Visible light active photocatalytic coatings for health care

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Introduction

Especially since the beginning of the coronavirus pandemic, the reduction of infections due to antimicrobial – and by this antiviral – surfaces in clinics and public buildings are a present topic [1], [2]. One possibility to minimise the contamination of surfaces by pathogens is the application of antimicrobial surface finishes or coatings. Currently available surface finishes with an antimicrobial effects are mostly based on the successive release of active ingredients as metal ions, metal nanoparticles (e.g. silver), or organic substances. The successive release of active substances leads to their consumption and consequently to a limited lifetime. Another negative effect is the release of substances into the environment, where they can have a harmful effect. Especially the toxicity of silver ions and nanoparticulate silver is a serve problem, e.g. for aquatic organisms [3]. The application of surface finishes without successive release of active substances is a promising and environmentally friendly alternative to the current standard. Photocatalytically active coatings are such an environmentally friendly alternative technology.

In the research project "Interior coatings with antiviral effect by using visible light active photocatalytic coatings with high long term stability", funded by the "Ministry for Economics, Labour and Tourism of Baden-Württemberg", the antiviral and antimicrobial effects of photocatalytic coatings for indoor applications were investigated. In this project, a consortium of the industrial partners Griwecolor GmbH, IBT Deutschland GmbH, and Fraunhofer IPA developed and studied the effectivity of water based photocatalytic active coatings as surface finishings for walls. The antimicrobial testing was performed at Mikrobiologisches Labor Dr Michael Lohmeyer GmbH. The aim of the project was to develop an antiviral coating to reduce pathogens on surfaces, and therefore reduce the risk of infections in public buildings and medical facilities.

Modification of test setups for visible light photocatalysis

To investigate the photocatalytical activity of the coatings, new measurement setups with visible light sources for interior application were installed. For that, the test setup according to DIN ISO 22197-1, to investigate the photocatalytic degradation of NO, was modified with a visible light source. As in modern room lighting LED illumination is state of the art, visible light LEDs were applied in the new measurement setup (Figure 2). As an LED light source a dimmable LED array (10 cm x 11 cm) with visible light LED type LXML PWN2 (4100 K, neutral white) and a max. output of 49 mW/cm^{2,} was constructed. In contrary to DIN ISO 22197-1 no pretreatment of the coating before the measurement was performed, and the degradation phase was shortened to 90 min (instead of 5 h), as the equilibrium of the degradation was reached after 90 min for the investigated coatings. The NO-degradation, photon efficiency and deposition velocity were calculated to evaluate and compare the efficiency of the new coatings.

The same light source as for NO-degradation was used to investigate the isopropanol degradation in the FPL reactor method (Figure 5). The experimental procedure with isopropanol in the FPL reactor was performed as described in literature [5].

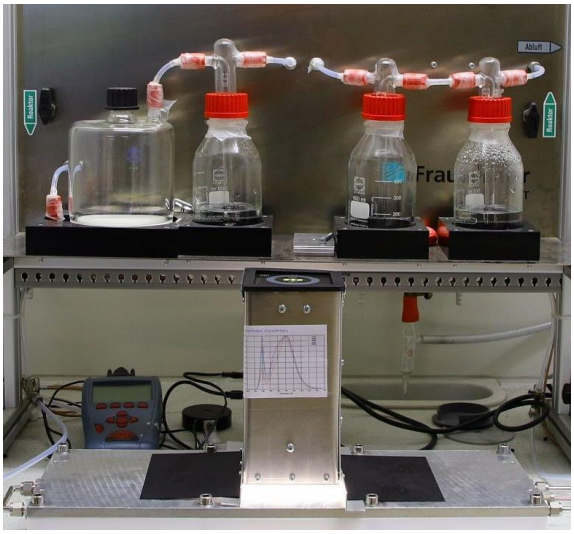

Figure 1: Modification of the NO-degradation setup with visible light source

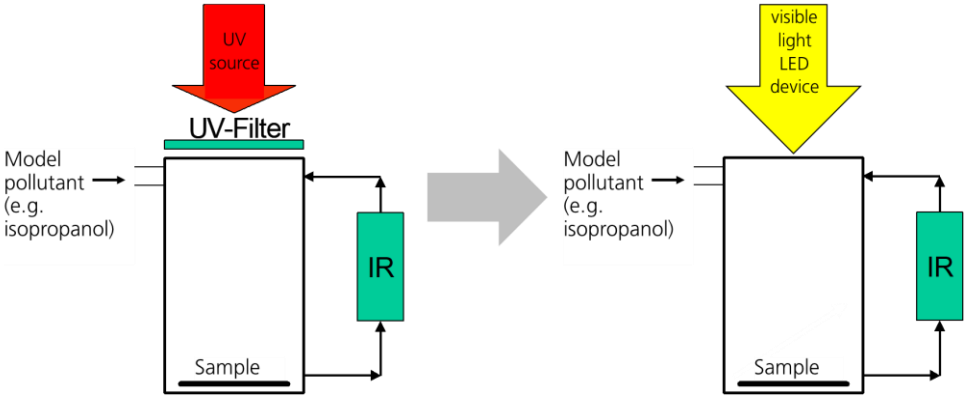

Figure 2: Modification of the FPL reactor setup with visible light source

As the investigation of the NO-degradation is the faster test method, it was used as a screening method. The FPL method only was applied for the most promising coatings.

The development of the antiviral test setup for the new coatings samples was a process with multiple iterations. As a starting point the setup of ISO 22196 was chosen. As the bacteriophage Pseudomonas Phage phi6 was selected as replacement of human pathogen viruses, as e.g. corona virus, and as a host bacteria Pseudomonas syringae (P. syringae) according to Vatter et al. was used [4]. A phage lysate was produced, the phage titer was determined, and the lysate was diluted. The lysate was incubated for 24 h covered with a 4 cm x 4 cm foil on a 5 cm x 5 cm sample surface. The phage titre on the test surface was determined at times t = 0 h and t = 24 h and compared to the control surface (reference). The number of plaque-forming units (pfu) was quantitatively determined using the host strain P. syringae in the cultural plaque assay method (double agar overlay technique) [4]. As reference, a test surface with known anti-bacterial effect was used to verify the developed test method with optimal recovery rate. Figure 3 shows the influence of the phage phi 6 on the host bacteria P. syringae. In the presence of the phage phi 6 a significant reduction of the bacterial lawns can be observed.

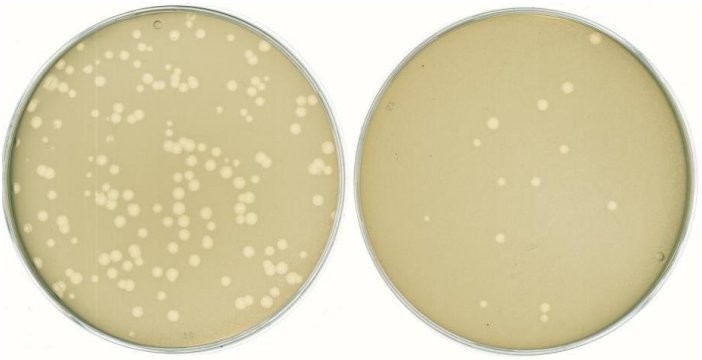

Figure 3: Agar plates with bacterial lawns of P. syringae; left: reference with 10^{-5} dilution; right: 10^{-6} dilution after applying a phage solution

In the second step, the method was adapted to the procedure according to ISO 18071 for determining the antiviral properties of photocatalytic coatings with visible light. As a light source the same LED device as for NO-degradation was used. The samples were placed in a Petri dish above a moistened filter, the phage suspension was pipetted onto the sample surface and covered with a foil to ensure even contact of the suspension with the surface and prevent drying out. It was incubated for 4 h each under light influence or in darkness (Figure 4).

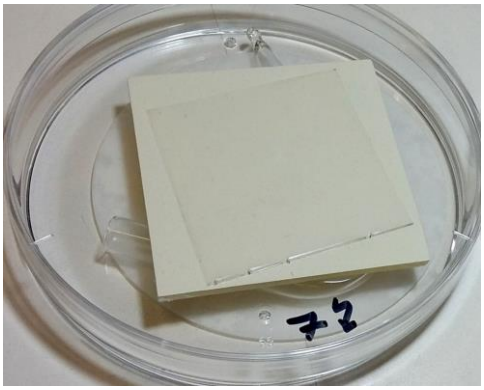

Figure 4: Test setup for testing the antiviral activity of the new coatings

As the antiviral activity did not correlate with photocatalytic activity, a modification of the test setup was necessary. The investigations of the influence of the buffer solution on the photocatalytic activity showed, that the buffer reduces the activity of the coatings. In addition, a negative effect of a liquid film on the surface was assumed. Due to this, the buffer concentration and the liquid volume were reduced to a minimum.
The final test setup “stamp test” of the antiviral test used P. syringae as host bacteria for Pseudononas phage Phi6. The concentration of the phage solution was about 10^6 pfu /ml in a volume of 300 µl. The surface of the sample was wet, but no film forming water was visible. The sample was exposed for 15 min to visible light (LED-light source). To recover the phage, 5 ml rinsing solution was used.

Formulation of the new coatings
The first step of the formulation of the new coatings was the selection of visible light active photocatalysts. Two candidates were found, KronoClean 7000 (KC) and Pretiox CG 300 (CG). Both are titanium dioxide photocatalysts with a high specific surface in the modification anatas. These two photocatalysts were combined with various binders.

As the new coatings were formulated as water based coating systems, the compatibility of nine water based binders with the two photocatalysts was investigated. The dispersion of the photocatalysts in the binders with up to 30 wt% of the photocatalyst was possible. The mixture was applied on aluminium substrates and the photocatalytic activity (NO-degradation with visible light) of the films was tested. As the photocatalyst KC showed significantly higher activity in all combinations, except for binder 8, KC was chosen as the photocatalyst for formulating the new coating systems (Figure 5).

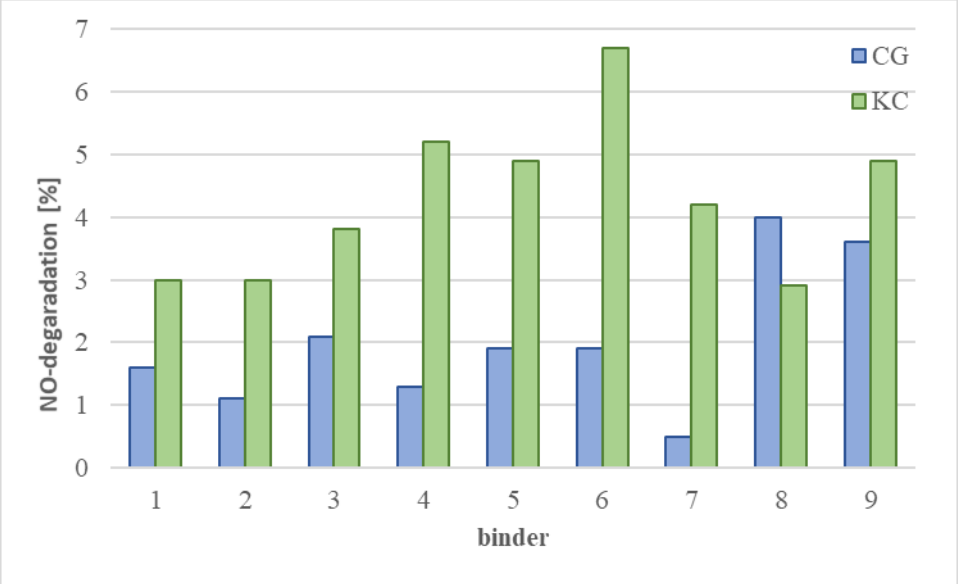

Figure 5: NO-degradation of binder/photocatalyst combinations with visible light

Due to the compatibility tests, coating formulations were developed. The first aspect for the further investigations of the new formulations was their stability. Stable coating formulations were applied on test panels.

Investigations

To investigate the functionality and properties of the new coatings, various test methods were used. The first selection criteria for coating films, with good film forming properties, was the photocatalytic activity. From the coatings, which showed photocatalytic activity, the most promising variants were tested for antiviral activity. Besides activity and structural investigations, further important characteristics of the coatings were investigated. Important characteristics for the application as wall paints are water vapour diffusion and optic effects. For the application in public buildings, also the mechanical stability, chemical resistance, and cleanability are relevant factors. Therefore, these properties were investigated and compared to standard wall paints.

Most of the investigated coating films showed photocatalytic activity with visible light irradiation. During the project, coating films with more than 20 % NO-degradation, a photon efficiency more than 0.5 % and a deposition velocity more than 0.005 m/s were found. These values are comparable to the “high standard” from a former research project for the development of a calibration standard for NO-degradation according to DIN ISO 22197-1 [6]. Outstanding is, that the new coatings show a comparable high or even higher photocatalytical activity under indoor lighting as the state of the art coatings under UV-light (outdoor lighting). The new coating LR 90, which was also investigated in the FPL reactor, showed a very high adsorption of isopropanol. This indicates a high adsorption of other organic molecules, as e.g. proteins on the surface of pathogens. A high adsorption of pathogens indicates a good

antimicrobial effect of the new wall paints. As the adsorption of the pathogens on the surfaces leads to a longer contact time and thus to a higher probability of degradation.
The antiviral tests were performed on the most promising coatings. Dark values and with LED light were determined. As the tests showed that some samples already show activity in the dark, it was not sure if the photocatalyst is responsible for the antiviral effect (Table 1). Additionally, some photocatalytic active coatings did not show antiviral activity. Therefor the test was further adapted to the "stamp test" (touch transfer test) and more reliable test results were possible, but still some samples showed antiviral activity in the dark.

sample	pfu/ml after 24 h	log	Log reduction compared to reference
Reference	$1{,}1 \times 10^6$	6	-
IVB 63 dark	$< 4{,}4 \times 10^3$	<3,6	>2,4
IVB 63 2 vis LED (70% output)	$< 4{,}4 \times 10^3$	<3,6	>2,4
IVB 28/1, without photocatalyst, dark	$6{,}6 \times 10^6$	6,8	0
IVB 28/1 without photocatalyst, vis LED (70% output)	$1{,}1 \times 10^6$	6,1	0

Table 1: Investigation of antiviral efficacy using phage Phi 6 (host bacterium P. syringae), stamp method with 15 min of illumination time

As the investigations of the antiviral effect did not give reliable information of the antimicrobial activity caused by the photocatalyst, electro spin resonance (ESR) spectroscopy as a further method for indirect proof of the antiviral effect was used.
To clarify, if the antiviral effect is caused by the photocatalyst or by other ingredients of the coating formulation (e.g. biocides which are used in the water based binders), ESR spectroscopy was chosen to investigate the photocatalytic effect of the coatings. ESR spectroscopy is a method to investigate the presence of unpaired electrons. As in the photocatalytic process, the light excites electrons from the valence band of the titanium dioxide in the conduction band, which leads to the formation of free radicals; these radicals (unpaired electrons) can be observed via ESR spectroscopy. To see, if the effect is created by the photocatalyst or other components of the coating, the catalyst and coating films were investigated. For that, glass capillaries were coated with a suspension of KC, as the reference, and with the new coatings. The spectra were taken in the dark (conditioning overnight in the testing chamber) and after lighting with a visible light source (gooseneck lamp for microscopy).The spectra of KC and the coatings showed, that even in the dark unpaired electrons are present (Figure 6). The signal between 334 and 337 mT can be assigned to delocalised electrons. That means that even in the dark radicals are present on the surface of the photocatalyst. The smaller signal between 330 and 335 mT occurs only by lighting and can be assigned to the Ti^{3+} of the excited photocatalyst. The intensity of the signal increases with increasing visible light irradiation. The coatings showed the same effects. The intensity of the signal depended on the coating. The ranking of the ESR intensity correlated with the ranking of the photocatalytic activity of the coating. These results explained that some coatings showed an antiviral effect even in the dark.

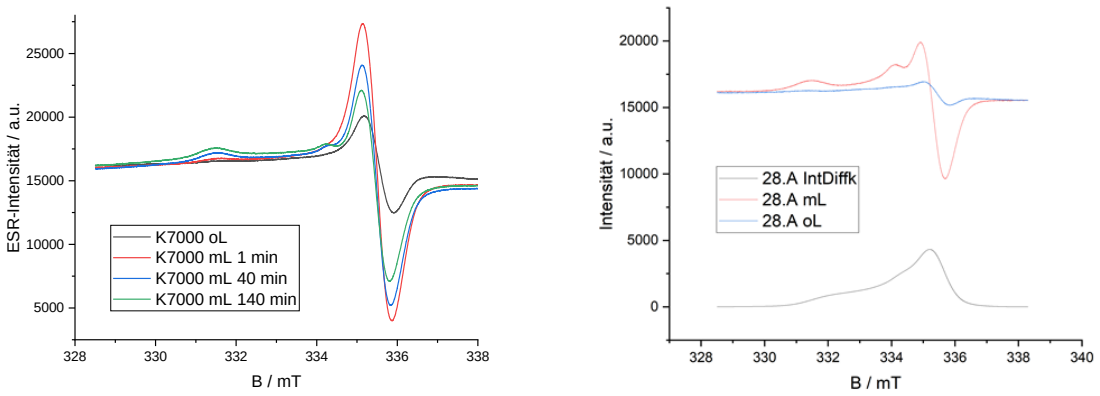

Figure 6: ESR spectra of KC (left) and the new coating IVB 28/A (right) in the dark (oL) and under visible light irradiation (mL)

It is known, that radicals have a negative effect on pathogens [7], [8]. Especially oxygen radicals are known to have antimicrobial effects. In the photocatalytic process, the photocatalyst induces the creation of hydroxyl radicals, which are described in literature as antimicrobial active [8]. The ESR spectra proved, that the new coatings show an antimicrobial effect caused by the photocatalyst and that even in the dark an antiviral effect is available.
In addition structural investigations compared to standard wall paints showed, that the new coatings have a rougher and more porous structure than standard wall paints. This structure has the positive effect, that pathogens dehydrate faster on the surface of the new wall paints than on the smother surface of standard products [9],[10].

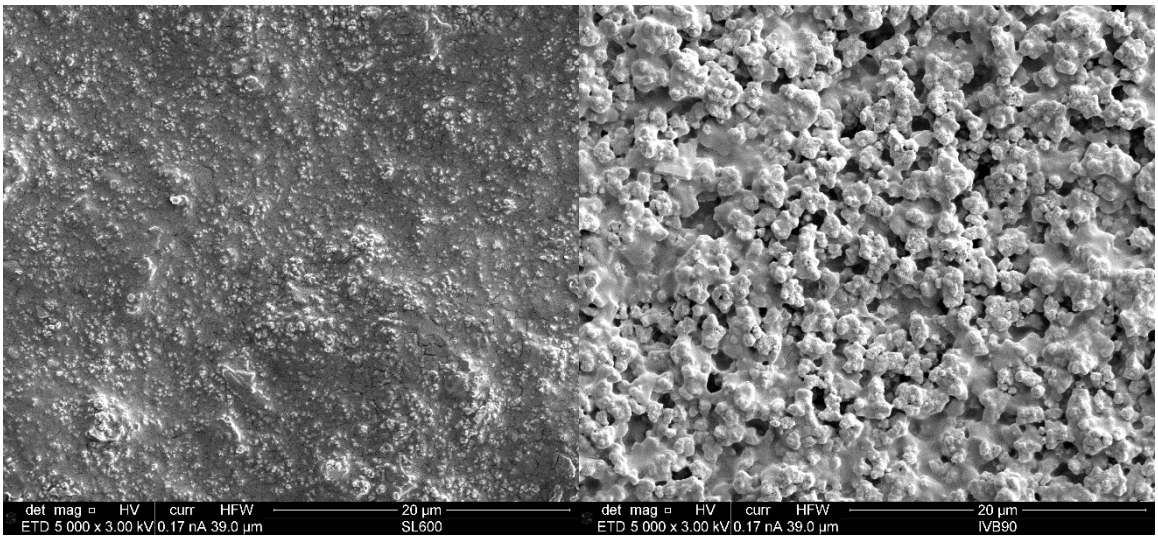

Figure 7: SEM of the surface of a standard (left) and an antimicrobial wall paint (IVB 90) (right).

One important property of wall paints is the water vapour diffusion. The water-vapour transmission properties were determined according to DIN EN ISO 7783. The water-vapour transmission rate V and water-vapour diffusion-equivalent air layer thickness, sd were determined. As V was higher than the maximal value 680 g, the water-vapour transmission rate, Vcs, of the substrate plus coating was also compared to get a ranking of the coatings. According to DIN EN ISO 1062-1 the new coatings have a high (V > 150 g/m²d) water-vapour transmission rate which is comparable to silicate wall paints. The standard wall paint is classified as middle with V = 85 g/m²d (V_{middle} = 150 – 15 g/m²d).

Wall paint	Vcs [g/m²d]	V [g/m²d]	sd [m]
IVB 90	259	> 680	0,076
IVB 28/A	271	> 680	0,069
Standard	67	85	0,2906
Silicate	306	> 680	0,068

Table 2: Water-vapour transmission properties of antimicrobial (IVB 90, IVB 28/A), standard and silicate wall paints

Another aspect, which is an interesting property for wall paints, is the cleaning effect. Photocatalytic coatings are known to have a self-cleaning effect. The self-cleaning effect was tested with the media blood, coffee, mustard, red wine, and black shoe polish. The test duration was 5 min and 30 min. After that, the test substances were wiped off. The new coatings IVB 90 and IVB 91 showed a very good cleanability for blood, no stain was visible. The other substances left stains on the coatings. The strongest stains were caused by coffee, followed by red wine and shoe polish. The mustard stains were the weakest. After one week of indoor lighting the stains for all substances, except for shoe polish, faded. On IVB 90 only the stain of shoe polish was still clearly visible. Due to this good cleanability and self-cleaning effect, IVB 90 and an improved version of IVB 90 (IVB 96) were chosen for a field test.

The resistance to abrasion and chemicals was also tested. The test was performed with the crockmeter. A good dry abrasion resistance of the new coatings was found. The abrasion resistance with water and neutral cleaning agent was also very good. Only the abrasion resistance with disinfection gel (Sterillium Gel Pure) was poor. The chemical resistance with disinfection gel was ok. The new coatings seem stable enough for the application as wall paints.

For long-term stability, various test scenarios were implemented. The temperature stability at 40 °C, lighting with visible LED light (49 mW/cm^2) and indoor light next to the window in the laboratory were tested for twelve weeks. In addition, artificial weathering with indoor filter was performed.

The new coatings are temperature stable at 40 °C. The other long-term tests lead to a change in colour. The largest change occurred in the first week of the testing with ΔE between 3.5 and 4.5. Then a slight increase was observed. After twelve weeks, the colour stabilised. The colour changed from slightly yellowish to a whiter shade.

After artificial weathering under indoor conditions, the new coatings showed chalking after 300 h. Due to this, at the end of the project investigations on the improvement of the long-term stability by modifying the formulation of the new coating were in the focus of the project. It was possible to improve the stability and reduce the chalking after artificial weathering by adding a more stable binder to the formulation of IVB 90.

Field Test

At the end of the project, the effectivity of the wall paints was tested in field tests. The field tests were performed in a kindergarten and two hospitals. Two walls were painted with two variants of photocatalytically active wall paints and one reference wall paint in the kindergarten (Figure 8). In the hospitals, acrylic substrates were painted and applied in picture frames. For testing the antimicrobial effectivity, smear tests were taken in periodic intervals. Additionally to that, parts of the test plates in the picture frames were cut off and their antiviral activity was tested. The analysis of the smear tests showed remarkable low concentrations of bacteria and fungal pathogens.

Figure 8: Test wall in the kindergarten

Summary
Most of the investigated coatings showed a high photocatalytic activity under indoor lighting. These coatings were investigated for an antiviral effect. Although the test setup is susceptible to faults, the antiviral activity of some coatings could be proven in laboratory. The antiviral effect due to the photocatalyst could be proven indirectly by ESR spectroscopy. The processability and mechanical stability of the coatings as wall paints were comparable to commercially available products. Some active coatings even show a high chemical resistance and a remarkable self-cleaning effect under indoor illumination. In field tests remarkable low concentrations of pathogens were found on the new wall paints.

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The project was carried out by the project partners Griwecolor GmbH, IBT Deutschland GmbH, Mikrobiologisches Labor Dr. Michael Lohmeyer GmbH, and Fraunhofer IPA.
The field tests were performed at St. Marien Kath. Kindergarten Döggingen (Döggingen), Oberschwabenklinik St. Elisabethen-Klinikum (Ravensburg), and the Kantonsspital Graubünden (Chur).

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