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Development of testing procedures for assessing the thermal and optical performance of thermochromic coatings for buildings

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ABSTRACT

In climates where cooling and heating demands are balanced, thermochromic (TC) building coatings represent a promising solution to reduce the overall energy consumption for space conditioning. The main TC type proposed for building application, based on leuco dye, is however affected by photodegradation and there is an increasing research interest towards more durable TC solutions. This study suggests outdoor and laboratory measurement procedures to characterize the performance of TC building coatings. In an outdoor experimental campaign, roof and façade components with leuco dye-based TC coating were tested for 13 consecutive days. Moreover, spectrophotometric measurements were carried out to: i) characterize the solar, light and near-infrared reflectance and color properties of TC panels in pristine conditions and at different aging stages in the colored/colorless phases; and ii) assess the switching process under transient thermal conditions with the newly developed procedure. In the outdoor monitoring campaign, a maximum surface temperature difference between TC panels (colorless phase) and reference ones of ~35 °C was found. Moreover, a 0.1 reduction in solar reflectance of TC panel in the colorless phase was reported after 3 days of outdoor exposition due to photodegradation, and the hysteresis of the TC panels undergoing the switching process was measured.

1. Introduction

The interest towards innovative design solutions to reduce building energy demand is increasing, given the large impact of the building sector, which nowadays accounts for about 30–40% of the global energy end use [1]. Moreover, in cities, it is of crucial importance to counteract urban overheating, which further increases building cooling demand and compromises thermal comfort conditions. In this frame, innovative building envelope materials, such as thermochromic (TC) ones, can benefit both indoor and outdoor settings, thus contributing to more comfortable and sustainable urban environments.

TC technologies have been proposed for both opaque and transparent building components, in the attempt to manage the amount of solar radiation either absorbed by the envelope or entering the building, and improve energy efficiency [2,3]. While TC glazing have been object of several past studies and is increasingly gaining popularity and market position [3], the application of TC coating for opaque components has emerged more recently.

In climates with balanced cooling and heating demand, thermochromic coatings applied to the external surfaces of buildings can be used to reduce energy consumption for heating and cooling and to improve the urban microclimatic conditions. TCs can reversibly change their optical properties based on their surface temperature and are considered to belong to the next generation of construction materials [2]. TCs exhibit a dark-colored appearance (colored phase) at temperatures lower than the design switching temperature, to maximize solar gains in winter, and a light-colored appearance (colorless phase) at higher temperatures, to minimize solar gains in summer. TC building coatings have the potential to overcome the limitation of high albedo ones in climates where both heating and cooling demands are relevant throughout the year; indeed, in such climates, high albedo materials, while being effective energy-saving solutions during summertime, are reported to result in a heating penalty, i.e., an increase in heating demand during winter [4]. In scenarios where cooling and heating needs are balanced, TC building coatings can modulate the sensible heat flow through the envelope in different seasons, thus reducing both cooling and heating demands [5–7]. For instance, the potential annual energy saving for a TC roof with respect to a high albedo one was estimated up to 8.5% in [5] and up to 11% in [6]. As concerns the indoor air temperature, a TC building envelope was predicted to provide reductions up to 11 °C during summertime, and increases up to 2.7 °C during

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Nomenclature

UHI	Urban heat island
TC	Thermochromic
ETICS	External thermal insulating composite system
XPS	Extruded polystyrene layer
NIR	Near-infrared
a*	CIELAB coordinate for green – magenta. [-]
b*	CIELAB coordinate for blue – yellow. [-]
I_{sol_h}	Solar irradiance on horizontal plane. [W/m^2]
I_{sol_v}	Solar irradiance on vertical plane. [W/m^2]
L*	CIELAB coordinate for color lightness. [-]
RH	Relative humidity. [-]
T_{a_o}	Outdoor air temperature. [°C]
T_s	Surface temperature. [°C]
$T_{sol\text{-}air}$	Sol-air temperature. [°C]
w	Wind speed. [m/s]
ΔE*	CIELAB color distance. [-]
ρ_e	Solar reflectance. [-]
ρ_{NIR}	Near-infrared reflectance. [-]
ρ_v	Light reflectance. [-]

wintertime [7]. Moreover, considering the outdoor environment, the color change of TCs can counteract UHI during summertime, and support it in wintertime, which would in turn have a positive effect on energy demands and carbon emissions [8,9]. It must be however highlighted that the energy saving potential of TC coatings greatly depends on the climatic scenarios, and TCs are not effective in either cooling- or heating-dominated climates, where materials with static optical performance are preferable [5,10].

TC materials can be divided into two categories: those based on dyes, and non-dye types [2]. The working mechanism of dye based ones depend on the interplay between the components (i.e. pH-indicator dye and polymer matrix), while non-dye ones work mostly based on molecular re-arrangement or nano-scale optical effects [2,11]. Reviews on the state of the art of dye and non-dye TC materials are presented in [2,11].

Leuco dye-based TC materials belong to the category of dye-based TC solutions, and their working principle is grounded on a proton transfer reaction. These materials can switch from a colorless phase (also called “leuco”, or “bleached”) to a colored (“zwitterionic”) one as a result of temperature change. Leuco dyes TC materials are composed of a color former (leuco dye), a color developer, and a co-solvent. The color former is an electron-donating component, the color developer is an electron-acceptor (proton donor), the co-solvent is a long chain alkyl alcohol whose melting point determines the transition temperature [2]. Despite their dynamic behavior is promising for building coating application [12], photodegradation is a major limitation of leuco dye-based materials, that results in a quick loss of switching properties due to solar exposition. As reported in [13], the photodegradation causes the colored state of dye-based TCs to gradually fade, while the colorless state gradually becomes darker. The phenomenon occurs especially in the first hours of exposition [14] and it is thought to be caused by an irreversible photochemical reaction activated by UV radiation [2]. Several studies report that applications of dye-based TC materials have been investigated comparing their optical, thermal and mechanical properties with cool or common samples, either in outdoor environments or climatic chambers [13,15,16]. According to [2], leuco dyes-based TC materials were the only type of TCs tested for applications in the built environment, either as the building envelope coating [13] or for pavement application [15,16]. In this framework, little attention has been given so far in an defining an outdoor and laboratory testing procedure for TC building coatings and on systematic studies on the effect of photodegradation on their performance, considering longer period of outdoor exposition.

Since the practical application of leuco dye-based TCs to the building sector is currently hindered by photodegradation, there is an increasing research effort towards strategies to improve the optical stability of these materials using UV and optical filters [17] and protective topcoats [18], as well as towards the development of non-dye based TCs, such as nanoscale engineerable ones (e.g. temperature sensitive quantum dots [19–22], plasmonics [23,24], and photonic crystals [11,25,26]). All these research lines let suggest that in the future the current limitations of TC materials will be addressed, allowing for their application in the built environment. However, despite the dynamic performance and durability of these materials were already investigated, the literature lacks studies aimed at sharing among the research community both laboratory characterization procedures and outdoor testing methods. This paper aims to contribute to filling this research gap by suggesting testing methodologies for the characterization of the dynamic behavior of TC coatings for building application in the laboratory and in an outdoor test facility, where the TCs are tested for several consecutive days. This study presents the results of a measurement campaign on a set of TC paints based on leuco-dye, that were used as a building envelope external coating, and includes the assessment of the photodegradation impact on their properties. The objectives of the study are:

a) The identification of a procedure for the outdoor measurement of the dynamic behavior and performance of TC materials applied as outer coating of building envelope components, including the monitoring of their surface temperatures and the solar reflectance variations.
b) The definition of experimental techniques to assess the progressive impact of the photodegradation process on the TC performance occurring over time, when exposed to solar irradiance.
c) The development of a laboratory method to characterize the dynamic optical properties of TC paints as a function of their surface temperature.

2. Materials and method

The research study is composed of an outdoor experimental campaign and a laboratory testing of panels coated with TC paint, that are addressed separately in § 2.1 “Thermochromic panels”, § 2.2 “Outdoor experimental campaign” and § 2.3 “Laboratory testing”. In the outdoor campaign, TC paints were employed as external coating on multilayer components for roof and façade application; the experimentation was performed in an outdoor test facility during summer

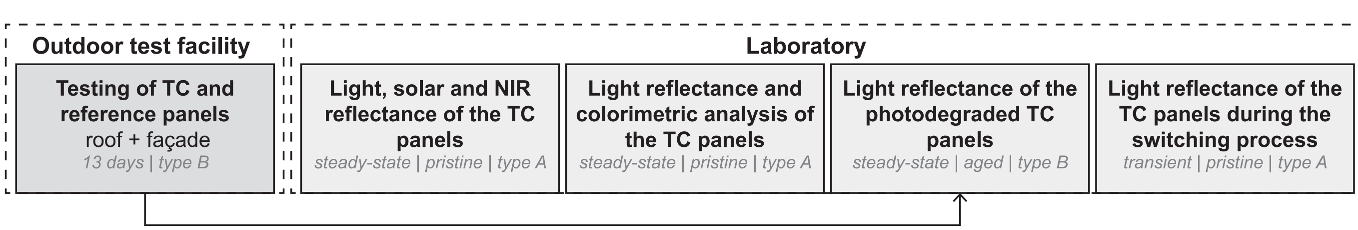

Fig. 1. Scheme of the outdoor and laboratory experimental campaigns.

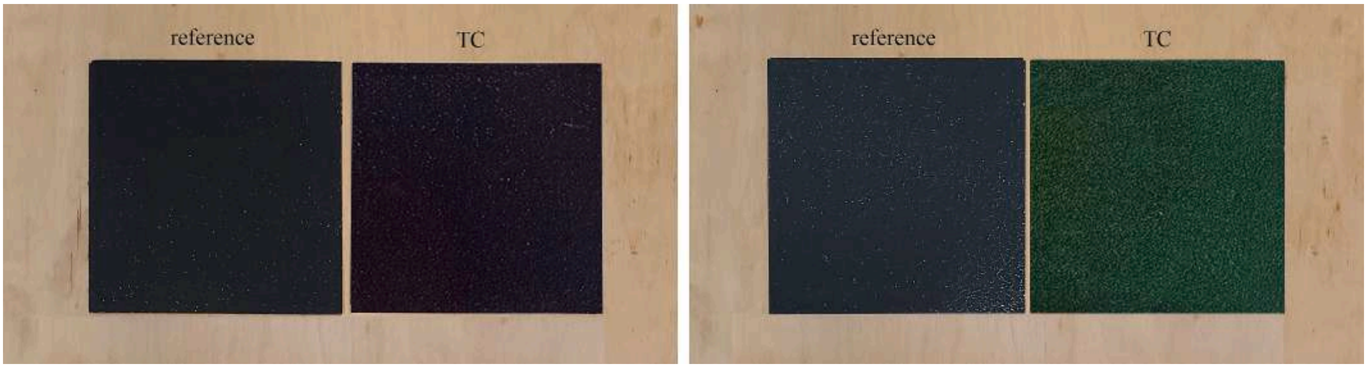

Fig. 2. Pictures of the black (left) and green (right) reference and TC panels (type A).

conditions in Turin, Italy. The laboratory, spectrophotometric measurements were conducted to characterize the outdoor exposed (naturally aged) TC panels and on unexposed (pristine) ones. Tests were carried out both in steady state and in transient thermal conditions. For clarity, a scheme of the outdoor and laboratory measurement campaigns, detailing some useful information on the tests, is provided in Fig. 1.

2.1. Thermochromic panels

The tested samples are squared aluminum panels coated with a TC paint composed of microencapsulated leuco dye with a nominal switching temperature of ~25 °C. The TC paint and the panels were manufactured in different colors and sizes. All the aluminum panels were coated with the following functional layers:

- an elastic white layer (Solar Reflectance Index > 100), with a thickness of about 1 mm, applied directly over the aluminum panels;
- a TC paint (3 layers) which coat the first elastic layer.
- a protective finishing transparent top coat (2 layers) which contains additives working as UV filter and HALS (Hindered-Amine Light Stabilizer).

For the sake of simplicity, the above-described panels will be referred to in the following as "TC panels". The panels are in black and green colors. Those for the laboratory testing, identified as type A, have a side

Fig. 3. Picture of the outdoor test facility with the experimental set-up highlighted in red; the picture was taken on the first day of experimentation.

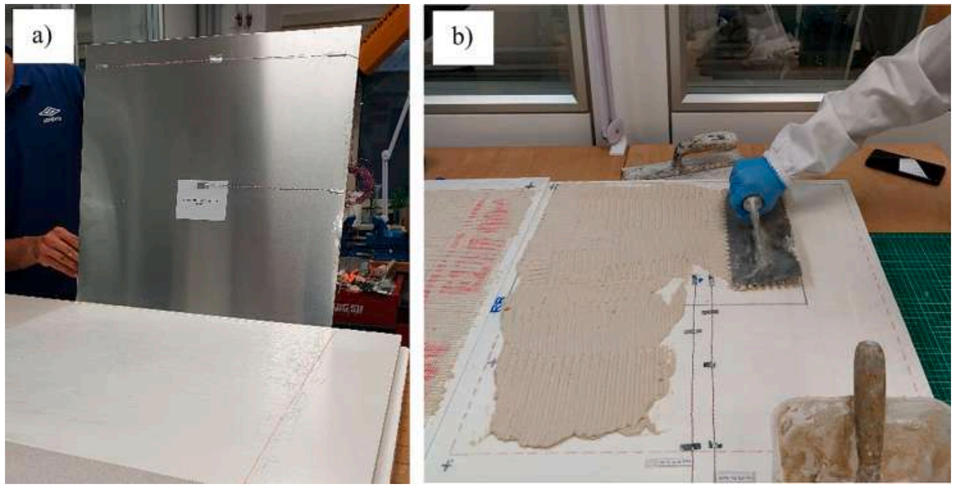

Fig. 4. Pictures of the preparation of the façade components (a) and roof components (b), showing the position of the thermocouples used to measure the external surface temperature.

length of 20 cm, while those meant to be tested outdoors, identified as type B, have a side length of 55 cm. The overall thickness of the coated samples is ~1.6 mm. It must be highlighted that, the optical properties of the green and black TC panels were different between type A and B, as a result of different production batches. Therefore, for the sake of completeness, the laboratory testing was conducted on both panel types, i.e., green type A and B, black type A and B. A set of panels with static optical properties were used as reference for the outdoor testing and the laboratory measurements. The reference panels are coated with a conventional static paint of the same color of the TC ones in the colored phase and are in the same dimensions. Pictures of TC and reference panels type A in black and green colors are shown in Fig. 2.

2.2. Outdoor testing

For the outdoor testing, the TC and reference panels were used as cladding solutions on the exterior sides of multilayer components for façade and roof application, that are described in detail in § 2.2.1. The components were installed on an outdoor experimental facility of the Department of Energy of Politecnico di Torino in Turin (Italy). The façade components were installed on a test cell (non-conditioned space) while the roof ones were applied directly over the roof slab of the university building. For the façade components, black and green TC/reference panels were applied as exterior layer, while for the roof application only black TC/reference panels were installed. In all tested positions, TC and reference panels of the same color were located close to each other to minimize the variation of the boundary conditions. The experimental setup is shown in Fig. 3. The experimental campaign was carried out for 13 days, between June 30 and July 12, 2021. During the campaign, the variation of surface temperatures and solar reflectance of the panels were continuously monitored, along with the environmental boundary conditions.

At the end of each monitoring day of experimentation, a patch of aluminum tape (~30 × 40 mm) was used to screen and protect a small portion of the panel from solar radiation and to stop the photodegradation process at different natural aging stages and collect data on its development over time (see § 2.3.1).

2.2.1. Multilayered components

Two types of envelope components with the TC/reference panels were prepared for the testing, i.e., a façade component and a roof one, consisting of multiple layers, where the TC/reference panels are the exterior one. The components were designed in the attempt to represent typical building thermal insulating solutions (insulated roof and façade External Thermal Insulating Composite System, i.e., ETICS).

The roof components are composed of a 50 mm thick extruded polystyrene layer (XPS) over which the black TC/reference panels type B (side length of 55 cm) are directly fixed with adhesive silicone, as shown in Fig. 4a. The roof components are cladded by 4 black TC/reference panels, that results in squared panels with a side length of 110 cm. The

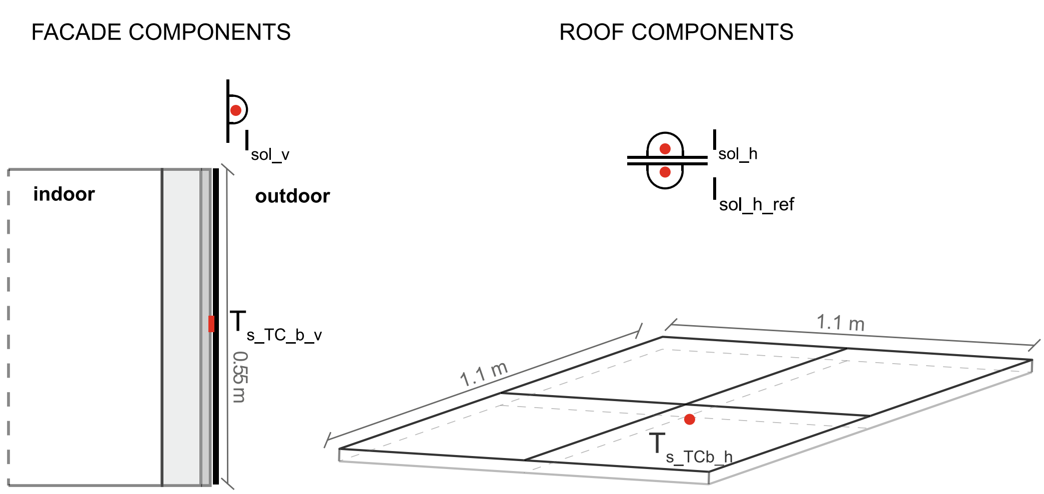

Fig. 5. Scheme of the experimental setup with the sensor positions. Please note that the identification codes used are referred to black TC panels, as an example.

Table 1
Details of the measurements on the TC/reference panels during the outdoor experimental campaign.

Measurement	type	color	Application	ID code
External surface temperature [°C]	TC	black	roof/ horizontal	$T_{s\_TC\_b\_h}$
	reference			$T_{s\_R\_b\_h}$
	TC	black	façade/ vertical	$T_{s\_TC\_b\_v}$
	reference			$T_{s\_R\_b\_v}$
	TC	green		$T_{s\_TC\_g\_v}$
	reference			$T_{s\_R\_g\_v}$
Solar reflectance [-]	TC	black	roof/ horizontal	$\rho_{e\_TC\ b}$
	reference			$\rho_{e\_R\ b}$
Reflected solar irradiance [W/m^2]	TC	black	roof/ horizontal	$I_{sol\_ref\_TC\_b}$
	reference			$I_{sol\_ref\_R\_b}$

roof components are leant horizontally against the roof slab of the university building.

The façade components are composed of a 50 mm thick layer of XPS covered by ~3 mm thick layer of ETICS render. The façade components were cladded with TC/reference panels that are fixed to the external render substrate with adhesive silicone layer. The panels applied over the façade are of type B and are in green and black color. A picture taken during the preparation of the façade components is shown in Fig. 4b, in which a layer of mortar is being laid on the XPS panel.

2.2.2. Experimental setup

During the experimentation, the external surface temperature of the TC/reference panels applied on the façade and roof components and the solar reflectance of the roof component was monitored, along with the environmental boundary conditions. The surface temperatures of the TC/reference panels were measured using T-type thermocouples, with ± 0.3 °C accuracy in the range between 0 and 60 °C, in accordance to ASTM E220-19 Standard [27]. In both the roof and the façade multilayer components, the thermocouples used to measure the external surface temperature (T_s) of each panel were installed below the thin aluminum coated panel, to avoid the disturbance of the direct solar radiation. Both sensors were set in correspondence to the center of the TC/reference panel to minimize the edge effect.

Furthermore, on the roof component, a double pyranometer set-up was used to estimate the in-situ solar reflectance of the TC/reference panels (ρ_{e_TCb} and ρ_{e_Rb}), which is calculated as the ratio between the horizontally reflected solar irradiance (I_{sol_ref}) and the global horizontal irradiance (I_{sol_h}). The set-up consists of two second class pyranometers (model: Hukseflux LP02-05) installed 20 cm above the panel's surface, one upward and one downward oriented, over the center of the panels. The height of the sensors was set to ensure for the downward oriented one a view factor of the panel equal to 90%, to minimize the influence of the radiation reflected by the surrounding surfaces. To estimate solar reflectance of the panels, a self-shading correction was applied to the reading of the downward-oriented sensor, following the indications found in [28]. The location of the thermocouples and pyranometers used to measure the behavior of the TC/reference panels is shown in Fig. 5 for the façade and roof components.

In addition, an infrared (IR) camera (model: Testo 882) was used to visually account for the surface temperature variation of the panels during the switching period. The thermal images were elaborated assuming a long-wave thermal emissivity of 0.9, which was calibrated by comparing the surface temperature measured with the thermocouples with that estimated with the IR camera.

The boundary conditions were measured for the entire duration of the experimentation, consisting of outdoor air temperature, relative humidity, wind speed and the solar irradiance incident on the façade and roof. The outdoor air temperature (T_{a_o}) was monitored with a calibrated T-type thermocouple placed outdoors in a shaded position.

Table 2
List of the boundary conditions monitored during the outdoor experimental campaign.

Measurement	Application	ID code
Air temperature [°C]	outdoor	T_{a_o}
Solar irradiance [W/m^2]	roof/horizontal	I_{sol_h}
	façade/vertical	I_{sol_v}
Wind speed [m/s]	outdoor	w
Relative humidity [-]	outdoor	RH

The relative humidity (RH) and wind speed (w) were measured by a weather station located over a nearby building in the university campus. The global solar irradiance on the façade of the test cell (I_{sol_v}) and that incident on the roof (I_{sol_h}) are measured using second Class pyranometers (model: Hukseflux LP02-05).

The details and identification codes of the measurements carried out during the experimental campaign with respect to the TC/reference panels and boundary conditions are summarized in Table 1 and Table 2, respectively.

All the measured data was continuously monitored using a datalogger (model: Datataker DT85) with a time-step of 5 min, except for wind speed and relative humidity values that were collected with a time-step of 15 min by the campus weather station.

2.3. Laboratory testing

The laboratory testing consists in four spectrophotometric campaigns that were carried out directly on the aluminum panels coated with the TC paints. The campaigns consisted of:

- a spectral reflectance measurement of the unexposed TC panels in the visible, solar and near-infrared (NIR) ranges (§ 2.3.1);
- a light reflectance measurement of TC panels in different colors in the colored and colorless phases (§ 2.3.2);
- a study in the visible range of the exposed TC panels at the different stages of photodegradation in steady state thermal conditions (§ 2.3.3);
- a study in the visible range of the switching process on unexposed TC panels in transient thermal conditions (§ 2.3.4).

The spectral reflectance measurements were conducted in the 300–2500 nm range with a Perkin Elmer Lambda 900 spectrophotometer equipped with a 150 mm diameter integrating sphere, suitable to carry out measurements on diffusing and scattering samples. The light reflectance measurements (400 nm to 700 nm wavelength) were carried out in the laboratories of Politecnico di Torino with a portable spectrophotometer (model: Minolta CM 600d). Based on the spectral reflection coefficients, the broad band coefficients (i.e., light/solar/NIR reflectance) are calculated after being weighted with the normalized relative spectral distribution of global solar radiation, following the procedure in ISO 9050:2003 Standard [29].

2.3.1. Measurement of light, solar and NIR reflectance under steady state conditions

As a preliminary step, the spectral reflectance of the TC panels was assessed in their colored and colorless phases considering the light (ρ_v), solar (ρ_e) and NIR ranges (ρ_{NIR}) to analyze the wavelength distribution of the optical properties. The analysis is performed at 15 °C and 50 °C, i.e., at temperature far below and above the switching temperature of 25 °C. This test was conducted on black and green TC panels, i.e., green TC type B, black TC type B. In addition, the same analysis was conducted on the reference panels, for comparison purposes.

Fig. 6. Pictures of the two testing conditions for the measurements used to assess the unexposed panels and the photodegradation of the exposed ones (shown in the pictures)., i.e., a) the ice basin, b) the ventilated oven.

2.3.2. Light reflectance measurement and colorimetric analysis of TC panels in the colored and colorless phases

A light reflectance analysis was conducted to study the color variation in the colored and colorless phases of the unexposed TC panels of type A in two different colors, i.e., black and green. The color variation of these panels was analyzed through the light reflectance (ρ_v) and, in more detail, through a colorimetric analysis, using the CIELAB coordinates. The latter method describes the color using L*, a* and b* coordinates, where L* quantifies the lightness, and the two coordinates for color a* and b* range respectively from green (-a*) to red (+a*) and from blue (-b*) to yellow (+b*) [30]. The panels were tested after being exposed to steady state thermal conditions at 0 °C and 50 °C for 4 h, by placing the panels in a thermally insulated basin filled with ice, and in a ventilated oven set at 50 °C, respectively. For each panel, the CIELAB coordinates were calculated as the arithmetic average of three measurements carried out in different positions of the panel, to account for potential color inhomogeneity of its surface. In order to have an overall assessment of the color difference exhibited by the panels between the colored and colorless phases, the color distance ΔE* was determined based on the measured L*, a* and b* coordinates of each panel. According to the CIE 1976 definition, ΔE* is the Euclidean distance between the coordinates exhibited by each panel in the colored phase (L_1^*, a_1^* and b_1^*) and colorless one (L_2^*, a_2^* and b_2^*), according with Eq. (1):

$$\Delta E^* = \sqrt{\left(L_2^* - L_2^*\right)^2 + \left(a_2^* - a_2^*\right)^2 + \left(b_2^* - b_2^*\right)^2} \tag{1}$$

2.3.3. Light reflectance measurement and colorimetric analysis of the outdoor exposed TC panels at different photodegradation stages

After the conclusion of outdoor experimental campaign, a laboratory testing was carried out to study the photodegradation effect on the green and black TC panels type B, that were previously tested in the outdoor experimental campaign. Light reflectance (ρ_v) measurements were performed in the areas of the panels that were protected by the patches applied during the outdoor exposition, which were meant to block the photo-degradation process at different stages. The measurements were performed at steady state thermal conditions far below and above the switching temperature of the TC paint, for the colored and colorless phases, respectively. The measurement procedure is the same described previously, i.e., the panels were tested at 0 °C (colored phase) and 50 °C (colorless phase), and three measurements were carried out in each

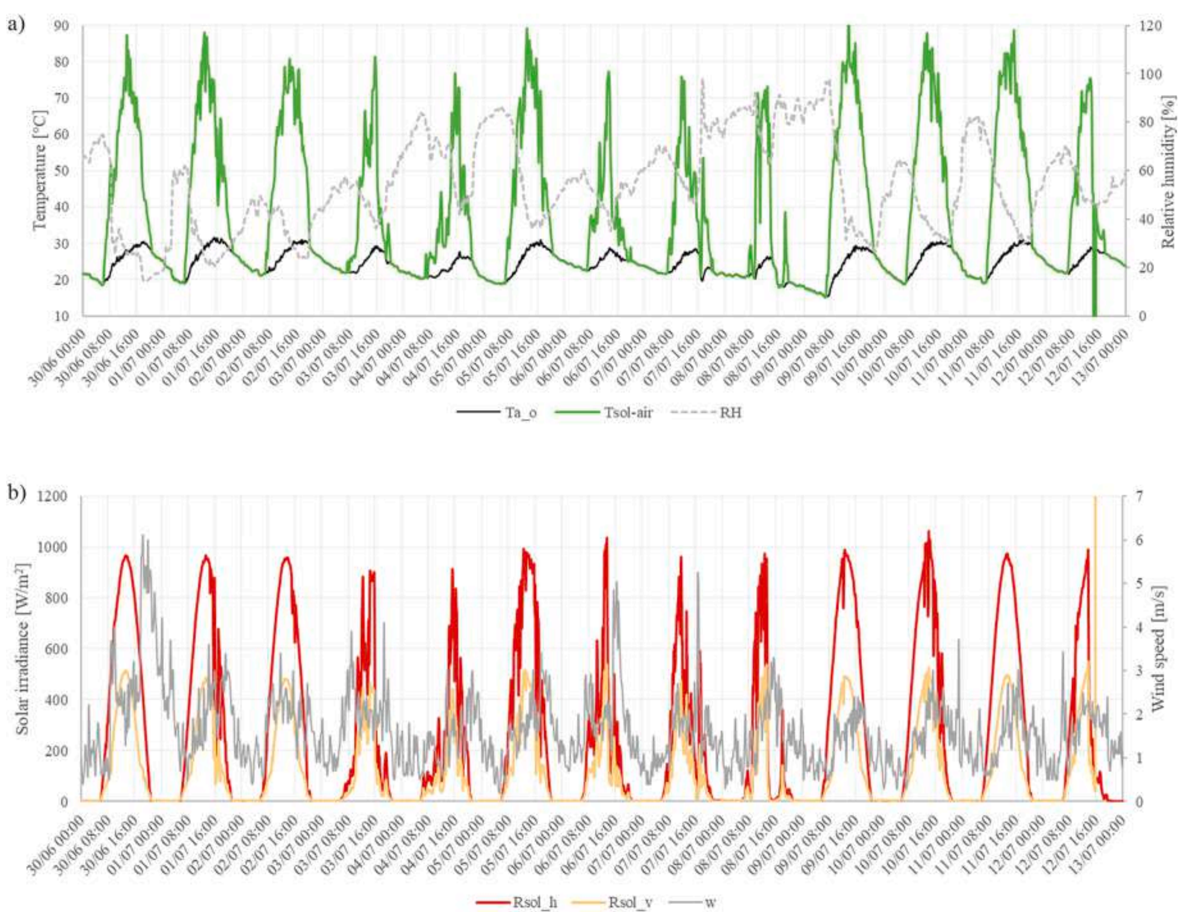

Fig. 7. Variation of the boundary conditions during the outdoor experimental campaign, with respect to a) outdoor air temperature (T_{a_o}), sol–air temperature ($T_{sol\text{-}air}$) and relative humidity (RH); b) the solar radiation on the horizontal plane (I_{sol_h}) and on the façade (I_{sol_v}) and of wind speed (w).

Fig. 8. Picture of the experimental set-up on the first day of the campaign, before and after the switching process.

portion of the panel, i.e., photodegradation stage; the two testing conditions are shown in Fig. 6. Besides the light reflectance (ρ_v) of the panel in the colored/colorless phase at each photodegradations stage, also the CIELAB were reported, for a more detailed evaluation on the color degradation exhibited by the panels.

2.3.4. Measurement of the light reflectance of the TC panels under transient thermal conditions

The switching process of the unexposed TC panels was studied in the laboratory by measuring the light reflectance (ρ_v) of the coating under transient thermal conditions for green TC panels type A and B and black TC panels type A and B. The panels were placed inside a climatic chamber (model: ATT DM340) performing temperature ramps in the range between 15 °C and 35 °C with a temperature variation of 0.1 °C/min. Considering the operating temperature of the spectrophotometer, the upper temperature of the transient temperature range was limited to 35 °C and a punctual data of ρ_v measured in steady state conditions at 50 °C (see § 2.3.1) was added for completeness. The panels were tested at every 1 °C variation of the climatic chamber under increasing and decreasing temperature ramps, to evaluate the behavior of the TC panels switching from the colored to the colorless phase and vice-versa. To have a more accurate accounting of the surface temperature variation, a calibrated T-type thermocouple (as described in § 2.2.2) was glued on the bottom side of each panel to collect temperature data every 30 s. The surface temperature of the panels was calculated as the average value of three acquisitions, considering the time needed to conclude the testing of the panels. The light reflectance of each panel is calculated as the average of three light reflectance measurements taken in different points.

3. Results

3.1. Outdoor testing

3.1.1. Boundary conditions

The graph in Fig. 7 shows the variation of the boundary conditions from June 30 to July 12. The outdoor air temperature (T_{a_o}), relative humidity (RH) and sol–air temperature ($T_{sol\text{-}air}$) calculated using the global horizontal solar irradiance (I_{sol_h}) are plotted in Fig. 7a, while I_{sol_h}, the solar irradiance incident on the façade (I_{sol_v}) and the wind speed (w) are shown in Fig. 7b. $T_{sol\text{-}air}$ allows to describe the environmental boundary conditions with a single figure, and it was calculated considering the measured solar absorbance of the black reference panel applied on the roof, equal to 0.9, and the horizontal or vertical solar irradiance (I_{sol_h} or I_{sol_v}), depending on the position of the samples. The radiative and wind-dependent convective coefficients used in the $T_{sol\text{-}air}$ calculation were determined according to ISO 6946:2017 [31] assuming an emissivity of 0.85, and considering the mean thermodynamic

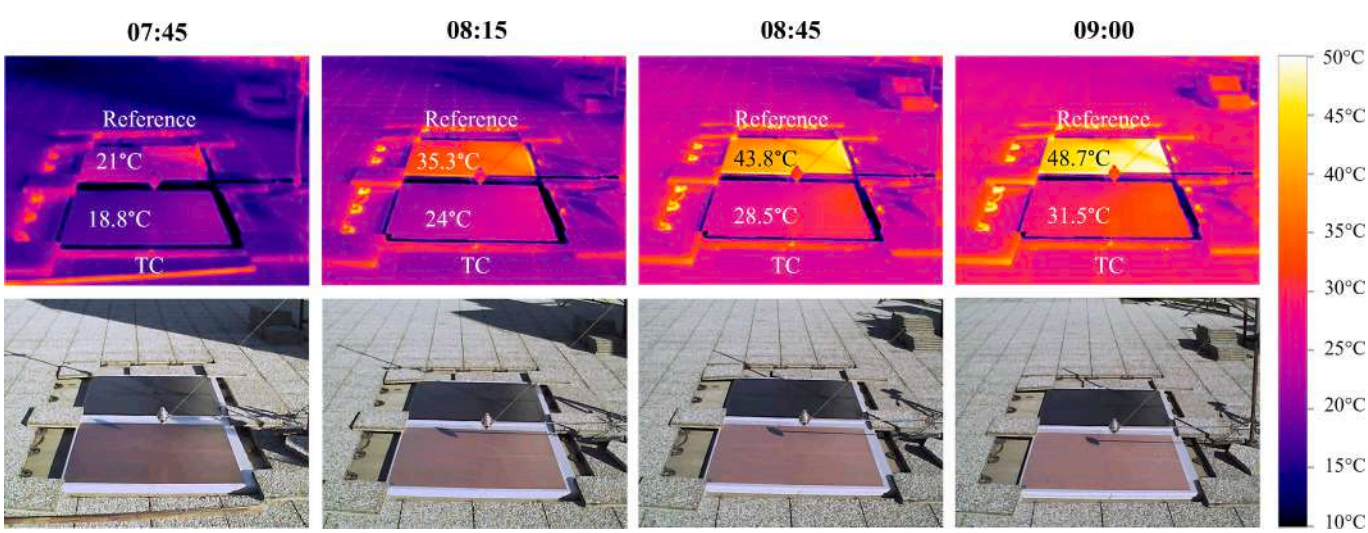

Fig. 9. Thermal images and corresponding true-color pictures of the TC/reference roof components during the switching process on the 2nd day of experimentation.

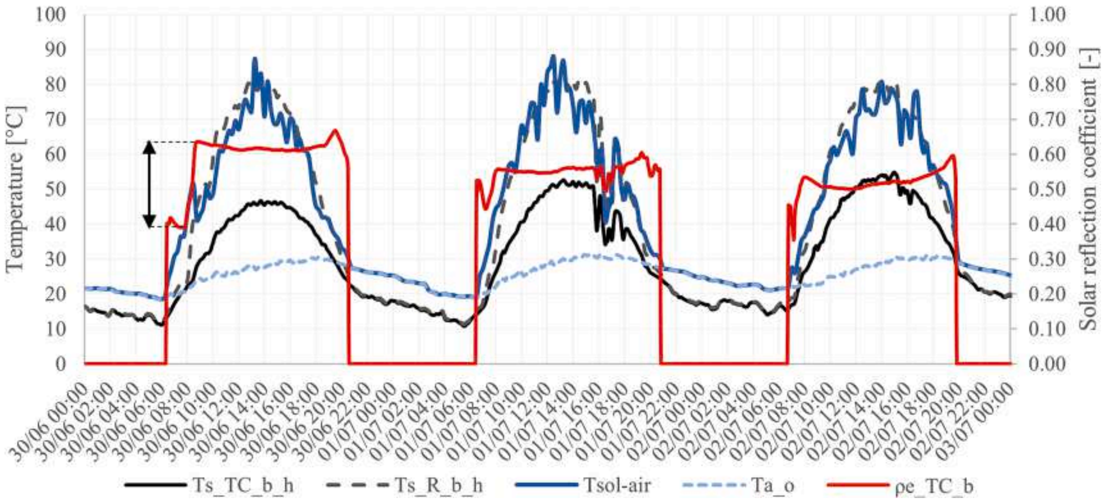

Fig. 10. Variation of the $T_{s\_TCb\_h}$, $T_{s\_Rb\_h}$ and ρ_e of the TC roof component and of T_a and $T_{sol\text{-}air}$ in the first three days of experimental campaign. Tsol-air and Ta_o are also plotted for completeness.

temperature of the surface and of its surroundings equal to the outdoor air temperature. The daily trends of the environmental variables suggest that the starting three days of the campaign exhibit comparable conditions, being sunny days with a clear sky. In the following days, the weather conditions are less stable, with a cloudy sky leading to a less regular solar radiation profile.

3.1.2. Roof components monitoring results

The appearance of TC panels installed on the roof and façade cladding components at the beginning and after the switching process on the first day of experimentation is shown in Fig. 8. As it can be noticed, the TC panels shift from a color comparable to that of the reference ones to a markedly lighter one at the end of the switching process.

Fig. 9 shows the thermal images, taken every 30 min, between 7:45 a.m. and 9:00 a.m. during the switching process on the second day of experimentation (please notice the impact of photodegradation in comparison to the photographs in Fig. 8). The images demonstrate how the temperature difference between the TC and reference panels quickly increases after sunrise, ranging from about 2 °C at 7:45 to around 17 °C at 9:00 a.m.

Fig. 10 shows the plots of the variation of the external surface temperature of the TC and reference roof components (i.e., $T_{s\_TC\_b\_h}$ and $T_{s\_R\_b\_h}$) and the solar reflectance of the TC panel applied on the roof component (ρ_{e_TCb}) as a function of $T_{sol\text{-}air}$ during the first three days of experimental campaign. For the sake of clarity, the I_{sol_ref} has been omitted from the graph, since ρ_{e_TCb} is calculated as the ratio between the I_{sol_ref} and I_{sol_h} (see Fig. 7b), and thus the former can be easily derived from this relation. As already pointed out, the $T_{sol\text{-}air}$ trend confirms that the boundary conditions during the first three days were favorable and comparable to each other. Since during those days the photodegradation effect was still relatively limited, the dynamic behavior of the TC panels was analyzed in this timeframe only. Due to the jeopardized switching performance of the TC paint, the data collected during the remaining days of experimentation (from July 3rd to July 12th) was used to study the photodegradation effect only (see § 3.2.2).

The plot shows the switching process of the TC panels, reported as the increase in solar reflectance occurring after sunrise, as a result of the surface temperature increase induced by the absorbed solar radiation. This variation in optical properties results in remarkably different

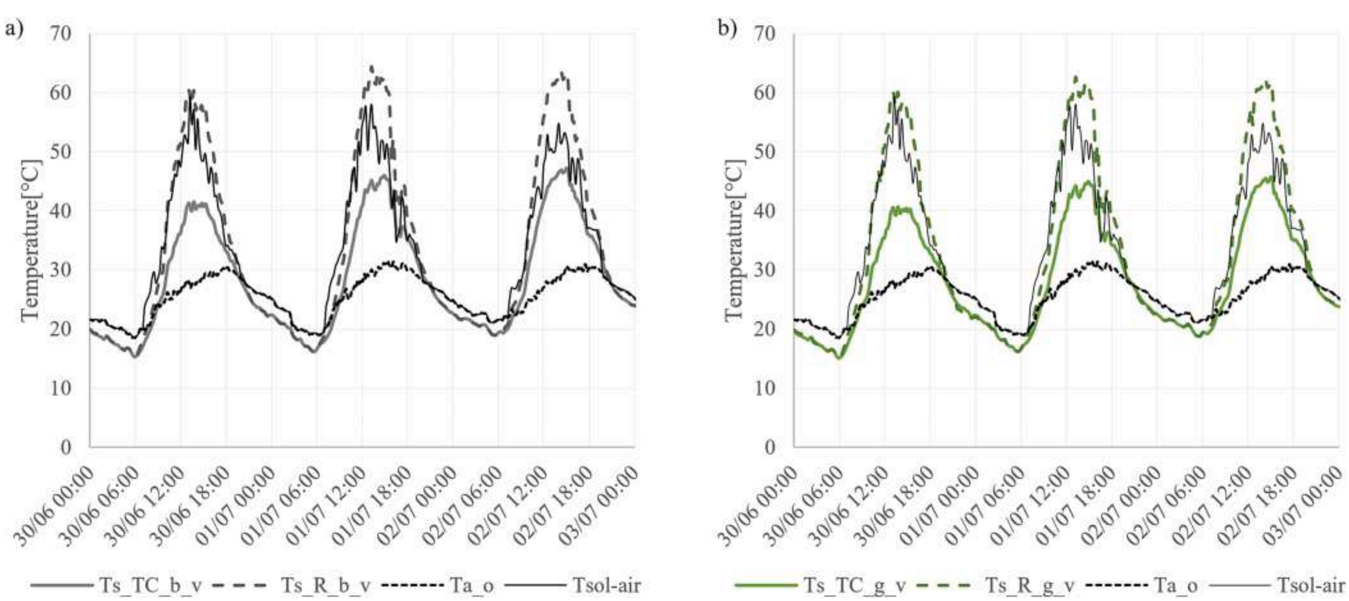

Fig. 11. Surface temperature of the TC/reference panel for façade application during the first three days of outdoor experimentation.

Table 3
Reflectance of the black unexposed TC panel and reference panels in the solar/visible range (laboratory measured) and on day 1 of exposition (in-situ measured solar reflectance). (*Value measured at about 45 °C).

	Black TC panel				Black reference panel			
	ρ_e (in-situ, 1st day)	ρ_e (lab)	ρ_v (lab)	ρ_{NIR} (lab)	ρ_e (in-situ)	ρ_e (lab)	ρ_v (lab)	ρ_{NIR} (lab)
colored phase	~0.40	0.39	0.05	0.71	0.10	0.05	0.05	0.05
colorless phase	0.62*	0.70	0.66	0.75				

surface temperatures between the TC panels and the reference ones during daytime. Conversely, at nighttime no sensible difference in surface temperature between the TC and reference panels is observed, thus indicating comparable long-wave thermal emissivity between the two panels' surfaces.

The ρ_{e_TCb} trend reveals that the switching phase occurred over a very short time frame (around 30 min) just after sunrise. Therefore, it can be generally considered that the ρ_{e_TCb} readings between 8:50 a.m. and 8:15p.m. describe the colorless phase of TC panels, while those referred to the colored phase can hardly be evaluated due the limited number of data collected in this short phase. Nevertheless, only for the first monitoring day, ρ_{e_TCb} in the colored phase of ~0.4 could be measured, while in the second and third day the occurred photodegradation has limited the difference between the colored and the colorless phases.

Despite the plot is limited to the first three days of outdoor experimentation, the effect of photodegradation is already visible. The solar reflectance of the TC panel in its colorless phase tends to decrease by 0.1 in three days, varying from a mean value of about 0.62 on the first day of exposition to about 0.52 on the third day. This reduction is caused by the photodegradation process that gradually compromises the TC panel's performance, whose colorless phase tends to become darker over time.

The external surface temperature of the reference panel reaches peaks of about 80 °C during the central hours of the days, while the maximum surface temperatures reached by the TC one range between 45 °C on day one to 55 °C on the third day. The maximum surface temperature difference between the TC ($T_{s\_TCb\_h}$) and the reference panels ($T_{s\_Rb\_h}$) is about 35 °C on the first day, when the effect of photodegradation is relatively limited in comparison to the following days. Indeed, in the third day of experimentation, the surface temperature difference between the reference and the TC panel is reduced to about 25 °C.

To convey information on the statistic distribution of the measured quantities for each day of outdoor experimental campaign, $T_{s\_TCb\_h}$ $T_{s\_Rb\_h}$ and $T_{sol\text{-}air}$ collected during the first three days have been also represented using boxplots in Fig. 15 in the Appendix.

3.1.3. Façade components monitoring results

The trend of external surface temperatures of the TC/reference panels applied over the façade of the test cell during the first three days of experimentation is shown in Fig. 11a for the black TC/reference panels ($T_{s\_TC\_b\_v}$ and $T_{s\_R\_b\_v}$, respectively) and in Fig. 11b for the green TC/reference panels ($T_{s\_TC\_g\_v}$ and $T_{s\_R\_g\_v}$, respectively). The $T_{sol\text{-}air}$ trend is added for completeness. The surface temperatures of the black and green TC/reference panels follow comparable trends, suggesting that, regardless the color difference, the reflectance of the coatings is similar.

As observed in the case of the roof components, the surface temperature of the TC panels is markedly lower than that of the corresponding reference components during daytime. In absolute terms, the surface temperature exhibited by the panels applied over the façade are lower than those applied horizontally on the roof, given the different amount of solar radiation impinging on them. The maximum temperature observed for the reference panels ($T_{s\_R\_b\_v}$ and $T_{s\_R\_g\_v}$) is around 60–62 °C while that measured on the TC panels ($T_{s\_TC\_b\_v}$ and $T_{s\_TC\_g\_v}$) is between 40 °C (day 1) and 47 °C (day 3), for both color options, depending on the day. The maximum temperature difference between the reference and TC panels shifts from about 20 °C on the first day, to about 15 °C on the third one, independently of the color. Overall, the graph shows that the absolute surface temperature values and relative loss of thermochromic performance over the days (i.e. trends in maximum surface temperature difference) are smaller in case of the façade panels with respect to the roof ones, as a result of the reduced amount of solar radiation impinging on them.

As for the roof components, $T_{sol\text{-}air}$, $T_{s\_TC\_b\_v}$ and $T_{s\_R\_b\_v}$ on the first three days of outdoor experimentation are shown using boxplots in Fig. 16 in the Appendix.

3.2. Laboratory testing

In the following sections, the results of the laboratory analysis are collected by grouping the results concerning the light and solar reflectance of TC panels (§ 3.2.1), the colorimetric analysis (§ 3.2.2), the photodegradation study (§ 3.2.3) and the analysis of the switching process of the TC panels (§ 3.2.4).

3.2.1. Light, solar and NIR reflectance of the TC panels

The result of the reflectance measurement for the black TC panels type B and corresponding reference panels are collected in Table 3, considering the solar, visible and NIR ranges. The results on the same analysis on green TC panels type B and reference panels is reported in Table 4. For the black TC panel, the solar reflectance (ρ_e) in the colorless and colored measured in the laboratory can be also compared to that measured in-situ on the first day of experimentation with the double pyranometer setup on the horizontal roof component, showing a good matching.

The reference panels were meant to be comparable to the corresponding TC ones in the colored phase. Nonetheless, despite a good agreement between the reference and TC panels is reported in the visible range (ρ_v), a marked mismatch is observed in the near-infrared one (ρ_{NIR}), where the TC panels exhibit a reflective behavior in contrast to the absorptive one of the reference panels. While these properties highlight a questionable degree of comparability between the reference and TC panels in the colored phase, they were however considered acceptable given the methodological purpose of the present research

Table 4
Reflectance of the green unexposed TC panel and reference panels in the solar/visible range (laboratory measured).

	green TC panel			green reference panel		
	ρ_e (lab)	ρ_v (lab)	ρ_{NIR} (lab)	ρ_e (lab)	ρ_v (lab)	ρ_{NIR} (lab)
colored phase	0.42	0.08	0.73	0.07	0.06	0.08
colorless phase	0.72	0.75	0.74			

Table 5
CIELAB coordinates and light reflectance of the unexposed TC panels type A in green and black color in the colored phase (0 °C) and colorless one (50 °C).

	0 °C				50 °C				Δ 0–50 °C	
	L*	a*	b*	ρ_v	L*	a*	b*	ρ_v	ΔE*	$\Delta\rho_v$
green type A	25.05	−9.76	5.01	0.06	84.00	0.34	9.69	0.64	59.99	0.58
green type B	27.61	−16.81	9.29	0.07	88.90	−3.02	7.12	0.73	62.85	0.66
black type A	19.43	1.49	−0.33	0.05	79.39	2.31	10.64	0.57	60.96	0.53
black type B	21.69	1.50	1.75	0.06	87.21	−0.77	6.22	0.70	65.72	0.64

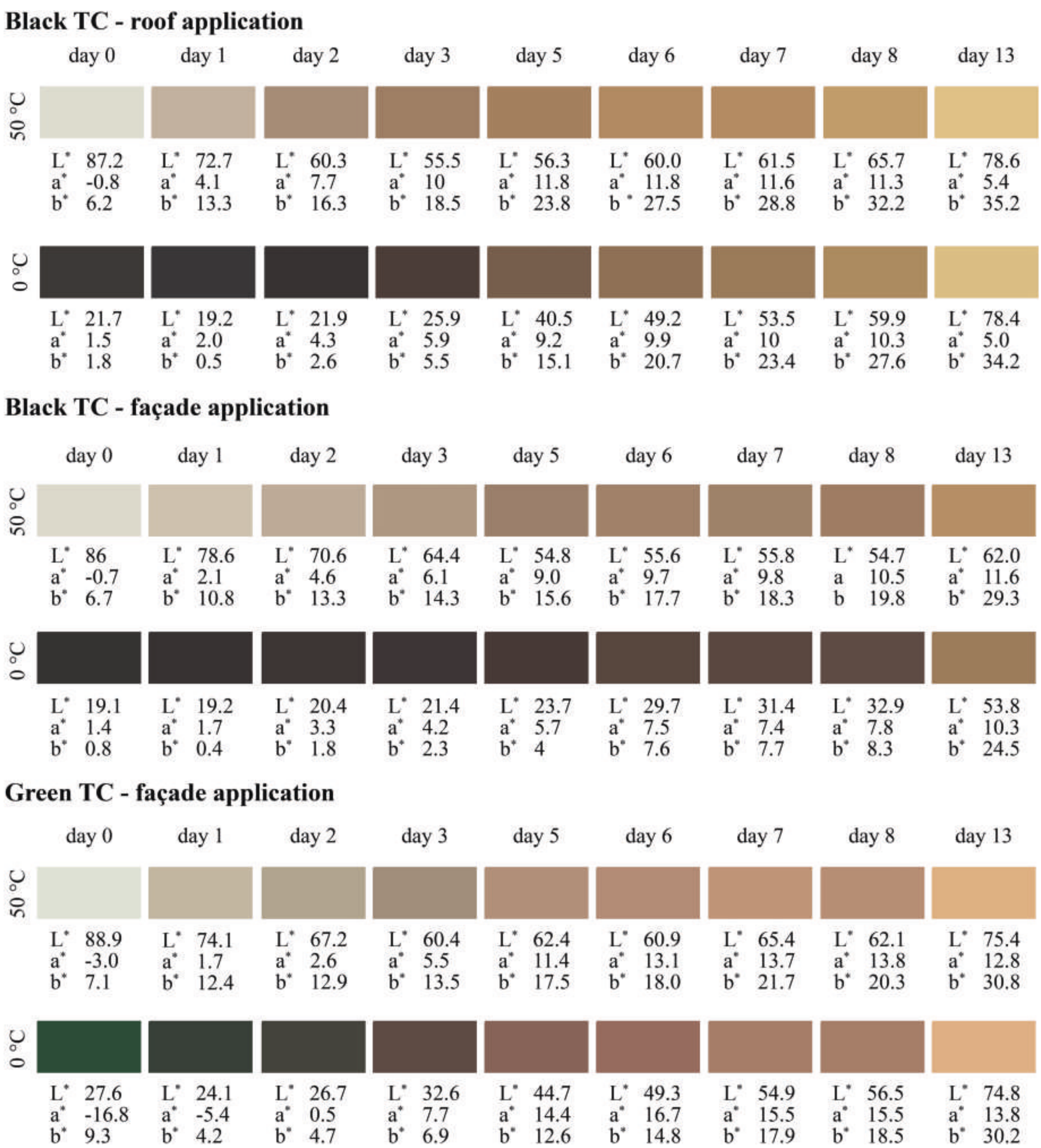

Fig. 12. Visual appearance and corresponding CIELAB coordinates of the TC panels at the different stages of photodegradation, in the colored and colorless phases.

contribution.

As concerns the TC panels, a good agreement between the in-situ measured and laboratory measured solar reflectance (ρ_e) of the black TC panel is found, with a maximum difference of 0.08 in case of the colorless phase, which confirms the reliability of in situ measured data. Moreover, the comparison of the reflectance in the different ranges for the colored and colorless phases highlights that the switching process affects the reflectance of both TC panels only in the visible range (ρ_v), while spectral reflectance of the TC panels in the NIR range (ρ_{NIR}) remains unaltered. In case of the black TC panel, ρ_v varies between 0.66 (colorless phase) to 0.05 (colored one), while for the green TC panels, ρ_v varies between 0.75 (colorless phase) and 0.08 (colored phase). This

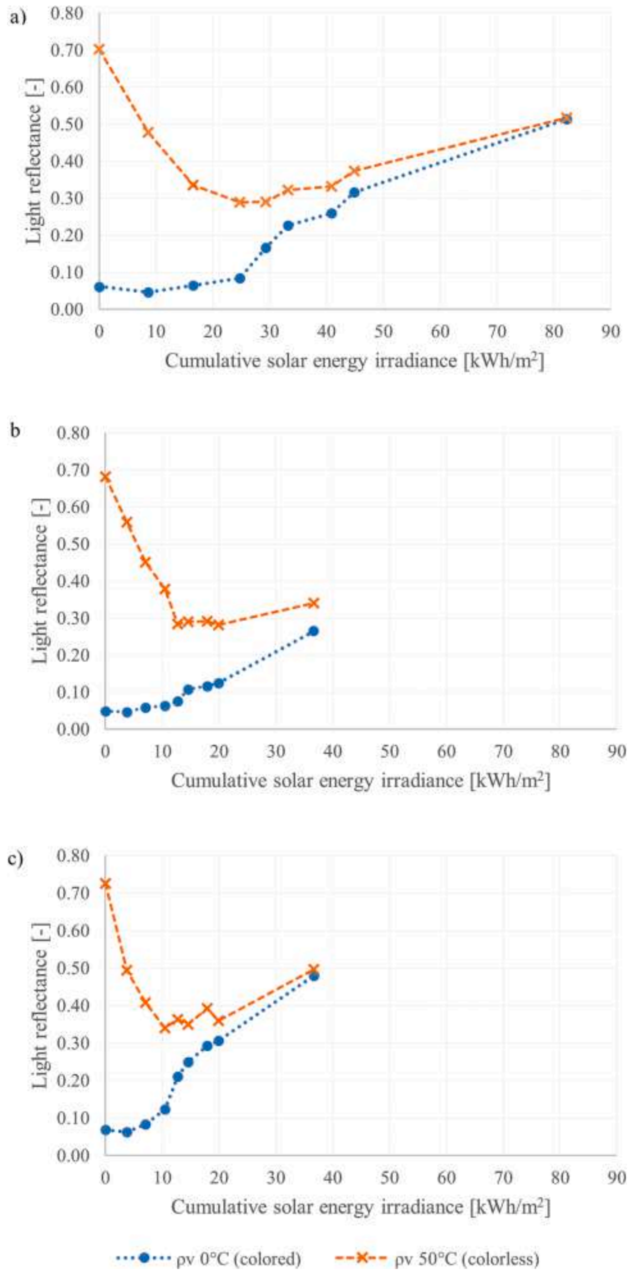

Fig. 13. Light reflectance plotted as a function of the cumulative solar irradiance for a) black TC panel type B installed on the roof; b) black TC panel type B installed on the façade; c) green TC panel type B installed on the façade.

result suggest that the dynamic properties of the tested TC materials can be adequately investigated through reflectance measurements limited to the visible range.

3.2.2. Light reflectance and colorimetric analysis of the TC panels of type a in the colored and colorless phases

Table 5 collects the results of the spectrophotometric investigation of the unexposed TC panels in green and black color, carried out in steady state thermal conditions at 0 °C and 50 °C to characterize them in the colored and colorless phases, respectively.

The results highlight that the differently colored panels show, in the colored phase, ρ_v values in the range of 0.05 to 0.07, while a greater dispersion of the ρ_v values in the colorless phase is observed, with values ranging from 0.57 to 0.73. Overall, the difference of light reflectance between the colored and colorless phases ($\Delta\rho_v$) is between 0.53 and 0.66, that corresponds to a color distance ΔE^* in the range between ~60 and ~66. The smallest variation in $\Delta\rho_v$, equal to 0.53 ($\Delta E^*=$ ~61), occurs for the black TC panel type B, while the greatest ones, i.e., 0.66 and 0.64 ($\Delta E^*=$ ~ 63 to 66), are exhibited by the green and black TC panel type B. The comparison between the green and black TC panels type A and B show marked differences in the ρ_v values in the colorless phases, evidencing a different production process for the two panels' types.

3.2.3. Light reflectance of the photodegraded TC panels in the colored and colorless phases

The analysis on the photodegraded TC panels aims to assess the extent to which the photodegradation processes had affected their color switching ability of the TC over time. In Fig. 12 the visual appearance and CIELAB coordinates of the TC panels type B used in the outdoor experimentation in the colored and colorless phases is shown at the different stages of photodegradation, i.e., days of experimental campaign. The image shows how the color difference exhibited by the pristine panel in the two phases gradually vanished due to the photodegradation process when exposed to outdoor conditions, leading to a final stage, at the end of the experimentation (13 days of exposure), where the dynamic properties of the TC panels are heavily compromised and the color difference in the two phases is barely noticeable.

To provide a more quantitative evaluation of the photodegradation process, the graphs in Fig. 13 plots the light reflectance of the TC panels of type B used for the outdoor experimentation, in the colored and colorless phases, as a function of the cumulative solar irradiance at the different stages of photodegradation. The cumulative solar irradiance quantifies the amount of solar radiation to which the panels were exposed at the different photodegradation stages and is referred to the horizontal irradiance (I_{sol_h}) in case of the roof component and to the vertical one (I_{sol_v}) in case of the façade ones. The data referred to the TC panel applied on the roof component is shown in Fig. 13a, while in Fig. 13b and Fig. 13c are reported those of the black and green TC panels applied on the façade, respectively. The results show progressive loss of switching ability of the TC panels due to photodegradation. The light reflectance of the TC panels before the outdoor exposition (i.e., the value plotted for a cumulative solar irradiance of 0 kWh/m^2) varies between ~0.7 in the colorless phase to ~0.05 in the colored one, as noted in § 3.2.2. Starting from the first day of exposition to solar irradiance there is a marked drop of the ρ_v of the panels in the colorless phase; the reduction of ρ_v in the colorless phase continue over the following days, with a slightly more attenuated trend until it tends to the stabilization. These more stable data were collected from the 4th day to the 7th day, where the weather was often cloudy, so the solar irradiance was quite limited. The ρ_v of the panels in the colored phase seems to be affected more gradually by the photodegradation effect, as the variation is much more limited during the first days of outdoor exposition, while for most panels seems to increase from the 4th day to the 7th day, i.e., the days in which the photodegradation impact on the colorless phase was less significant. The ρ_v values for the colored and colorless phases collected on the 7th day (~20 kWh/m^2 for the façade component and of ~45 kWh/m^2 for the roof one) are very close to each other with a difference smaller than 0.1 in case of the black TC panel applied on the roof and the green one installed on the façade, and of about 0.15 in case of the black TC panel applied on the façade. The final value plotted in the graphs, referred to the end of the outdoor experimentation (on the 13th day, at ~82 kWh/m^2 for the roof panel, and ~37 kWh/m^2 for the façade one), clearly show that the ρ_v in the colored and colorless phases have converged to a single value, meaning that the panels have fully lost their ability to switch their optical properties.

3.2.4. Light reflectance of the TC panels during the switching process

The graphs in Fig. 14 plots the measured variation of ρ_v under transient thermal conditions, of the green and black TC panels type A and green and black TC panels type B as a function of their surface

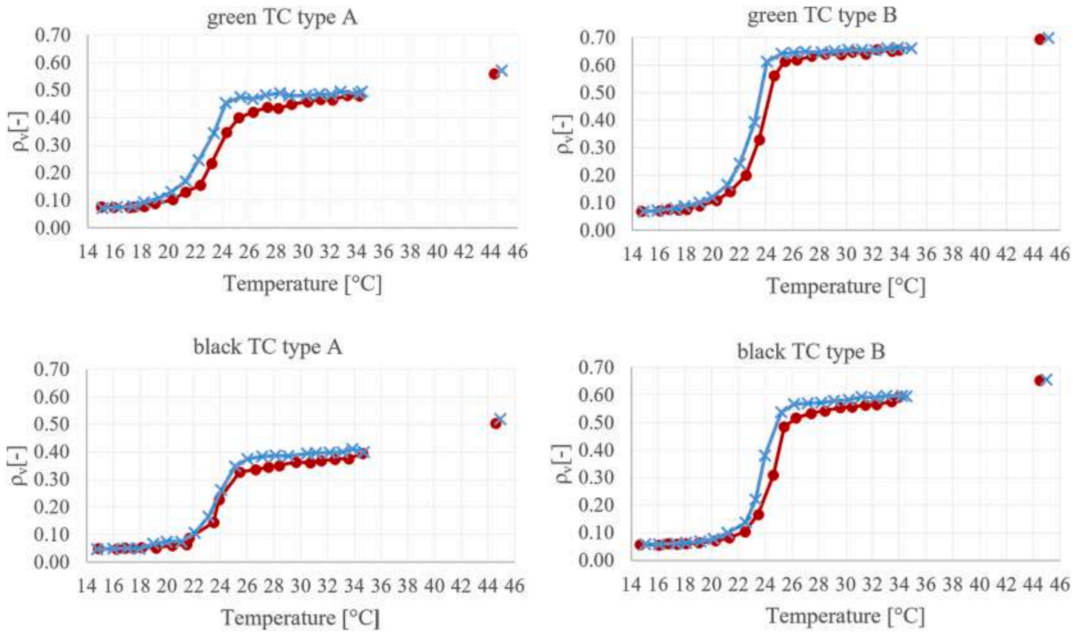

Fig. 14. Graphs of the light reflectance of the test TC panels in either decreasing (blue line) or increasing (red line) thermal conditions.

temperature. The graphs show the measured value of ρ_v considering an either increasing (i.e., heating, shown in red color) or decreasing (i.e., cooling, shown in blue) temperature variation. The switching process of the panels, that in the graphs corresponds to a steep variation of ρ_v, occurs for most TC panels at around 24 °C, i.e., slightly below the nominal switching temperature of 25 °C. At temperature far above and below such temperature, almost no variation of light reflectance was observed. The comparison of the ρ_v values measured following the increasing and decreasing temperature trends, highlights that the switching process is not instantaneous and occurs around slightly different temperatures, with a variation of 0.5 to 1 °C, suggesting that they are subject to a limited thermal hysteresis phenomenon, whose magnitude is comparable for all the tested panels. While the phenomenon of hysteresis is reported to occur in other thermochromic solutions, such as TC glazing [32], and has been included in the simulation model of TC roofs in [5], to the best knowledge of the authors, it has not been studied experimentally on TC coatings so far.

4. Conclusions

This study focuses on TC materials for building cladding applications that present dynamic optical properties and are a promising energy-saving solution to reduce the heating and cooling demands in climates where they are balanced throughout the year, while also contrasting urban overheating in summer. This research presents a methodology to monitor the behavior of TC materials in outdoor conditions and to characterize their dynamic performance in the laboratory. Despite being originally developed for TC materials, the proposed methodology may be adapted for other types of switchable coatings.

In an outdoor experimental campaign conducted during summertime, TC and reference panels were applied as the outer layer of roof and façade components to monitor the external surface temperature and solar reflectance of the panels over the days. Different laboratory studies were carried out, with the goals of characterizing the spectral and light reflectance of the TC panels in the colored and colorless phases, investigating the progressive performance loss exhibited by the outdoor exposed thermochromic panels caused by the photodegradation, and studying the switching process of unexposed TC panels under transient thermal conditions. The results of the outdoor experimentation suggest that the application of TC building cladding is an effective strategy to reduce building energy consumption to achieve indoor thermal comfort without occurring in heating penalties in wintertime. While a maximum difference in the surface temperature of TC in their colorless phase and reference panels of about 35 °C was found in case of the roof application, this result should be considered specific of this study. Indeed, it was observed that the TC paint shows a greater near infrared reflectance compared to the reference (conventional) paint, meaning that the measured temperature difference is influenced also by this property and not only by TC behavior. Therefore, the results of this study should be interpreted in light of these considerations.

A methodological approach to assess the in-situ reflection properties of TC coatings is also presented, showing good agreement with the values measured in the laboratory.

The spectral reflectance analysis on the TC panels in the colored and colorless phases have highlighted that the panels exhibit dynamic properties in the visible range, while a negligible switching behavior is observed in the near infrared region. The light reflectance of TC panels in the colored and colorless phases was measured on a set of panels in green and black colors; in addition, a colorimetric investigation was performed on them to gather more information on the visual appearance of the panels in the two phases. Overall, the difference of light reflectance between the colored and colorless phases ($\Delta\rho_v$) is between 0.53 and 0.66, that correspond to a color distance ΔE* in the range between ~60 and ~66.

Despite their potential, the dynamic performance of TC materials based on leuco dye quickly degrade when exposed to solar radiation. This phenomenon was observed in the outdoor testing, where the solar reflectance of the TC panel was reduced by 0.1 after three days of outdoor exposition. Consequently, the difference in surface temperature between the TC and reference panel applied on the roof was reduced by 10 °C. A light reflectance analysis on the degraded panels at different photodegradation stages in the colored/colorless phases suggests that, at first, the process mainly affects the ability of the TC dye to fully reach the colorless phase, while it impacts on its ability to switch to the colored phase at a later time.

To conclude, a light reflectance study was conducted to investigate the switching process of the TC panels under transient thermal conditions, with increasing and decreasing temperature variations. The study has allowed to observe a limited hysteresis phenomenon exhibited by the TC panels, evidencing that the switching process is noninstantaneous and occurs at slightly different temperature based on the previous thermal state of the panel.

Further investigations may include the extension of the monitoring campaign to both summer and winter condition, the testing of more stable TC paint solutions and the characterization of TC behavior in outdoor settings over longer period of time.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix

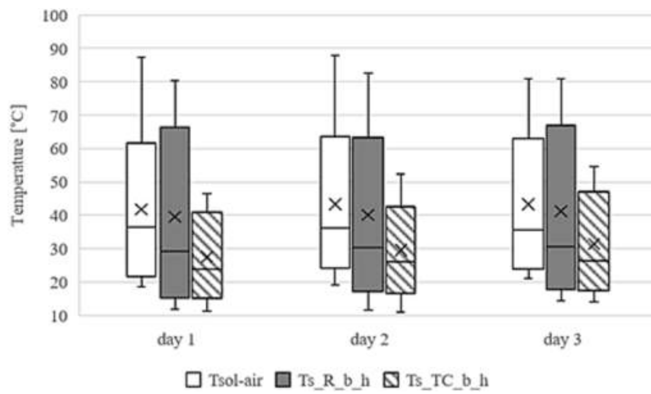

Fig. 15. Boxplots showing the sol–air temperature and the surface temperature of the TC and reference roof panels (Ts_TC_b_h and Ts_R_b_h, respectively) during the first three day of outdoor experimentation.

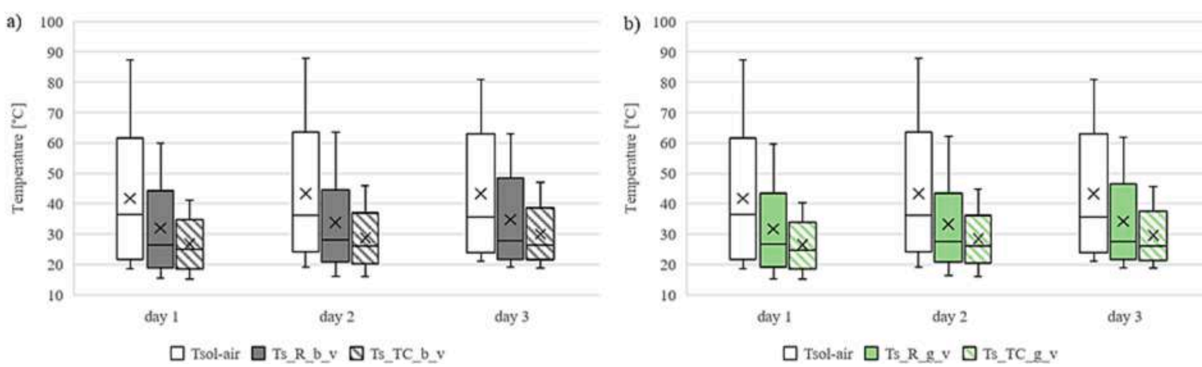

Fig. 16. Boxplots showing the sol–air temperature and the surface temperature of the TC and reference façade panels in a) black color (Ts_TC_b_v and Ts_R_b_v, respectively) and b) in green color (Ts_TC_g_v and Ts_R_g_v, respectively) during the first three day of outdoor experimentation.

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