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A Lab Study of Photo-Catalytic Oxidation and Removal of Nitrogen Oxides in Vehicular Emissions and Its Fieldwork on Nanjing No.3 Bridge of Yangtze River

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Abstract: This paper reports the results of experiments (conducted on road surface materials) that may effectively reduce the concentration of nitrogen oxide (associated with vehicular traffic) in the air. The performances of Portland cement concrete and bituminous mixtures as carriers of nano-TiO_2 for the removal of NO_2 are compared. Portland cement concrete was found to be superior to bituminous materials because of its porous microstructure. In the absence of light, the porous concrete specimen adsorbs more NO_2 and also forms a higher concentration field of NO_2 around the specimen. Even after a significant surface weight loss per unit of area from abrasion, the photo-catalytic oxidation efficiency of the concrete that carried nano-TiO_2 remained stable because the nano-TiO_2 particles were fixed in the exterior pores and fissures due to permeation. The nano-TiO_2 photo-catalyst composite that was placed on the concrete road of the north toll square was found to efficiently reduce the nitrogen oxide concentration and control the air quality in accordance with the China National Air Quality Standard Grade I.

***Key words**: Asphalt admixture; Nano-TiO_2; Nitrogen oxides; Photo-catalysis and oxidation; Portland cement concrete.*

Introduction

The primary air pollutants mainly derive from poisonous gases (such as hydrocarbons and other vehicular emissions) that are produced by transportation traffic, industrial activities, and other human activities. In China, per-capita car ownership has sharply increased in recent years. It has been estimated that total car ownership in China will reach 50,000,000 by the year 2010 [1]. The statistical report showed that vehicular emissions account for three quarters of air pollution. In populous and developed cities within China (e.g., Beijing, Shanghai, and Tianjin), 40% of the nitrogen oxide, 80% of the carbon monoxide, and 70% of the hydrocarbon are attributed to vehicular emissions.

In this paper, a nano-TiO_2 photo-catalyst was fixed to road surface material in order to photo-catalyze the oxidization of nitrogen oxide. The efficiency of the photo-catalytic oxidation depended on the specific area of the contact surface not only because nitrogen oxide came from vehicular emissions but also because the photo-catalytic oxidization reaction took place at the contact surface between the photo-catalyst and the nitrogen oxide. If the photo-catalyst is fixed to the road surfacing material, it is easy for the vehicular emissions to be adsorbed by the photo-catalyst. Combined with the effects of ultraviolet light in solar rays, nitrogen oxide was photo-catalytically oxidized and thus removed from the air. Laboratory studies have been conducted [2] on the oxidation of nitrogen oxide to HNO_3 via nano-TiO_2 photo-catalyst-treated concrete under conditions that simulating the actual highway environment (including light intensity, velocity of gas flow, NO_2 concentration, temperature, and relative humidity). Based on these studies, a premixed photo-catalyst composite was sprayed onto the north square of the toll station of the Nanjing No.3 Yangtze River Bridge both when the road was being cast and during the curing time. After the bridge was opened to traffic, nitrogen oxide concentrations [3] and other correlative parameters on the south and north toll squares were recorded in order to evaluate the photo-catalytic oxidization effects.

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Materials and Methods

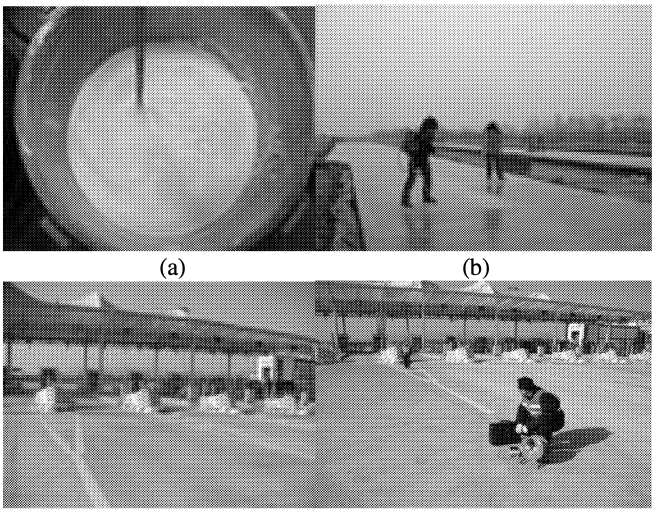
Material Preparation

Preparation of Concrete Samples

Concrete samples that carry $10g/m^2$ of nano-TiO_2 within a maximum depth of $3mm$ were prepared as follows. The concrete was first cast and cured. Then, at the appropriate curing time, $20\times 40\times 400mm$ concrete cubes were cut, which were then suitable for the photo-catalysis reactor. After spraying nano-TiO_2 water-like composite on the $40 \times 400mm$ surface of the concrete, the samples were dried at room temperature (20°C) for one week, washed in tap water for 2hrs, and finally dried in an oven. The concrete samples that had been surfaced with nano-TiO_2 were then ready for use.

Preparation of Bitumen Samples

An immobilized photo-catalyst in a bituminous mixture was prepared by blending Fe-ion-modified nano-TiO_2 particles with melted asphalt or asphalt emulsion. Asphalt-I was prepared by blending a 6%-nano-TiO_2 (by weight fraction of asphalt) with melted



(a) (b)

(c) (d)

Fig. 1. Photos of Photo-Catalysis Functional Road Preparation and Nitrogen Oxides Concentrations Detection; (a) Photo-Catalyst Composite, (b) Spraying Photo-Catalyst Composite on Curing Concrete Road (the Woman in Yellow is the Author Herself), (c) the Bridge Opening to Traffic, and (d) a Technician Adjusting the Nitrogen Oxides Sampling Set.

asphalt. Densely graded AC13 I was prepared by blending 5.1% by weight asphalt-I with aggregate. The open-graded asphalt mixture OGFC (open-graded friction coarse) was prepared by blending 4.6% by weight asphalt-I with open-graded aggregate. Asphalt-II was prepared by blending emulsified asphalt with 2.5%-nano-TiO_2.

Photo-Catalyst Composite Volume per Road Unit

For the photo-catalyst composite to be applied to the road surface, it was decided to adopt the recommended photo-catalyst weight proportion of $10g{\cdot}L^{-1}$ [4], which amounts to $1g$ of nano-TiO_2 per square meter of road surface. The photo-catalyst-treated road was prepared while the toll square was under construction and while the concrete was in moist curing (see Figs. 1(a) and 1(b)).

Methods

Photo-Catalysis Mechanism

The photo-catalytic oxidation reaction takes place on the concrete in two steps (see Fig. 2(a)). In the first step, the NO_2 that is nearest to the nano-TiO_2 is directly photo-catalytically oxidized. In the second step, the NO_2 is transferred to the nano-TiO_2 via a concentration gradient and is continuously photo-catalytically oxidized. In comparison with the concrete, the bituminous mixture that carries nano-TiO_2 lacks step two (see Fig. 2(b)).

The photo-catalytic oxidation reactions are illustrated below by Eqs. (1) to (3). To neutralize the system, HNO_3 is removed by mixing $Ca(OH)_2$ into the photo-catalyst composite, which reacts to produce $Ca(NO3)_2$ and H_2O.

$$TiO_2 \xrightarrow{solarenerg\ y} electrons\ (-) + cavities\ (+) \tag{1}$$

$$cavity(+) + H_2O \rightarrow \bullet OH + H^+ \tag{2}$$

$$\bullet OH + NO_2 \leftrightarrow HNO_3 \leftrightarrow H^+ + NO_3^- \tag{3}$$

Definition of the Degree of Abrasion of the Concrete Samples

The degree of abrasion is defined as the weight loss divided by the abrasion area, which is in accordance with the accordance with the state standard of JT1053T0527-94 [5] that is shown in Eq. (4).

$$G = \frac{m_0 - m_1}{0.0125} \times 100 \tag{4}$$

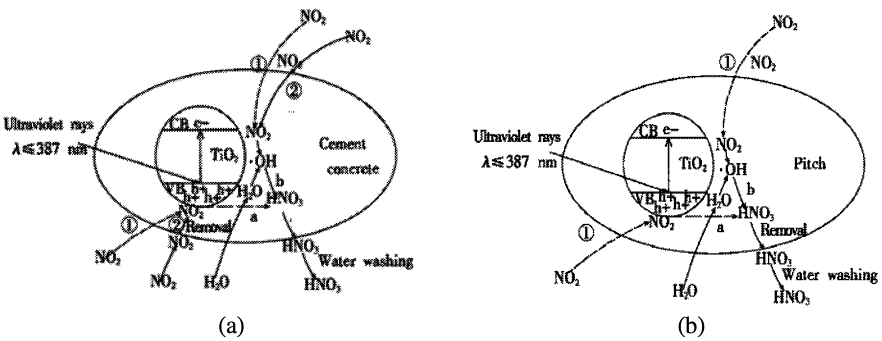
G is the weight loss per unit area ($kg{\cdot}m^{-2}$), m_0 is the initial weight of the specimen (kg), and m_1 is the weight of the specimen after abrasion (kg) and 0.0125 is the abrasion area of the specimen (m^2).

Photo-Catalytic Oxidation Efficiency

The photo-catalytic oxidation efficiency is defined as the reduction in the concentration of NO_2 between the entrance and the outlet of the photo-catalytic reactor when the concentration at the entrance is constant. Eq. (5) defines the photo-catalytic oxidation efficiency:

$$\eta = \frac{Ci - Co}{Ci} \times 100\% \tag{5}$$

where η is the efficiency of photo-catalytic oxidation, %, C_i is the concentration of NO_2 at entrance, $\mu g{\cdot}m^{-3}$, and C_o is the concentration of NO_2 at outlet, $\mu g{\cdot}m^{-3}$.



(a) (b)

Fig. 2. Photocatalysis and Oxidation Mechanism of Nano-TiO_2 Photocatalyst Immobilized on (a) Concrete and (b) Asphalt.

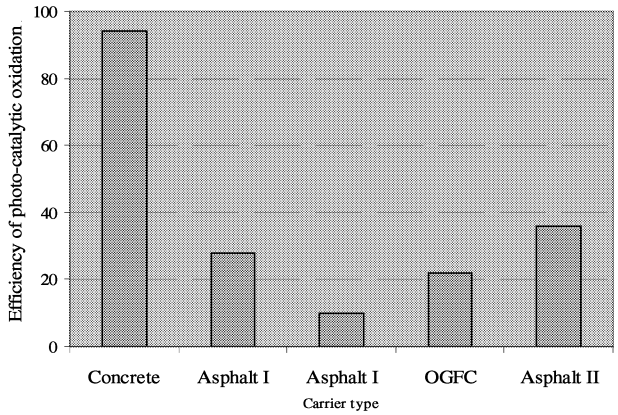


Fig. 3. Relationship between Efficiency of Photo-Catalytic Oxidation and Carrier Types.

Table 1. Maximum Saturation Molecular Adsorptive Quantity Q_{max} and Adsorptive Equilibrium Coefficient K.

Photocatalyst/Carrier	$K(\times 10^6 m^3 \cdot mol^{-1})$	Q_{max} $(\times 10^{-6} mol)$
TiO_2/-	0.1022	0.091
TiO_2/Concrete	0.0785	0.381
-/Concrete	0.0114	0.428
TiO_2/Asphalt	0.0032	0.006
-/Asphalt	0.0021	0.007

Adsorption Capability of Concrete and Bitumen Samples in Darkness

In the absence of light, the adsorption capability was evaluated by Q_{max} and K of Eq. (6), which was deduced from the Langmiur adsorptive isothermal function:

$$\frac{1}{Q_{ads}} = \frac{1}{K \cdot Q_{\max}} \times \frac{1}{C_{eq}} + \frac{1}{Q_{\max}} \tag{6}$$

where Q_{ads} is the molecular quantity that was adsorbed onto the surface (mol), Q_{max} is the maximum molecular quantity that was adsorbed onto the surface (mol), K is the adsorptive equilibrium coefficient, and C_{eq} is the concentration of NO_2 gas at the adsorptive equilibrium ($mol \cdot m^{-3}$).

Determination of Nitrogen Oxides on the Bridge

After the bridge was opened to traffic in October of 2005 (see Fig. 1(c)), technicians from the China Jiangsu Provincial Environment Evaluation Institution examined the nitrogen oxide concentrations on the concrete road by using the Japanese Industrial Standard JIS K0104-2000 [6] for Determination of Nitrogen Oxide in Flue Gas (see Fig. 1(d)).

Results and Discussion

Results

The photo-catalytic oxidation efficiency of the concrete specimens, which had nano-TiO_2 fixed onto the surface, was tested after they were abraded to various degrees. Energy dispersive X-ray analysis (EDXA) was used to determine the concentration of Ti (from the nano-TiO_2 that was fixed onto the concrete specimen) after the surface of the concrete had been abraded to a weight loss of $1.6 kg \cdot m^{-2}$, which equated to a depth loss of $1 mm$. Fig. 3 shows the relationship between the efficiency of the photo-catalytic oxidation and the carrier types.

Data showing the maximum saturation molecular adsorptive quantity, Q_{max}, and the adsorptive equilibrium coefficient, K, for the concrete and asphalt pavement sections (with or without the nano-TiO_2 treatment) are listed in Table 1. The data recorded (from Dec. 2005 to Nov. 2006) for the ultraviolet radiation index, wind speed, and traffic flow on the north and south toll squares of the Nanjing No.3 Yangtze River Bridge in China are shown in Fig. 4.

Discussion

Photo-Catalytic Oxidation Efficiency of Concrete and Bitumen

It is apparent from the data in Fig. 3 that the cement-based material was a more efficient carrier. The reason for this is that the nano-TiO_2 particles were embedded in the bituminous mixture, which prevented good contact with the NO_2. Based on the results of the laboratory experiments, it was reasonable to expect that the photo-catalytic oxidation efficiency might reach 90% in 20 minutes under the conditions of 10°C, 60% relative humidity, less than $200 \mu g \cdot m^{-3}$ NO_2 concentration and about $1{,}400 \mu W \cdot cm^{-2}$ of UV-A intensity (an average in December at 1:00 pm in Nanjing China).

The photo-catalytic oxidation efficiency of the concrete specimens, which were surfaced with nano-TiO_2, slightly dropped off (by 10%) when the weight loss per unit of area, G, increased from 0 to $2.5 kg \cdot m^{-2}$. The reason for this was that the nano-TiO_2 particles permeated into the fissures and pores of the concrete. This was confirmed by measuring the concentration of Ti at the surface of the concrete specimen by EDXA after the specimen had been abraded to $1.6 kg \cdot m^{-2}$ of surface loss, which equates to a $1 mm$ depth loss.

Nitrogen Oxides Adsorption Capability of Concrete and Bitumen in the Absence of Light

It can be seen from Table 1 that in the absence of light the adsorptive equilibrium coefficient (K) of the concrete specimen, which was surfaced with nano-TiO_2, is only one tenth as large as the adsorptive equilibrium coefficient of nano-TiO_2 itself while the maximum saturation molecular adsorptive quantity (Q_{max}) of the former is four times as much as for the latter. This indicates that the absorbability of the NO_2 (gas) of the former was poorer than that of the latter. However, the NO_2 (gas) adsorptive capacity of the former was higher than that of the latter. Furthermore, the K and Q_{max} for the bituminous mixture, which contained the photo-catalyst, were much smaller than those of the photo-catalyst itself.

In darkness, when the lights were off, the porous concrete specimen adsorbed more NO_2 and had a higher concentration field of NO_2 around the specimen. As soon as the lights were turned on, NO_2 was adsorbed at the surface of the specimen and in darkness, was photo-catalytically oxidized right away. Meanwhile, under the

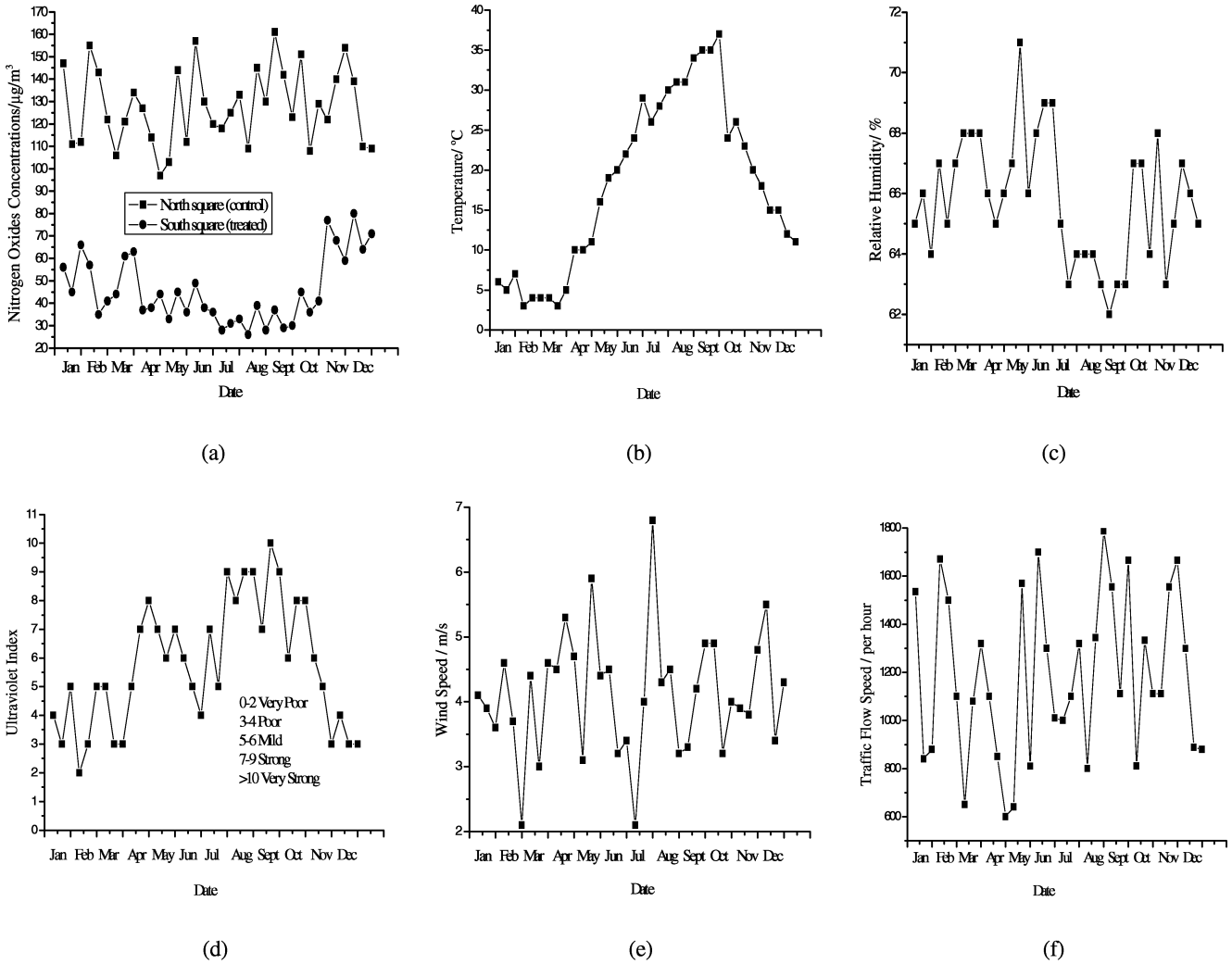


Fig. 4. Graphs of Nitrogen Oxides Concentrations and Meteorologic and Traffic Factors Data (Dec. 2005-Nov. 2006).

effect of a concentration gradient, NO_2 in a higher concentration field was transferred to the lower NO_2 concentration field, where the photo-catalytic oxidation reaction continued. In comparison, in darkness, NO_2 (gas) was adsorbed only on the photo-catalyst that was exposed to the surface of the bituminous mixture. The difference in the ability to absorb NO_2 (gas) between the cement-based materials and the bituminous mixture was entirely attributed to the differences in their structures [7]. Cement-based materials are porous. The pore size was around 100*nm*; the pores at this scale provide good gas circulation. Also, the hydration-product of the CSH gel particles was on the nanometer scale. These factors can explain the high NO_2 adsorbing capacity of the concrete. However, the bituminous mixture, which is usually used as a waterproof material, was compact with no permeation and gas circulation.

Road Test Results Discussion

The north square of the toll station was sprayed with the photo-catalyst composite while the south was not. There were two reasons to choose the north toll square. First, it was made of concrete. Second, it was an area with heavy air contamination due to vehicular emissions. The samples were set up on the 10^{th}, 20^{th}, and 30^{th} day of each month at 1:00pm, when the ultraviolet radiation was possibly the strongest. As shown in Fig. 4, the nitrogen oxide concentrations (average during one hour) at the south square were considerably higher than those at the north square during the 12-month sampling period, which started in Dec. 2005 and ended in Nov. 2006. This indicated that the photo-catalyst composite on the north square evidently contributed to the reduced the nitrogen oxide concentrations.

Conclusions

Nitrogen oxide from vehicular emissions, which are a major source of air pollution, is one of the most harmful toxic gases affecting the health of people. After the first air decontamination, which was marked by the use of catalytic converters in the tail pipes of motor vehicles, a second decontamination could be realized by treating concrete road surfaces with a photo-catalyst material. The

photo-catalytic oxidization efficiency of the concrete base that was treated with nano-TiO_2 in laboratory experiments remained at over 90%, even when the weight loss from the concrete surface per unit area was up by $2.5kg \cdot m^{-2}$. This indicated that even after visible abrasion with vehicular tires, the concrete road that was treated with nano-TiO_2 still exhibited excellent performance in removing NO_2 by photo-catalytic oxidation. Laboratory experiments also showed that Portland cement concrete was a superior carrier of the nano-TiO_2 photo-catalyst as compared to the asphalt road surface material because of the porous microstructure of the cementitious material. In the concrete, the pore size was centralized in the 100-*nm* range. These pores are found to be helpful by allowing the gas and the light to penetrate through the pavement and interact with the photo-catalyst. The NO_2 maximum saturation adsorbing quantity (Q_{max}) of the porous concrete that carried nano-TiO_2 was four times as much as for the nano-TiO_2 itself. The NO_2 adsorbed by the concrete surface was transferred to the nano-TiO_2, which had been fixed onto the concrete surface or in the pores, in order to continue the photo-catalytic oxidation reaction once the NO_2 closest to the concrete was first oxidized by the nano-TiO_2.

Recommendations and Perspectives

Vehicular tail pipe gas is first decontaminated with catalytic converters. Then the gas is emitted and contacts the material of the road surface (usually concrete or asphalt). When the road material is treated with a photo-catalyst composite, a second decontamination is expected to take place. After these two decontaminations, it is reasonable to believe that the pollution from the vehicular emissions is at a minimum. Portland cement concrete was found to be superior to asphalt road surface material as a carrier of nano-TiO_2 photo-catalyst because of the porous microstructure of the cementitious material. In concrete, the pore size was in the 100*nm* range. The pores were found to be helpful when allowing airborne emissions and light to penetrate through the mixture and contact the photo-catalyst. Since variations in the meteorological conditions might affect the results, a long-term sampling and determination is obviously necessary.

For a complete removal of HNO_3, it is suggested that by watering the photo-catalyst treated road twice a day, most of the HNO_3 would be neutralized by $Ca(OH)_2$ as soon as it is produced. Another important issue that concerns the proposed pavement treatment was whether or not the catalytic procedure would lead to an increase in ozone. As is well known, atmospheric VoCs (hydrocarbons especially), nitrogen oxide and oxygen in the air could possibly cause the photochemical reactions to occur with ultraviolet radiation of less than a 250-*nm* wavelength; thus, ozone could be produced. However, in the laboratory experiments, conditions were simplified so that no by-product like ozone was produced in the photo-catalytic reaction. This was because NO_2 was the only reactant and UV-A, with a wavelength range of 320 to 400*nm*, was used to induce the photochemical reaction. Further research is needed to validate the feasibility of the proposed application.

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