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## **An experimental study on the removal of NO and NO<sub>2</sub> content from ambient air using the photocatalytic reaction on the surface of Protectam FN® photocatalytic coating.**

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### **Introduction**

The study focuses on the possibility of removing nitrogen oxide pollutants from the air using photocatalytic technology. ISO 22197-1 and proposed CEN standards, as well as some modified methodology, were used.

### **A. Analysis of the initial situation**

The primary product of combustion in motor vehicle engines is nitrous oxide (NO). This oxide may be further oxidized into nitric oxide (NO<sub>2</sub>). The rate of this secondary oxidation depends on a number of meteorological parameters (intensity of solar radiation, humidity, presence of pollutants in the air, air flow). NO and NO<sub>2</sub> oxidation is not instantaneous but all the NO present in the air oxidizes to NO<sub>2</sub> in a few hours. Therefore the proportion of both oxides varies considerably throughout a given day. In the morning peak hours NO significantly prevails and in the afternoon, NO<sub>2</sub>.

This fact implies *that it is necessary to substantially decrease NO concentrations because NO<sub>2</sub> is created solely from NO and all NO is converted to NO<sub>2</sub>*. Therefore, if we can remove NO from the air, the subsequent concentration of NO<sub>2</sub> is reduced as well, because there is nothing else from which it can be created.

This decrease of NO can be achieved using photocatalysis, on a photocatalytically active surface. When using the photocatalytic process, NO is gradually oxidized to nitric acid, which eventually is neutralized in the presence of alkali metal ions or alkali soil into various nitrates.

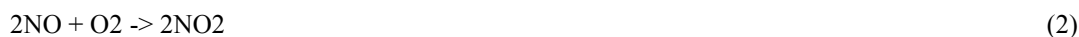


(NO<sub>2</sub>)<sub>ads</sub> is an adsorbed product of the first step in oxidation of NO on the surface of the photocatalyst, which is subsequently oxidized to nitric acid or nitrates.

To a limited extent, if there are enough water droplets in the air (rain or artificial sprays of water, e.g. fountains) the breakdown of NO<sub>2</sub> to nitric acid and NO occurs according to the equation



This reaction is very advantageous to the environment because there is a radical reduction in NO<sub>2</sub> concentrations in the air. Because of the subsequent oxidation of NO to NO<sub>2</sub>



it is possible to remove even more NO<sub>2</sub> according to reaction (1).

*Note: Although there are disputes as to whether NO or NO<sub>2</sub> is more dangerous, nitric oxide exhibits significant toxicity to plants and also binds to blood, causing internal suffocation like CO.*

On sunny days at high concentrations of nitrogen oxides, ground ozone (O<sub>3</sub>) is formed due to the action of ultraviolet radiation B (UVB) on the molecules of organic compounds. Although it is beyond the scope of this study, it is necessary to emphasize that photocatalysis effectively oxidizes such organic substances into harmless mineral products (H<sub>2</sub>O and CO<sub>2</sub>), thereby preventing an increase of ozone concentrations in the air.

## **B. Reduction of pollutants using photocatalysis and the methodology of the experimental studies**

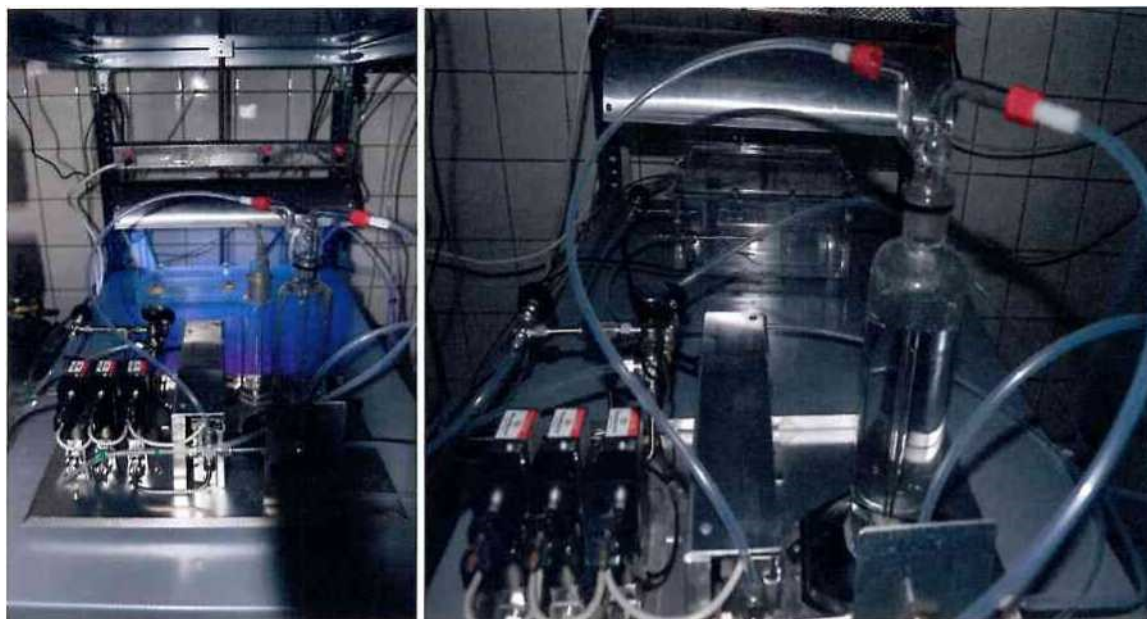
The experimental study whose results are presented in the attached protocol (see Appendix 1) show that when we use photocatalysis **it is possible to significantly reduce both nitrogen oxides in the air**. The decrease in the total **concentration of nitrogen oxides on contact with the photocatalytic surface (i.e. the decrease of the total NO and NO<sub>2</sub> concentration)** is expressed by a **DeNO<sub>x</sub> factor** that reaches 20-50% in a steady state, i.e. at a concentration of 100 ppb the decrease in NO and NO<sub>2</sub> is 20-50 ppb.

This was a very systematic study that - unlike the commonly conducted tests in accordance with ISO or CEN standards - reflects a number of important influences and comprehensively describes all the phenomena occurring on the surface of the photocatalyst.

The parameters of the process are as follows:

1. The input NO concentration - in contrast to the standards, which assume a concentration of 1 ppm, the study also focuses on the lower concentration of 100 ppb that is commonly found in polluted air in certain locations.
2. The influence of air flow - laboratory experiments were conducted simultaneously in two reactors:
  - in a reactor with laminar flow (ref. no. 112)
  - in a flowing, ideally mixed reactor (of the CSTR type) where a high degree of turbulence is modelled.

In both reactors the sample photocatalytic surface was 50 cm<sup>2</sup>, the volume of air flow was 3 L/min and the UV radiation intensity was 1.5 mW/cm<sup>2</sup>. The delay (space time) is 1 min, the space rate was 1 min<sup>-1</sup>. The space velocity is at the ratio of the volume flow rate (in e.g. L/min) and the volume of the reactor (in litres). Therefore, the unit is min<sup>-1</sup>. The space time is the reciprocal value of space velocity (the unit is time, e.g. min).



*Fig. 1 Photocatalytic apparatus for the study of nitrogen oxides removal from the air, equipped with a laminar gas flow reactor (on the left) and a turbulent gas flow reactor (on the right).*

3. The length of the experiment - instead of short-term experiments of in 3-5 hours in accordance with the usual standards, the experiments in the study were prolonged to 25 hours. Similar long experiments are not commonly conducted because they are expensive and more difficult because of the enormous consumption of gas. ***The prolongation of the experiments allowed reaching a steady state where the rate of the photocatalytic reaction was constant as well as more realistic quantitative results.***

4. Experiments with nitrogen oxide that have never before been conducted - according to the data of the Czech Hydrometeorological Institute the limit of concentration of NO<sub>2</sub> is 40 µg/m<sup>3</sup>. The absolute highest concentration recorded in the field was in Prague - Smíchov, 219 µg/m<sup>3</sup>. In our experiments we chose a concentration of NO<sub>2</sub> of 0.1 ppm, which corresponds to 190 µg/m<sup>3</sup>. The reason for choosing such a significantly higher concentration is are the critical dispersion conditions that may occur. The data are from the Czech Hydrometeorological Institute from 2013.
5. Inclusion of the impact of adsorption and desorption of the nitrogen oxides on the photocatalytic surface.
6. Impact of the substrate on which the photocatalytic surface is applied. The experiments were conducted on common construction materials (façade coating on plaster and concrete, supplied by the party contracting for the study). ***The results of the experiment can be compared to experiments on glass that exclude any influence of the substrate*** (i.e., having minimum roughness and chemically inert). This comparison was measured in an independent study (see Appendices 2, 3, 4).
7. Impact of the thickness of the applied photocatalytic coatings of Aeroxide TiO<sub>2</sub> P25 and Protectam FN®. The comparison between the two coatings was measured in an independent study (see Appendix 3).
8. Comparison of particular product types with a pure photocatalyst (Aeroxide TiO<sub>2</sub> P25) that has very high photocatalytic effectiveness and is recognized as an industry standard). The comparison was measured in an independent study (see Appendix 4).
9. Assessment of the final products of photocatalytic oxidation captured on the photocatalytic surface of the sample. The comparison was measured in an independent study.

### **C. Analysis of the experimental study results**

The analysis was carried out in accordance with the aforementioned parameters.

1. Photocatalysis at low NO concentrations that correspond to the real pollutant situation in the field, taking into account the critical situation, is an independent concentration process. That means that when contaminated air comes into contact with the photocatalytically active surface, the same percentage decrease in nitrogen oxides concentration occurs as in the field. The conversion factor, i.e. the proportion of the NO oxidized on the monitored surfaces according to reaction (2), which is the first step in the removal of nitrogen oxides, averages 50%. Because the DeNO<sub>x</sub> factor reaches values from 0.02 to 0.05 ppm depending on the substrate (plaster or concrete), at the initial concentration of 0.1 ppm the photocatalytic process removes 20-50% of nitrogen oxides from the air.

*Note: In the ISO 22197-1 test with an input concentration 1 ppm of NO, the minimum parameter for air cleaning is a decrease in NO concentration of 0.5 µmol/m<sup>2</sup>/h. All the measured samples showed much higher efficiency.*

2. Comparison of the impact of laminar and turbulent flows on the effectiveness of the process showed that the ***effect of the flow is not critical at common concentrations***. With a photocatalytic surface applied on concrete, at an initial concentration of 0.1 ppm of NO, the DeNO<sub>x</sub> factor was virtually the same in both cases - 0.04 ppm, i.e. a 40% decrease in NO<sub>x</sub>.
3. Study of the impact of the length of the experiment showed that the common short-term experiments of 3-5 hours do not provide completely reliable results, because during long term experiments significant changes in activity occurred after this time. To achieve an equilibrium steady state approximately 20 hours are necessary. Therefore activity was evaluated only after achieving this steady state, i.e. in the range of 15-25 hours.
4. Experiments with nitrogen oxides (NO<sub>2</sub>) showed that it is possible to achieve a significant decrease in their concentration using photocatalysis. The DeNO<sub>x</sub> factor is typically 0.04 ppm at the initial concentration of 0.1 ppm, i.e. 40 %. It turns out that the humidity of air is very important (with 100% relative humidity the decrease in concentration is higher than at 50% relative humidity). The experiments conducted with NO<sub>2</sub> show that the retroactive reduction of NO<sub>2</sub> to NO is negligible.
5. Before the photocatalytic experiments, NO or NO<sub>2</sub> were always absorbed onto the surface of the photocatalyst so as to achieve balance (i.e. to prevent the loss of nitrogen oxides due to adsorption during the measurement of activity). Thus ***the removal of nitrogen oxides in this study was due solely to photocatalysis***,

***not to physical adsorption onto the surface.*** It was found after the photocatalytic experiments that the quantity of nitrogen oxides desorbed from the surface of the photocatalyst is negligible.

6. Measurements of the photocatalytic layers applied on various substrates show that the impact of the substrates commonly used in construction on the photocatalytic surface is not very significant. Comparison of the impact of substrates shows that the most important thing is the thickness of the surface. The chemical nature of the substrate does not influence the measure as much and the results for plaster and concrete are almost the same. However, on glass the active surface available is approximately half as much as on concrete or plaster due to its smoothness, which is reflected proportionately in the measurement of the photocatalytic activity. For example, the effectiveness for 3 layers of the photocatalytic coating using Protectam FN® is 2x higher on plaster than on glass.

7. The total thickness of the photocatalytic layer influences its activity. There is an increase in activity in the range from 1 to 7 applied layers. As the number of layers applied increases from 1 layer to 7, the conversion of NO was almost six times greater. The 3 layers recommended by the manufacturer is a reasonable compromise between high effectiveness and acceptable price.

8. The comparison of the products Protectam FN® with the pure photocatalyst Aeroxide TiO<sub>2</sub> P25 shows that the Protectam products have very high efficiency, which is even higher than the efficiency of the pure photocatalyst P25. For example the photocatalytic efficiency of three layers of Protectam FN® is 25% higher than that of three layers of P25. The morphology of the layer and the openness of the surface have a positive impact when the Protectam FN® products are used.

9. The independent study using the Dionex ICS-2000 methodology of ion chromatography showed that the final product of NO oxidation on the photocatalytic surface is nitric acid. Formation of nitrous acid has not been detected at all.

#### **Conclusion:**

The experimental study conducted showed that the photocatalytic oxidation on the surface of the photocatalytic coating Protectam FN® is an effective method for the removal of nitrogen oxides from contaminated air. The experiments showed that in a steady state and under conditions simulating a real environment the monitored surfaces are able to decrease the concentration of nitrogen oxides (NO<sub>x</sub>) in the air by 20-50% of the original value. This effectiveness is not significantly influenced by process parameters such as air flow and the nature of the substrate on which the coating is applied, and is independent of the amount of concentration of nitrogen oxides under normal conditions. The nitrogen oxides are oxidized up to their highest oxidation state, i.e. to nitric acid (or nitrates) and undesirable nitrous acid is not formed at all.



Ing. Jiří Rathouský CSc., Chairman of the Scientific Board of CSAP

Prague, 22 June 2015

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## Protocol from the test of the photocatalytic activity in samples of Protectam FN1 and FN2 in the removal of nitrogen oxides

Experimental conditions:

### substrate

- concrete 50 cm<sup>2</sup>
- plaster 50 cm<sup>2</sup>

photocatalytic coating (see composition in the safety data sheet of the manufacturer - Advanced Materials-JTJ, S.r.l.)

- *Protectam FN1*
- *Protectam FN2*

### reactor

- laminar gas flow (Re=12), ISO 22197-1
- turbulent gas flow (ideal mixed flow reactor) reactor in accordance with the proposed CEN standard

### concentration NO/air

- 1.0 ppm
- 0.1 ppm

### concentration NO<sub>2</sub>/air

- 0.1 ppm

### carrier gas

- air

### flow

- 3.0 L/min (NO, NO<sub>2</sub>)
- 2.0 L/min (NO<sub>2</sub>)

intensity of radiation 365 nm

- 1.5 mW/cm<sup>2</sup>

### relative humidity of gas mixture

- 50%
- 0 and 100% (NO<sub>2</sub>)

### length of the experiment

- in accordance with ISO and CEN - 5 hours
- for quality results - up to 25 hours

### results based on the aforementioned conditions of the test

- using the DeNO<sub>x</sub> coefficient (real decrease of total concentration of nitrogen oxides - NO<sub>x</sub> in the air in percent)
- the absolute quantity of nitric oxide removed per 1 m<sup>2</sup> of the photocatalytic surface per hour is stated in mg/m<sup>2</sup>/h and μmol/m<sup>2</sup>/h.

| initial concentration NO/air <b>1 ppm</b> which corresponds to 45 mg NO/m <sup>2</sup> /h*** |                     |  |  |                     |  |  |
|--|---------------------|--|--|---------------------|--|--|
| sample   | laminar gas flow    |  |  | turbulent gas flow  |  |  |
|  | DeNO <sub>x</sub> % | decrease of NO <sub>x</sub> mg/m <sup>2</sup> /h**** | decrease of NO <sub>x</sub> μmol/m <sup>2</sup> /h****<br>(x times in comparison with minimum parameter) | DeNO <sub>x</sub> % | decrease of NO <sub>x</sub> mg/m <sup>2</sup> /h**** | decrease of NO <sub>x</sub> μmol/m <sup>2</sup> /h**** |
| concrete @FN1<br>RH=50%)   | 10<br><b>8</b>      | 4.6<br><b>3.6</b>                                    | 153 (306 x)**<br><b>120 (240 x)</b>  | 43                  | 19.1   | 640 (1280 x)   |
| concrete @FN2<br>(RH=50%)  | 11                  | 5.0  | 168 (236 x)  | 43                  | 19.4   | 650 (1300 x)   |
| plaster @FN1 (RH=50%)  | 27                  | 12.2   | 407 (814 x)  | 54                  | 24.9   | 830 (1660 x)   |
| plaster @FN2 (RH=50%)  | 25<br><b>8</b>      | 11.3<br><b>3.6</b>                                   | 377 (754 x)<br><b>120 (240 x)</b>  | 35                  | 15.9   | 530 (1060 x)   |

\* The data in bold obtained from long-term experiments (after reaching the steady state)

other data obtained from experiments of a length according to ISO and CEN standards

\*\* The data in parentheses are calculated from the total balance of nitrogen oxide because they better reflect the real situation in the field. The minimal parameter for air cleaning according to the standard ISO 22197-1 applies only to the concentration of NO. If this parameter was used in the same way, the data in parentheses would be 2-3x higher.

\*\*\* The mass flow rate of NO is related of 1 m<sup>2</sup> of the photocatalytic coating.

\*\*\*\* The decrease in the mass or molar flowrate of NO<sub>x</sub> is related of 1 m<sup>2</sup> of the photocatalytic coating

| initial concentration NO/air <b>0.1 ppm</b> which corresponds to 4.5 mg NO/m <sup>2</sup> /h *** |                  |  |  |               |   |   |
|--|------------------|--|--|---------------|---|---|
| sample   | laminar gas flow |  |  | turbulent gas |   | flow  |
|  | DeNOx %          | decrease of NO <sub>x</sub> mg/m <sup>2</sup> /h**** | decrease of NO <sub>x</sub> μmol/m <sup>2</sup> /h**** | DeNOx %       | decrease of NO <sub>x</sub> mg/m <sup>2</sup> /h **** | decrease of NO <sub>x</sub> μmol/m <sup>2</sup> /h **** |
| concrete @FN2 (RH=50%)   | 50               | 2.3  | 75   | 50            | 2.3   | 75  |
|  | <b>40</b>        | <b>1.8</b>   | <b>60</b>  |               |   |   |
| plaster @FN2 (RH=5 0%)   | 20               | 0.9  | 30   | 30            | 1.4   | 47  |

\*\*\* The mass flow rate of NO is related of 1 m<sup>2</sup> of the photocatalytic coating.

\*\*\*\* The decrease in the mass or molar flowrate of NO<sub>x</sub> is related of 1 m<sup>2</sup> of the photocatalytic coating.

| initial concentration NO <sub>2</sub> /air - <b>0.1 ppm</b> which corresponds to 6.9 mg NO <sub>2</sub> /m <sup>2</sup> /h *** |                  |  |  |               |   |   |
|--|------------------|--|--|---------------|---|---|
| sample   | laminar gas flow |  |  | turbulent gas |   | flow  |
|  | DeNOx %          | decrease of NO <sub>x</sub> mg/m <sup>2</sup> /h**** | decrease of NO <sub>x</sub> μmol/m <sup>2</sup> /h**** | DeNOx %       | decrease of NO <sub>x</sub> mg/m <sup>2</sup> /h **** | decrease of NO <sub>x</sub> μmol/m <sup>2</sup> /h **** |
| concrete @FN2 (RH=50%)   | 20               | 1.4  | 30   | 50            | 3.5   | 76  |
| concrete @FN2 (RH=100%)  | 40               | 2.8  | 61   |               |   |   |
| plaster @FN 1 (RH=0%)  | 3                | 0.02   | 0.4  |               |   |   |
| plaster @FN2 (RH=0%)   | 60               | 4.1  | 90   |               |   |   |
| plaster @FN2 (RH=50%)  |                  |  |  | 70            | 4.8   | 104   |
| plaster @FN2 (RH=100%)   | 40               | 2.8  | 61   |               |   |   |

\*\*\* The mass flow rate of NO<sub>2</sub> is related of 1 m<sup>2</sup> of the photocatalytic coating.

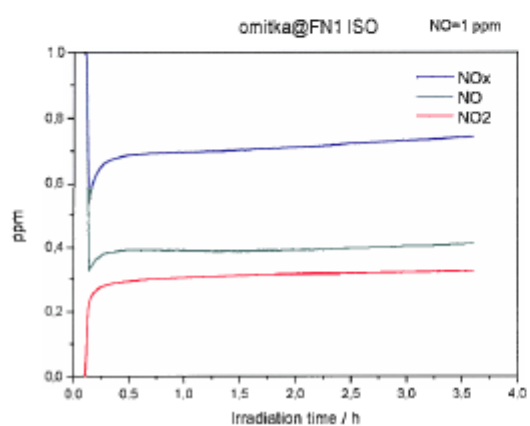
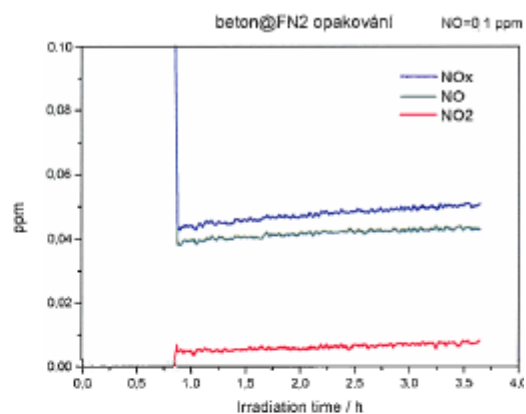
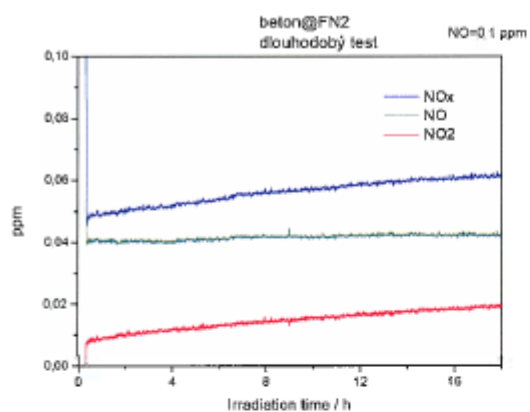
\*\*\*\* The decrease in the mass or molar flowrate of NO<sub>x</sub> is related of 1 m<sup>2</sup> of the photocatalytic coating.

## APPENDIX 1

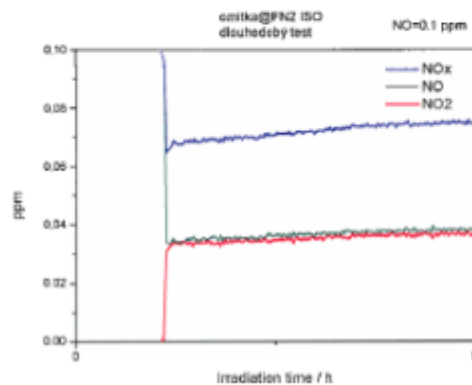
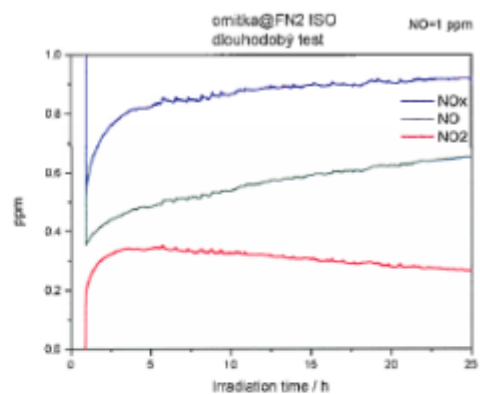
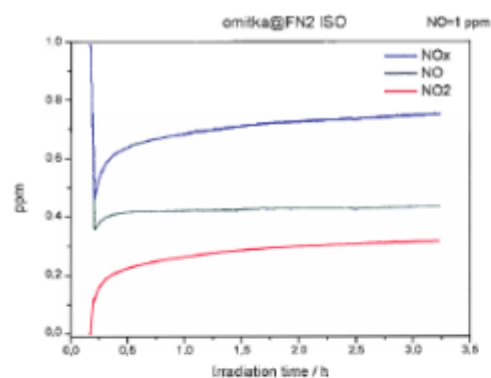
Times of NO, NO<sub>2</sub>, NO<sub>x</sub> concentrations.

The beginning of curves are the moment of exposure to ultraviolet light radiation.

Laminar gas flow - NO  
Initial concentration NO = 1 ppm  
Initial concentration NO = 0.1 ppm



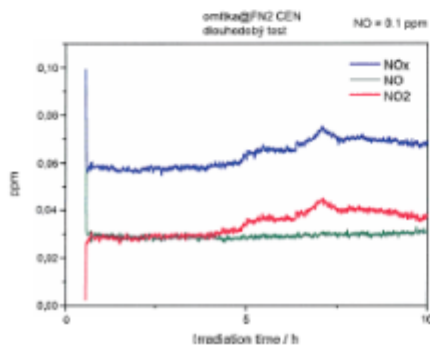
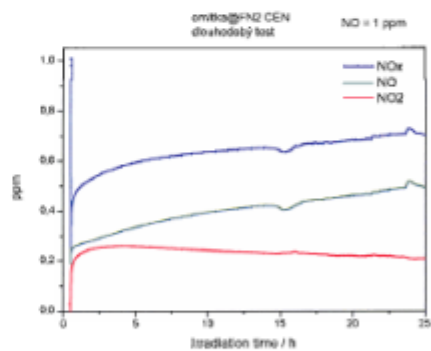
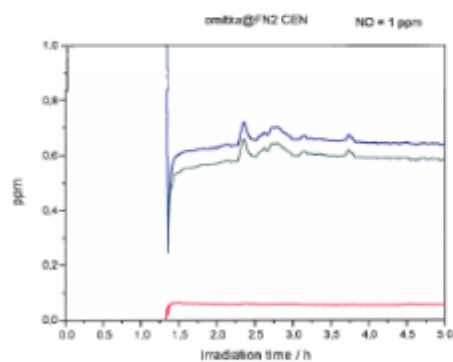
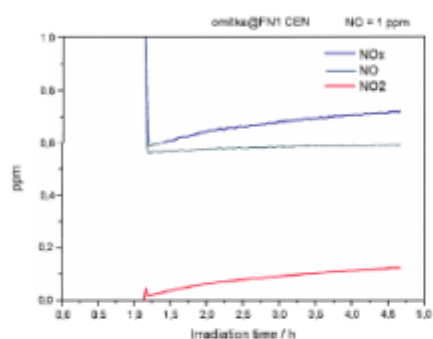
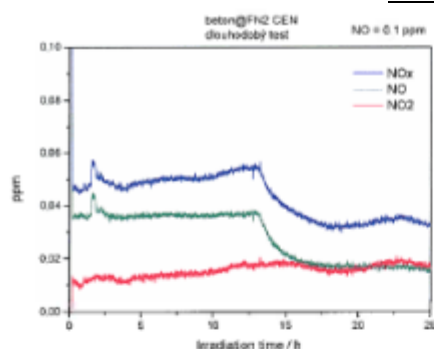
|  |   |
|--|---|
| beton@FN2<br>dlouhodobý test<br>NO=0.1 ppm | concrete @FN2<br>long-term test<br>NO=0.1 ppm |
| beton@FN2 opakování                        | concrete @FN2 repetition                      |
| omítka@FN1 ISO                             | plaster @FN1 ISO                              |



|                    |                    |
|--------------------|--------------------|
| omítka@FN1 ISO     | plaster @FN1 ISO   |
| omítka@FN2 ISO     | plaster @FN2 ISO   |
| Dlouhodobý test    | long-term test     |
| Doba ozařování / h | radiation time / h |



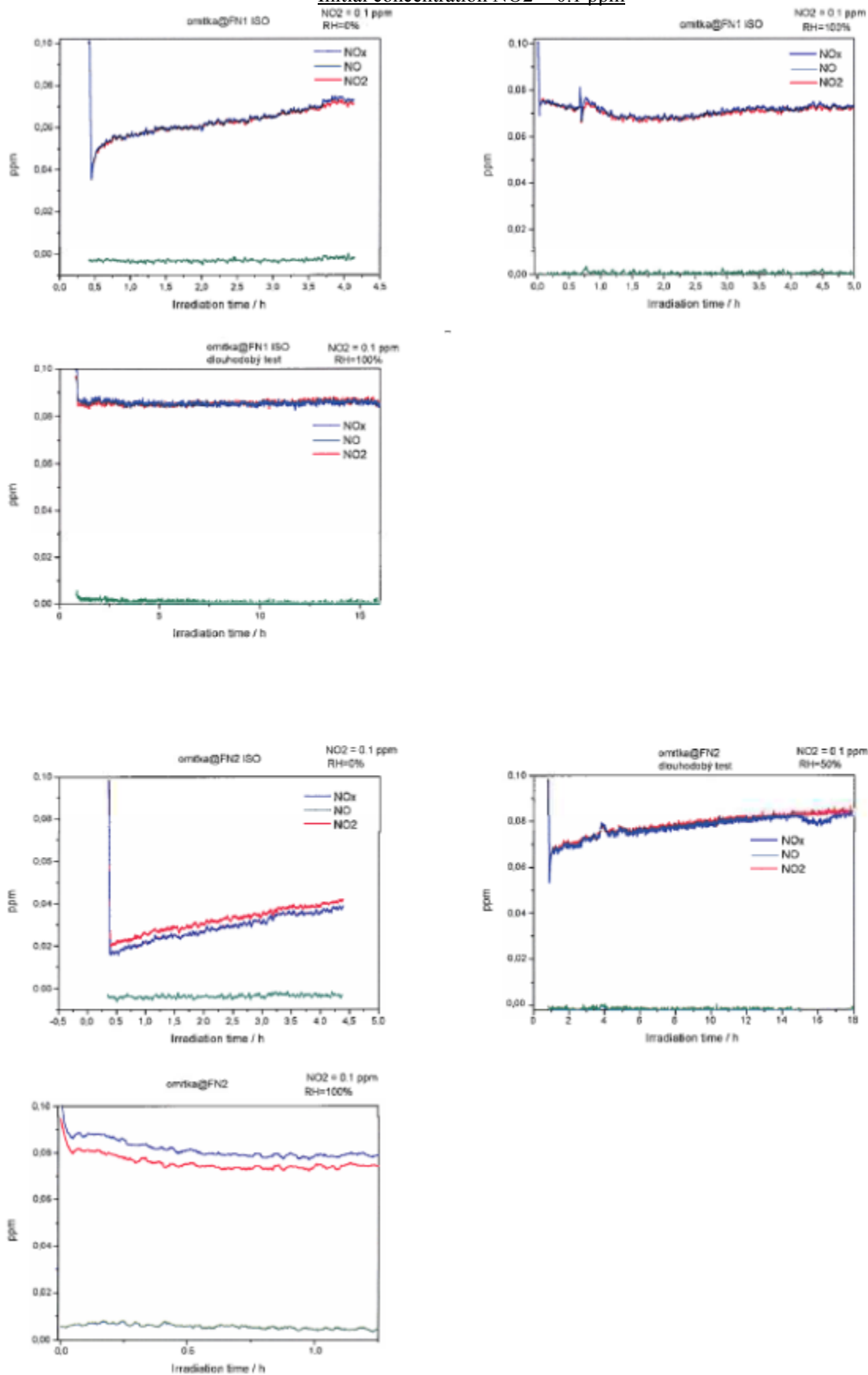
Turbulent gas flow - NO  
Initial concentration NO = 1 ppm  
Initial concentration NO = 0.1 ppm



|                 |                  |
|-----------------|------------------|
| beton@FN2 CEN   | plaster @FN2 CEN |
| Dlouhodobý test | long-term test   |
| omítka@FN1 CEN  | plaster @FN1 CEN |
| omítka@FN2 CEN  | plaster @FN2 CEN |

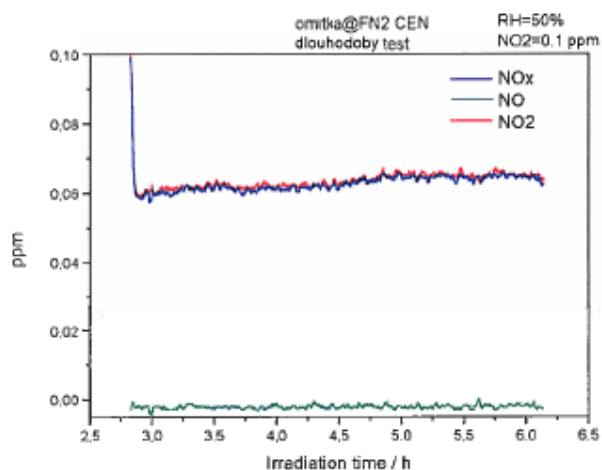
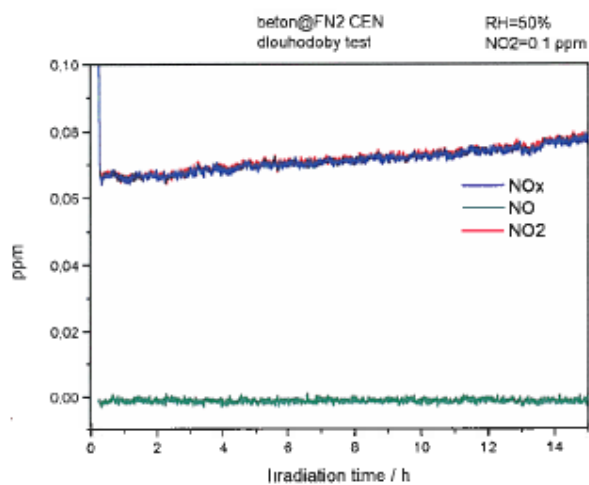
|                    |                    |
|--------------------|--------------------|
| NO = 1 ppm         | NO = 1 ppm         |
| Doba ozařování / h | radiation time / h |

Laminar gas flow - NO<sub>2</sub>  
Initial concentration NO<sub>2</sub> = 0.1 ppm




|                         |                          |
|-------------------------|--------------------------|
| omítka@FN1 ISO          | plaster@FN1 ISO          |
| Dlouhodobý test         | long-term test           |
| omítka@FN2 ISO          | plaster@FN2 ISO          |
| omítka@FN2 ISO, RH=100% | plaster@FN2 ISO, RH=100% |

Turbulent gas flow - NO<sub>2</sub>  
Initial concentration NO<sub>2</sub> = 0.1 ppm

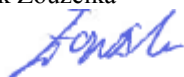


|                 |                  |
|-----------------|------------------|
| beton@FN2 CEN   | concrete@FN2 CEN |
| Dlouhodobý test | long-term test   |

Prague, 22 June 2015

  
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## APPENDIX 2



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### Protocol from the test of the photocatalytic activity in samples of Protectam FN1, FN2 and FN3 supplied by the company Advanced Materials-JTJ, s.r.o., Kamenné Žehrovice

| Standard         | Sample | Initial conversion (%) | Conversion in steady state (%) |
|------------------|--------|------------------------|--------------------------------|
| ISO 22197-1:2007 | FN1    | 50                     | 21                             |
| CEN              | FN1    | 27                     | 13                             |
| ISO 22197-1:2007 | FN2    | 38                     | 23                             |
| CEN              | FN2    | 58                     | 15                             |
| ISO 22197-1:2007 | FN3    | 45                     | 40                             |
| CEN              | FN3    | 39                     | 24                             |

Table: Results of the test of photocatalytic activity.

The results of the photocatalytic activity measurements of the supplied samples of Protectam FN1, FN2, FN3 according to the ISO 22197-1:2007 standard and the proposed CEN standard. The measurements according to the ISO standard were conducted in a reactor with laminar gas flow. The test according to the CEN proposed standard were conducted in the flow mixing reactor with a volume of 3.5 l, a space rate of  $0.874 \text{ min}^{-1}$  and space time of 1.14 min. The space velocity is at the ratio of the volume flow rate (in e.g. L/min) and the volume of the reactor (in litres). Therefore, the unit is  $\text{min}^{-1}$ . The space time is the reciprocal value of space velocity (the unit is time, e.g. min).

The results of the tests are based on conversion of nitrous oxide corresponding to the proportion of the nitric oxide in the gas mixture that was photocatalytically oxidized.

An overview of the results obtained is shown in the table above. The initial conversion corresponds to the maximum value achieved in the short-term interval after initiation of the test.

The conversion in the steady state is the proportion of oxidized nitric oxide in the air after approximately 2-3 hours, which is practically constant. For operational reasons the intensity of the UV radiation chosen for the reactor with laminar gas flow was  $0.9 \text{ mW/cm}^2$  with a wavelength of 365 nm. In the mixing reactor the intensity of the UV radiation was  $1.0 \text{ mW/cm}^2$ . The proportion of conversion in the steady state as measured in the reactor with laminar flow and in the mixing reactor was the same for all samples - approximately 1.6.

Prague, 6 May 2014

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# APPENDIX 3



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## Protocol from the test of photocatalytic activity in samples of Protectam FN3 supplied by the company Advanced Materials-JTJ, s.r.o., Kamenné Žehrovice

| Standard         | Sample       | Initial conversion (%) | Conversion in steady state (%) |
|------------------|--------------|------------------------|--------------------------------|
| ISO 22197-1:2007 | FN3 1 layer  | 15                     | 10                             |
| ISO 22197-1:2007 | P25 1 layer  | 9                      | 4                              |
| ISO 22197-1:2007 | FN3 2 layers | 20                     | 13                             |
| ISO 22197-1:2007 | P25 2 layers | 17                     | 6                              |
| ISO 22197-1:2007 | FN3 3 layers | 25                     | 20                             |
| ISO 22197-1:2007 | P25 3 layers | 19                     | 16                             |
| ISO 22197-1:2007 | FN3 4 layers | 33                     | 25                             |
| ISO 22197-1:2007 | P25 4 layers | 30                     | 21                             |
| ISO 22197-1:2007 | FN3 5 layers | 40                     | 29                             |
| ISO 22197-1:2007 | P25 5 layers | 35                     | 25                             |
| ISO 22197-1:2007 | FN3 6 layers | 70                     | 54                             |
| ISO 22197-1:2007 | P25 6 layers | 58                     | 41                             |
| ISO 22197-1:2007 | FN3 7 layers | 80                     | 60                             |
| ISO 22197-1:2007 | P25 7 layers | 65                     | 53                             |

Table: Results of the test of photocatalytic activity.

Measurements are of the photocatalytic activity of the supplied samples of Protectam FN3 and Aeroxide TiO<sub>2</sub> P25 (Evonik Industries - pure active nano-material TiO<sub>2</sub> - an industry-recognized standard) according to standard ISO 22197-1:2007.

Measurements according to the ISO standard were conducted in a reactor with laminar gas flow. The results of the tests are based on conversion of the nitric oxide corresponding to the proportion of the nitric oxide in the gas mixture that was photocatalytically oxidized. An overview of the results obtained is shown in the table. The initial conversion corresponds to the maximum value achieved in the short-term interval after initiation of the test. The conversion in the steady state is the proportion of the nitric oxide after approximately 2-3 hours, which is practically constant. For operational reasons the intensity of the UV radiation chosen for the reactor with laminar gas flow was 1.5 mW/cm<sup>2</sup> with a wavelength of 365 nm.

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## APPENDIX 4



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### Protocol from the test of photocatalytic activity in samples of Protectam FN3 manufactured by the company Advanced Materials-JTJ, s.r.o., Kamenné Žehrovice

| Standard          | Sample       | Initial conversion (%) | Conversion in steady state (%) |
|-------------------|--------------|------------------------|--------------------------------|
| ISO 22197-1:2007  | FN1 7 layers | 50                     | 21                             |
| CEN               | FN1 7 layers | 27                     | 13                             |
| ISO 22197-1:2007  | FN2 7 layers | 38                     | 23                             |
| CEN               | FN2 7 layers | 58                     | 15                             |
| ISO 22197-1:2007  | FN3 7 layers | 45                     | 40                             |
| CEN               | FN3 7 layers | 39                     | 24                             |
| ISO 22197-1:2007  | FN3 1 layer  | 15                     | 10                             |
| ISO 22197 -1:2007 | P25 1 layer  | 12                     | 8                              |
| ISO 22197-1:2007  | FN3 2 layers | 19                     | 11                             |
| ISO 22197-1:2007  | P25 2 layers | 20                     | 10                             |

Table: Results of the test of photocatalytic activity.

The results of photocatalytic activity measurements of the supplied samples of Protectam FN1, FN2, FN3 and P25 (Evonik Industries - industrial standard of pure nano TiO<sub>2</sub>), according to ISO standard 22197-1:2007 and the proposed CEN standard. The measurements according the ISO standard were conducted in a reactor with laminar gas flow. The test according to the proposed CEN standard were conducted in a flow turbulent reactor with a volume of 3.5 l and at the space rate of 0.874 min<sup>-1</sup> and space time of 1.14 min. The results of the tests are based on conversion of the nitric oxide corresponding to the proportion of nitric oxide in the gas mixture that was photocatalytically oxidized. The space velocity is at the ratio of the volume flow rate (in e.g. L/min) and the volume of the reactor (in litres). Therefore, the unit is min<sup>-1</sup>. The space time is the reciprocal value of space velocity (the unit is time, e.g. min).

An overview of the gained results is shown in the table. The initial conversion corresponds to the maximum value achieved in the short-term interval after the initiation of the test. The conversion in the steady state is the proportion of nitric oxide after approximately 2-3 hours that is practically constant. The steady state was achieved after 2-3 hours. The conversion in the table correspond to the value in this steady state. For operational reasons the chosen intensity of the UV radiation was 0.9 mW/cm<sup>2</sup> with a wavelength 365 nm for the reactor with laminar gas flow. In the mixing reactor the intensity of the UV radiation was 1.0 mW/cm<sup>2</sup>. The proportion of conversion in steady state measured in the reactor with laminar flow and in the mixing reactor was the same for all samples - approximately 1.6.

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