Photocatalytic plaster for indoor air purification

Authors:
Wolfram Maier, maxit Group, Germany, wolfram.maier@maxit.de
Claes-Göran Nilsson, maxit Group, Sweden, c-g.nilsson@maxit-group.com
Michael Holzer, maxit Deutschland, Germany, michael.holzer@maxit.de
Jan Lind, Cementa Research AB, Sweden, jan.lind@research.scancem.com
Kim Rosenbom, maxit Group, Portugal, kim.rosenbom@maxit.pt

Abstract: This work describes that by selecting suitable semiconductor-binder-combinations, it is possible to develop decorative thin layer final coat plasters with high photocatalytic activity. It is shown that this innovative plaster is able to degrade indoor air pollutants such as VOC’s, Ammonia and Formaldehyde efficiently even at low UV intensities. The simultaneous formation of harmless CO₂ indicates the complete mineralisation of organic compounds during this photocatalytic oxidation process. As demonstrated in a field test, the indoor air improving effect of the commercial product maxit airfresh is working in practice.

Keywords: photocatalytic plaster maxit air-fresh.

1. INTRODUCTION

It is well known that outdoor air in urban or industrial regions can be heavily polluted by substances such as volatile organic compounds (VOC’s). Recent studies show that indoor air is often more contaminated than the surrounding outdoor air. This is even more important taking into consideration that modern humans spend 80 % to 90 % of their lifetimes indoors [1]. Even if the concentrations of those indoor air pollutants are in a concentration range that cannot be smelled, they can cause symptoms like teary eyes, headache, etc. This impact of bad indoor climate on the health is known as "sick building syndrome" [2].

On the other hand, a new technology called “photocatalytic oxidation” is being used mainly in Japan [3] for water purification and other applications [4 - 7]. With the help of photocatalysts such as special TiO₂-modifications, light and oxygen from air, organic substances are said to be oxidised into CO₂ and water.

The task of this work was to find out if it is possible to develop an internal plaster having photocatalytic properties, so that indoor air pollutants such as VOC’s are decomposed into harmless CO₂ and water.

2. Development of a photocatalytic plaster for indoor air purification
2.1 Photocatalysts and photocatalytic oxidation

It is well known since a long time that there are substances that can promote chemical reactions as soon as they are activated by light, without being consumed themselves. These materials are nowadays called “photocatalysts” and they belong to the substance class of “semiconductors”.

The most well-known example of photocatalytic oxidation is probably the undesired paint chalking, which is caused by photocatalytic oxidation of the polymer binder [4]. In those cases, the TiO₂ pigment acts as a photocatalyst. In order to avoid this phenomenon, modern TiO₂ pigments are coated with silica, alumina and others.

On the other hand, since the seventies and eighties, there are research efforts to use this photocatalytic oxidation for degradation of organic pollutants into harmless CO₂ and water. This reaction is sometimes called “photomineralisation”:

\[
\text{Photocatalyst} \quad \text{light} \\
\text{Organic pollutants} + \text{O}_2 \quad \text{--------------------------} \quad \text{CO}_2 + \text{H}_2\text{O}
\]

There are many different semiconductors which are potential candidates for the use as photocatalysts, among them are CdS, ZnS, ZnO, WO₃ and others. But it turned out that nanoparticles of TiO₂ – preferably in the Anatase modification – have many advantages such as non-toxicity, stability, non-solubility and high photocatalytic activity. Therefore, most of the commercial available photocatalysts are based on TiO₂.

Activation of a semiconductor photocatalyst such as TiO₂ is achieved by absorption of light energy, resulting in the promotion of an electron e⁻ from the valence band into the conduction band, thus leaving a hole h⁺ in the valence band.

In humid air, the initial reactions will be that involving the hole with water to form highly reactive hydroxyl radicals and the reaction of the electron in the conduction band with oxygen creating hydroperoxy radicals.

\[
\text{Light} + \text{semiconductor} \quad \text{--------------------------} \quad \text{h}^+ + \text{e}^-
\]
\[
\text{h}^+ + \text{H}_2\text{O} \quad \text{--------------------------} \quad \cdot\text{OH} + \text{H}^+
\]
\[
\text{e}^- + \text{O}_2 + \text{H}^+ \quad \text{--------------------------} \quad \cdot\text{OOH}
\]

As soon as organic molecules come into contact with those highly reactive radicals, chain reactions are promoted leading to complete decomposition of the organic molecules and formation of CO₂ and water.

2.2 Indoor air pollutants

The effects of indoor air pollution have been dealt with by a large number of publications [8 - 10]. Volatile organic compounds may have effects ranging from unpleasant odour and irritation in the mucous membranes of eyes, nose and throat to effects on the nervous system and long-term effects. Substances causing allergic reactions and, most specifically, those with carcinogenic or mutagenic potential belong to this category.
There are no legal threshold values for concentrations of indoor air pollutants, but at present there are two different approaches for evaluation of indoor air quality: the health-related (or toxicological) evaluation concept [11] and the statistical evaluation concept [12].

Most of those concepts have in common to evaluate three substance groups, that are the concentrations of TVOC, Formaldehyde and Ammonia. In table 1, those groups are shown according to the Finnish FiSIAQ evaluation system [13]. The three indoor climate categories are defined as:

S1: individual indoor climate  
S2: good indoor climate  
S3: satisfactory indoor climate

<table>
<thead>
<tr>
<th>Substance</th>
<th>Category S1 max. conc. [µg/m³]</th>
<th>Category S2 max. conc. [µg/m³]</th>
<th>Category S3 max. conc. [µg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TVOC</td>
<td>200</td>
<td>300</td>
<td>600</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>30</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Ammonia</td>
<td>30</td>
<td>30</td>
<td>40</td>
</tr>
</tbody>
</table>

### 2.3 Suitable binders for photocatalytic coatings

The goal of this work was to develop a photocatalytic coating for walls and ceilings. For reasons mentioned in section 2.1, we focused on using TiO₂ as photocatalyst. But the most challenging task was to find suitable binders. Polymer dispersions, which are used as binders in paints and plasters, are known to be degraded by photocatalysts resulting in chalking [4]. Alkali-silicates (water glasses) are also commonly used binders for paints and plasters. But it is known that the alkali-ions are significantly reducing the activity of photocatalysts [14].

Furthermore there are ongoing efforts to use cement as a binder for photocatalytic coatings [15]. On the other hand, examinations at the TU Munich showed that the activity of photocatalyst in cement goes down significantly during cement carbonation [16]. For our own preliminary tests, we chose to use the speed of photo bleaching of the red organic dye “Rhodamin B” [17] in order to compare the photocatalytic activities with different binders. As an example, we produced powder mixtures containing 10 % TiO₂ photocatalyst and 90% binder (e.g. Portland cement or Calciumsulfate hemihydrate or other binders) as well as the reference samples without photocatalyst. After mixing with water, hardening and drying of the samples, two drops of Rhodamin B solution were put onto the surface of each sample. One drop was covered with a porcelain-cup so that it was not illuminated. All the samples were exposed at the same time to identical illumination conditions, e.g. ordinary laboratory light near the window. The speed of the bleaching of Rhodamin B can be watched visually or measured with a colorimeter.
With this simple test method, we surprisingly found that the Rhodamin bleached fastest on the photocatalyst containing samples with gypsum as binder [18]. As the stains on the samples without photocatalyst as well as the covered stains did not bleach under those conditions, the fast bleaching on the gypsum samples can indeed be interpreted as photocatalytic oxidation.

This general finding was the starting point to develop decorative gypsum based thin layer final coat plasters with photocatalytic properties.

2.4 Measurements for proving the degradation of indoor air pollutants

In the next step, it was necessary to measure the degradation of indoor air pollutants in laboratory scale. The measurements with Formaldehyde and Ammonia were performed at the “Institut für Umweltschutz und Agrikulturchemie” and the tests with Acetaldehyde and Butanol were performed at “Cementa Research AB”. If not stated otherwise, the photocatalytic gypsum plasters are called “maxit airfresh”

2.4.1 Degradation of Ammonia and Formaldehyde

Airfresh samples with and without photocatalyst were applied on glass plates and put into excicators, which were used as test chambers. Ammonia or Formaldehyde was injected into the excicators and their concentrations were determined after defined time intervals. These experiments were carried out under ordinary laboratory conditions without any additional illumination.

As can be seen in diagrams 1 and 2, there is a small decrease of the concentrations of Ammonia or Formaldehyde even for airfresh without catalyst. This is probably due to absorption of those gases at the surface of the test chamber and the sample. But the decrease of both indoor air pollutants is significantly faster in case of airfresh with photocatalyst.
Diagram 1: Degradation of Formaldehyde, initial concentrations set as 100 %

Diagram 2: Degradation of Ammonia, initial concentrations set as 100 %

2.4.2 Degradation of Acetaldehyde and Butanol
Again, airfresh samples with and without photocatalyst were applied on glass plates and put into the test chambers. Acetaldehyde or Butanol was injected into the test chambers and their concentrations were determined after defined time intervals either by GC or IR spectroscopy.
As can be seen on diagrams 3 and 4, there is again an initial decrease of the concentrations of the test substances even for airfresh without catalyst, which is due to absorption. But in case of airfresh with photocatalyst, a very fast and complete removal of the indoor air pollutants takes place.
Diagram 3: Degradation of Butanol, initial concentration = 10 ppm

Diagram 4: Degradation of Acetaldehyde, initial concentrations set as 100 %

2.4.3 CO₂ detection as a prove for photomineralisation
In previous sections it was shown that indoor air pollutants such as Formaldehyde and the VOC’s Acetaldehyde and Butanol can be removed from the gas phase very efficiently with airfresh. But it was not proven yet that those substances are really completely mineralised to harmless CO₂. In order to be able to prove this, a special test equipment
was built up at Cementa Research. This closed loop flow system enables to continuously monitor the concentrations of the test substance (Acetaldehyde) and CO₂ simultaneously by FTIR spectroscopy (path length of the gas cell: 8 m).

As can be seen from diagram 5, indeed the concentration of Acetaldehyde goes down from 150 ppm to zero and at the same time, the concentration of CO₂ goes up from approx. 550 ppm to approx. 850 ppm. This is according to theory, because from 1 molecule Acetaldehyde, 2 molecules of CO₂ are being produced.

In a second test (diagram 6) Cementa research was able to prove that only with the airfresh containing photocatalyst, CO₂ is being produced during the degradation of Acetaldehyde, whereas no CO₂ was formed with airfresh containing no photocatalyst.

2.4.4 Impact of the UV-intensity on the speed of photocatalytic oxidation

The speed of the CO₂ production during photocatalytic oxidation of Formaldehyde was used as a measure for the photocatalytic activity of airfresh using different light sources. The UV-intensity was determined with a Lutron UV-meter (290 – 390 nm).

As expected, the speed of CO₂ production is faster, the higher the UV intensity is. But on the other hand, the airfresh shows a high photocatalytic activity also under illumination with ordinary light sources such as fluorescence tubes or diffuse natural light behind a window (Table 2).

Diagram 5: Simultaneous decrease of Acetaldehyde- and increase of CO₂-concentration
Diagram 6: CO₂ production during PCO of Acetaldehyde only for airfresh containing photocatalysts

Table 2 – Speed of CO₂ production [ppm/h] during degradation of Formaldehyde

<table>
<thead>
<tr>
<th>Light source</th>
<th>Brand name</th>
<th>UV intensity [µWcm²]</th>
<th>New CO₂ production [ppm/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence tube</td>
<td>Osram 965</td>
<td>21</td>
<td>70</td>
</tr>
<tr>
<td>Fluorescence tube</td>
<td>Osram 840</td>
<td>37</td>
<td>100</td>
</tr>
<tr>
<td>Diffuse natural light</td>
<td>0,5 m behind window</td>
<td>80</td>
<td>240</td>
</tr>
<tr>
<td>Solarium tube</td>
<td>Osram eversun</td>
<td>570</td>
<td>680</td>
</tr>
</tbody>
</table>

2.4.5 Indoor air improving effect of airfresh in practice

In order to show the indoor air improving effect of airfresh in practice, a field test at the Radisson Grand Hotel in Helsingborg, Sweden, was carried out. Two identical non-smokers rooms were chosen, one of them being plastered with airfresh and the other left without airfresh.

Passive collectors (active Charcoal tubes) were fixed in both rooms at the same time and left there for two weeks. The analysis and evaluation was performed by “Umweltanalytik Ingenieurbüro Oetzel”
It turned out that even in the room without airfresh, the concentration of VOC was low (67 µg/m³). But compared to that, in the room with airfresh, the VOC concentration was reduced down to nearly 1/3 (26 µg/m³).

It is also worth to mention that the concentrations of all individual substances from different substance groups (Aromatic, aliphatic and chlorinated hydrocarbons, Terpenes and others) are significantly lower in the room with airfresh.

In table 3, the concentrations of some selected substances are given.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Room without airfresh</th>
<th>Room with airfresh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>8,9</td>
<td>2,3</td>
</tr>
<tr>
<td>Pinen</td>
<td>10,0</td>
<td>1,5</td>
</tr>
<tr>
<td>Tetrachlorethan</td>
<td>6,3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Benzene</td>
<td>1,7</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Methylcyclohexan</td>
<td>4,4</td>
<td>2,2</td>
</tr>
<tr>
<td>n-Butylacetate</td>
<td>3,4</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>TVOC</td>
<td>67,0</td>
<td>26,3</td>
</tr>
</tbody>
</table>

3. Summary

The task of this work was to examine the possibility to develop a photocatalytic plaster which is able to improve indoor air quality. It could be shown that by choosing a suitable binder, which is neither being destroyed photocatalytically nor reducing the activity of the photocatalyst, it is possible to develop final coat plasters with high photocatalytic activity.

It was shown that this plaster is able to degrade indoor air pollutants such as VOC’s (Butanol, Acetaldehyde), Ammonia and Formaldehyde efficiently even under low UV intensities. The simultaneous degradation of Acetaldehyde and formation of harmless CO₂ indicates the complete mineralisation of organic compounds during this photocatalytic process. As demonstrated in a field test, the indoor air improving effect of the commercial product maxit airfresh is working in practice.

4. References


[14] Ref. [3], page 53