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REPORT

Kreo White Active:
self-cleaning tests performed
by means of contact angle measurement

ISO 27448-1

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1. Introduction

GranitiFiandre S.p.A. (Castellarano, Reggio Emilia) commissioned a series of tests to assess and quantify the self-cleaning performance of some of its products (ceramic tiles of the series Kreo White Active). The test was performed by the team headed by Prof. C.L. Bianchi in the laboratories of the University of Milan, Department of Chemistry.

Tests were performed strictly following the ISO 27448-1 rules "Test method for self-cleaning performance of semiconducting photocatalytic materials. Part 1 – Measurement of water contact angle".

2. Operating Procedure

The surface of the sample is coated with a film of oleic acid (Fig. 1) by a suitable method. The degradation of this substance in the presence of UV irradiation is a sign that the substrate has photocatalytic properties. This is measured, according to the mentioned ISO Standard, by monitoring the change in the contact angle of a drop of water allowed to fall onto the surface of the sample, illuminated by a UV source at known wavelength and power.

The *self-cleaning* action is assessed by measuring the contact angle generated by the film of pure oleic acid (at zero time) and by monitoring the changes in the angle due to any degradation of the deposited acid due to the UV irradiation, which occurs only if the substrate has photocatalytic properties.

In the event that a variation in the contact angle has occurred during the test, further measurements are taken once the angle returns to the initial value obtained on the clean original sample, as measured before coating with oleic acid.

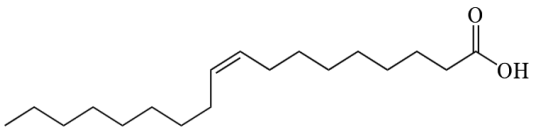

Fig.1 –Oleic acid structure

A photocatalytic material can be defined as *self-cleaning* when a variation in the contact angle due to the degradation of the oleic acid applied to its surface can be shown to occur, experimentally, between the beginning and the end of the test (duration 76 hours).

As a control, the measurement is repeated on a sample coated in oleic acid in the same way but left in the dark throughout the duration of the test (76 hours). This provides the certainty that the change in the contact angle value is due solely to the photodegradation of the contaminant molecule triggered by the combined effect of both UV radiation and photocatalytic action of the material being tested, and not to natural degradation of the oleic acid caused by factors unrelated to photocatalysis.

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3. Experimental Procedure

The test was performed in accordance with the ISO 27448-1 standard.

A sample of Iris Ceramica Kreo White Active tile (size 100x100 mm), randomly taken from an industrial production batch, is irradiated for 24 h by a UV lamp (2.0 mW/cm^2) in order to remove any superficial organic contaminant.
At the end of this pre-treatment, the sample is placed in a suitably prepared solution containing 0.5 vol% of oleic acid (Fluka reagent, purity >80%) in n-eptane (Fluka reagent, purity > 99%), in order to obtain a uniform coating of oleic acid on the surface. The amount of oleic acid thus applied resulted to be 2.0±0.2 mg, (value measured by means of a Gibertini Elettronica precision balance).

The contact angle is measured by means of a Kruss instrument equipped with high resolution TV camera.

The sample is analyzed immediately after the cleaning pre-treatment by UV irradiation, after contact with the oleic acid (zero time) and after irradiation with UV lamp at 2.0 mW/cm^2 at 2, 4, 6, 24, 48, 72, 74 and 76 hours. At each time, the measurement is repeated on 5 random points on the surface of the tested material.
An additional sample of Kreo White Active was pre-treated and then coated with the oleic acid using the same method as described above. At the end of this procedure, the sample was then placed in a vessel with controlled air and humidity, in the dark, throughout the duration of the whole test (76 hours).
The value of the contact angle (expressed in degrees (°)) of the two tested samples of Kreo White Active, before coating their surface with oleic acid, was of: 31.3° ± 0.9°.

4. Self-cleaning properties

The results of the measurements on Kreo White Active tiles, subject of this investigation, are summarized in the following. Fig. 2 reports a few pictures taken and processed by the instrument used for the contact angle measurements (Water Contact Angle Kruss).

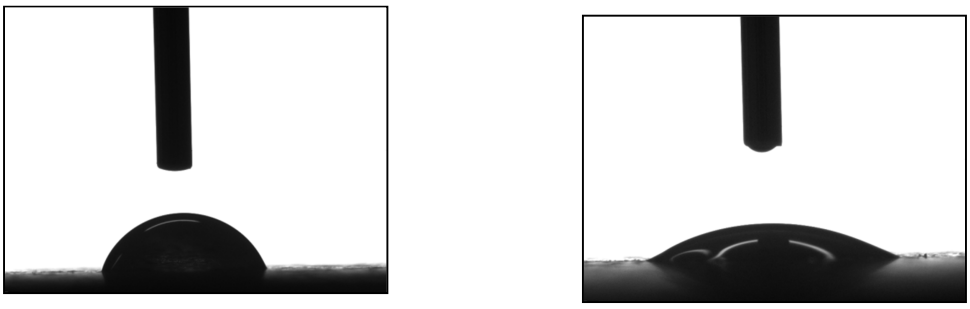

Fig.2 – Profile of the water drops at time 0 (image on the left) and at 76 hours (image on the right) on a Kreo White Active slab.

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Contact angles data and the results obtained by processing them as required by the ISO standard are listed in Tab. 1.

Tab.1

Kreo White Active		5 (five) contact angle measurements at each time (°)					θ_n	S	$\bar{x}$	$S/\bar{x}$
		1	2	3	4	5	(°)	(°)	(°)	(%)
UV irradiation time (h)	0	67.8	70.1	68.4	67.6	68.8	68.5	-	-	-
	2	68.9	71.0	64.7	66.0	67.2	67.6	-	-	-
	4	67.2	59.1	57.6	67.8	60.2	62.4	3.3	66.2	5.0
	6	64.4	68.0	64.2	68.0	59.6	64.8	2.8	64.8	4.3
	24	52.0	52.9	44.8	53.8	46.6	50.0	7.9	58.9	13.3
	28	51.5	53.6	45.9	51.0	48.6	50.1	8.5	55.0	15.5
	48	41.3	42.3	44.3	36.3	41.0	41.0	5.2	47.1	11.1
	72	29.4	31.9	24.7	33.5	32.8	30.5	9.8	40.5	24.3
	74	31.9	26.9	32.0	26.8	31.4	29.8	6.3	33.8	18.7
	76	27.7	31.4	27.2	34.2	30.0	30.1	0.3	30.1	1.1
	Starting slab	32.3	31.8	31.6	29.9	30.9	31.3	-	-	-

θ_n = mean of the contact angle value measured on 5 (five) measurements made on 5 points chosen randomly on the surface of the material
s = standard deviation
$\bar{x}$ = mean of the values of θ_n obtained at three consecutive time

Contact angle value of the Kreo Active White sample stored in the dark was also examined, but only at the end of the 76 hours. Comparison between the two tested slabs is listed in table 2:

Tab.2 – Summarizing table

Sample	UV	Original slab contact angle	Contact angle t_0	Contact angle t_{48}	Contact angle t_{76}
Kreo White Active	yes	31.3°± 0.9°	68.5°±1.0°	41.0°±2.9°	30.1°±2.8°
Kreo White Active	no	31.3°± 0.9°	67.8°±0.9°	-	68.2°±1.1°

It can be seen that the value of the contact angle gradually decreases in the irradiated sample of Kreo White Active from time t_0 to t_{76}, achieving the original value measured before the application of oleic acid onto the surface. This is due to the photocatalytic efficiency of the material, which is then able to degrade the oleic acid under UV irradiation (see Watanabe et al. J. Sol-Gel Sci.& Tech. 19, 2000, 71).
After 76 hours, the oleic acid can be considered totally degraded and, in fact, the contact angle returns to the original value measured on the as received samples.

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The contact angle value at 72, 74 and 76 hours is more or less the same, demonstrating that it has returned to the value of the Kreo White Active surface at the start of the test, and that the oleic acid molecule has been completely degraded.

Conversely, there were no obvious changes in the value of the contact angle of the sample of Kreo White Active treated with oleic acid but kept in the dark between t_0 and t_{76}, confirming that natural degradation is not effective and that the photocatalytic process is needed to activate the photodegradation of the organic contaminant.

5. *Conclusions*

Kreo White Active tiles can be defined as a *self-cleaning* material under the ISO 27448-1 standard.

With regard to the data obtained after 76 hours of testing, the value of the contact angle falls by over 38 degrees, returning to the material's original value before the start of the test. This fact proves that the oleic acid applied onto its surface had undergone photodegradation due to the photocatalytic efficiency of the material.
The control (dark test) sample shows a contact value which remains unchanged from the start to the end of the test.

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