RAPPORTO TECNICO
Technical Report

Protocollo			
Titolo	**Hydrophilic behavior and photocatalytic activity of the ceramic sample Collection NEVE tono 704, Laminam 3+**		
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INTRODUCTION

This report refers to the characterization of a ceramic tile surface, named **Collection NEVE tono 704 Laminam 3+**, bearing a TiO_2-based coating. The determination of the contact angles with water (WCA) and the analysis of the hydrophilic behavior of the surface was performed according to the **ISO 27448-2009** Standard, while the photocatalytic activity against a Methylene Blue (MB) solution was determined according to the **ISO 10678-2010** Standard.

1. OBJECTIVES

The objective is to verify the self-cleaning ability and the photocatalytic properties of the surface according to the following Standards:
ISO 27448-2009: "Fine ceramics (advanced ceramics, advanced technical ceramics) - Test method for self-cleaning performance of semiconducting photocatalytic materials - Measurements of water contact angle"
ISO 10678-2010: "Fine ceramics (advanced ceramics, advanced technical ceramics) - Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue"
The results of photocatalytic activity against MB have been further elaborated according to the Japanese standard **JIS R 1703-2: 2007**.

2. SAMPLING

The sampling - requested by ISTEC and delivered by LAMINAM - consists of ceramic pieces measuring approximately 10 x 10 cm for the determination of the contact angle (ISO 27448-2009) and approximately 5 x 5 cm for the determination of the photocatalytic activity (ISO 10678-2010).

3. INSTRUMENTS

3.1 Determination of contact angles and induced hydrophilicity under UV irradiation
- KRUSS DSA 30S tensiometer (Krüss GmbH) by the sessile drop method (drop volume = 2µl).
- Osram Ultra-Vitalux 300 Watt Lamp emitting in the UV-A range at $\lambda < 400$ nm.

3.2 Determination of the photocatalytic activity against a methylene blue (MB) solution
- Single-beam spectrophotometer (Boeco S-22) with wavelength λ centered at 664 nm.
- Osram Ultra-Vitalux 300 Watt Lamp emitting in the UV-A range at $\lambda < 400$ nm.

4. EXPERIMENTAL METHODOLOGIES

4.1 Determination of contact angles and induced hydrophilicity under UV irradiation (operators: Guia Guarini, Federico Veronesi)
All test pieces were cleaned with deionized water under slight rubbing with a cotton cloth, then dried with a flow of hot air.
The hydrophilic degree of the ceramic surface was determined by measuring the contact angle with water (WCA) (KRUSS DSA 30S tensiometer, GmbH) using the sessile drop method. A 300 Watt Osram Ultra-Vitalux lamp, emitting in the UV-A range at wavelength <400 nm and with an intensity (I) experimentally measured on the test surface of 2.0 mW/cm^2, was used for irradiation. Before the measurement, all pieces were kept in the dark for one night. The wettability of the ceramic surface was monitored through WCA measurements before and after irradiation.
The irradiation was conducted for 7 hours, measuring the WCA every 60 minutes. For each experimental condition, the WCA was measured by depositing a volume drop of 2 ml on a number of points equal to 10, randomly distributed on the sample surface in order to ensure the statistical significance of the results. The labelled values of WCA represents the average of the different measurements.

The final contact angle x is defined as the average of the last three WCA values whose ratio between the standard deviation and the average is lower than 10%:

$x = (\theta_1+\theta_2+\theta_3)/3$

The lower the WCA, the greater the hydrophilic degree. In many papers, which can be taken as reference, samples are defined as superhydrophilic when their WCA is lower than 5°.

4.2 Determination of the photocatalytic activity against a methylene blue (MB) solution (operator: Federico Veronesi)
The variations of the absorbance (A) of the MB solution were followed by spectrophotometric evaluation (single-beam Boeco S-22 Instruments, λ centered at 664 nm). For the irradiation of the samples, a 300 Watt Osram Ultra-Vitalux lamp with UV-A emission in the wavelength range <400 nm was used, with an intensity (I) measured experimentally on the test surface of 1.0 mW / cm^2.
The sampling consists of two pieces with a surface of about 5x5 cm^2, cleaned with deionized water under light rubbing with a cotton cloth, then dried with a flow of hot air. The samples were previously irradiated with the OSRAM Ultra-Vitalux 300W lamp for at least 24 hours with an incident intensity of 2.0 mW/cm^2. Two aqueous solutions of MB were prepared, a "conditioning" MB solution with a concentration of 20 μmol /l and a "test" one with a concentration of 10 μmol /l.
A plastic cylinder (diameter = 4 cm, height = 2.8 cm), containing 35 ml of the conditioning solution, was glued onto the sample surface with high vacuum grease. The sample was then left in the dark for at least 16 hours. The conditioning phase is considered to be complete if the absorbance of the MB solution is greater than that of the test solution.
For only one of the two test samples, the conditioning solution was replaced with 35 mL of test solution. The sample was then placed under the lamp by setting the irradiation intensity on the surface to 1.0 mW /cm^2. The other cylinder was kept in the dark. The absorbance of aliquotes of the test solutions in contact with the samples was measured at fixed intervals of 20 minutes. The total irradiation length was established in 3 hours.
In accordance with the requirements of ISO10678-2010, the following parameters have been calculated:

- Specific degradation rate $\mathbf{R} = \Delta A \lambda V / \Delta t \varepsilon d A$

- UV photons intensity, $\mathbf{E_p} = \lambda_{max}\ E \cdot 30074$

where:
λ_{max} is the wavelength corresponding to the maximum emission of the lamp (λ_{max} = 351 nm)
V the volume of the solution (V = 35 mL)
ε the absorption coefficient of the MB solution at 664 nm (ε = 7402.8 m^2/mol)
d the length of the cuvette (d = 1 cm)
A the surface of the sample in contact with the solution (A = 12.56 cm^2)

These parameters allow to calculate the specific photoactivity $\mathbf{P_{MB}}$ and the photonic efficiency $\boldsymbol{\zeta_{MB}}$**:**

- Specific photoactivity $\mathbf{P_{MB} = R_{irr}-R_{dark}}$
- Photonic efficiency $\boldsymbol{\zeta_{MB} = P_{MB}/E_P \cdot 100}$

For comparison, the results were also processed according to the Japanese standard JIS R 1703-2: 2007, calculating the MB index according to the formula:

MB index = $|a| \times 1000$

where:
a is the slope of the fitting line in Figure 3 showing the MB concentration as a function of time.
According to JIS R 1703-2: 2007, a surface can be defined as photocatalytically active if the value of MB index is at least 5.

5. Results

5.1 Contact angles values and hydrophilicity induced under UV irradiation

The average values of WCA measured on the sample surface at t = 0 and after irradiation with the UV lamp are shown in Table 1.
The experimental trend highlights that at t=0 WCA is about 66° and that, after 6 hours of irradiation, it reaches the final value of 15.2°. Notwithstanding the ISO standard does not provide any specific reference, such a value indicates that a somehow limited activation of the surface is occurring during UV irradiation.

Table 1. Experimental value of WCA (°) at different irradiation times. The value that, according to the ISO 27448-2009 standard, was taken as the final contact angle is highlighted in red

Irradiation time (h)	θ_n (°)	S (°)	x (°)	s/x (%)
0	66.7			
1	55.3			
2	26.5	20.7	49.5	41.9
3	19.2	19.1	33.7	56.7
4	16.8	5.1	20.8	24.2
5	14.7	2.3	16.9	13.3
6	14.0	1.5	**15.2**	9.6
7	12.1	1.3	13.6	9.9

5.2 Determination of the photocatalytic activity against a methylene blue (MB) solution
The values of specific photoactivity $\mathbf{P_{MB}}$ and photonic efficiency ζ_{MB} are labelled in Table 2. The values are, respectively, 3.3 x10^{-5} mol/m^2h e 0.030906%.

Table 2. Specific photoacivity ($\mathbf{P_{MB}}$) and photonic efficiency (ζ_{MB}) of the ceramic surface

t (min)	t (h)	A_{irr} (AU)	A_{dark} (AU)	E (W/m^2)	E_P (mol/m^2*h)	R_{irr} (mol/m^2*h)	R_{dark} (mol/m^2*h)	P_{MB} (mol/m^2*h)	ς_{MB} (%)
0	0,00	0,771	0,75	10,0	0,106				
20	0,33	0,743	0,757	10,0	0,106	3,16E-05	-7,90E-06	3,95E-05	0,03744
40	0,67	0,71	0,758	10,0	0,106	3,73E-05	-1,13E-06	3,84E-05	0,03637
60	1,00	0,673	0,756	10,0	0,106	4,18E-05	2,26E-06	3,95E-05	0,03744
80	1,33	0,646	0,761	10,0	0,106	3,05E-05	-5,65E-06	3,61E-05	0,03423
100	1,67	0,611	0,759	10,0	0,106	3,95E-05	2,26E-06	3,73E-05	0,03530
120	2,00	0,586	0,762	10,0	0,106	2,82E-05	-3,39E-06	3,16E-05	0,02995
140	2,33	0,558	0,758	10,0	0,106	3,16E-05	4,52E-06	2,71E-05	0,02568
160	2,67	0,532	0,759	10,0	0,106	2,94E-05	-1,13E-06	3,05E-05	0,02888
180	3,00	0,520	0,759	10,0	0,106	1,36E-05	0,00E+00	1,36E-05	0,01284
MEDIA								**3,26E-05**	**0,030906**

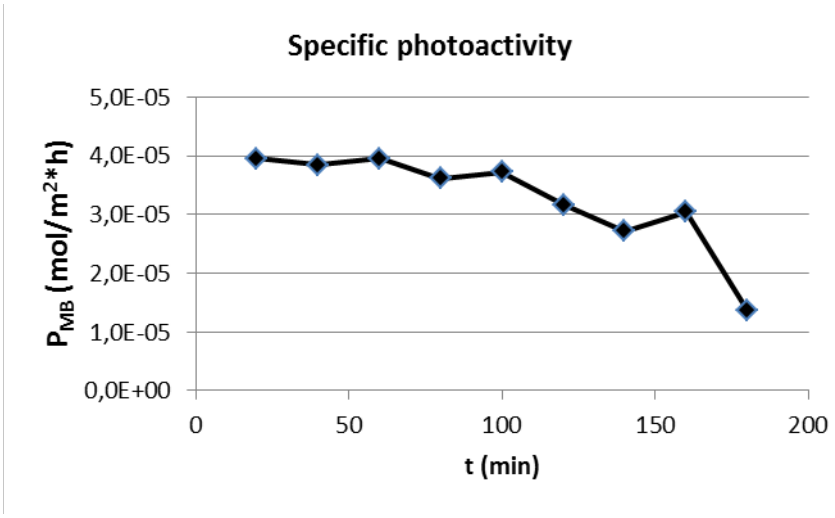

Figure 1. Specific photoactivity $\mathbf{P_{MB}}$ of the ceramic surface as a function of the time

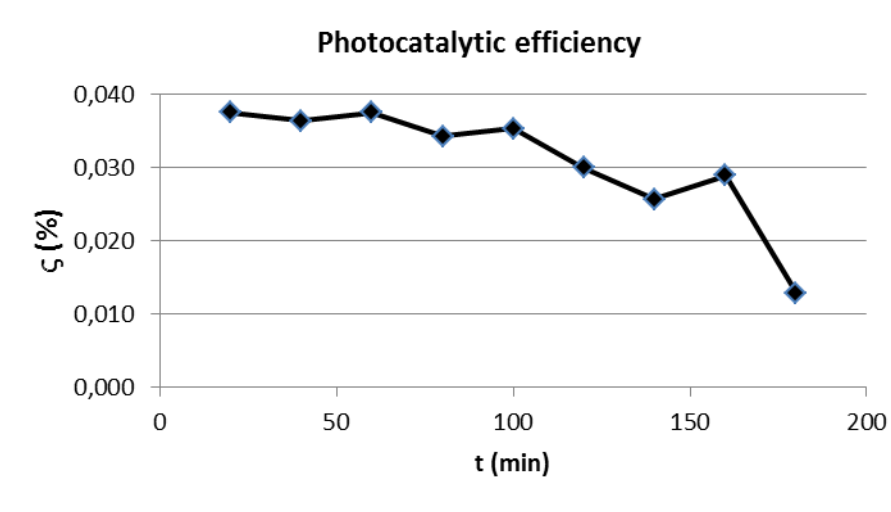

Figure 2. Photocatalytic efficnecy ζ_{MB} of the ceramic surface as a function of the time

It should be emphasized that the ISO 10678-2010 standard, unlike the Japanese JIS R 1703-2: 2007, does not provide a minimum reference value that allows to classify a material as photocatalytically active or inactive. For this reason, the specific photoactivity and the photonic efficiency data should be evaluated not in an absolute way, but in relationship with those of other surfaces that have been found to be active.
The calculation of the methylene index MB according to the JIS R 1703-2: 2007 standard was carried out from data of Figure 3, where the trend of the methylene blue concentration is reported as a function of time, and from Table 3. According to the JIS standard a surface can be defined photocatalytically active if MB Index> 5. The MB index of the ceramic sample here considered is equal to 19, much higher than the minimum value of 5.

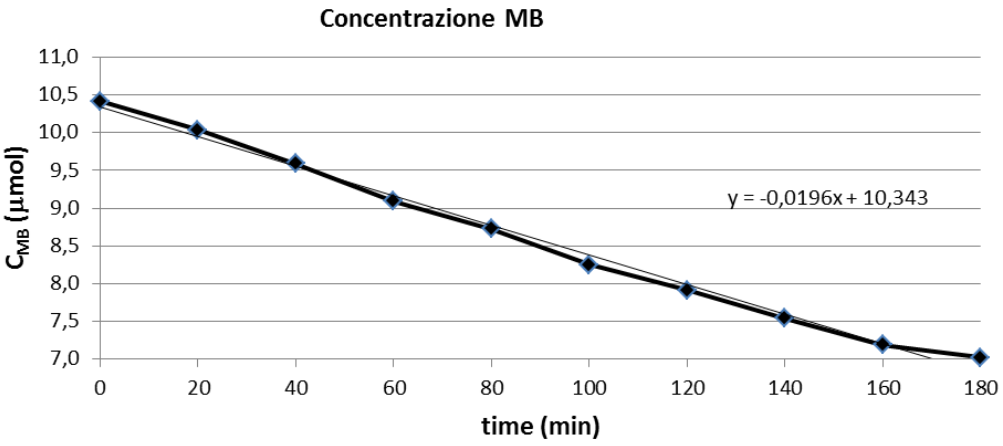

Figure 3. Variation of MB concentration as function of the time

Table 3. MB index calculated according to the JIS R 1703-2: 2007 standard

t (min)	A_{irr} (AU)	C_{MB} (µmol)
0	0,771	10,41
20	0,743	10,04
40	0,71	9,59
60	0,673	9,09
80	0,646	8,73
100	0,611	8,25
120	0,586	7,92
140	0,558	7,54
160	0,532	7,19
180	0,520	7,02
	MB Index	**19,6**

6 Notes

The results reported in this technical report refer only to the samples here described and the specified instruments. Any extrapolation and extension to other samples and instruments are outside the scope of this document.