Study of the effect of nano surface morphology on the stain-resistant property of ceramic tiles

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Abstract. In this study, six types of commercially available ceramic tiles, including nano-structured ceramic tiles and regular ceramic tiles, were selected to investigate the effect of surface morphology on their stain-resistant property. The stain-resistant efficiencies of various ceramic tiles with nano-size surface were measured in order to determine the appropriate method for testing ceramic tiles with nano-structure surface.

1. Introduction
Taiwan is warm and humid due to its location in the subtropical area. Owing to the rapid industrial development as well as the increasing number of motor vehicles in recent years, Taiwan’s air pollution is becoming worse, leading to many problems including the fouling of ceramic tiles used by metropolitan buildings. As a result, the Professional Executing Agencies of Nano Mark has received several public suggestions regarding this matter, such as applying nano technology to the treatment of ceramic tile surface in order to solve the fouling problem of ceramic tiles. For this reason, the Professional Executing Agencies of Nano Mark began to study methods for testing the stain-resistant efficiency of ceramic tiles with nano-structure surface. It is hoped that the appropriate method found can be used as the standard testing method for the verification of ceramic tiles with nano-structure surface.

To transform regular ceramic tile into nano-structure ceramic tile, the key technology is to deposit a layer of hydrophilic or hydrophobic nano material on the ceramic tile surface via coating or spraying technique. The stain-resistant effect of ceramic tile with hydrophilic nano surface is resulted from the fact that the hydrophilic nano layer can react with water molecules in air to form a thin layer of water film. Such water film not only can prevent the adhesion of stains (pollutants) on the ceramic tile, but also make the removal of stains on the ceramic tile easier by rain. On the other hand, the stain-resistant effect of ceramic tile with hydrophobic nano surface is due to its self-cleaning nature, which also prevents stains from attaching onto the ceramic tile. Such phenomenon is analogous to the well known Lotus effect. Both nanotechnologies can be applied to improve the stain-resistant effect of ceramic

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tiles, which enhances not only its quality but also its competitiveness when the product is promoted to the global market.

2. Experimental design

2.1. Experimental parameters
The test conducted in the beginning of this study to investigate the stain-resistant property of ceramic tiles was based on Chinese National Standard (CNS) 3299-9: Methods of Test for Ceramic Tiles-Part 9[1]. The following stains are requested by CNS 3299-9: (1) stains (Cr$_2$O$_3$ or Fe$_2$O$_3$) in the form of light oil or test cream that can generate clear marks, (2) stains that can cause chemical reaction (alcohol solution containing 13 g/L of iodine), and (3) stains that can form thin film (olive oil).

Six types of commercially available ceramic tiles were collected in this study. Among them, samples labeled A, B and C claimed that they have been treated by nano process, while samples labeled A1, B1 and C1 were regular ceramic tiles. The methods and stains used in the stain-resistant tests for all the samples were as requested by CNS 3299-9. The results indicate that all ceramic tiles exhibited level-5 stain-resistant efficiency as shown in Table 1, which is the highest level in CNS 3299-9.

Table 1. Testing results of various ceramic tiles according to the method of CNS 3299-9

| Testing method | Stain       | Ceramic tile sample |
|----------------|-------------|---------------------|
| CNS 3299-9     | Iodine      | Level 5             |
|                | Cr$_2$O$_3$ | Level 5             |
|                | Olive Oil   | Level 5             |
|                |             |                     |
| A              | Level 5     | B                   |
| A1             | Level 5     | B1                  |
| B              | Level 5     | B1                  |
| B1             | Level 5     | C                   |
| C              | Level 5     | C1                  |

According to the results in Table 1, all the ceramic tiles have excellent stain-resistant property. Therefore, it is difficult to determine whether the good stain-resistant property is resulted from nano-structure of the ceramic tile surface or not. To solve the problem, we have studied many literatures (domestic and international) and visited several ceramic tile manufacturers in Taiwan to collect their testing methods and standards for ceramic tiles. Finally, we found that in order for the ceramic tile manufacturers to sell their products in Taiwan, the products must meet the highest stain-resistant level of CNS 3299-9. For this reason, we decided to abandon the testing methods of CNS 3299-9 as an option for the verification of nano products.

2.2. Experimental parameter update
To further understand the composition of stains on the contaminated ceramic tiles, stains from ceramic walls of the buildings near Kuang Fu Road of Hsinchu were collected in this study (as shown in Figure 1). The samples collected were then analyzed by SEM-EDS (Scanning Electron Microscope-Energy Dispersive Spectrometer) to determine the chemical compositions of the stains. From EDS results, elements such as C, K, Si, Al, Mg, Na, Fe and Cu were detected as shown in Table 2 (mostly carbon black compound). In addition, according to the results of the supersite monitoring project reported by the Environmental Protection Administration (EPA), Executive Yuan [2], and the stains of metropolitan ceramic tiles are mainly substances resulted from exhaust emission, dust, coal smoke, and carbon black. Moreover, from the method of JSTM J 7602[3] reported by the Japan Testing Center for Construction Material, carbon black compound is used as a stain for the standard testing procedure. Therefore, we decided to change the experimental parameters of this study by replacing the stains requested by CNS 3299-9 with carbon black, a common stain that is easily observed in the environment. Two types of carbon black compound were selected in this study:
(1) Aqueous type stain: 25 wt % carbon black in pure water (volatile: 18% ± 1%, particle size: 15 nm ± 2 nm, specific surface area: 350 m²/g ± 40 m²/g).

(2) Oil (organic) type stain: 25 wt % carbon black in neutral silicon oil (volatile: 3% ± 1%, particle size: 15 nm ± 2 nm, specific surface area: 350 m²/g ± 40 m²/g).

Figure 1. Stain on ceramic tiles of building wall.

Table 2. EDS results of stains from ceramic walls of the buildings in Hsinchu

| Element | Weight% | Atomic% |
|---------|---------|---------|
| C K     | 39.63   | 50.47   |
| O K     | 42.56   | 40.68   |
| Na K    | 0.33    | 0.22    |
| Mg K    | 0.39    | 0.25    |
| Al K    | 2.62    | 1.49    |
| Si K    | 10.73   | 5.85    |
| K K     | 0.66    | 0.26    |
| Fe K    | 1.77    | 0.48    |
| Cu K    | 1.31    | 0.32    |
| Totals  | 100.00  |         |

3. Method for testing the stain-resistant property of ceramic tile
According to the recommendation (European Committee No. 2011/696/EU) officially passed by the European Union on October 18, 2011[4], “Nanomaterial” refers to material containing particles with any given dimension of less than 100 nm. In order to prove that the stain-resistant property of nanotechnology treated ceramic tiles is resulted from its nano-structure surface, the correlation between the size of the nano structure and the stain-resistant property of ceramic tiles was investigated in this study. The testing methods are described as follows:

3.1 Nano-size measurement
The equipment recommended in this study to carry out nano-size measurement includes Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Atomic Force
Microscope (AFM). To ensure the accuracy of the electron microscope, magnification test must be performed in accordance with ISO 16700:2004(E)[5] prior to SEM/TEM analysis. Moreover, the analysis of samples can be conducted following the TNS M017001-2012[6] procedures reported by the Taiwan Nano Standard Council (TNSC). For those require using Atomic Force Microscope, the analysis of samples can be conducted following the ASTM E2859-11[7] procedures.

3.2 Stain-resistant efficiency measurement
To ensure the long-term workability of the product since ultraviolet (UV) from sunlight may speed up the aging of ceramic tile surface structure, it is recommended that accelerated weathering test of 500-hour UV irradiation must be implemented for ceramic tiles. Furthermore, to ensure that the product is anti-corrosive under acidic and basic conditions, it is also recommended that ceramic tiles must undergo chemical resistance (anti acid/base corrosion) test. After finishing the above mentioned tests, stain-resistant efficiency measurement can then be conducted for ceramic tiles. Detailed test and measurement procedures are described as follows:

3.2.1 Accelerated weathering test
In this study, the condition of sunlight irradiated on ceramic tile was simulated by carrying out the accelerated UV irradiation test. The UV irradiation tester selected in this study is able to simulate the UV intensity in sunlight and accelerate the weathering effect by employing thermal cycles on the testing material. Testing was conducted in accordance with conditions stated in the ASTM G154:06[8] procedure 1 (cycle 1), in which the wavelength of UV light source selected is 340 nm. The UV exposing conditions are shown in Table 3.

| Cycle | Light source | Intensity | Wavelength | Exposing cycle |
|-------|--------------|-----------|------------|----------------|
| 1     | UVA-340      | 0.89 W/m²/nm | 340 nm     | 8 h UV at 60 (±3)°C Black Panel Temperature; 4 h Condensation at 50 (±3)°C Black Panel Temperature |

3.2.2 Anti corrosion (chemical resistance) test
The anti corrosion (chemical resistance) tests for ceramic tiles were conducted in accordance with the rules specified in Section 7 of CNS 3299-10: the Methods of test for ceramic tiles - Determination of chemical resistance[9]. During the chemical resistance test, the testing samples and the control samples of ceramic tiles were first immersed separately into hydrochloric acid (HCl) solution, followed by potassium hydroxide (KOH) solution. The immersing period for each solution was 24 hours. After removing the samples from KOH solution, they were rinsed with water (flow) and dried by towel to complete the chemical resistance test. The next test to perform is stain-resistant test.

3.2.3 Stain-resistant test
To ensure that ceramic tiles can fulfil their application requirement, stain-resistant test was conducted in this study. During the stain-resistant test, stain (see section 2.2) was coated on the ceramic tile sample to cover an area of approximately 1 cm². The sample was then placed into the oven and baked at 50 °C for a period of 24 hours to simulate the scenario of sunlight drying up (hardening) the stain on ceramic tiles. After baking the sample, the washing procedure stated in CNS 3299-9: Methods of test for ceramic tiles - Determination of resistance to stains was conducted.

3.2.3.1 Washing procedure
(1) Procedure A: Rinse the ceramic tile by flowing water (at room temperature) through its surface for 5 minutes, and then clean its surface with a wet towel before making any observations.
(2) Procedure B: Use mild detergent to clean the ceramic tile surface manually with a sponge or soft towel. Rinse the ceramic tile by flowing water through its surface, and then clean its surface with a wet soft towel before making any observations.
(3) Procedure C: Use strong detergent to clean the ceramic tile surface through the help of mechanical equipment. The equipment implemented should be operated in accordance with the rules stated in CNS 3299-9 (Section 5.2.3). The cleaning period is 2 minutes. Rinse the ceramic tile by flowing water through its surface, and then clean its surface with a wet soft towel before making any observations.
(4) Procedure D: Immerse the sample into a prepared chemical solution for a period of 24 hours. The solution should be prepared in accordance with the rules stated in CNS 3299-9 (Section 5.1.4). Rinse the ceramic tile by flowing water through its surface, and then clean its surface with a wet soft towel before making any observations.

3.2.3.2 Stain-resistant level determination
After completing the washing procedure, the stain-resistant level of the sample is determined according to the rules stated in CNS 3299-9. There are 5 stain-resistant levels in CNS 3299-9. If the stain cannot be removed, proceed to the next washing procedure.
(1) If all stains can be completely removed by Procedure A, the sample is rated level 5.
(2) If all stains can be completely removed by Procedure B, the sample is rated level 4.
(3) If all stains can be completely removed by Procedure C, the sample is rated level 3.
(4) If all stains can be completely removed by Procedure D, the sample is rated level 2.
(5) If all stains cannot be removed by Procedure D, the sample is rated level 1.
If no stain is observed on the sample surface, it means that the stain has been completely removed. Record the corresponding washing procedure.

3.3 The basis of verification standards
The testing criteria for nano-size measurement and nano material performance described in Section 3.1 and 3.2 are summarized in Table 4.

| Table 4. Criteria of nano-size measurement and nano material performance for stain-resistant ceramic |
|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------------|
| Item                                      | Characteristic                                      | Criteria                                         | Note |
| Nano size                               | Size of the nano structure on the surface of stain-resistant ceramic tile | Any given dimension of nano surface structure with size of less than 100 nm |
| Nano performance                        | Stain-resistant performance | Stain-resistant performance is above level 4 |
| Other requirement                       | Weathering resistance, chemical resistance | After 500 hours of UV irradiation test and chemical resistance test, the stain-resistant performance is above level 4 |

4. Measurement results
In this study, six types of commercially available ceramic tiles were collected. Among them, samples labeled A, B and C claimed that they have been treated by nano process, while samples labeled A1, B1 and C1 were regular ceramic tiles. Tests were conducted according to the methods planed out in this study. The results of the stain-resistant tests are shown in Table 5. From the results, it is noted that
sample A is a commercially available ceramic tile with stain-resistant performance of level 4. By analyzing its surface structure with AFM, it was found that particles on the surface of sample A are closely arranged, with an average size of 20 nm as shown in Figure 2. This is believed to be the reason for its high stain-resistant performance.

**Table 5.** Results of the TN-041 stain-resistant test for various ceramic tiles with nano surface treatment

| Testing Methods | Stain          | Ceramic tile sample |
|-----------------|----------------|---------------------|
|                 | Hydrophilic   | A       | A1      | B       | B1      | C       | C1      |
| TN-041          | carbon black  | Level 4 | Level 1 | Level 1 | Level 1 | Level 1 | Level 1 |
|                 | Hydrophobic   | Level 4 | Level 1 | Level 1 | Level 1 | Level 1 | Level 1 |
|                 | carbon black  |         |         |         |         |         |         |

**Figure 2.** Surface structure of sample A (AFM analysis).

The stain-resistant performance of sample B and C is level 1 only, suggesting that they are more vulnerable to the attack of stain with smaller particle sizes. From the AFM analysis results shown in Figure 3 and 4, it is apparent that the size of particles on the surface of sample B and C is not consistent and the particles are not closely distributed. Such poor surface morphology is believed to be the reason lowering the stain-resistant performance of sample B and C.

**Figure 3.** Surface structure of sample B (AFM analysis).
5. Discussion
To investigate the effect of surface morphology on the stain-resistant performance of ceramic tiles, six
types of commercially available ceramic tiles, including nano-structured ceramic tiles and regular
ceramic tiles, were selected in this study. The testing results show that ceramic tiles with stain-
resistant performance of level 4 exhibit closely distributed surface particles and an average particle
size of 20 nm, which is believed to benefit the stain-resistant performance of ceramic tiles. On the
other hand, the particles on the surface of other ceramic tile samples show uneven distribution and
sizes, making these ceramic tiles to have lower stain-resistant performance.

6. Reference
[1] CNS 3299-9: 2011 Methods of test for ceramic tiles. Part 9: Determination of resistance to stains.
[2] Yuan, 2008 The stains of metropolitan ceramic tiles are mainly substances resulted from exhaust
emission.
[3] JSTM J 7602T: 1992 Pollution inspection methods of Construction with ceramic tiles.
[4] Recommendation, commission recommendation of 18 October 2011, Official Journal of the
European Union.
[5] ISO 16700: 2004(E) Microbeam analysis – Scanning electron microscopy – Guidelines for
calibrating image magnification.
[6] TNS M017001: 2012NanoProduct: Method of Dimensional Measurement of Nanoparticles on
Surface - Scanning Electron Microscope
[7] ASTM E2859: 2011 Standard guide for size measurement of nanoparticles using atomic force
microscopy.
[8] ASTM G154:2006 Standard practice for operating fluorescence light apparatus for UV exposure of
nonmetallic materials.
[9] CNS 3299-10: 2011 Methods of test for ceramic tiles-Part 10: Determination of chemical
resistance.

Figure 4. Surface structure of sample C (AFM analysis).