

Novel self-cleaning coatings

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Abstract

Decorative and functional coatings with self-cleaning or easy-to-clean properties are presently in growing demand. These properties can be achieved according to the concepts of superhydrophobicity, superhydrophilicity or photocatalysis. The self-cleaning or easy-to-clean properties of such coatings are however significantly degraded, when the coated surfaces are exposed to chemical or mechanical loading, as by contact with surfactants or by scratching, which changes the surface tension and topography. The present attempt aimed at the generation of surfaces with self-cleaning properties, which are less prone to scratching or contact with surfactants. The underlying concept bases on the use of UV/IR-reflecting additives in coatings which cause the weakening or degradation of a dirt bonding. The self-cleaning properties of coatings are evaluated by outdoor exposure and a new laboratory short-time test. A further focus is also on the UV protection of coatings.

Introduction

Furnishing of modern coatings with self-cleaning properties is highly desired [1-12]. Within the last decade, different principles were utilized to generate self-cleaning or at least "easy-to-clean" coated surfaces.

One principle bases on a usage of hydrophobic polymers, waxes and particles, which introduce micrometer scale structures to the coated surfaces [7,10,11], resulted in the minimized adhesion of organic and inorganic dirt particles (cf. "lotus effect" [13]) and their easy removal with water.

In contrast, the self-cleaning properties of superhydrophilic surfaces are generated by a combination of photocatalytic surface activity and increased hydrophilicity [5,7,8,9,10]. For this purpose, photocatalytically active pigments (e.g. anatase) are either directly incorporated into the coating or an additional thin coating with such pigments is applied.

Both principles, however, are not universally usable. In biological systems hydrophobic surfaces are for example able to regenerate. By synthetic hydrophobic coatings, mechanical and UV impact may reduce their self-cleaning properties irreversibly [11]. Hydrophilic systems, however, are known to lose their efficiency in case of contamination with silicones or silanes [10]. Therefore, there is a demand for alternative concepts of more robust and durable self-cleaning coatings.

In this work, a novel attempt to develop self-cleaning coatings is presented, which bases on the principle of UV and IR reflexion. By this concept, a bottom site of dirt particles is irradiated from beneath by the reflected UV/IR energy, causing the degradation of the binding forces and loosening of adherence. Fig. 1 illustrates this principle schematically for an automotive coating system.

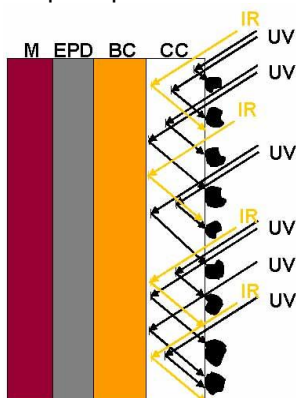


Fig. 1 Generation of self-cleaning properties by the principle of UV/IR reflexion; M: metal substrate, EPD: electrophoretically deposited primer, BC: basecoat, CC: clearcoat

Since the UV/IR-reflecting particles are not necessarily located at the surface of the top coating, surface affecting impacts like scratching or chemical contamination do not principally deteriorate the self-cleaning properties of such coatings.

Experimental

Test panels with an electrophoretic coating of 15 μm thickness were overcoated with a basecoat/clearcoat system as depicted in Fig. 1. The basecoat was a 20 μm thick waterbased white system, the clearcoat was a 2K PUR system of 40 μm thickness. 16 UV/IR-reflecting pigments and powders were tested at PVC of 7 w%. These additives can be described as follows:

1 - 9: pigments (almost colourless, mainly industrial trial products)

10 - 12: metal salts (powder)

13: colour pigment

14 - 16: aluminium flakes

For comparison a system without UV/IR-reflecting pigments or powders ("0") as well as commercial self-cleaning coatings were tested. The latter consisted of two coatings basing on the concept of superhydrophilicity (Shphi1 and Shphi2, whose superhydrophilicity is generated by surface nanostructuring), one float glas sample functionalized photocatalytically and superhydrophilically (ShphiP) and two superhydrophobic coating samples (Shpho1 and Shpho2, whose superhydrophobicity was generated by structure-modified hydrophobic pyrogenic silicic acids).

After conditioning for 7 days at 23°C and 50% r.h., the panels were characterized colorimetrically using an Online Spectrocolorimeter Teleflash T130 (X-Rite) by detecting L^* at 22.5°. By a fixed distance of 42 cm the diameter of the measured spot accounted for 6 cm.

The panels were exposed to outdoor weathering in Stuttgart, Germany. The orientation was to south at 45°. Further series of the same panels were tested using an apparatus described later. In both cases one series was scratched reproducibly using the Rota-Hub scratch test (Bayer AG, Germany) as displayed in Fig. 2.

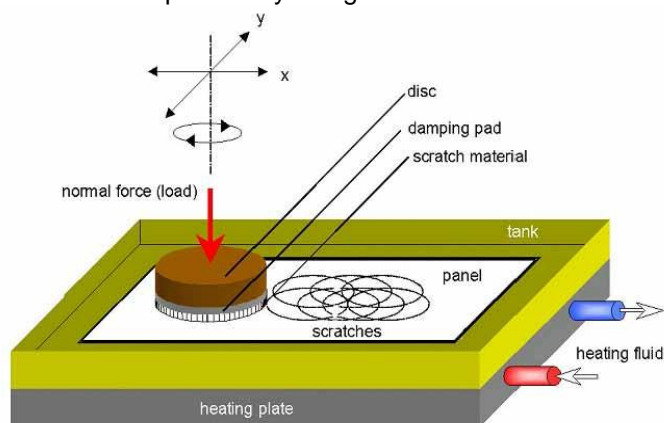


Fig. 2 Schematic of the Rota-Hub scratch testing device

By the scratching, the damping pad (3M Typ 2500 A) impacted by a normal force of 10 N at 48 rpm uniformly within the relevant area. The scratching was performed at 23°C and 50% r.h.. This procedure is abbreviated by "RH".

A self-constructed instrumentation for the characterization of the self-cleaning properties of coatings represents a further development of a device described by Nakaya [12]. It is depicted in Fig. 3.

An aquarium (40 cm x 25 cm x 30 cm) was provided with four circular holes. The hole diameter for the spectrocolorimetric detection and for the UV/IR irradiation accounted for 11 cm, whereas the hole diameters for the rotating axis accounted for 3 cm. This rotating axis was mounted to an electric motor, which was run at 0.28 rpm and 1.43 rpm, respectively. The axis was provided with two brackets, by which two test panels (10 cm x 10 cm) were fixed in rotational symmetry. The brackets were equipped with containers for dirt suspension, which were mounted in terminal position. By each rotation these containers were filled with the dirt suspension at the bottom of the aquarium. The test panels were wetted with the dirt suspension at each rotation.

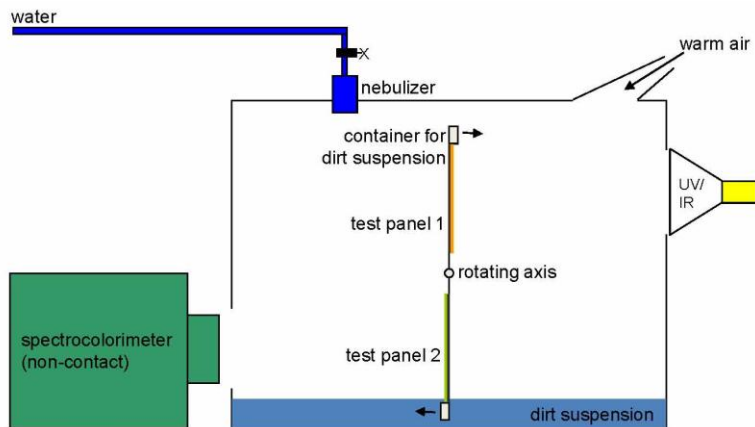


Fig. 3 Schematic of the instrumentation for the characterization of the self-cleaning properties of coatings

In order to obtain a good correlation with the outdoor weathering, the dirt used was collected in the following manner:

Pebbles from the weathering station were collected and washed with deionized water under impact of ultrasonic sound. The dirt suspension obtained was filtered through a 1 mm mesh and evaporated at 60°C. The residue was collected and powdered in a mortar. In order to inhibit biological activity 200 g of this powder were suspended in 500 ml of a 0.01% solution of NaN_3 and dried by evaporation again. The powder obtained was homogenized by mechanical shaking at 5 Hz for 80 min and stored at -15°C in a polymer flask. The dirt suspension was prepared in the following manner: 1.5 g of the dirt powder were suspended in 1 l of deionized water and treated with ultrasound for 20 min. Afterwards the suspension was diluted to 2.5 l, which is the adequate volume for the test.

Each test cycle consisted of a pollution and a cleaning phase, which were performed in following steps:

1. detection of L^*
2. 30 rotations through the dirt suspension at 1.43 rpm
3. 10 rotations through the dirt suspension at 1.43 rpm interrupted by drying with warm air (32°C)
4. waiting for cooling down and detection of ΔL^* (= „pollution“)
5. removal of the dirt suspension
6. 20 h rotation at 0.28 rpm under sunlight-simulating UV/IR irradiation (UV-A: 0.3 mW/cm^2 , UV-B: 0.1 mW/cm^2)
7. ten times impact of nebulizer for 10 s under rotation at 1.43 rpm; each time followed by drying with warm air (32°C)
8. waiting for cooling down and detection of ΔL^* (= „cleaning“)

Before performing this procedure, the samples were pretreated by the Rota-Hub scratching (RH) and/or one of the methods described as follows:

- a.) thermocyclic loading including UV irradiation (“TC/UV”): This loading was processed using the instrumentation shown in Fig. 4. Temperature cycles were performed by the impact of IR-lamps, which are controlled by a temperature sensor located at the surface of the coated samples. This sensor is connected to a PID control, which operates the IR lamps (6 x 500 W) following a user defined temperature program. Here, sinusoidal temperature cycles (20°C... 70°C in periods of 1 h) were performed for 24 h. Each 4 h a 15 min lasting UV irradiation (UV-A: 2.4 mW/cm^2 , UV-B: 1.0 mW/cm^2) was acted upon the samples additionally.
- b.) UV irradiation (“UV”): This loading was processed by a 24 h lasting UV irradiation (UV-A: 2.4 mW/cm^2 , UV-B: 1.0 mW/cm^2).

The UV-induced degradation of the organic matrix of the coating system was characterized using a special instrumentation, by which the formation of CO_2 and CO was detected in dependence of the irradiation time. This assembly is depicted schematically in Fig. 5.

The reactor and FTIR spectrometer, which analyses the volatile components of the air circulating over the sample in the reactor, are the main parts of the instrumentation.

After inserting the sample into the reactor, the instrumentation is purged with the carrier gas (here: synthetic air) accurately. While still in the flow mode, the desired water vapour concentration is adjusted via the injection pump. A real-time FTIR detection allows the evaluation of the resulting concentration changes of the gaseous species continuously. After switching to a circular flow, the radiation starts to act upon the

sample. The decomposition of the organic matrix indicated by the increase of the CO₂ and CO concentration is monitored quantitatively using the continuously recorded FTIR spectra.

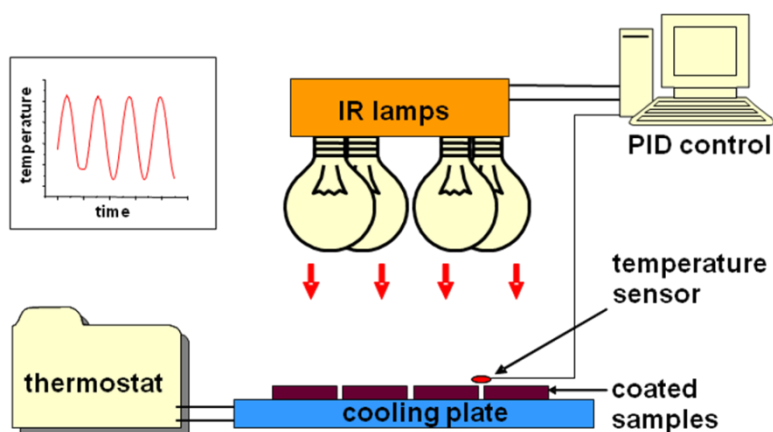


Fig. 4 Set-up for carrying out a thermocyclic loading of coated samples

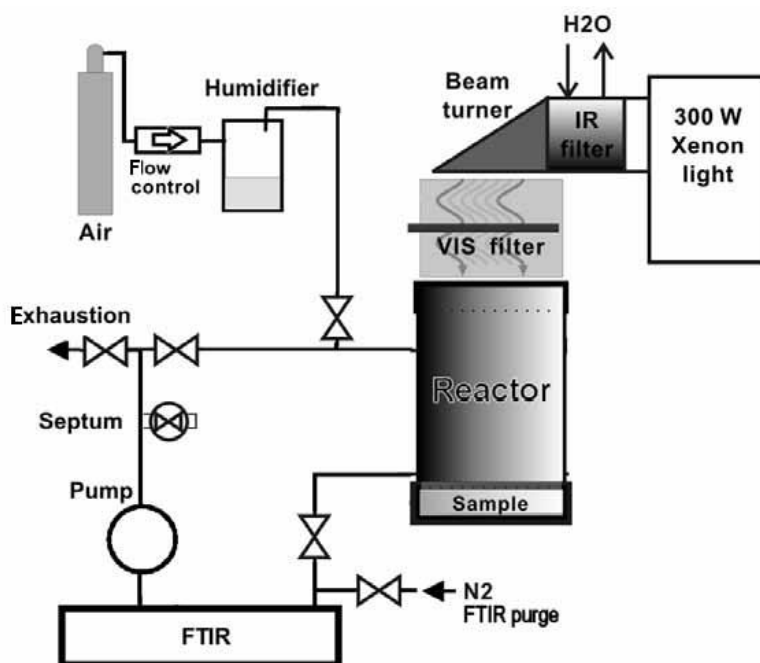


Fig. 5 Instrumentation for the detection of the UV-induced formation of CO₂ and CO

The FTIR spectrometer (Gasmeter FT IR gas analyzer, Temet Instruments Oy, Finland) was used to read spectra in intervals of 20 s, which were analysed on the basis of reference spectra by the computer programme CALCMET V2005 (Ansyco Karlsruhe, Germany) continuously. The optical path length accounts for 10 m; the spectrometer is sensitive enough to detect the concentration changes of approximately 1 ppm. The concentrations of CO₂ and CO can be then displayed in dependence of the irradiation time.

Reflection spectra were recorded from the samples as 12% dispersions in nitrocellulose lacquer. Freestanding films (thickness: 40 µm) were generated by use of a doctor blade and characterized in a Perkin Elmer UV/VIS/NIR Spectrometer Lambda 900 using an Ulbricht sphere (reflection mode).

Results and Discussion

The self-cleaning properties of the 22 samples, described at the beginning of the experimental part, were tested following the column headings listed in Table 1. In each column, the ΔL^* values obtained from the differences between the colorimetric measurements after and before the respective treatment are given. Positive values reflect a brightening whereas negative values comply with a brightness loss of the coating system.

The first experimental column reflects the results from a 24 h lasting UV irradiation, followed by the short-time test (Fig. 3). Due to the weak adhesion of the dirt on the clearcoat surface a prior trial without preceding UV irradiation resulted in no significant ΔL^* values.

The results displayed in the second experimental column were obtained from the short-time test, after the above described TC/UV, RH and again a TC/UV procedure were performed. Due to the quite strong UV impact in the preceding short-time test, here, the UV impact was decreased and accompanied by a thermocycling. In order to further improve the correlation with real-world loading, a defined scratching was applied between the two TC/UV periods.

These two short-time test series were followed by two outdoor weathering series performed as described in the experimental part. The second outdoor weathering series was processed after the coating samples were exposed to the defined Rota-Hub scratching (Fig. 2) as also performed within the second short-time test series (cf. Table 1, experimental columns 2 and 6-8).

Rank	UV Short-time test	TC/UV, RH, TC/UV Short-time test	Outdoor 6 months	Outdoor 12 months	Outdoor 18 months	RH Outdoor 6 months	RH Outdoor 12 months	RH Outdoor 18 months
1	Shphi2: 0.98	2: 1.70	ShphiP: 2.20	4: 3.24	4: 2.25	ShphiP: 2.63	4: 1.21	4: 0.27
2	8: 0.81	13: 0.28	4: 1.42	Shpho2: 1.35	Shphi2: 1.12	4: 0.08	ShphiP: 1.05	ShphiP: 0.15
3	3: 0.63	Shphi2: 0.16	Shphi2: 0.19	14: 0.71	2: 0.86	Shpho1: -0.38	Shpho1: 0.58	Shpho1: 0.04
4	Shphi1: 0.04	10: 0.00	Shpho2: -0.28	ShphiP: 0.68	Shpho2: 0.71	8: -1.11	8: -0.81	14: -0.55
5	ShphiP: -0.01	Shphi1: 0.00	8: -0.34	3: 0.62	3: 0.53	13: -1.94	14: -1.35	15: -1.34
6	5: -0.01	11: -0.02	3: -0.80	2: 0.53	16: 0.37	Shphi2: -2.07	13: -1.47	13: -1.37
7	4: -0.72	12: -0.08	2: -0.86	Shphi1: 0.30	10: 0.32	16: -2.22	10: -1.58	10: -1.46
8	7: -0.88	0: -0.12	14: -1.03	Shphi2: 0.29	14: -0.16	14: -2.28	15: -1.64	2: -1.47
9	10: -1.10	9: -0.18	16: -1.13	16: -0.05	ShphiP: -0.53	Shphi1: -2.36	Shpho2: -1.67	Shpho2: -1.57
10	Shpho1: -1.14	Shpho2: -0.20	Shpho1: -1.33	10: -0.07	Shphi1: -0.75	10: -2.46	Shphi1: -1.70	0: -1.70
11	0: -1.35	Shpho1: -0.26	10: -2.01	8: -0.10	11: -1.02	2: -2.65	2: -1.78	Shphi2: -1.75
12	1: -1.39	5: -0.39	Shphi1: -2.36	Shpho1: -0.44	Shpho1: -1.25	15: -2.69	0: -1.80	6: -1.77
13	15: -1.62	6: -0.48	0: -2.36	11: -1.18	8: -1.32	11: -2.71	11: -1.84	11: -1.79
14	6: -1.75	4: -0.49	11: -2.76	7: -1.76	7: -1.53	3: -2.82	6: -1.85	12: -1.81
15	Shpho2: -1.90	14: -0.50	5: -3.09	5: -1.78	0: -1.54	Shpho2: -2.93	12: -1.92	5: -1.84
16	11: -2.35	ShphiP: -0.56	9: -3.15	0: -1.92	6: -1.64	6: -3.00	5: -2.05	8: -2.02
17	12: -2.57	1: -0.56	6: -3.36	9: -1.92	5: -1.76	12: -3.06	Shphi2: -2.06	7: -2.10
18	16: -2.64	8: -0.12	7: -3.47	12: -2.48	9: -1.94	7: -3.14	7: -2.13	Shphi1: -2.14
19	9: -2.81	7: -0.79	1: -3.78	6: -2.51	12: -2.27	0: -3.22	16: -2.26	16: -2.16
20	14: -7.31	16: -1.02	12: -3.90	1: -2.93	1: -2.61	5: -3.41	3: -2.26	3: -2.50
21	2: -9.88	15: -1.10	15: -3.99	15: -3.37	15: -3.18	9: -3.65	9: -3.20	9: -3.41
22	13: -10.80	3: -1.57	13: -7.95	13: -7.55	13: -7.53	1: -4.17	1: -4.40	1: -4.49

Table 1: ΔL^* values obtained from the two short-time test series and the two outdoor weathering test series

Comparing the results of the four test series, several coherences become obvious:

First, the self-cleaning properties of some of the samples are apparently strongly affected by scratching. In general, samples like 3 or Shphi2 are characterized by significantly lower ΔL^* values in series with RH than in comparable series without RH. Other samples do not show such effects (e.g. 4) or exhibit even contrary effects (e.g. Shpho1). These findings should be ascribed to the features of the respective samples. The UV/IR-reflecting pigments of the samples 3 and 4 are plate-like, however they differ in thickness. The plate thickness in sample 3 accounts for 0.5 μm or smaller, whereas in sample 4 it accounts for more than 1 μm . Conceivably, the mechanical impact of the scratching procedure causes breaks in the thinner plate-like pigments of sample 3, which may result in a lower proportion of surface-directed UV/IR reflection during the short-time test procedure and the outdoor exposure, if a RH loading was performed before.

In case of Shphi2, whose self-cleaning superhydrophilic properties are induced by surface nanostructuring, the lower ΔL^* values in series with RH are most likely due to the scratching-induced destruction of the

surface nanostructure. In contrast, Shpho1, whose self-cleaning properties are caused by structure-modified, hydrophobic pyrogenic silicic acids, shows improved activity in case of a preceding surface scratching. Apparently, this scratching increases the hydrophobicity and therefore the self-cleaning effect.

In general, many non-commercial systems show self-cleaning properties, which are comparable with commercial products. This means that the concept of generating self-cleaning properties, as shown in Fig. 1, can be regarded as principally confirmed. However, some of the systems exhibit smaller ΔL^* values than sample 0. This means that the self-cleaning properties of the clearcoat was decreased by the addition of the respective pigment or powder.

For a better understanding of the ranking among the non-commercial systems, UV reflexion spectra were recorded for a selection of the used substances. The spectra are shown in Fig. 6.

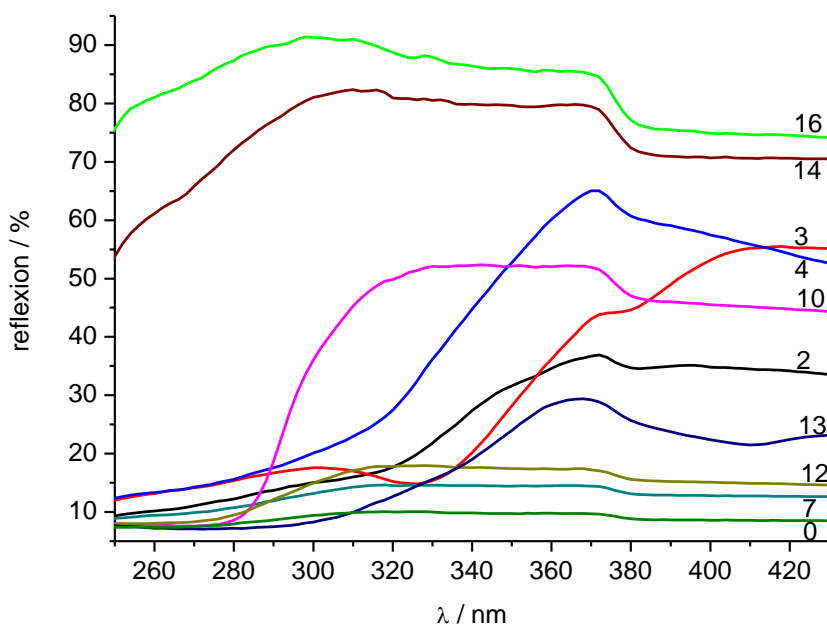


Fig. 6 UV reflexion spectra of several pigments and powders recorded for 12% dispersions in nitrocellulose films

As one might expect, the samples of the two aluminium flakes 14 and 16 are characterized by the strongest reflexion in the recorded range. By outdoor exposure these systems in fact cause quite large ΔL^* values (cf. Table 1), which indicate good self-cleaning properties. In the short-time test, however, they don't perform as good. This might be due to UV irradiation, which causes the formation of dark oxidation products. Apparently, they can't be easily washed off by the nebulizer action (cf. experimental part).

Excellent self-cleaning properties are found for the samples containing pigment 4. This sample shows relatively low losses of brightness under strong UV irradiation and its self-cleaning properties under long-term outdoor exposure conditions are better than any other - including the commercial ones. Outdoor exposure testing of this sample results in thoroughly positive ΔL^* values - even for the previously scratched sample. One may suppose that the absence of a significant UV-B reflexion band ($\lambda < 315$ nm), which could cause the formation of dark matrix oxidation products, and the presence of a quite strong UV-A reflexion band ($315 < \lambda < 400$ nm), which could induce the degradation of the adhesion between the dirt and the coating surface, contribute to overall advantageous self-cleaning properties (cf. Fig. 6).

Among the metal salt powders sample 10 exhibits the largest ΔL^* values. This sample is a nano powder, which is not the case for the metal salts 11 and 12, which show thoroughly worse self-cleaning properties. The UV reflexion spectrum of sample 10 shows a strong UV-A band, confirming the assumption that this contributes to good self-cleaning properties. Supposedly, the self-cleaning properties of 10 may be further improved by optimizing the dispersion and/or the concentration of this nano-powder in the clearcoat.

Although the intensity of the UV reflexion is significantly smaller for sample 2 than for sample 4, the shape of these two UV reflexion spectra is quite similar. In fact, pigment 2 exhibits also quite effective self-cleaning properties, although the results obtained from the first short-time test would suggest the opposite.

Sample 13 is also characterized by a similar UV reflexion spectrum. The test results for this sample show similarities to those of Shpho1, because both systems are characterized by larger ΔL^* values in case the

samples were previously scratched as in case they were not. Since sample 13 is the only colour pigment in this study, this finding cannot be evaluated systematically.

Samples with additives like 12 and 7, whose UV reflexion spectra show poor reflexion, are typically ranked around sample 0, which means that their presence in the clearcoat does not induce a significant positive contribution to the self-cleaning properties of the clearcoat. For many of these samples the short time test as well as the outdoor exposure result in ΔL^* values, which are lower than the ΔL^* value of sample 0. This means that the presence of these additives does even diminish the self-cleaning properties of the clearcoat surface.

In order to quantify the extend of UV-induced photooxidation, a sample of each system was characterized using the instrumentation as shown in Fig. 5. Exemplarily, the results for the samples 12 and 13 are given in Fig. 7.

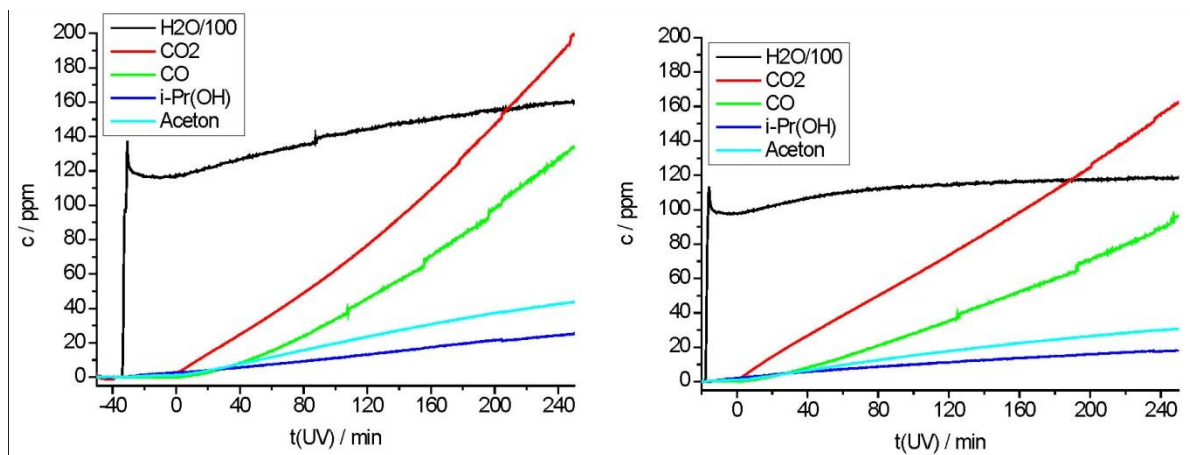


Fig. 7 Results of the photooxidation test obtained for the samples 12 (left) and 13 (right)

From these diagrams it becomes apparent that the degradation starts immediately after the aperture is removed ($t(\text{UV}) = 0$ min). The concentrations of the final oxidation product CO_2 as well as of CO and of the intermediate products as isopropanol and acetone increase at different rates but at an almost constant relation to each other. This indicates a similar degradation mechanism.

The increase of CO_2 occurs almost linear in case of sample 13, whereas for sample 12 one observes a more exponential increase of the CO_2 concentration. This may be explained either by an increase of the sample temperature within the test duration or by an auto-catalytical progress of the photooxidation. In any case the reaction rate is affected by the specific properties of the pigment or powder dispersed in the clearcoat. Fig. 8 shows the results of the photooxidation test for all systems.

The commercial systems Shphi2 and ShphiP, for which a very low extent of CO_2 formation is observed, are also characterized by quite good self-cleaning properties (cf. Table 1). This can be also stated for the non-commercial samples 2 and 3 (without RH). This is contrasted by the finding for sample 4, which shows the strongest UV-induced formation of CO_2 and CO but also the overall largest ΔL^* values (cf. Table 1). For these three samples the ranking regarding the photooxidation can be correlated with the reflexion intensities of these samples in the short-wave UV-A range ($315 \text{ nm} < \lambda < 350 \text{ nm}$).

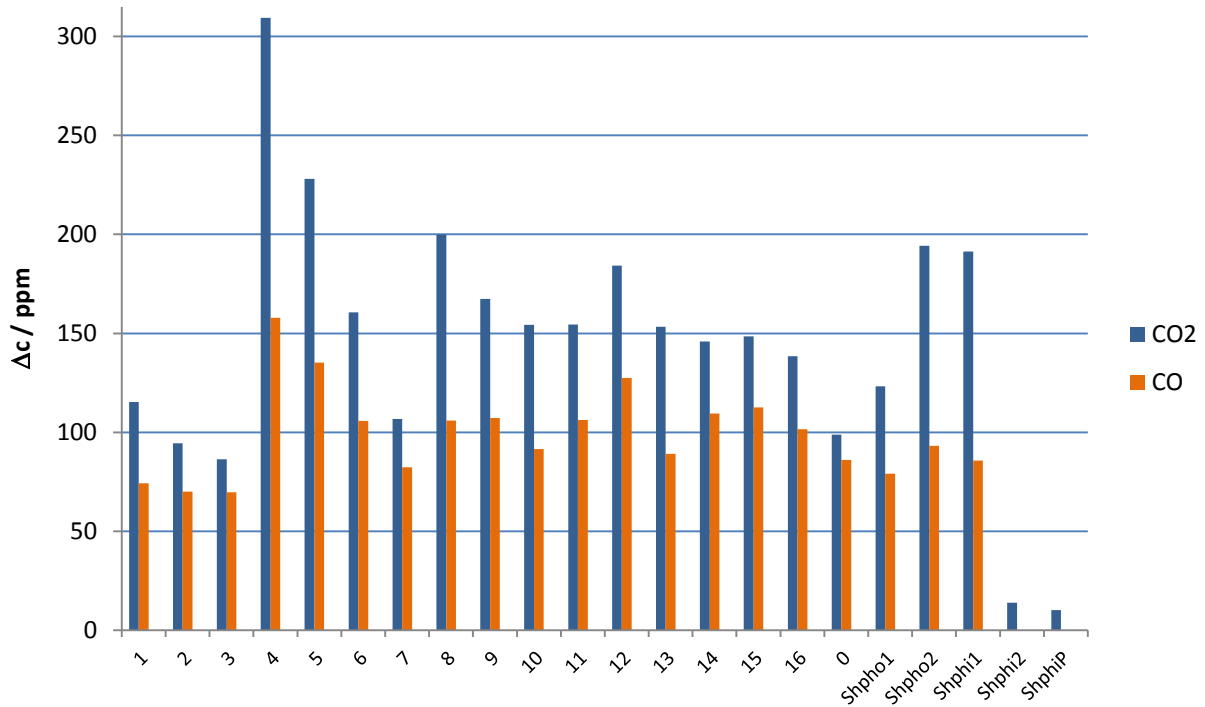


Fig. 8 Quantitative photooxidation results for all tested samples

One may speculate that the strong self-cleaning properties of 4 base on the surface oxidation of the clearcoat. Since the first step oxidation products are hydrophilic, they may be removed by rain during the outdoor exposure or by the nebulizer action during the short-time test. It can be assumed that dirt, which is deposited naturally (outdoor exposure) or artificially (short-time test), is removed together with these first step oxidation products by water.

Conclusion

The present work proved the feasibility of the new concept of self-cleaning coatings, based on the internal UV/IR reflection for the deadsorption and removal of dirt. Special additives were selected to functionalize coatings for such reflective activity. It was found that UV/IR reflective functionalized coatings exhibit a comparable or even better self-cleaning efficiency as commercial systems, which function on the principle of superhydrophilicity, superhydrophobicity or photocatalytically induced hydrophilicity. Since the origin of the self-cleaning activity by a UV/IR reflexion comes from inside of the coating, the scratching and other mechanical loading of the surface causes less detrimental effects as in the case of commercial systems. A new methodology for testing and evaluation of self-cleaning coatings has been also worked out.

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