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Long term exposure of self-cleaning and reference glass in an urban environment: A comparative assessment

Anne Chabas [a,*], Stéphane Alfaro [a], Tiziana Lombardo [a], Aurélie Verney-Carron [a], Estifania Da Silva [a], Sylvain Triquet [a], Hélène Cachier [b], Eric Leroy [c]

[a] *Laboratoire Interuniversitaire des Systèmes Atmosphériques, Université Paris-Est Créteil, Université Paris Diderot, UMR CNRS 7583, 61 Avenue du Général de Gaulle, 94010 Créteil, France*
[b] *Laboratoire des Sciences du Climat et de l'Environnement, CNRS-CEA, Orme des Merisiers, bât 701, 91191 Gif-sur-Yvette, France*
[c] *Institut de Chimie des Matériaux Paris-Est, UMR CNRS 7182, Université Paris Est Créteil, 2-8 rue Henri Dunant, 94430 Thiais, France*

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ABSTRACT

Nowadays, the self-cleaning glasses are commonly used for outdoor and indoor applications. If their initial efficiency has been clearly demonstrated in the laboratory and on the field, information on their durability is still lacking on the long term. This work compares the short (12 months) and long (100 months) term exposures of uncoated and TiO_2-coated glasses in urban conditions. Dry as well as wet atmospheric conditions are both tested. The deposit present on the surface is characterized using a combination of optical and chemical methods. Chemical analysis of the glass substrate is also performed in order to document a potential washing out of the TiO_2-coating. After long exposures, the affinity of the self-cleaning glass for water vapor and its superhydrophilic properties are maintained. This does not affect the transparency of the glass on the short term but eventually favors the development, in dry conditions, of local embryonic gypseous crusts (giant clusters of salt deposit) impairing the glass optical properties on the long term.

1. Introduction

It is common knowledge that air pollution causes a premature aging of building materials. Primary gaseous pollutants such as SO_2, NOx, CO_2, VOCs and secondary ones such as O_3, HNO_3, H_2SO_4, H_2CO_3, aldehydes … are involved in the acidic attack of the substrates [1]. Airborne particulate matter (PM) associated mainly with vehicle emission (diesel soot) may adhere to the surface of the material, thereby changing its optical, physical and chemical properties [2]. Moreover, parameters such as radiation, temperature and humidity are known to increase the kinetics of weathering, particularly in the current context of climate change [3]. An abundant literature has been produced in the last 20 years on the development of active materials able to remove pollutants through a de-polluting and/or a self-cleaning action and provide better resistance to climate change.

The de-polluting action consists in the decomposition or the deactivation of atmospheric components such as NO_x [4,5] and VOCs (benzene, toluene and hexane) as well as in the removal of bacteria [6], formaldehyde [7] from the surface of materials covered with TiO_2 films. The appearance of gaseous or inorganic components has been highlighted. Indeed, the reduction of NO_2 by TiO_2 leads to the production of HNO_3, HONO, NO and nitrate [8–10]. The UV-induced formation of ozone has also been evidenced [11]. The photolysis of HNO_3 involving the formation of NO_2, OH and possibly HONO has been underlined on proxies and on real urban grime films [12]. These experiments are more specifically conducted in the research field of atmospheric sciences through numerous short time experiments (10 mn to 1 day max).

The study of the durability of materials and of their self-cleaning efficiency belongs more to the field of material sciences. As mentioned by Ref. [13], factory-finished photocatalytic self-cleaning glazing products are advertised as having a self-cleaning property lifespan equal to the one of the window itself, which is to say approximately 25–30 years. The self-cleaning action can be described as follows: when exposed to natural UVA radiation, the TiO_2 film reacts with atmospheric O_2 and H_2O and produces free radicals, among which $^{\bullet}OH$. These radicals are able to break C-bonds and transform the organic pollutants deposited on the glass into

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[*] Corresponding author. Tel.: +33 1 45 17 16 74; fax: +33 1 45 17 15 64.
E-mail address: anne.chabas@lisa.u-pec.fr (A. Chabas).

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volatile H_2O and CO_2. Another consequence of the self-cleaning process is a photo-induced superhydrophilicity enhancing in turn the wettability of the glass surface [6,13–18].

The photocatalytic properties of TiO_2 make it a choice component for being applied on opaque materials used in the building sector [19], or on transparent ones, such as glazing [20]. For the float silica-soda-lime glass currently used for the fabrication of window panes (glass with $[SiO_2] > 60\%$ defined as durable according to Ref. [21]), the atmospheric pressure chemical vapor deposition (ACV) technique is used to create a film of TiO_2 on the glass surface itself. With the exception of the Picada European project [22] focused on the de-soiling and the de-polluting action of TiO_2 deposited on facade coatings, of the Self-Cleaning Glass European Project [23], and of a recent study dedicated to solar panels [24], very few cases of outdoor exposure are reported. Therefore, this under-investigated field approach could prove to be a useful and promising complement to the already available laboratory studies.

In the previous field works, the behaviors of uncoated “reference” glass and of “self-cleaning” TiO_2-coated glass (with anatase nanoparticles) exposed to the same polluted urban environment were compared [25–28]. In the frame of these relatively short duration (up to 2 years) experiments, the ability of the self-cleaning process to slow down the optical degradation (haze) was evidenced, especially in the case of the glass samples sheltered from the rain. The first aim of the current work is to assess the de-soiling efficiency of the TiO_2 coating in the long term, namely over 8 years of exposure in urban conditions. A combination of physical and chemical analyses is used in order to quantify the optical impairment, the repartition, the accumulation and the nature of the deposit. The sensitivity of the deposit to relative humidity is investigated by means of isotherm adsorption measurements. Finally, the study is completed by an analysis of the substrates of the reference-glass and of its TiO_2-coated self-cleaning version in order to determine if the glass material underlying the deposit has undergone a chemical aging during the 8 years of exposure.

2. Field exposure, materials and methods

The field exposure test consisted in exposing to the urban environment pairs of 10 × 10 cm float glass samples, an uncoated (Planilux®) and a self-cleaning one (Bioclean®). One series of samples was exposed to the rain (wet atmospheric deposit) and the other one was protected from it (dry atmospheric deposit). These experimental conditions reproduce those defined by the ISO 8565 norm which was adopted jointly by a consortium of 24 European research groups in the frame of the International Cooperative Program on Materials [29–31]: the samples submitted to wet exposure are exposed facing south on a rack inclined at 45° from the vertical so that they can receive both the vertical and the driving rains. Samples exposed in dry conditions are set-up vertically in a ventilated box. Nevertheless, for allowing the photocatalytic activity and the development of the photoinduced superhydrophilicity of the self-cleaning glass samples, the boxes have been adapted for our experiments and made of UV-transparent glass. The exposure site was located in a pedestrian area at the top (elevation 40 m) of the Saint Eustache Church in downtown Paris.

Before the experiment, each glass sample was cleaned using soft paper soaked with deionized water and then alcohol. The field experiment was carried out from June 2004 to September 2012. Withdrawals of the glass samples were planned every 3 months for the first two years, and the following removals were performed after 4, 5, and 8 years. After each withdrawal, samples were transported carefully and horizontally inside individual boxes. In the laboratory, the back sides and edges were cleaned again with deionized water and alcohol, and then the samples were stored horizontally in desiccators.

2.1. Haze measurement

A VIS Spectrometer (Lambda 650 PerkinElmer, accuracy 0.1units) calibrated with a light source D65 was used to measure optical parameters of all the samples every 10 nm between 380 and 780 nm. These parameters include the total $TL(\lambda)$ and diffuse $Td(\lambda)$ transmittances from which the spectral haze $H(\lambda)$ is calculated as the ratio of $Td(\lambda)$ to $TL(\lambda)$. The integration of $H(\lambda)$ between 380 and 780 nm yields the value of the average haze (H) used in the industry as a standard quantification tool of the optical impairment of the glass panels. On each sample, three measurements of the haze were performed. The physically-based model proposed for explaining the increase of H with time [30] was adjusted to represent the measurements. This adjustment involves the determination by an iterative procedure of two parameters only: the initial deposition flux (CV_0) of particles on the surface of the clean glass and a parameter (α) taking into account the alteration of the glass surface properties induced by the progressive deposition of particles. Note that CV_0 is in fact an apparent deposition flux taking into account the deposition of particles but also other processes such as removal by the rain in unsheltered conditions or destruction by the photoactive coating on self cleaning-surfaces.

2.2. Optical microscope observations and calculation of the percentage of covered surface

The reference and self-cleaning glass samples were observed directly under an optical microscope (Leica Leitz Laborlux 12POLS) used in the reflection mode and connected to the Histolab-Microvision® image processing system. Observations were made at the 526× magnification (eyepiece 12.5; objective 20; camera 2.104), which allowed detecting particles with diameters larger than 0.06 μm. On each sample, 100 areas were chosen at random and a focus area of 72,581 μm^2 was selected for applying the gray-level thresholding method classical in image processing. The sum of the areas covered by individual particles and by clusters was divided by the focus area, which yields the percentage of covered surface (%CS) for each of these areas. The 100 values of %CS obtained in this way was distributed in bins of width 2%. Then a combination of normal modes was fitted to this statistical distribution using an automated least square iterative routine. This procedure yields the amplitude (absolute and relative), the median value and the standard deviation of the normal modes whose combination reproduces best the statistical distribution of the measurements. Using an analytical Table Top Scanning Electron Microscope (Hitachi TM3000), low vacuum observations were realized directly on the samples without any prior carbon or metallic coating. The conditions of observation were 5 kV for accelerating voltage, charge-up reduction mode, 15 mm for working distance. Some punctual elemental analyses were also performed at 15 kV.

2.3. 3D areal surface texture

The potential of optimized combination of confocal microscopy and AFM for assessing the topographic characteristics of glass samples has already been demonstrated [31]. In this work, a similar method based on the use of an interferometric microscope has been chosen in order to determine the evolution of the roughness of the glass resulting from the accumulation or destruction of deposited matter. This non-destructive method allows detection of