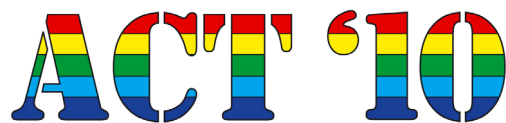


# ADVANCES IN COATINGS TECHNOLOGY



## NOVEL SELF-CLEANING COATINGS: DEVELOPMENT AND TESTING

**Nowoczesne powłoki samoczyszczące: rozwój i badania**

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# Novel self-cleaning coatings: development and testing

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## ABSTRACT

Self-cleaning coatings, which follow the concepts of photocatalysis, superhydrophobicity or superhydrophilicity, are commercially available. The self-cleaning properties of such coatings, however, are significantly degraded, when they are exposed to scratching or surface tension affecting substances. Within this work a novel concept to generate surfaces with self-cleaning properties is proved. This concept bases on a usage of UV/IR-reflecting additives in organic or inorganic/organic hybrid coatings. The self-cleaning properties of these coatings are evaluated by the outdoor exposure and with a novel quantitative short-time test. The results obtained show a good correlation. Additional methods for the quantification of the UV-induced degradation of coatings are proposed.

## 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.

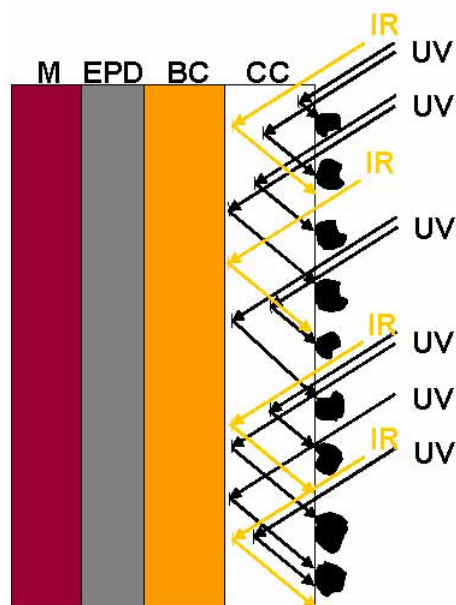


Fig. 1 Generation of self-cleaning properties by the principle of UV-/IR-reflexion; M: metal substrate, EPD: electrophoretically deposited primer, BC: basecoat, CC: clearcoat

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 coated with a corrosion inhibiting primer of 15  $\mu\text{m}$  thickness applied via electrophoretic deposition, were evaluated with a basecoat/clearcoat system as depicted in Fig. 1. The basecoat was a 20  $\mu\text{m}$  thick waterbased white system, the clearcoat was a 2K PUR system of 40  $\mu\text{m}$  thickness. UV/IR-reflecting pigments and powders were inserted at PVC of 7 w%. For comparison a system without UV/IR-reflecting pigments or powders as well as commercial self-cleaning coatings were tested. These were the systems AEROXIDE<sup>®</sup> LE1 and AEROXIDE<sup>®</sup> LE2 (Evonik), Col.9 (BASF), Pilkington Aktiv<sup>™</sup> (Pilkington) as well as the test version VP BO 9587 of the NANO-X company.

After conditioning for 7 days at 23°C, 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.

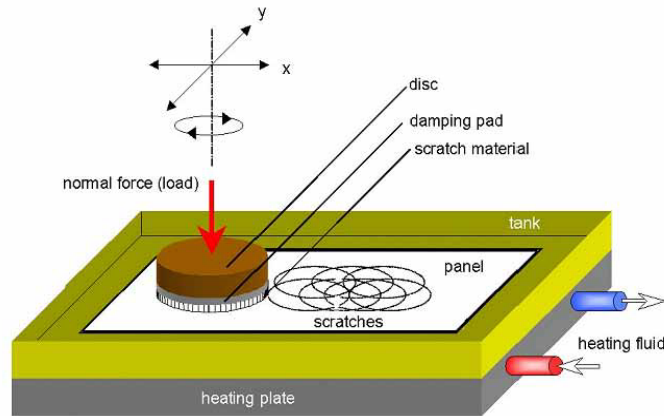


Fig. 2 Schematic of the Rota-Hub scratch testing device

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.

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.

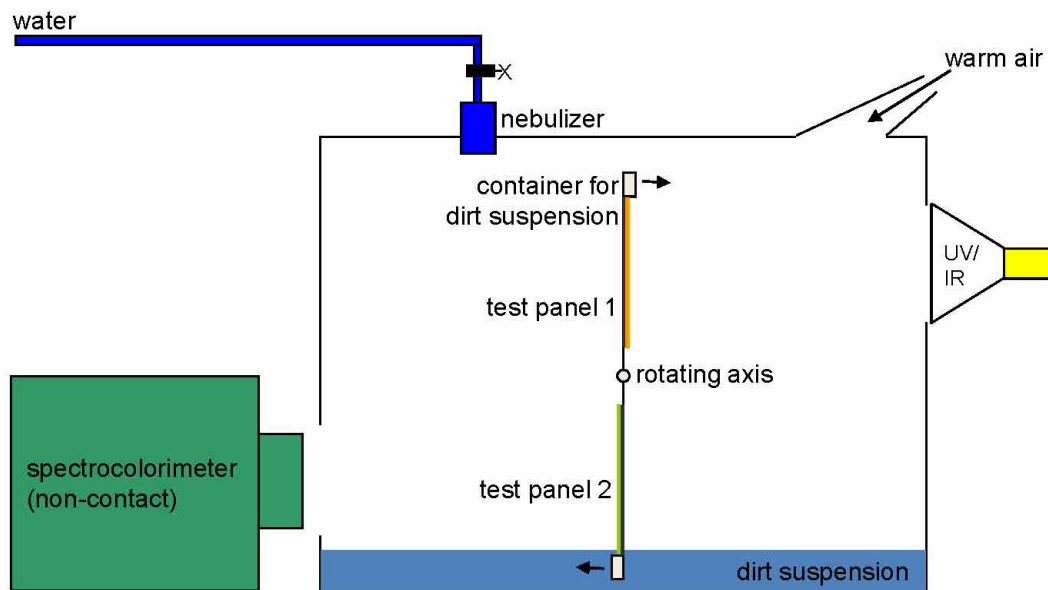


Fig. 3 Schematic of the instrumentation for the characterization of the self-cleaning properties of coatings

An aquarium (40 cm x 25 cm x 30 cm) was provided with three circular holes. The hole diameter for the spectrocolorimetric detection and for the UV/IR irradiation accounted for 11 cm, whereas the hole diameter 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 × 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.

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<sub>3</sub> 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  $\Delta L^*$  (= „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<sup>2</sup>, UV-B: 0.1 mW/cm<sup>2</sup>)
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  $\Delta L^*$  (= „cleaning“)

The UV-induced degradation of the organic matrix of the coating system was characterized using a special instrumentation, by which the formation of CO<sub>2</sub> and CO was detected in dependence of the irradiation time. This assembly is depicted schematically in Fig. 4.

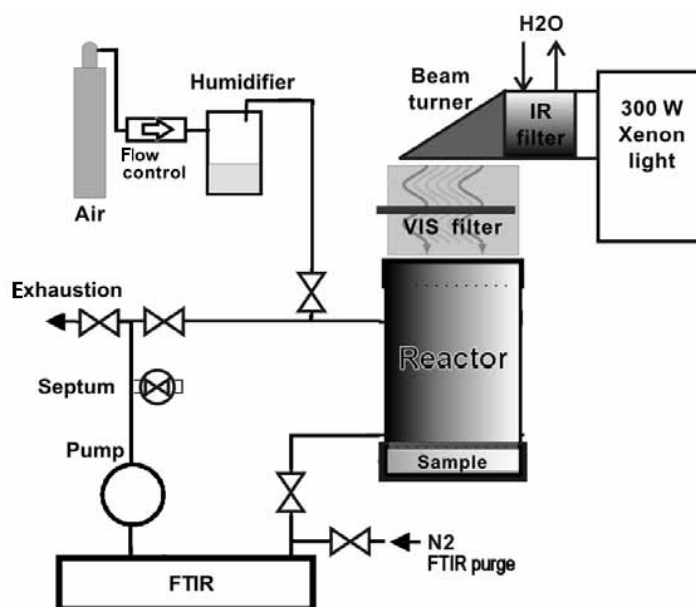


Fig. 4 Instrumentation for the detection of the UV-induced formation of CO<sub>2</sub> and CO

The reactor and FTIR spectrometer, which analyses the volatile components of the air 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 (e.g. 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 is monitored quantitatively using the continuously recorded FTIR spectra.

The FTIR spectrometer (Gasetm 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 CO<sub>2</sub> and CO can be then displayed in dependence of the irradiation time.

## RESULTS AND DISCUSSION

The results obtained from the so far performed six months weathering are depicted in Fig. 5. Samples of the tested coatings were exposed to the natural weathering after defined scratching (cf. Experimental) and in original state.

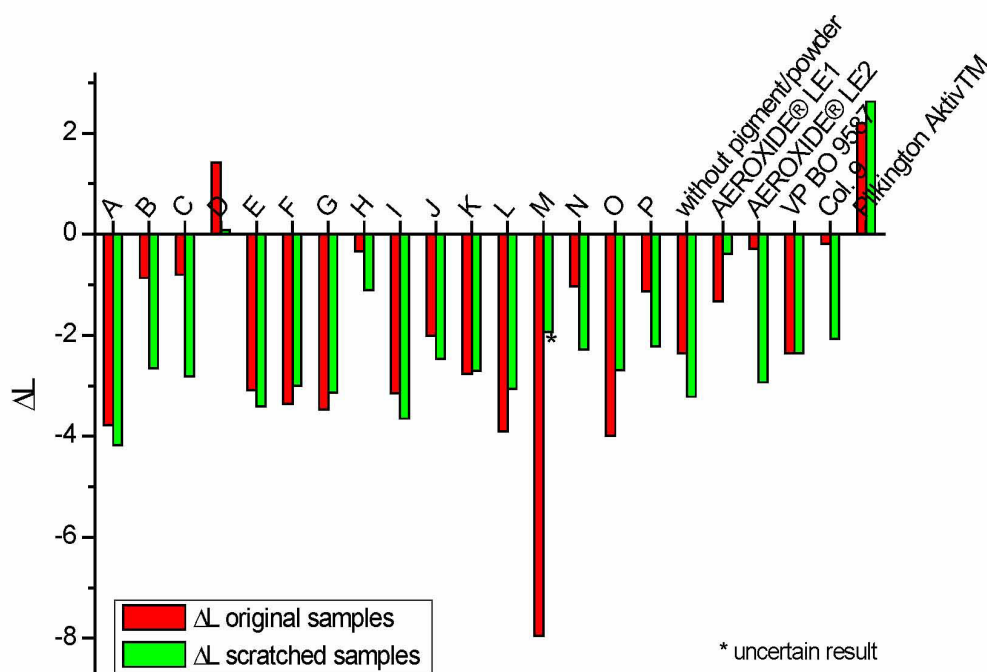


Fig. 5 Results of the colorimetric characterization of the naturally weathered samples after six months exposure

Due to the rougher surfaces the scratched samples generally show a stronger decrease of  $\Delta L^*$  than the original samples. In the few other cases, the opposite phenomenon can mostly be explained by an originally rough surface (caused e.g. by large pigments), which is “smoothed” by the scratching procedure. Sample M, which showed the by far strongest decrease of  $\Delta L^*$ , could not be characterized unambiguously in the case of the prescratched

surface, since the  $L^*$  values detected did very much depend on even lightest changes of the measuring angle.

Generally, it can be stated that all of the commercial products show a lower decrease of  $\Delta L^*$  than the reference sample without UV/IR-reflective pigment or powder. This means that the effectiveness of these products, which base on the self-cleaning concepts of superhydrophobicity, superhydrophilicity or photocatalysis, is confirmed principally. Pilkington Aktiv™, which is a transparent coating for glass surfaces, shows even positive  $\Delta L^*$  values. This finding applies also for the best of the non-commercial systems, the sample D. For this sample both the scratched and non-scratched variants show the same high self-cleaning efficiency. Additionally, systems H, B, C as well as N and P exhibit significantly enhanced self-cleaning properties in comparison with the reference sample without UV/IR-reflecting pigments or powders.

The first laboratory trials resulted in very low  $\Delta L^*$  values, indicating that the dirt used is almost non-adherent to the original coating surface. Therefore the following 24 h lasting pretreatment was performed for all samples identically:

1. detection of  $L^*$
2. sinusoidal temperature cycling:  $20^\circ\text{C} < T < 70^\circ\text{C}$  at a cycle duration of 1 h
3. after periods of 4 h: 15 min UV irradiation (UV-A:  $15 \text{ mW/cm}^2$ , UV-B:  $0.8 \text{ mW/cm}^2$ ).
4. detection of  $\Delta L^*$  (“yellowing”)

The results of the accelerated test, including the procedure described in the experimental part, are depicted in Fig. 6.

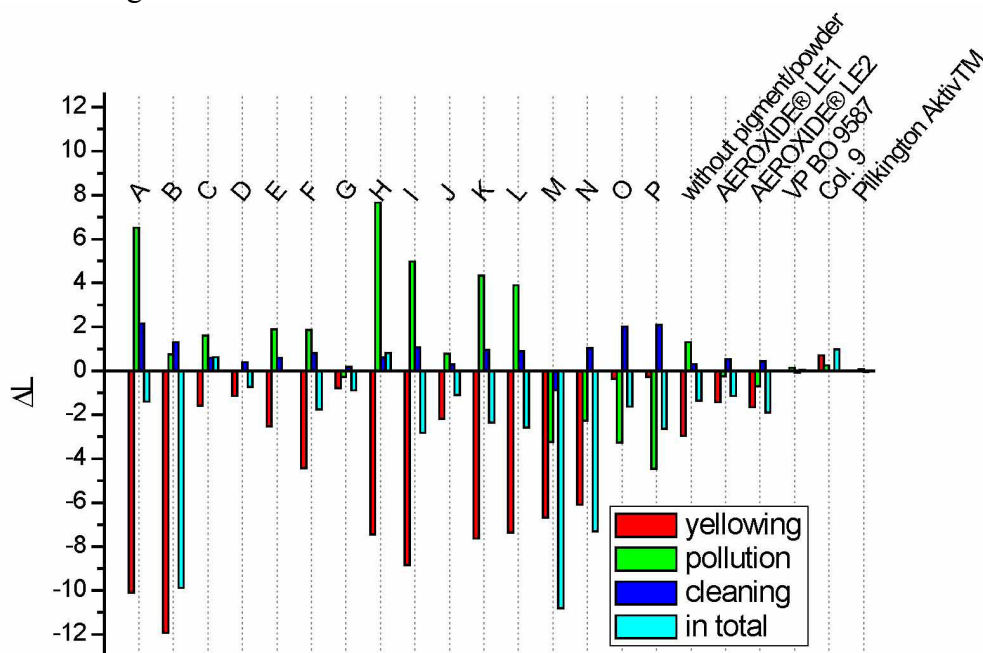


Fig. 6 Results of the colorimetric characterization of the samples exposed to the pretreatment and the accelerated test

Again, Pilkington Aktiv™ – among other commercial systems like Col.9 and VP BO 9587 – performs at the best. It does not show any yellowing, due to the absence of an organic matrix in this silicon-based coating. In the case of Col.9 a positive  $\Delta L^*$  value evidences a high photoresistance of this dispersion. In contrast, many other systems are characterized by a significant yellowing. In numerous cases the extent of yellowing exceeds that observed for the reference system without UV/IR-reflective pigment or powder. This indicates an increased photodegradation of the polymeric matrix, caused by multi-reflection phenomena. However,

for some systems (e.g. C, D, G, O and P) the extent of yellowing was found to be lower than for the reference. In these cases a part of the UV irradiation seems to be absorbed by the additives.

In many cases the pollution procedure resulted in an increase of the  $L^*$  value. This may be explained by the hydrophilic nature of the photooxidation products formed at the surface of the UV irradiated samples. Apparently, the dirt suspension removed the hydrophilic components from the surface of the yellowed samples.

In nearly all cases the cleaning procedure resulted in the expected increase of  $L^*$ , where M again is the exception. Apparently this system with quite weak UV reflectors did not exhibit remarkable self-cleaning properties. The calculated total self-cleaning effect is given in Fig. 6. Regarding this parameter, the best systems characterized by the largest total  $\Delta L^*$  values are C, H and D. This correlates well with the natural weathering, however by the ranking D, H and C.

A further improvement of the correlation can be probably reached by a prolonged natural weathering and a less intense UV-irradiation before the accelerated test.

The extent of the photodegradation by the laboratory test can be monitored by the detection of  $CO_2$  and  $CO$ , generated by UV/IR-irradiation of coatings (cf. Fig. 4). The results of this detection are displayed in Fig. 7.

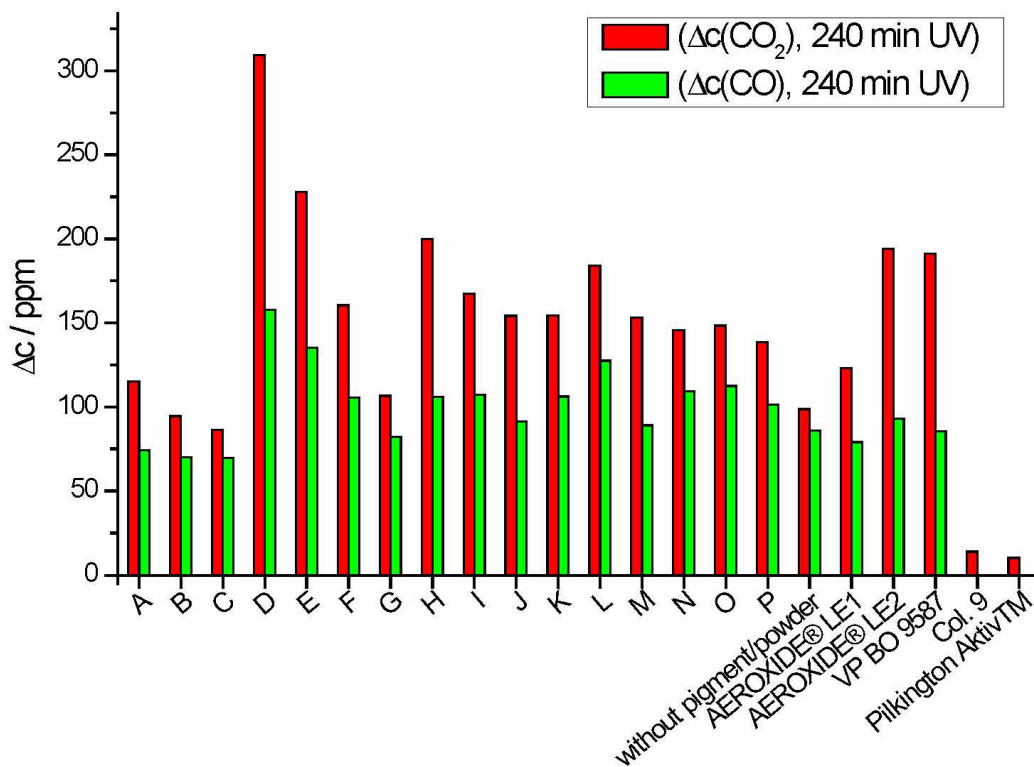


Fig. 7 Results of the photodegradation test

Low values of  $CO_2$  rise for Pilkington Aktiv<sup>TM</sup> and Col.9 (cf. Fig. 6) correlate well with a yellowing resistance of these samples. Since no  $CO$  was found for both samples, it may be concluded that the detected small amount of  $CO_2$  desorbs from the surface of the sample.

For non-commercial systems a rough correlation between the self-cleaning efficiency and the photodegradation, indicated by the  $CO/CO_2$  detection, is apparent. For more precise concluding is however a further research necessary.

## CONCLUSION

Self-cleaning properties of commercial and non-commercial systems – the latter basing on UV/IR-reflective pigments and powders – were evaluated colorimetrically by natural weathering and laboratory testing. A relatively good correlation of both testing procedures can be further optimized by enhancing the duration of the natural weathering and adjusting the intensity of the UV loading. Both tests identify the non-commercial systems C, H and D as efficiently self-cleaning and point out at the possibility to reach this property by using UV/IR-reflective pigments or powders.

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