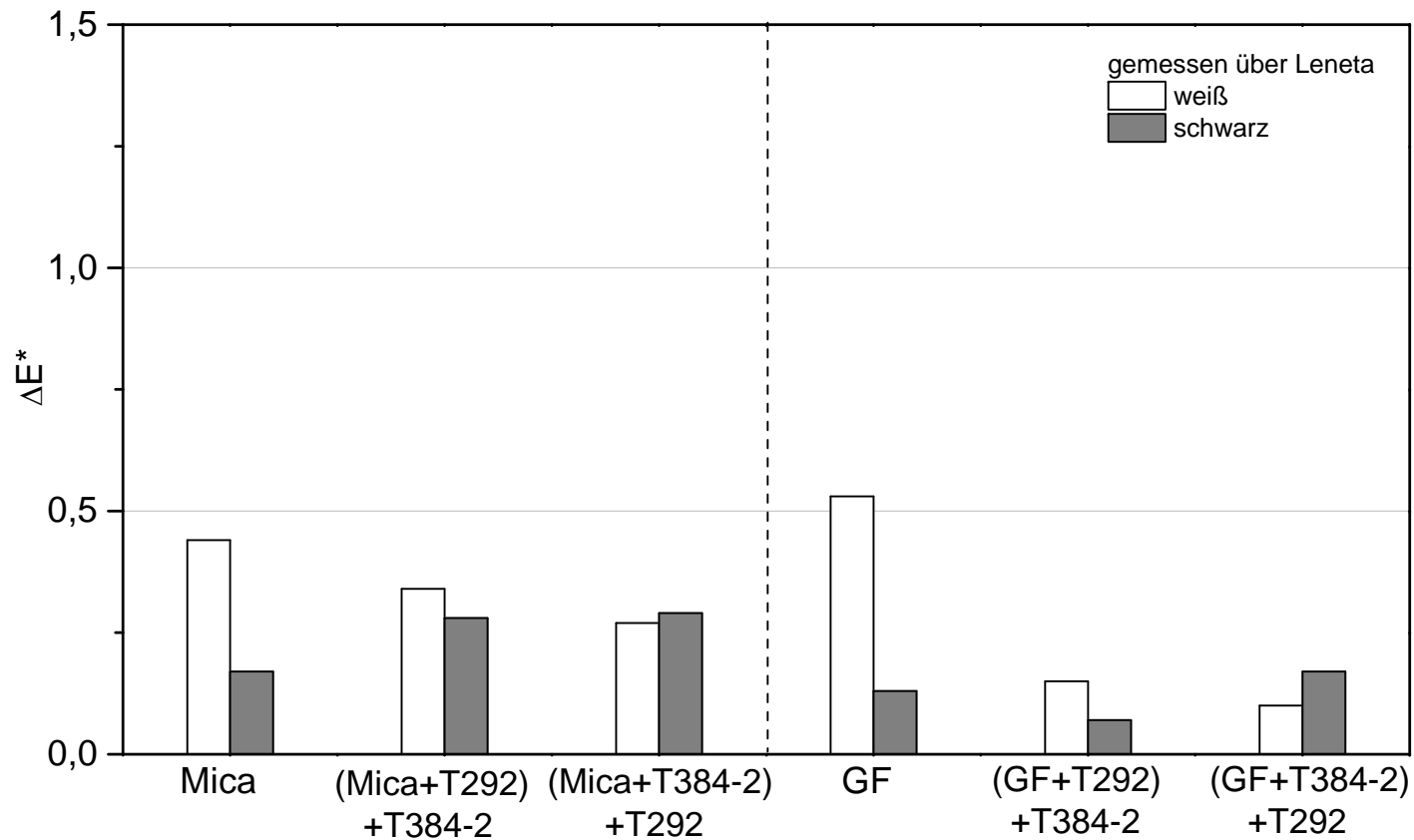
Coloristic influence of nanoscale inorganic UV-protection components in clear coats



*without org. UV-Absorber

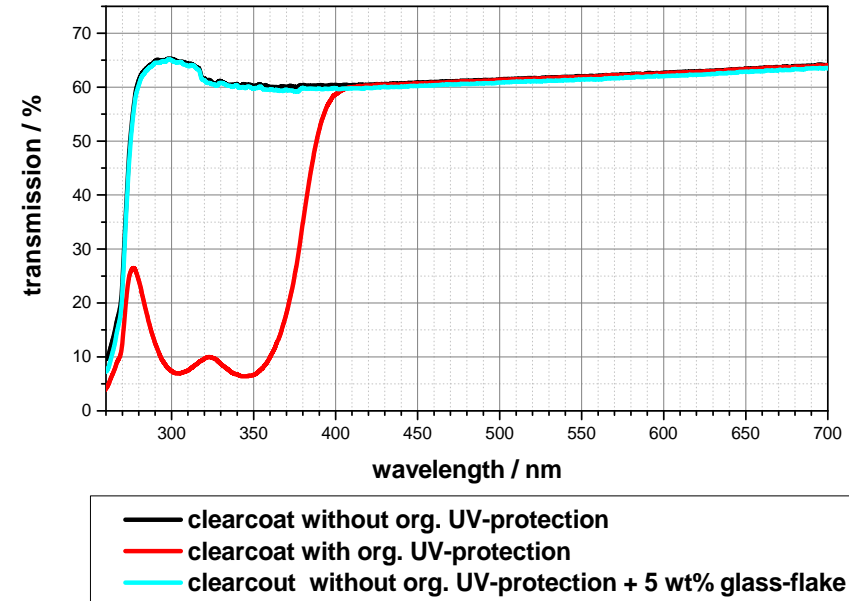
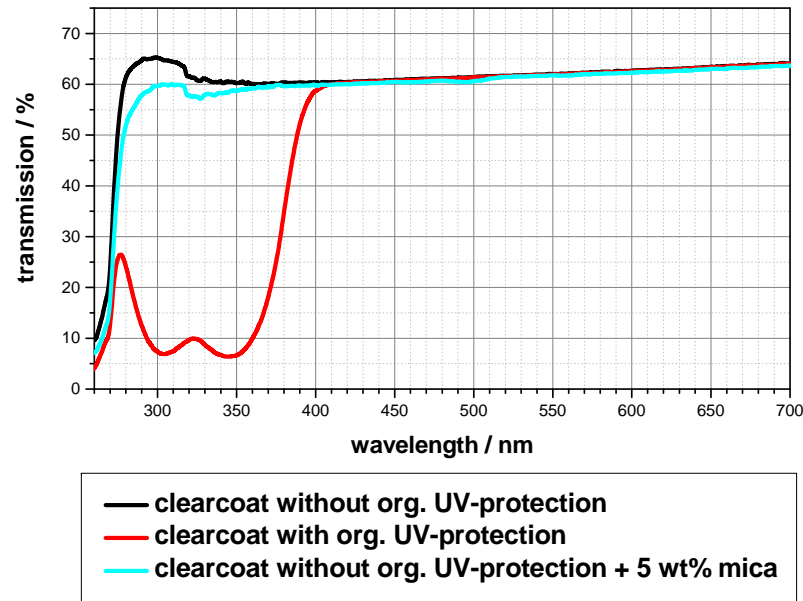
- The used nano-ZnO was not compatible with the organic UV-absorber Tinuvin 384-2
- The influence on transparency and colour mainly determines the maximum concentration of the different nanoscale components in the clear coat

Influence of platelet components to the appearance of the clear coat



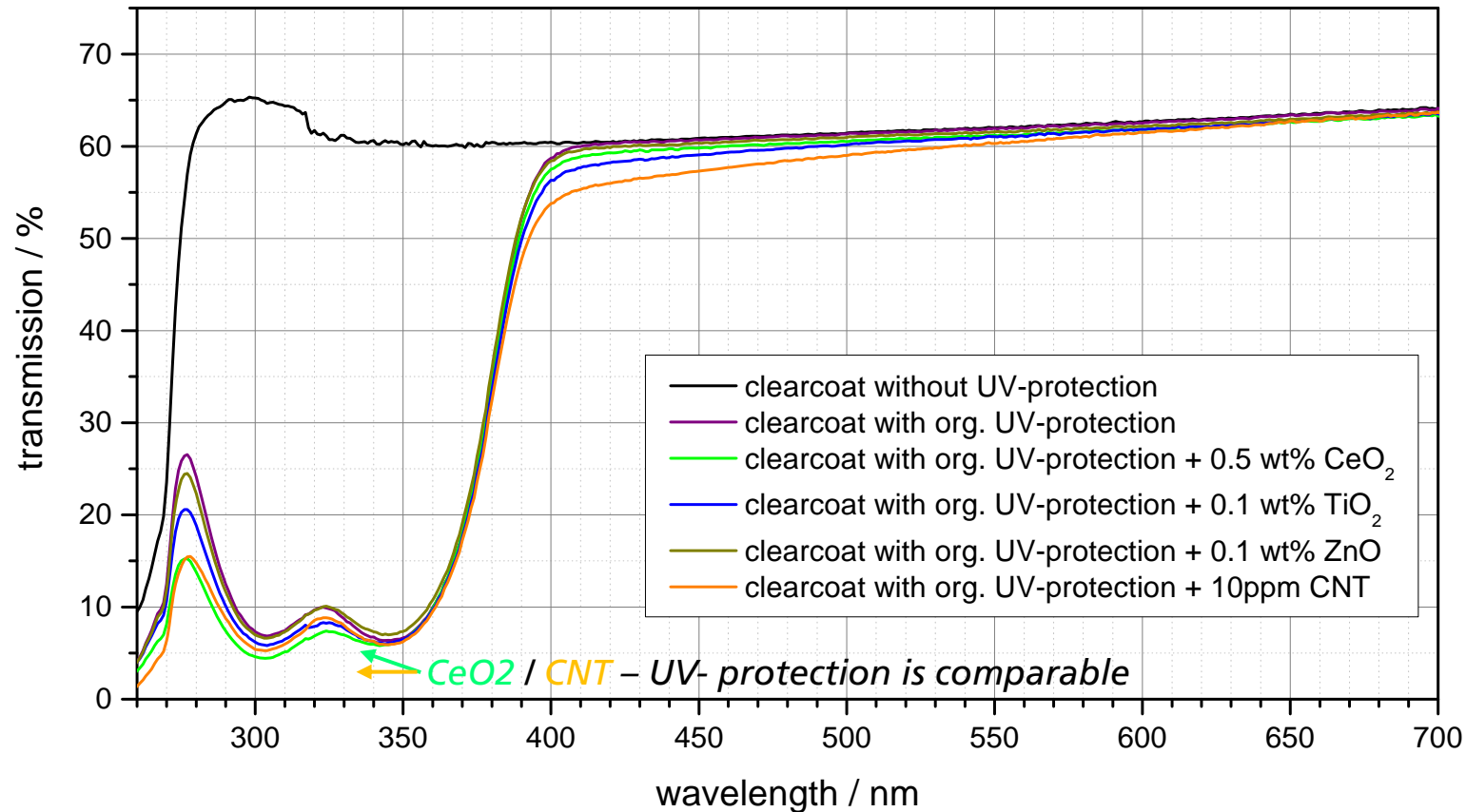
- Mica or glass-flakes (GF), do not influence the colour to a great extent.
- For thin platelet components, mainly the increasing surface roughness, causing scattering effects, limits the maximum concentration in the clear coat.

Transmission spectra of clearcoats with mica- and glass-flakes



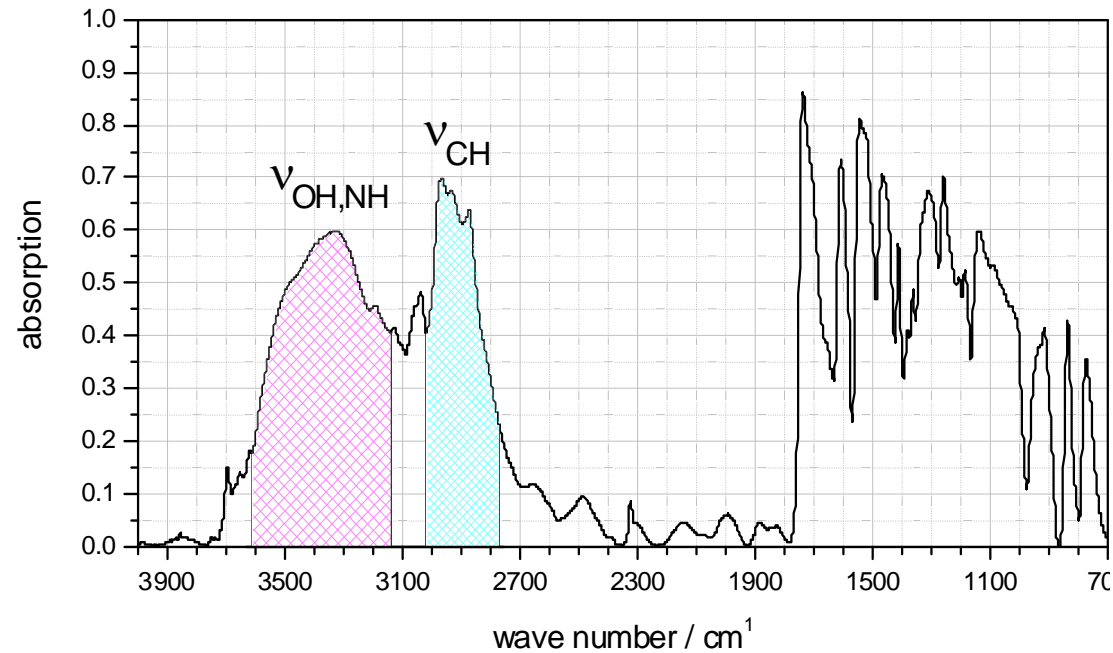
- Mica-flakes influence only slightly the transparency of the clearcoat in the UV- / Vis
- Glass-flakes do not influence the transparency of the clearcoat in the UV- / Vis

Transmission of different UV-protected clearcoats



- Small amounts of carbon derivate like CNT have a great influence on the transparency of clearcoat in the UV- / Vis-region
- CeO₂ combines excellent transparency in the Vis-, with good absorption properties in the UV-region of light.

Evaluation of the photooxidation index (POI)



$$POI_t^* = \frac{Q_t - Q_0}{Q_0} \cdot 100 \%$$

with

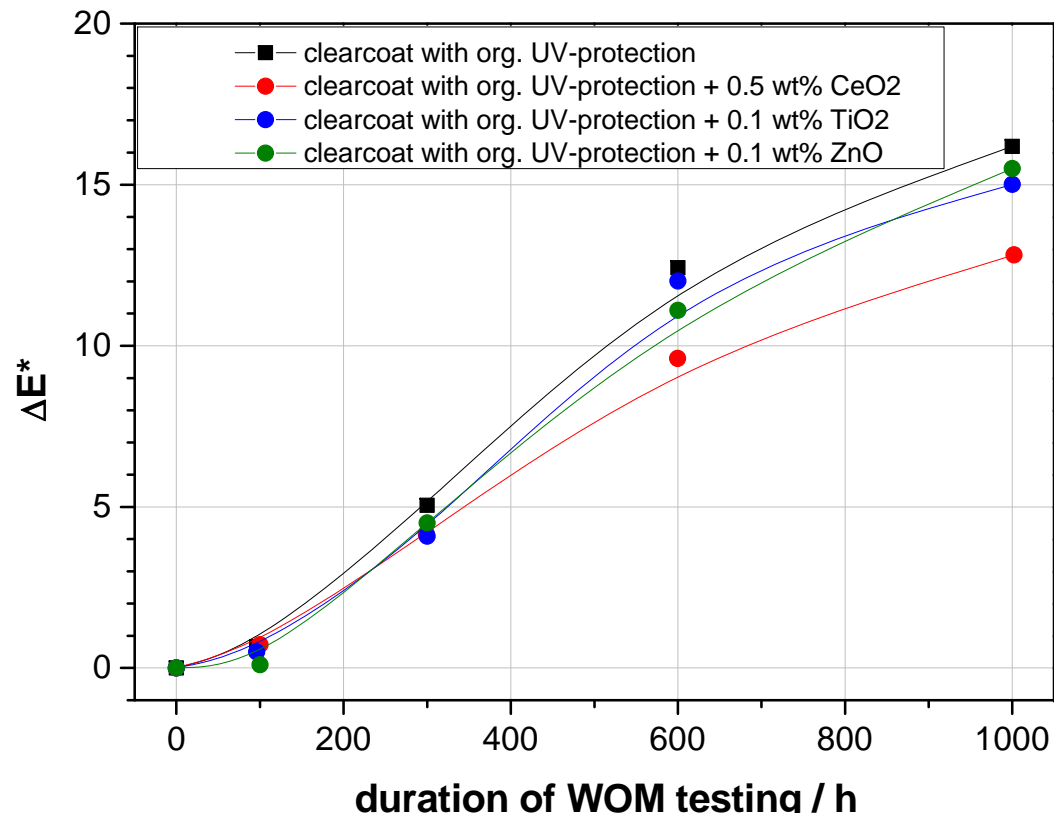
$$Q_t = \frac{A_{\text{variable}}}{A_{\text{internal standard}}}$$

variable = $\nu_{OH,NH}$

internal standard = ν_{CH}

For the evaluation of POI, the integrated valency vibration regions of hydroxy and amino groups are related to the valency vibrations of alkyl groups, which are taken as an internal reference.

Colouristic aspects of clear coats after Weather-Ometer (WOM) testing

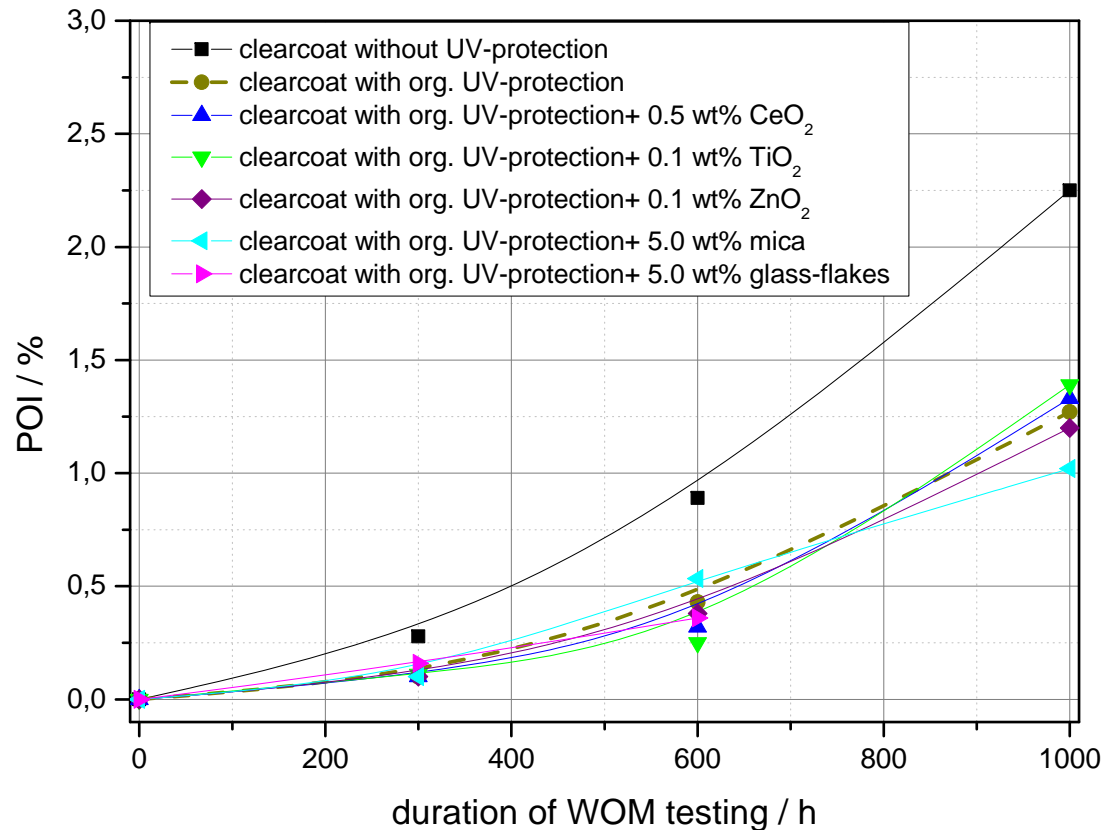


- A combination of both, inorganic and organic UV-protection provides enhanced weathering stability.

- The following ranking for the protection properties was found:

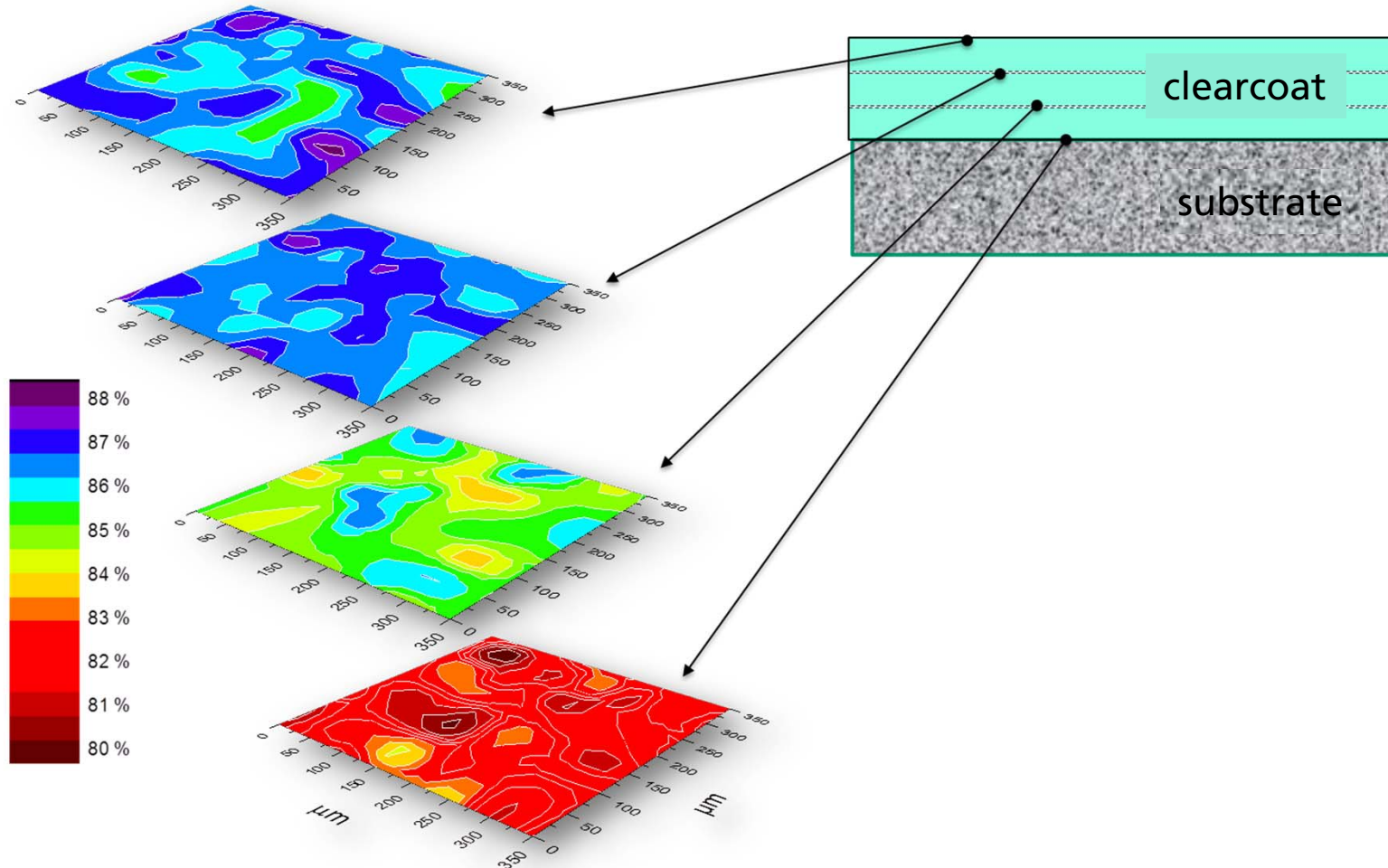
$CeO_2 + org. UV-protection > TiO_2 + org. UV-protection \approx ZnO + org. UV-protection > org. UV-protection$

POI of clear coats after Weather-Ometer (WOM) testing

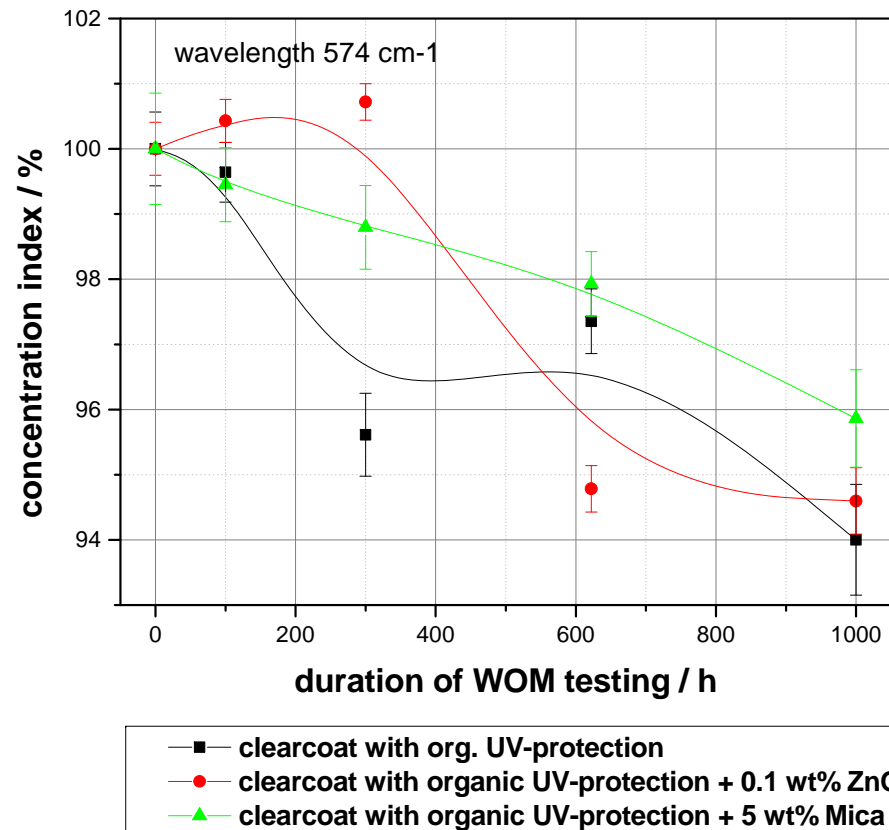


- Surprisingly, mica as well as glass-flake pigmented clear coats, show a relatively slow development of POI, although their UV-absorption properties are low.
- Therefore, the influence of barrier effects on the durability of clear coats have to be studied in detail.

The use of confocal Raman-spectroscopy for the evaluation of barrier properties in respect to organic UV-protection components



Evaluation of barrier effects in respect to organic UV-protection components through determination of a time dependent local concentration index (I_t)



$$I_t = 100 - \frac{Kk_t - Kk_0}{Kk_0} \cdot 100 \%$$

and

$$Kk_t = \frac{A_{\text{Tinuvin}}}{A_{\text{clearcoat}}}$$

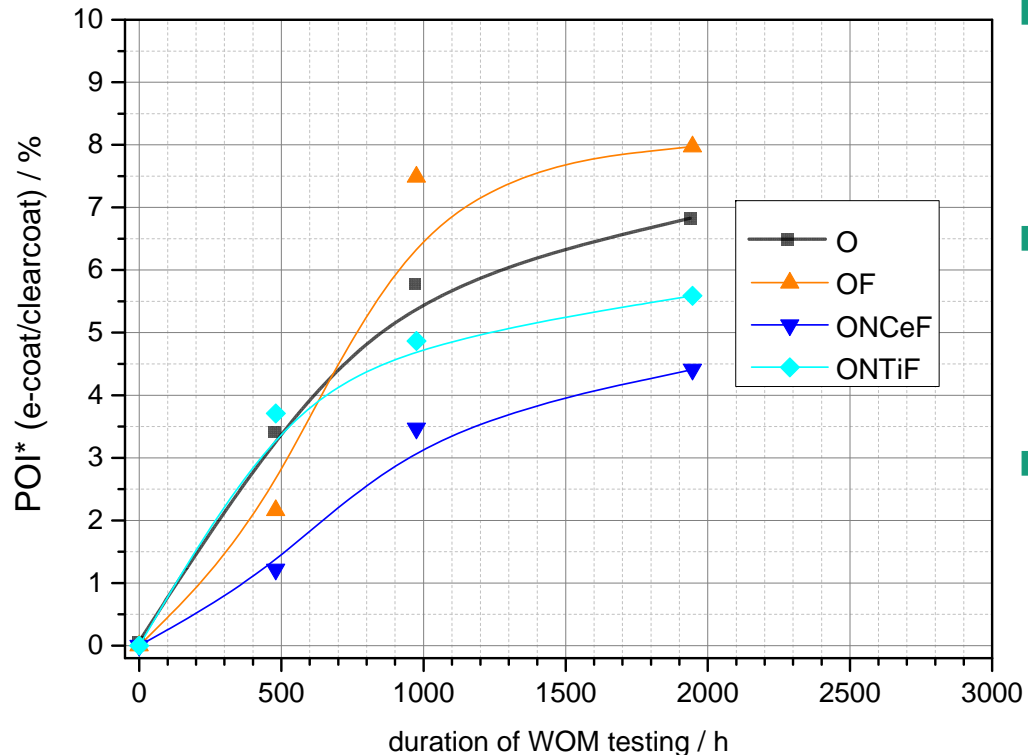
variable = v_{Tinuvin}
internal standard = $v_{\text{clearcoat}}$

- The measurements were performed in defined time intervals at a certain clear coat positions
- For the organic UV-protection components a differentiation between diffusion and decomposition effects was not possible
- Inorganic components, especially higher amounts of barrier flakes reduce the depletion of organic UV-protecting components

Coating formulations for detailed UV-protection studies

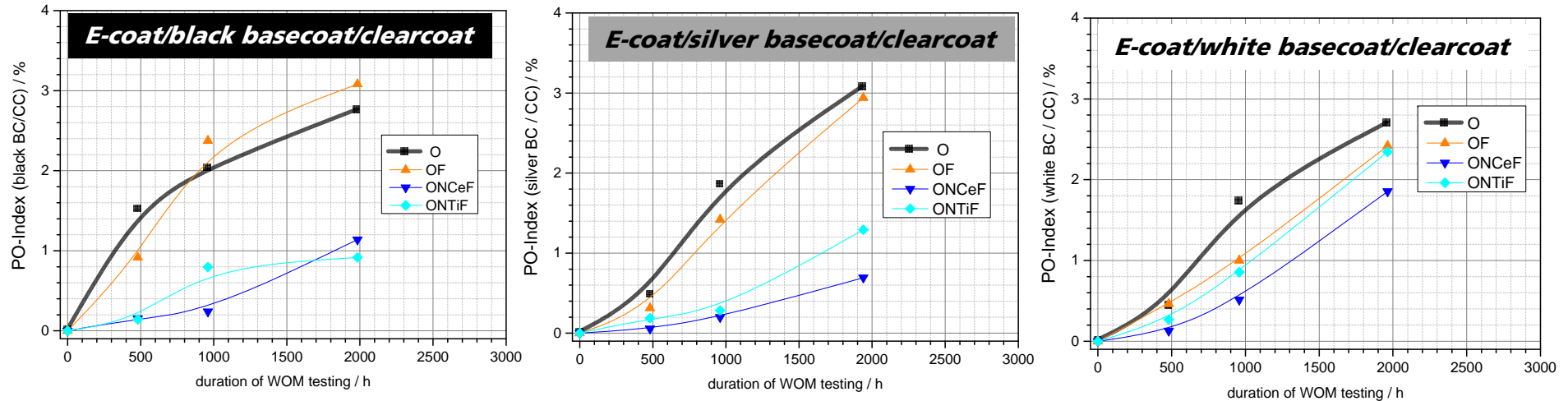
Clear coat	Organic UV-protection O	Inorganic nanoscale UV-protection NCe / NTi	Flake F
O	T292 T384-2	-	-
OF	T292 T384-2	-	Mica
ONCeF	T292 T384-2	CeO₂	Mica
ONTiF	T292 T384-2	TiO₂	Mica

Changes of POI for the e-coat, over-coated with different clear coat systems, with increasing exposure times in WOM testing



- The addition of mica to the clearcoat didn't have the same positive influence on the POI development for the e-coat as for the clearcoat.
- Therefore also the diffusion and influence of water and oxygen on the POI development of the e-coat has to be considered.
- The combination of organic and inorganic UV-protection, especially if CeO_2 was used in addition to barrier flakes, allows the formulation of a highly protective layer which increases the weathering-stability of the e-coat.

Changes of POI for the e-coat, over-coated with a black, silver, white basecoat and different clear coat systems, with increasing exposure times in WOM testing



- The POI development of the e-coat depends on the colour / pigmentation of the over-coated base coat.
- The combination of organic and inorganic UV-protection, especially if CeO₂ was used, with barrier flakes, allow the formulation of highly protective clear coat layers which increases, even if over-coated with a black, silver, or white base coat, the photooxidation stability of the e-coat.

Summary

- With the use of RAMAN- and IR-microscope devices a detailed study of photooxidation- (POI-measurements) and depletion-processes (concentration measurements) in organic coatings is possible.
- Inorganic components, especially higher amounts of barrier flakes, reduce the depletion of organic UV-protecting components.
- A combination of organic and inorganic UV-protection components with barrier flakes can protect the clear coat and the e-coat layer, even if the later one is over-coated with a black, silver, or white basecoat, from photodegradation, so the weathering-stability of the e-coat (or of epoxy-primer) and of the clear coat (or of the topcoat) can be improved.
- The POI development of the e-coat in weatherability testing depends on the colour / pigmentation of the over-coated basecoat.
- The influence on transparency and colour mainly determines the maximum concentration of nanoscale components in clear coats, whereas the maximum concentration of thin barrier-flake components in clear coats is mainly limited due to the increase in surface roughness, causing scattering effects.

The research work at Fraunhofer IPA was performed with the intention to have a better understanding of the degradation processes in protective coatings.

The results presented will be followed up by bilateral industrial co-operations, using the developed methods to study photodegradation effects on established multilayer coating systems.

Acknowledgements

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Thank you for attention -

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