Novel crosslinking additive for chemical resistant UV-curable clearcoats

M. Entenmann [1], H. Greisiger [1], R. Maurer [1], T. Schauer [1],

S. Schauhoff [2], J. Ohlemacher [2]

[1] Fraunhofer Institute for Manufacturing Engineering and Automation; Germany
[2] Evonik Industries AG; Germany

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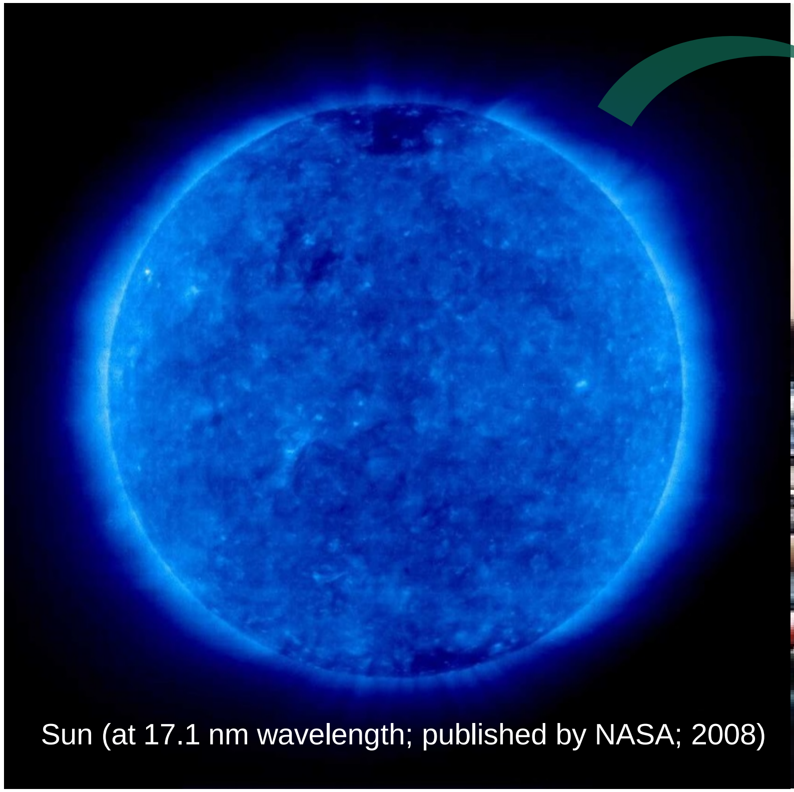
UV- and chemical stability properties are the most important parameters for the weather resistance of UV-cured coatings



Sun (at 17.1 nm wavelength; published by NASA; 2008)

General aspect and considerations about UV-cured coatings

To increase the durability and performance, usually UV-absorbers, as well as hindered amine light stabilizers (HALS) are added, which can additionally influence the crosslinking reactions in the UV-curing coatings.

Unlike solvent or waterborne coatings the options for formulation of solvent free UV-cured coatings are certainly limited, because properties like weathering and chemical stability, hardness, mechanical and adhesion properties, strongly depend on each other.

=> Therefore, components are highly desirable which selectively improve coating properties.

It is already known in the plastics industry, that triallyl isocyanurate can improve the crosslinking density, but so far experimental results for the properties of triallyl isocyanurate in coatings are still missing.

=> In this study the effect of triallyl isocyanurate in UV-cured coatings, which were stabilized with UV-absorbers and HALS, was investigated.

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Experimental aspects - materials and components

- **Trimethylolpropane triacrylate (TMPTA)** in the range of 20 % to 50 % was used in the UV-curing clearcoat formulations as reactive diluent.

- As **triallyl isocyanurate**, **TAICROS®** from Evonik Industries AG in concentrations between 2 % and 15 % and as **aliphatic urethane acrylate binder, Desmolux® XP2738** in the range 40 % to 65 % from Bayer MaterialScience AG was used.

- As **photoinitiator PI** for the trials with different UV-protection systems **Irgacure® 184** was used. For some trials, **Irgacure® 184** was substituted with **Irgacure® 754; Irgacure® 819; Lucirin® TPO-L** from BASF SE and **Genocure® ITX** from Rahn AG to evaluate the effect of the PI on the properties of the UV-cured coatings.

- For **UV-protection** the following **absorber/HALS-combinations** from BASF SE were used: **Tinuvin® 1130/123; Tinuvin® 400/152; Tinuvin® 384-2/292.**

The photoinitiator PI components in detail

- **Irgacure® 184**

  Phenyl**ketone**, alpha-**hydroxy**cyclohexyl

- **Irgacure® 754**

  Oxy-phenyl-acetic acid 2-[2-oxo-2-phenyl-acetoxy-ethoxy]-ethyl ester
  Oxy-phenyl-acetic acid 2-[2-hydroxy-ethoxy]-ethyl ester

- **Genocure® ITX**

  Isopropyl-9H-**thioxanthen**-9-**one**

- **Irgacure® 819**

  Phenyl**phosphineoxide**, bis(2,4,6-trimethylbenzoyl)

- **Lucirin® TPO-L**

  Phenyl**phosphinate**, ethyl (2,4,6-trimethylbenzoyl)

The UV protection components in detail

- **Tinuvin® 1130 / Tinuvin® 123**
  Tinuvin 1130
  (b-[3-(2-H-**Benzotriazole**-2-yl)-4-hydroxy-5-tert.butylphenyl]-propionic acid poly(ethylene glycol)300-ester)
  Tinuvin 123
  (**N-OR HALS**, Bis-(1-octyloxy-2,2,6,6-tetramethyl-4-**piperidinyl**) sebacate)

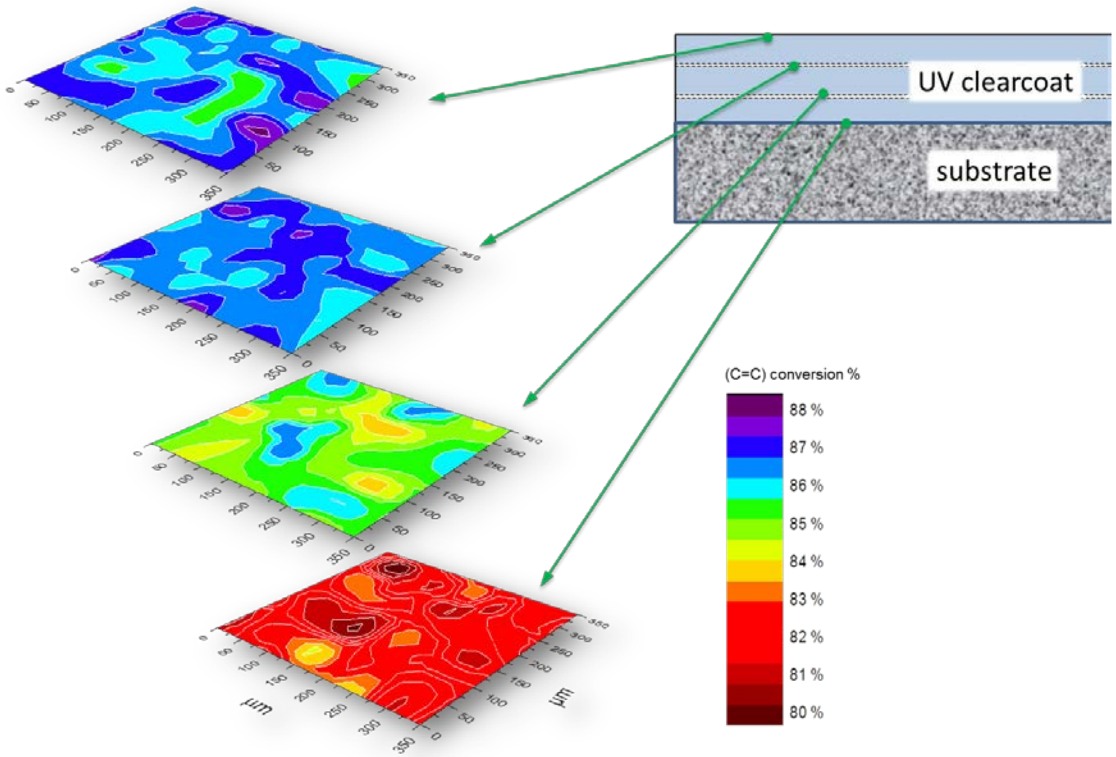
- **Tinuvin® 400 / Tinuvin® 152**
  Tinuvin 400
  (2-[4-[(2-Hydroxy-3-dodecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-**triazine**)
  Tinuvin 152
  (**N-OR HALS**, derivates of N-butyl-2,2,6,6-tetramethyl-4-**piperidinamine**)

- **Tinuvin® 384-2 / Tinuvin® 292**
  Tinuvin 384-2
  (3-(2H-**Benzotriazol**-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid)
  Tinuvin 292
  (**N-alkyl HALS**, mixture of two (1,2,2,6,6-pentamethyl-4-**piperidinyl**)-sebacates)

Experimental aspects - application and analytics

- The coating formulations were applied with a **doctor blade and with pneumatic spray application** on steel panels (layer thickness approx. 40 µm), which were pre-coated with an OEM automotive multilayer system, consisting of e-coat, primer surfacer and basecoat.
- **Crosslinking** was performed under nitrogen inert atmosphere using an IST Metz UV-curing device with a UV-dose of 4520 mJ/cm^2.
- For the **chemical stability testing**, the substances under investigation were contacted with the clearcoat surface at a certain temperature. The maximum temperature, for which no gloss reduction occurred, was taken as a measure for the chemical stability.
- The **Martens hardness measurements** were performed using a Fischerscope HM 2000.
- For the examination of the **double bond conversion**, a confocal Raman Spectrometer Senterra 785 from Bruker Optics was used.
- The **scratch stability testing** was performed with a Nano-Scratch-Tester NST from CSM Instruments.

Double bond conversion in a profile of an UV-curing clearcoat, measured with a confocal Raman microscope device



- The double bond conversion in this UV-curing clearcoat drops within the layer thickness of 40 µm from approximately 87 % near the coating surface to around 82 % conversion at the bottom.
- In each plane the distribution of the double bond conversion is non-homogeneous.

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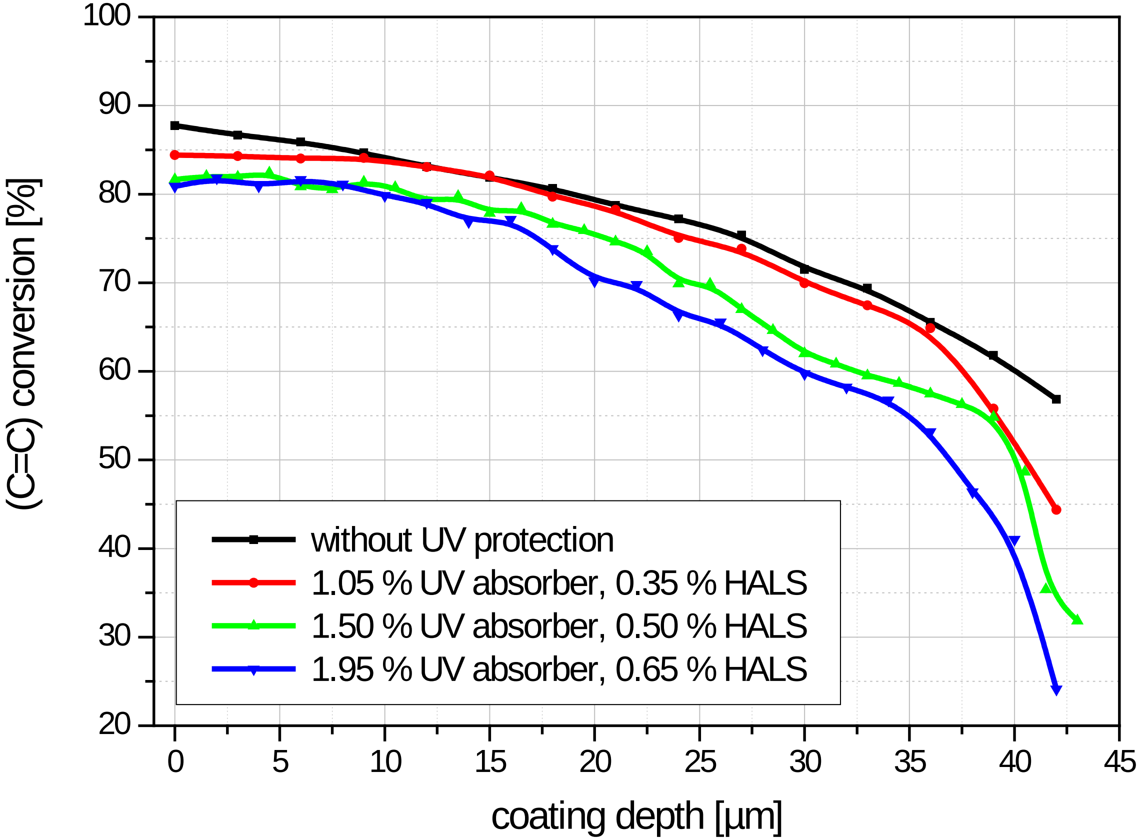
Influence of UV absorber and HALS on the double bond conversion



- With increasing UV-protection, the double bond conversion drops.
- For UV-curing coating with a good weatherability, the UV-absorber has to be selected carefully.
- For durable UV-curing coatings an urgent need for crosslinking improving components like triallyl isocyanurate, which reduce the influence of the UV-absorber exists.

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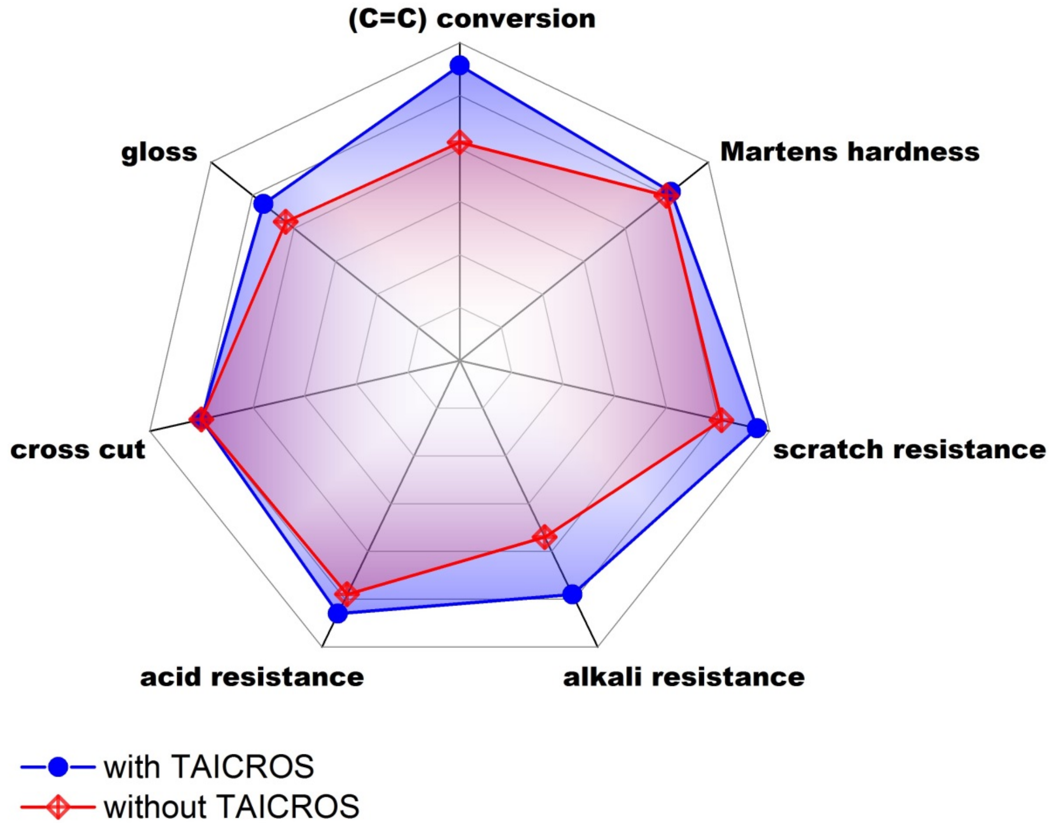
Influence of triallyl isocyanurate on the properties of an UV-cured clearcoat <u>without</u> UV protection



	☐ TAIC	☒ TAIC
(C=C) conversion [%]	72.2	86.8
Martens hardness [N/mm²]	181.9	183.8
Scratch resistance [mN // %]	56.4 // 93.3	70.7 // 93.5
Alkaline resistance [°C]	53	59
Acid resistance [°C]	51	53
Cross cut	GT 1	GT 0
Gloss at 20°	85.2	86.3

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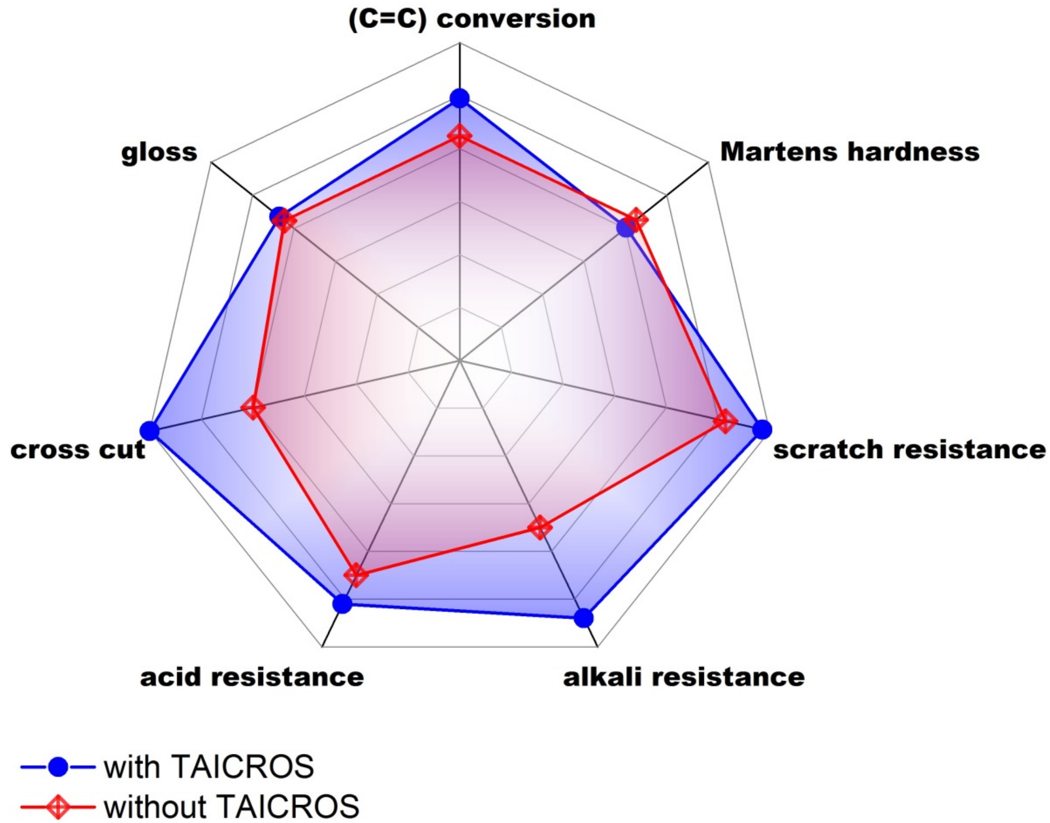
Influence of triallyl isocyanurate on the properties of an UV-cured clearcoat with UV protection (Tinuvin 1130 / Tinuvin 123)



	☐ TAIC	☒ TAIC
(C=C) conversion [%]	73.4	80.5
Martens hardness [N/mm²]	167.6	162.9
Scratch resistance [mN // %]	58.5 // 92.4	73.7 // 93.2
Alkaline resistance [°C]	52	62
Acid resistance [°C]	49	52
Cross cut	GT 2	GT 0
Gloss at 20°	85.3	85.7

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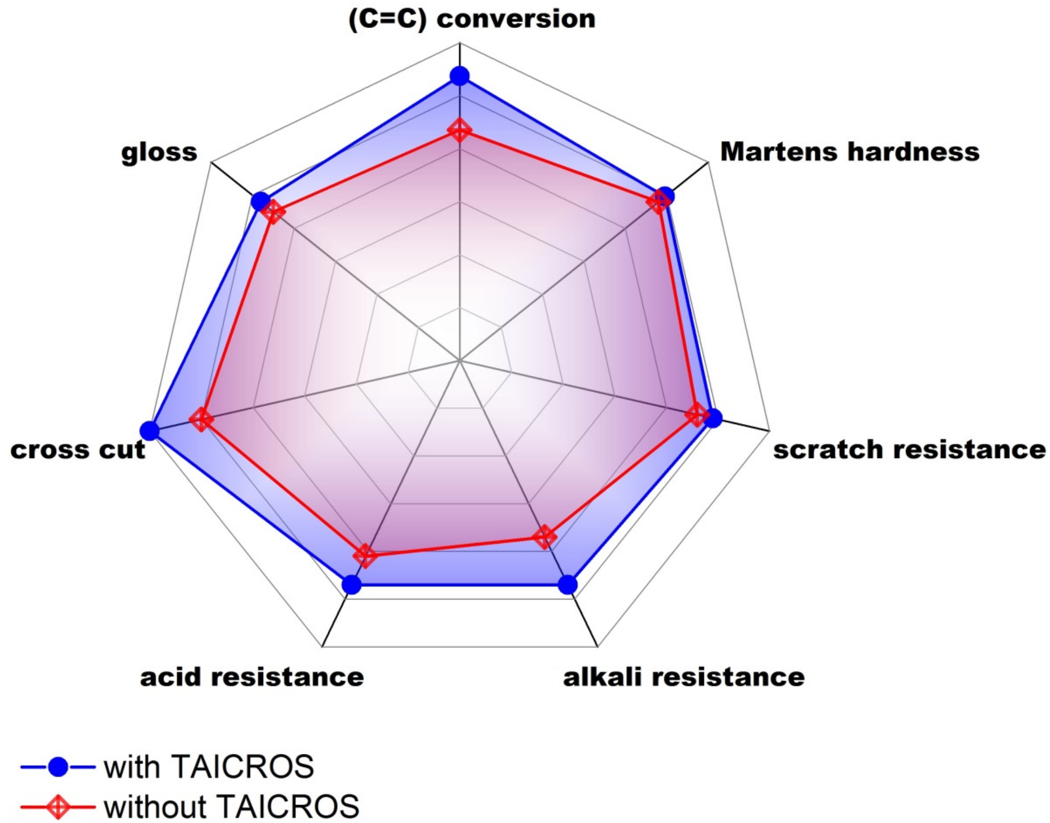
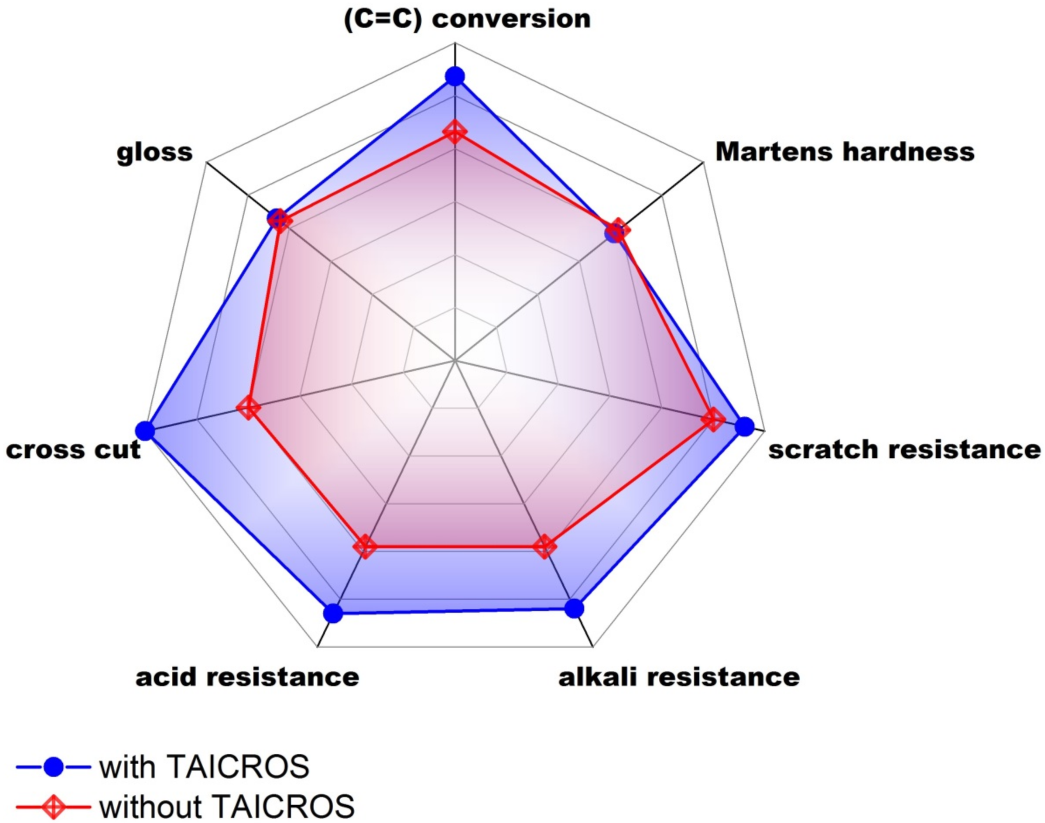
Influence of triallyl isocyanurate on the properties of an UV-cured clearcoat <u>with</u> UV protection (Tinuvin 400 / Tinuvin 152)



	☐ TAIC	☒ TAIC
(C=C) conversion [%]	74.5	84.8
Martens hardness [N/mm²]	178.1	181.1
Scratch resistance [mN // %]	47.7 // 90.2	53.0 // 92.6
Alkaline resistance [°C]	53	58
Acid resistance [°C]	47	50
Cross cut	GT1	GT0
Gloss at 20°	86.0	86.6

Influence of triallyl isocyanurate on the properties of an UV-cured clearcoat with UV protection (Tinuvin 384-2 / Tinuvin 292)



	☐ TAIC	☒ TAIC
(C=C) conversion [%]	74.2	84.6
Martens hardness [N/mm^2]	161.4	158.8
Scratch resistance [mN // %]	54.7 // 93.5	68.2 // 92.9
Alkaline resistance [°C]	54	61
Acid resistance [°C]	46	53
Cross cut	GT2	GT0
Gloss at 20°	85.4	85.8

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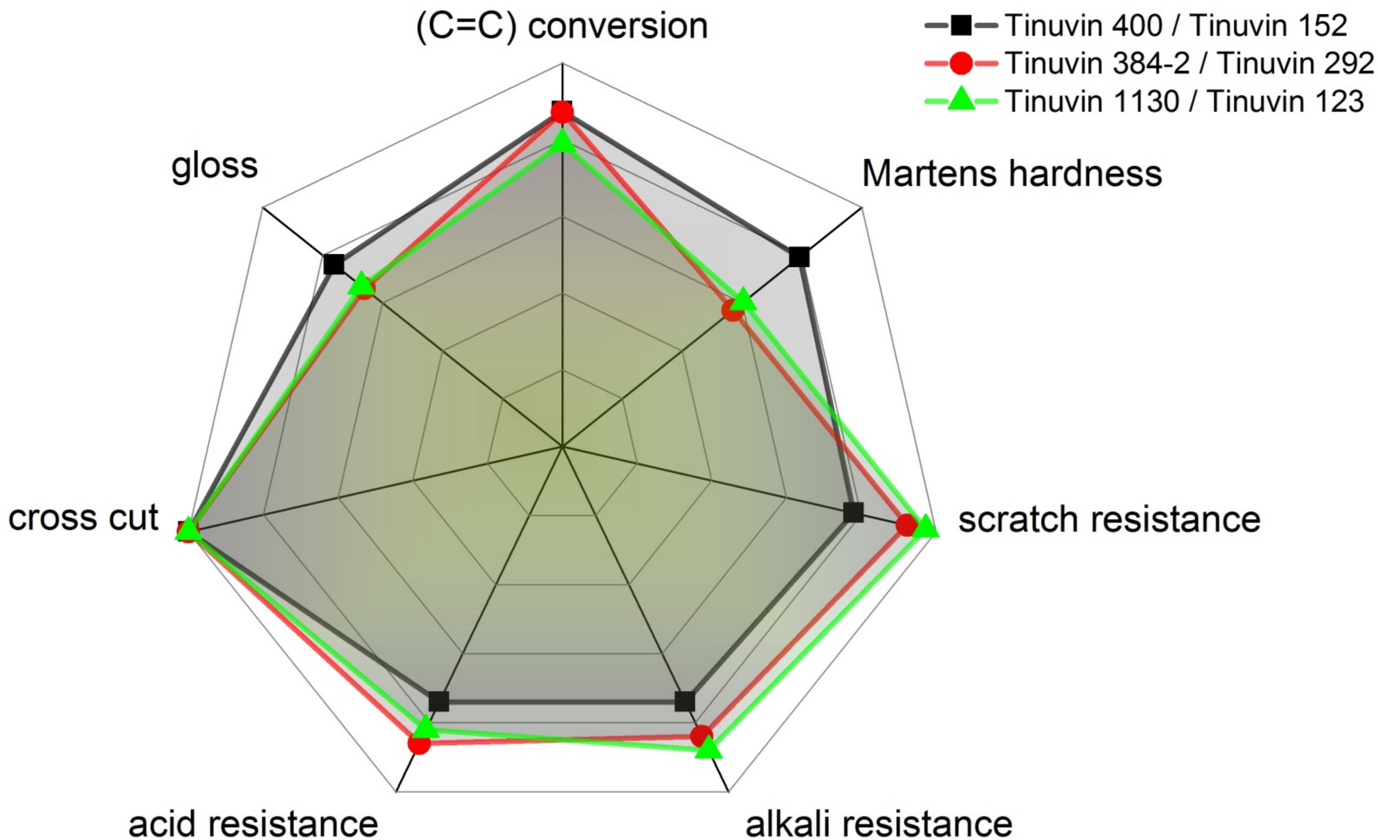
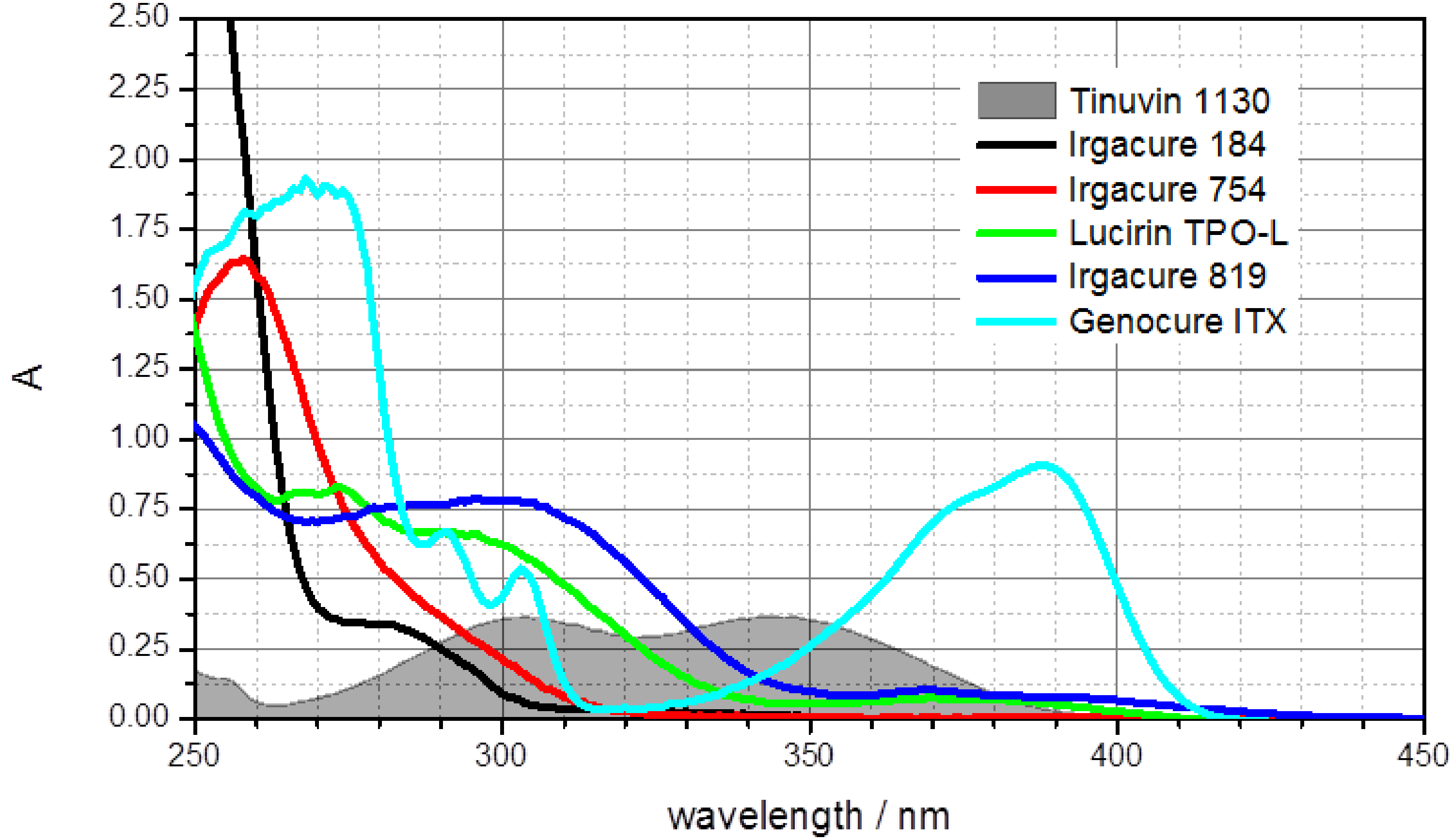
UV-cured clearcoats with different UV protection



- The UV-protection components influence the properties of the resulting UV-cured coatings.
- Because the (C=C) conversion doesn’t change significantly, an influence of the UV-protection components on the constitution of the polymer network should be considered.

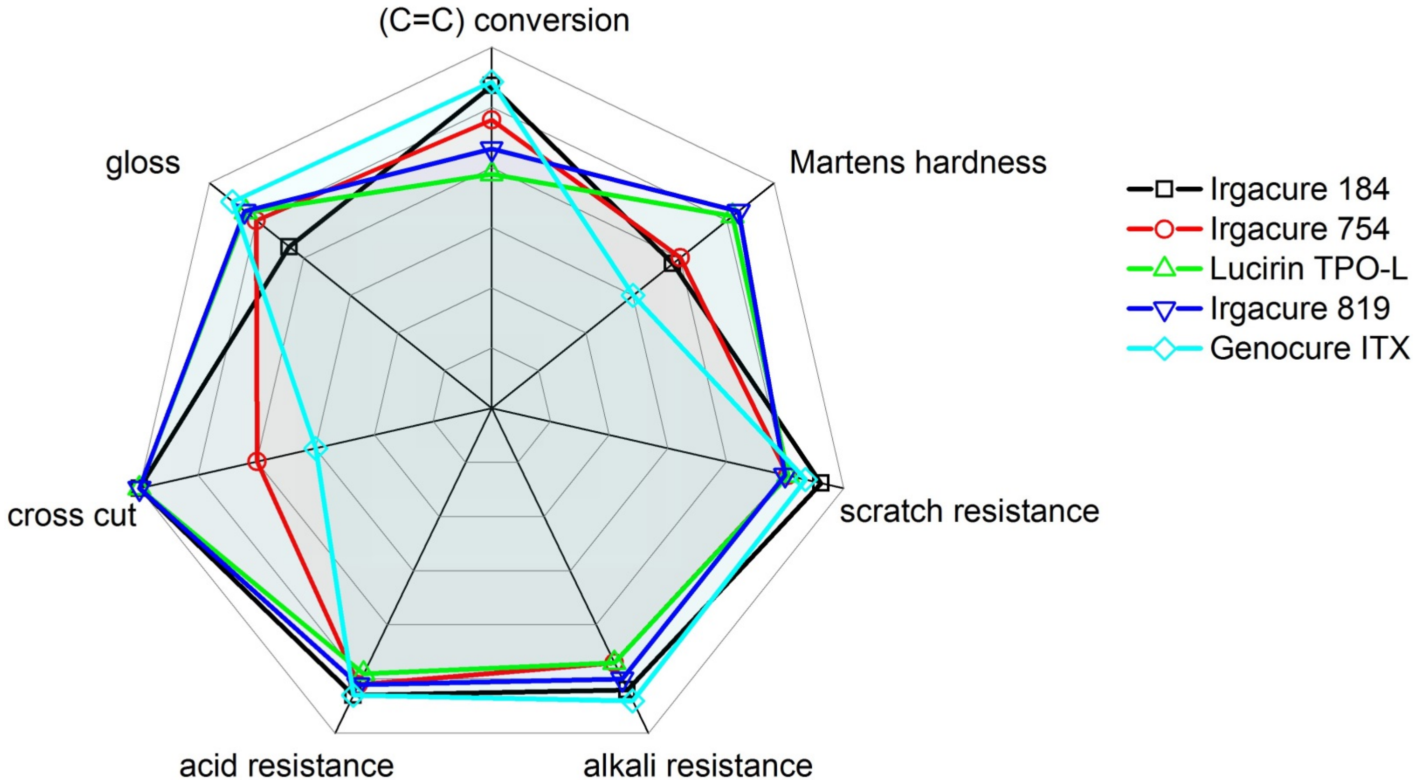
Comparision of UV-absorber and photoinitiators

(diluted in $CHCl_3$ at a concentration ratio 4/1.5)



- In contrast to the absorber Tinuvin 1130, most of the PI absorb mainly in the short (e.g. Tinuvin 184) and long wave UV-region (e.g. ITX).

UV clearcoats protected with Tinuvin 1130/123, cured with different photoinitiators



- The (C=C) conversion shows a significant dependency on the used PI.
- Even if the (C=C) conversion for ITX was quite high, the hardness as well as the adhesion properties dropped, whereas in the case of TPO-L with the lowest conversion, a high hardness and a good adhesion could be achieved. This indicates the different influence of the PI on the constitution of the polymer network.

Summary

- The addition of *triallyl isocyanurate* can improve mechanical (e.g. scratch resistance) and adhesion properties, as well as chemical stabilities of UV-curing coatings, by increasing the double bond conversion and by modifying the network of the crosslinked matrix.
- With increasing UV-protection, the double bond conversion drops. For durable UV-curing coatings an urgent need for crosslinking improving components, which reduce the negative influence of the UV-absorber, exists.
- The used UV-protection components and PI additionally affect the constitution of the polymer network, which influences the properties of the resulting UV-cured coatings.
- Optimized UV-cured coating formulations were developed, which contain UV-protection components and *triallyl isocyanurate* crosslinking agent.

Conclusions

-> *Triallyl isocyanurate improves important properties of non-protected and UV-protected UV-cured coatings. Therefore triallyl isocyanurate can be regarded as a valuable agent for the formulation of durable UV-cured coatings.*

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Acknowledgements

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Thank you for your attention …