Water and Dirt Repellent Treatments for Building Surfaces

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ABSTRACT

This paper describes important parameters in creating a water and dirt repellent treatment: surface free energy should be as low as possible and the chemical composition and molecule size of the treatment must correspond to the material to be treated. Commonly used hydrophobic agents such as silane and siloxane have low surface free energies, but fluorine-based polymers such as Teflon have a better potential.

Roofing tiles, which were supposed to be dirt repellent, have been tested. The surface of the tiles had a combination of a hydrophobic treatment and protrusions with height and spacing of approximately 25 µm. The self-cleaning method was inspired by the lotus flower. The tiles were naturally exposed for approximately two-and-a-half years and tested for soiling, water runoff, water uptake, porosity, pore size distribution, frost resistance, water vapor permeability, chemical composition, and topography.

The result was that the tiles with this self-cleaning method were neither hydrophobic nor self-cleaning. However, soiling was somewhat delayed. The tiles are no longer manufactured.

INTRODUCTION

It is well known that the service life of surfaces is highly affected by moisture. The most effective way to prevent moisture-induced deterioration is designing constructions in a way that quickly leads water away from the building. However, not all surfaces can be protected in this way, e.g., for architectural reasons or because the component (e.g., the roof) is used to protect other surfaces. An alternative is to choose surfaces that prevent water uptake, either by choosing materials with water-repellent properties or by applying a surface treatment that improves the surface properties.

Stone strengtheners combined with water repellents are widely used for the conservation of historical monuments (Toniolo et al. 2001), but, when it comes to contemporary buildings, building owners have been more reluctant to use hydrophobic agents, although their application has several potential advantages:

- Water is repelled at the surface, and, as a consequence, the bulk material is drier and the insulation properties are better.
- Deterioration caused by moisture is reduced.
- Biological growth at surfaces is inhibited.
- Repelled water might take particles with it, thus cleaning the surface.

Reasons for *not* using hydrophobic treatments are the risk of misapplication or unintentional chemical reactions. Many mishaps could be prevented if the choice of method and agent is guided by proper knowledge of which chemical and physical properties should be favored. This paper will outline some of the issues to be considered.

A general problem in scientific work is that to understand one mechanism thoroughly, the complexity of practical problems must be reduced to well-defined, relatively simple issues. However, by simplifying the subject, factors that are decisive for practical use can be overlooked. In the case of designed surface properties, these are very sensitive to smudge, e.g., surface treatments can become useless if another layer quickly covers the newly obtained surface. The term *soiling* is used to describe when surfaces are covered by environmental dirt or

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biological growth. This paper will therefore consider a combination of water *and* dirt repellent treatments.

Another reason for considering dirt repellency is that soiling can be seen as a failure and therefore influence the service life of surfaces. Soiling is a failure if:

- soiling accelerates deterioration or
- soiling is unacceptable for aesthetic reasons.

However, in some cases, soiling is seen as an advantage, and a general discussion of whether soiling is a failure is also a part of this paper.

THEORY

The experimental design and test procedures were chosen based on theoretical considerations on water and dirt repellence.

Hydrophobicity

By preventing transport of moisture into a porous material, several damaging processes can be stopped:

- *Frost damage.* Some materials, depending on porosity and pore size distribution, can develop frost damage if they are wet when subjected to low temperatures.
- *Transport of chemicals.* Through capillary activity, moisture can transport chemicals into a material. Chemical reactions between the substrate and the transported fluid might change the composition of the material. An example is the formation of gypsum: when water reacts with SO_2, typically caused by pollution, sulphate acid is formed, which can react with Ca, resulting in a gypsum layer. The layer might obscure the image of the building. The transport of chlorides into reinforced concrete is another example.
- *Salt transport.* Moisture in porous materials might dissolve salts in the material. When the moisture dries out, salt efflorescence occurs. If the efflorescence takes place inside the material, the material might disrupt.

However, not all materials will be damaged when subjected to moisture, and water-repellent treatment should therefore not be used uncritically.

A water-repellent surface is called hydrophobic, but there are two different definitions on when a treatment is hydrophobic—a practical definition: when a treatment reduces the water uptake by 50% or 80% (British Standard and Dutch regulations, respectively) (Gerdes 2001), and a more theoretical definition: the contact angle is >90° (Gottfredsen and Nielsen 1997). For scientific purposes, the latter definition is most interesting, as it helps explain why water is repelled.

Contact Angle. The contact angle describes the angle between the surface and a water droplet, as shown in Figure 1. Water at a surface will either wet the surface as droplets spread over the surface (contact angle <90°) or show non-wetting behavior, where droplets form beads at the surface. If this

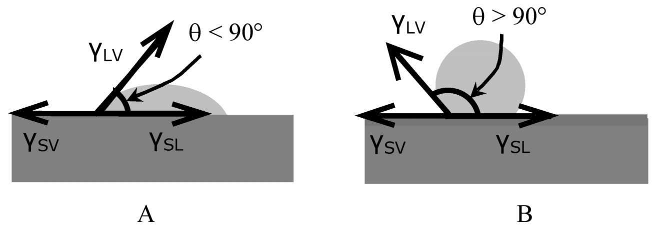

Figure 1 *Different contact angles. A: Wetting behavior, contact angle θ > 90°. The figure also shows the surface free energies γ needed to describe the contact angle according to Young's equation.*

behavior also is true in pores, the material with a contact angle <90° will be capillary active; water will be sucked into the material, while water will be repelled (capillary depression) when the contact angle is >90°. In porous materials, not only the outer surface must be treated, so must the pore walls, and the efficiency of a treatment is highly dependent on the penetration depth.

Surface Free Energy. The size of the contact angle is highly dependent on the surface free energy γ of the system, from which Figure 1, from Young's equation (Baer 1964), can be obtained.

$$\gamma_{SV} - \gamma_{SL} + \gamma_{LV}\cos\theta = 0 \Leftrightarrow \cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

where θ is the contact angle, γ is the surface free energy, L is liquid, S is solid, and V is vapor. As the liquid and the gas (vapor) are given, the only way to change the contact angle is by applying a treatment to the solid that changes the surface free energy. Treatments with low surface free energy increase the contact angle.

Soiling

How a surface is smudged depends on the environment, i.e., the nature of the soiling, and how soiling is able to adhere to the surface. Soiling is a broad field; for simplification it is here divided into biological growth and environmental particles, as the nature of these two kinds of soiling is very different. A fast indication of whether discoloration is caused by biological growth or environmental particles can be obtained by observing the smudging pattern. Environmental particles are transported by air and, to some extent, washed away by rain, leaving exposed surfaces cleaner than other parts. Biological growth, on the other hand, is typically seen on exposed surfaces that, for some reasons, are moist. However, this simple rule of thumb does not always apply, but through a microscope, the difference is often clear because of the biological characteristics of the growth.

Biological Growth. In this paper, the term *biological growth* is limited to algae, lichen, moss, and mold. Higher plants are generally seen as more than soiling, and bacteria are

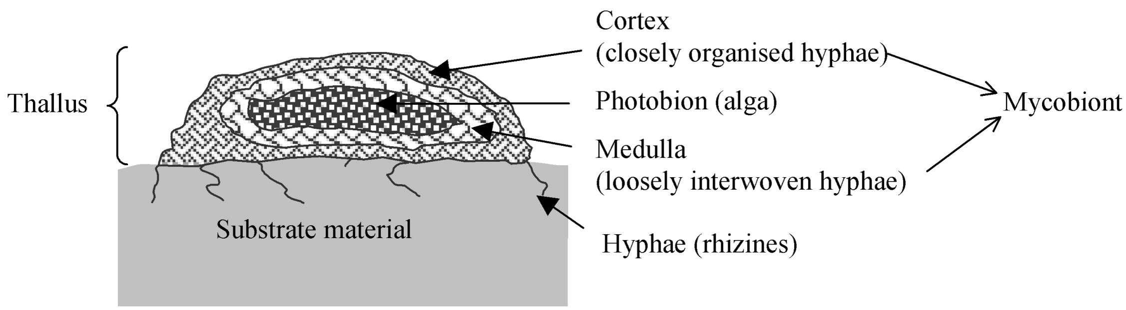

Figure 2 *Principles in the structure of lichen, based on Adamo and Violante (2000) and Frambøl et al. (2003). The mycobiont, especially the dense cortex, protects the photobiont (alga) from direct exposure to the environment. A lower cortex is not always present; in some lichen, the hyphae of the medulla form the attachment to the substrate.*

invisible to the naked eye. However, all three categories are a part of a chain: bacteria can be nourishment for other microorganisms, and higher plants can only establish themselves with other kinds of biological growth as first colonizers.

Describing the different groups of biological growth is beyond the scope of this paper. However, by using lichen as an example, the fundamentals of biological growth become clearer. Lichen is chosen because it is a symbiosis of a fungal component (mycobiont) and an alga (photobiont) and therefore has the characteristics of several kinds of biological growth. The structure of lichen is showed in Figure 2. The fungus feeds and protects the algae (as in a greenhouse) and, at the same time, lives off the algae. More specifically, the photobiont provides the mycobiont with organic nutrient created by photosynthesis. In return, the mycobiont provides the photobiont with minerals, procured via hyphae into the substrate and production of lichen acids (Warscheid and Krumbein 1994). This means that water can be retained in the medulla, reducing the risk of drying out, and that hyphae penetrate the substrate, making it possible for the biological growth to adhere to the surface.

The kind of biological growth that will appear at building surfaces—if any—is a combination of nourishment, moisture, temperature, light, and surface roughness.

Nourishment, in some form, will normally be abundant at exterior surfaces; sometimes the nourishment will favor some species (e.g., excessive algae growth at surfaces in the close vicinity of pig farms, where the air is very nitrogenous). But the microorganisms are often hardy species, which have found ways to extract nourishment from the surroundings in a way that restriction on nourishment is not a realistic way to prevent biological growth (Møller 2003).

Not all biological growth needs light—only those who photosynthesize, i.e., algae, lichen, and moss, but not molds. The surface roughness and porosity of the material will also only favor some species, but the variety of biological growth include species that have a thick mucilage, which they use as a system of suction cups to stick to smooth surfaces.

Although different species prefer different moisture and temperature levels, the most effective way to limit biological growth on building surfaces (beside biocides) seems to be to obtain a low moisture level and high temperature level >50°C (122°F).

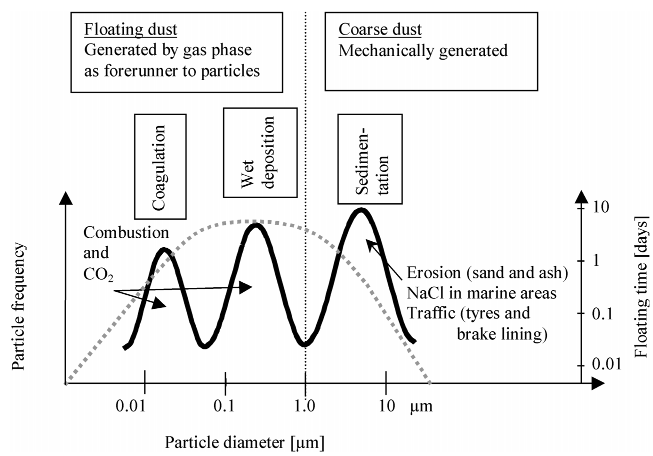

Figure 3 *Schematic depiction of particle frequency (by mass or volume) versus particle diameter in the atmosphere combined with deposition and floating times (dotted line). The particle frequencies by mass or volume are similar, while, e.g., the frequency by number would show a majority of small particles (Møller 2003).*

Environmental Particles. The term *environmental dirt* is used in this paper as opposed to *biological growth*; it describes dirt that does not consist of living organisms or the remains hereof. Although environmental dirt can be transported by water, e.g., in streams, only airborne environmental dirt will be considered. Airborne dirt that settles at surfaces and is transported by rain to other surface areas is included.

The origin, size, and chemical composition of environmental dirt interact, and particle frequency in the air varies considerably. However, the particle size distribution tends to be trimodal. Figure 3 shows a typical distribution and how particles deposit at surfaces. Large particles (coarse dust) deposit by sedimentation and are therefore located at horizontal surfaces. Rough surfaces will have horizontal parts where the particles will deposit. Very different from the mechanical adhesion of the coarse dust is the adhesion of floating dust; gravity has less importance, and these fine particles adhere to surfaces through intermolecular forces (chemisorption and physisorption). In this case, the surface properties at a molecular level become important (Møller 2003).

Van der Waals forces and chemical bonding depend on the surface of the substrate. Most "natural" exterior surfaces of building materials are polar and have a high surface energy and will therefore attract molecules from the air or rain. However, the processes can be inhibited in different ways, e.g., by lowering the surface energy and making the surface non-polar—a process that is possible by applying, e.g., a hydrophobic treatment. By applying a surface treatment, the adhesion of the soiling can be diminished; this does not mean that dirt is repelled, but it is more easily removed. Silicone-based polymers such as silane or siloxane are the most used hydrophobic treatments at porous building materials. They both fulfill the requirement of having a low surface energy. Siloxane has approximately 10% lower surface free energy than silane but has larger molecules, which can be important in porous materials with very fine pores (Carmeliet 2001).

But there are other alternatives, mainly with fluorine, that have even lower surface free energies, e.g., polytetrafluoroethylene (PTFT) has the lowest reported surface free energy for solid homogeneous organic materials (Drummond and Chan 1996). The CF_3 group in PTFT is responsible for the low surface energy; a treatment with as many CF_3 groups as possible will result in the lowest possible adhesion. However, not all treatments will adhere to the surface. Many porous building materials used for exterior surfaces contain silicon; chemical bonding, silicon-based polymers can adhere to the substrate, which makes silane and siloxane very suitable (Gerdes 2001).

The consequences of soiling vary; it can therefore be discussed whether soiling is a failure and, therefore, should be avoided.

Aesthetics. Whether one considers soiling as an aesthetic nuisance or a benefit as a "patina" is highly subjective and often dependent on the situation, material, and use of the building. Architects sometimes talk about how some materials patinate beautifully, mellowing the building. Materials are chosen for their ability to soil in a way that the building, with time, will not look brand new but age with dignity; the appearance of the surfaces will only change slowly, giving the building a kind of timeless expression.

Time is not unimportant when considering whether soiling is a nuisance or a benefit. The important thing is that the building owner can decide how the building would soil. Surfaces that soil very fast may have soiling patterns after three years, which are unacceptable at that time, but could have been accepted if the building was 15 years older.

Even in cases where soiling is accepted, the soiling layer will continue to grow and, at some point, soiling will dominate the expression of the building and become unacceptable. Therefore, after a short or long period of time, soiling will become an aesthetic problem.

Deterioration or Protection? It is well known that old monuments deteriorate with time. The deterioration is often a combination of wear-and-tear and soiling. Particles in the soiling may cause chemical deterioration, as described under moisture in this section, and higher plants that have found footing because of soiling can penetrate surfaces and start deterioration of building parts. Whether soiling caused by biological growth is damaging or protecting, the surface is highly discussed (e.g., Frambøl et al. [2003]). As summarized in Møller (2003), biodeterioration can be caused by the following:

- Hyphae penetrate the substrate.
- Moisture-induced volume change, e.g., the medulla can (Figure 2) contain up to 300% of the dry weight, which means that biological growth subjected to wetting and drying can induce tension in the substrate. Freezing and thawing will have a similar effect.
- The metabolism of some of the biological growth result in acids. These can cause decomposition of stone materials.
- Incorporation of mineral fragments into the biological growth. Grains of the substrate that have been loosened by different mechanisms become integrated in the substance of the growth.

On the other hand, biological growth can also result in bioprotection.

- *Protection against thermal stress.* In hot summers, with few but heavy showers, high surface temperature and the sudden cooling of the surface caused by the rain might induce thermal stress, enhancing existing fissures or creating new ones. If the substrate is covered with biological growth, retained water will reduce the thermal stress.
- *Protection against abrasion.* A surface covered with biological growth is not as exposed to wear and tear. Abrasion by, e.g., windborne particles, will therefore be reduced.
- Through chemical reactions with the substrate, biological growth can form metal oxalates, which are insoluble in water. The result is a visible layer at the surface, obscuring the visual appearance, but preventing the surface from further deterioration.

Whether one or the other occurs depends on the kind of biological growth and the extent of the growth. As the removal of soiling can be very expensive and damaging in itself (Young et al. 2003), one should consider if cleaning is necessary, i.e., if the failure is "only" aesthetic or also influences the durability. In new buildings, one might consider cleaning the surface regularly or, if possible, use surfaces that are self-cleaning.

A Self-Cleaning Effect

There are different possibilities for creating a self-cleaning surface—one practical approach is represented by a treatment that combines hydrophobicity with low adherence. The method is patented and thoroughly described in the European Patent Office (1998a and 1998b). The inspiration comes from the lotus flower, which is self-cleaning. The main principle is to combine surface roughness and hydrophobicity, which ensures that there is only little contact between the smudge and the surface and that water runs off easily.

Surface Roughness. A surface with this self-cleaning effect has protrusions. In the patent, the protrusions are described as having a spacing of 5-200 μm, preferably 10-100 μm, and height of 5-100 μm, preferably 10-50 μm. Moving water will catch particles that will adhere to the water instead of the surface, and the water will remove the contamination. The principle is shown in Figure 4. However, the scale in the patented method is different from the original description of the surface of the lotus flower by Barthlott and Neinhuis (1997), where the microrelief of wax crystals, as observed by others, is reported to have heights of 1-5 μm. However, some of the pictures in Barthlott and Neinhuis (1997) show considerably higher protrusions (≈ 25 μm), which correspond to the size used in the patent.

Water Runoff. The protrusions are combined with a hydrophobic treatment. If air is trapped between the protrusions, the result is a composite surface with a larger contact angle θ_r than the true angle θ_{true} (Adamson 1990).

$$\cos\theta_r = r_A \cdot \cos\theta_{true}$$

where r_A = ratio of actual to projected area. The phenomenon is illustrated in Figure 5. The result is that water runs off more easily from the micro-corrugated surface than if the surface was only hydrophobic in the traditional way. With this combination of little contact area and enhanced water runoff, rain is supposed to be able to clean the surface.

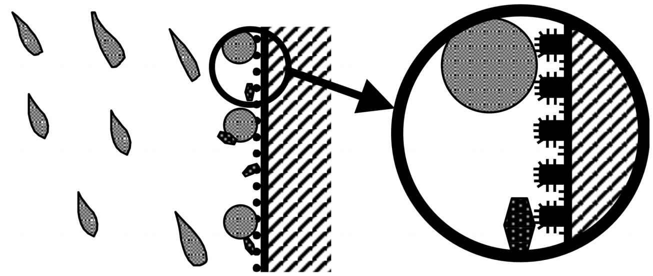

Figure 4 *Illustration of the Lotus effect. The hydrophobic effect of a treated surface is enhanced by protrusions. Larger particles stay at the top of the protrusions and have very little contact with the surface. As droplets run off the surface, the particles are carried away.*

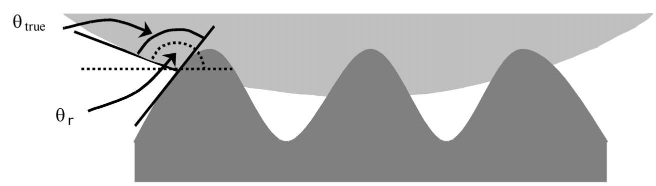

Figure 5 *The contact angle is increased from θ_{true} to θ_r when the surface has sufficient roughness on the microscopic scale (Adamson 1990).*

EXPERIMENTAL DESIGN

To test the effect of a dirt and water repellent treatment at a building surface, several experiments were conducted; the first step was to choose an appropriate test material—one with a self-cleaning and hydrophobic effect, and one without had to be chosen. The main considerations were:

- To minimize the differences between the two test materials, they had to be *similar* in any respect except for the treatment.
- The treatment had to be *well defined* to reduce differences due to application technique.

After considering different kinds of paints, the idea of testing paints was abandoned because the composition of paints is very complex; there would not be one paint with self-cleaning and/or hydrophobic properties and the same paint without. The chemical composition of the paints would differ considerably, and self-cleaning properties could be affected by, e.g., softener, extender, and pigment volume. An extra obstacle would be gathering complete information of the chemical composition on commercially available paints; this would probably not have been possible.

In spring 2001, roofing tiles with a self-cleaning effect, combining hydrophobicity and protrusions as described above, became commercially available. Ordinary roofing tiles from the same factory, with the same dimensions and almost the same color, were also available. According to the manufacturer, the ordinary and the self-cleaning tiles were similar; the only difference was that the latter had received an extra treatment, which would give them their self-cleaning properties (Heidtmann 2001). The treatment was applied under well-controlled conditions, ensuring a consistent level of quality. These two types of roofing tiles were therefore supposed to fulfill the requirements listed above and were used for further investigations.

In-Situ Testing

The work was a part of a Ph.D. study describing hygrothermal performance and soiling of exterior surfaces (Møller 2003); therefore, the experimental setup had to be designed to show differences in soiling on surfaces within two to three years. However, accelerated tests on soiling are not standardized (Eiselé et al. 1999), and tests used by the industry are too ambiguous to be used to predict soiling behavior in real time in natural environments; e.g., since horizontal surfaces soil faster than vertical surfaces, sloping test samples of facades is therefore a common way to accelerate soiling. However, Born (2001) has showed that there is no correlation between soiling rate at sloped surfaces and vertical surfaces. Using artificial dust, e.g., fly ash, at surfaces is dependent on the dust and methods of application and removal. Bagda (2001) has reported several experiments but did not find a reliable test method.

Instead of using accelerated tests, it was decided to test surfaces for soiling by natural exposure to rain and soiling.

Test Site. A test site where soiling would be likely to occur during the relatively short test period was found in an area near one of the most busy motorways in Denmark. The area was at the same time surrounded by trees. By this combination, smudge from environmental pollution as well as biological growth could appear as soiling at the surfaces.

Setup. Soiling and water runoff are dependent on the slope of the setup. Biological growth depends on the orientation; therefore, four different setups with ordinary roofing tiles and roofing tiles with self-cleaning were placed at the area:

- Setup with a 12° slope, facing south
- Setup with a 12° slope, facing north
- Setup with a 45° slope, facing south
- Setup with a 45° slope, facing north

The low slope of 12° was chosen as a minimum because this was the lowest slope the manufacturer recommended in roofs with this tiling. A 45° slope was chosen as a "normal" slope of a pitched roof with tiles.

The underside of the tiles was subjected to the outdoor climate, as the setup did not include underlay, insulation, or heating.

The setup was inspired by a Danish standard for test of frost resistance of roofing tiles in which three rows of tiles with at least three tiles per row is tested (Danish Standard 2000). In this case, the number of tiles was five per row; this gave the opportunity to remove some of the tiles for destructive testing during the experiment. Each tile measures 270 × 420 mm (0.89 × 1.38 ft). Because of overlays, the area of each setup was approximately 1 m^2 (35 ft^2). The tiles weighed approximately 2.9 kg (6.4 lb) each.

Besides soiling, the tiles were also tested for their water runoff and water uptake. Gutters were placed under each setup to measure differences in water runoff. The gutters, which all had the same length, were carefully placed under the three tiles in the middle of each setup to avoid boundary effects.

The tiles in the described setups were not to be touched for several years, as they were left exposed to natural conditions for soiling. Therefore, a separate water uptake test had to be performed on other similar tiles and with similar climatic exposure. The setup was extended with four individually mounted tiles of each type in each direction and slope—a total of 2 × 4 × 4 = 32 tiles.

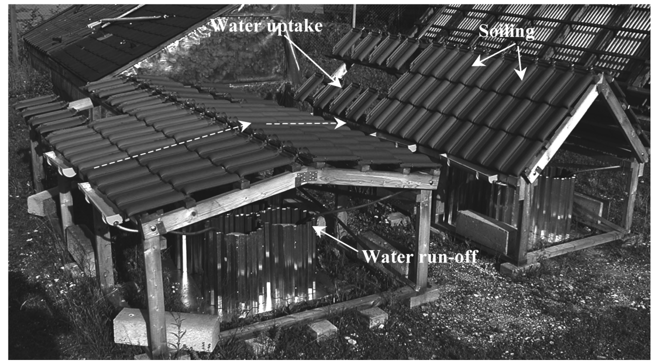

Figure 6 *The setup used for soiling and wetting tests. For the soiling and water runoff tests, three rows with five ordinary tiles and five self-cleaning tiles were placed in different slopes (12° and 45°) and two orientations (north and south). Gutters were placed under the central tiles in each setup, and the water was collected in plastic containers hidden by metallic sunscreens. Tiles for weighing in water uptake testing were placed on the same frames and can be seen at the back as two rows of four individual tiles.*

The complete outdoor setup is shown in Figure 6.

Laboratory Testing

In addition to tests in real time and natural environment, more specific material testing was conducted either at whole tiles (freeze-thaw testing), samples cut out of the tiles (typically 2500 mm^2 or 4 in.^{2}), or just fragments of the tiles (spectroscopy testing). The different laboratory tests are described in the section concerning test procedures. Most tests were performed on ordinary tiles as well as tiles with self-cleaning effect.

TEST PROCEDURES

Several experiments were conducted with the designs described above. If available, standardized tests were used. Further details on the test procedures can be found in Møller (2003).

Natural Exposure

Tiles subjected to natural exposure, as shown in Figure 6, were tested for their soiling and hydrophobic behavior; the main issue was the behavior of the self-cleaning roofing tiles compared to ordinary tiles, i.e., if a treatment that is supposed to be dirt and water repellent has the desired properties and the background for why it is possible to change the properties.

Soiling. The setups were left untouched for approximately two-and-a-half years. During that time, soiling was registered by visual inspections and documented with photographs. At the end, two tiles (one ordinary tile and one with self-cleaning effect) were cut in pieces (approximately 50 × 50 mm = 2 × 2 in.), and four areas were tested with light-emitting diode technology (LED). The pictures were compared to pictures from similar areas on new tiles. This part of the soiling test was to test if LED technology could be useful as an objective method to describe soiling. The technique is to take pictures with light of particular wavelengths and compare the pictures. Soiling of a specific color will be highly visible in only some of the pictures (in this case, pictures taken with red light with a wavelength of 630 nm were used). By using threshold values for color differences, the soiling appears in the digital pictures as pixels with another color, and the number of soiling spots and the size of the spots at the sample can be calculated. In traditional measurements with color meters, only the mean color in a very small area (usually described as a point) is determined.

With the LED technique, more information is obtained and the nature of soiling is determined (e.g., equally distributed or in spots). Unfortunately, the camera used in this case cannot be used onsite and could only handle smaller samples. The test was therefore destructive. Brechet et al. (1998) has described the development of an LED device for in-situ testing of soiling. As the device should be applicable to many different surfaces and thereby different colors, it only uses one wavelength of light and cannot be as optimized to the specific case as the camera used here.

Water Runoff. The amount of water that ran off the test tiles was registered by weighing the plastic containers in which the water was collected from the gutters. How often the containers were weighed depended on the weather—often in periods with heavy rain, and more seldom in drier periods. The registration of water runoff was carried out for one year.

Water Uptake. The single mounted tiles were weighed almost daily for nearly five months (from July to the end of November 2002) to register water uptake and drying when the tiles were exposed to natural weather conditions. The experiment was repeated one week in February and, again, one week in July the following year to determine whether frost or aging made any difference.

Material Testing

Most testing performed in the laboratory was material testing, i.e., either tests on the material behind the treatment (bulk material) or very specific surface tests. The frost-thaw test was an exception, as it involved whole tiles.

Freeze-Thaw Test. Four tiles of each type were mounted vertically in one row and subjected to an accelerated frost resistance test consisting of 168 cycles, each with a duration of six hours. The cycle is described in Figure 7.

Porosity. The porosity of the bulk material was tested by placing six 50 × 50 mm (2 × 2 in.) specimens of each tile type

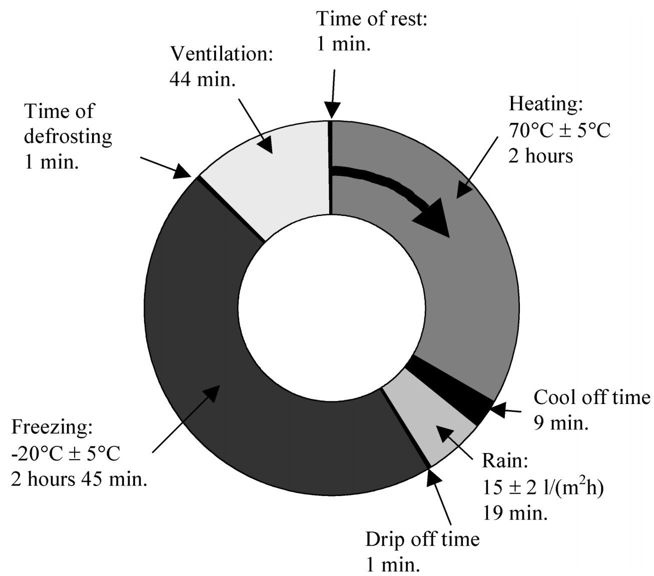

Figure 7 *Test of frost resistance. Description of one six-hour cycle. The tiles were subjected to 168 cycles.*

in an empty desiccator and evacuating the air; after three hours, water was let into the desiccator, and the specimens were left in the water, first with low air pressure and later with atmospheric pressure for a day. The specimens were weighed underwater and, after being wiped off with a moist cloth, they were weighed in air. Afterward, the specimens were dried at 105°C until constant weight. The porosity was calculated by the equation,

$$p_{open} = \frac{m_{ssd} - m_{dry}}{m_{ssd} - m_{sw}},$$

where p_{open} is open porosity, m_{ssd} is mass of specimen in saturated dry surface condition, m_{dry} is mass of dried specimen, and m_{sw} is mass of specimen weighed underwater.

Pore Size Distribution. In addition to the porosity, the pore size distribution was obtained by using pressure plate measurements as described in the method NT Build 481 (Nordtest 1997). Basically, the method relies on the pore water pressure to determine the size of a meniscus in a pore, i.e., by increasing the air pressure, water is pressed out of the small pores. By gradually increasing the pressure and measuring the water that is pressed out in each step, the volume of pores in a given size range can be determined. Simple capillary uptake measurements were also conducted by placing samples with one side in the water.

Water Vapor Transmission. To test if the water vapor transmission is changed by the surface treatment of the self-cleaning tiles, six specimens of each tile type were tested in a wet cup according to the European Standard EN ISO 12572 (CEN 2001) for determination of water vapor transmission properties. In the test, the amount of water that is transported by diffusion through the specimen is measured over time. The temperature is held constant and the relative humidity is constant but different above (RH = 50%) and below (RH = 94%) the specimen. The wet cup was chosen because the main interest is how the surface treatment influences the drying out possibilities of the tiles.

Chemical Composition of the Surface. X-ray-induced photoemission spectroscopy (XPS) was used for determination of the chemical composition of the surface of the two tile types. XPS is well suited for chemical analysis because it can be used without preparing the surface in any way and therefore excludes preparation as a source of error, which can be critical in a chemical analysis of an unknown substance. Furthermore, the method is very surface sensitive; the detected photoelectrons come from a depth of up to approximately 5-10 nm (Rehwinkel et al. 2000). For determination of the penetration depth, analysis on polished cross sections with a scanning electron microscope (SEM) was combined with an energy dispersive x-ray spectrometer (EDX).

Topography. SEM analysis on surfaces was used for determining differences in the topography of the two tile types.

RESULTS

The experiments listed above were used to test different hypotheses based on the theoretical considerations.

Natural Exposure

When working with natural exposure, the conditions are beyond the control of the researchers. During the test period, the weather had its usual fluctuations but was not extreme. Results are therefore likely to be representative of normal exposure in Denmark.

Soiling. During the test period, soiling became visible on both tile types, but the ordinary tiles soiled faster than the self-cleaning tiles. The soiling was algae growth; it was only visible at the north-faced tiles, and it was most noticeable in the setups with a steep slope. The difference in soiling can be seen in Figure 8. The soiling does not seem to be prevented by the self-cleaning effect—it was only delayed for a few months. The measurements with LED technique showed that larger areas were soiled on the ordinary tiles, especially at the rounded areas or at the edges, while the difference was small at the flat areas of the tiles. When the tiles were removed for LED testing, the difference in soiling of the two tile types was small to the naked eye, but, after a few months, the difference became clearer at the tiles left at the setup.

Water Runoff. The measurements of the runoff were very dependent on the nature of rain; in heavy rain, the differences were small (about 2%), but after a long period with almost dry weather and only occasional light showers, the differences were considerably higher (about 10%). Table 1 shows differences in water runoff in percent.

It should be noted that more water runs off the ordinary tiles than the self-cleaning tiles, independently of orientation and slope.

Water Uptake. There were only small differences in the water uptake from the different positions. Figure 9 shows the water uptake as an average of all ordinary tiles and all self-cleaning tiles. During the summer, heavy rain resulted in a 5% to 6% weight increase in tiles with self-cleaning effect and a 0.5% to 1% increase in ordinary tiles. In the late autumn,

Figure 8 *Soiling of north-facing roofing tiles after more than two-and-a-half years; a few tiles have been replaced by new tiles, as some of the exposed were used in destructive tests. Left: tiles with supposedly self-cleaning properties. Right: ordinary tiles.*

Table 1. Difference in Water Runoff Between Ordinary Tiles and Self-Cleaning Tiles

	North Low	North Steep	South Low	South Steep
Average (%)	3.26	4.56	4.03	4.18
Maximum (%)	10.37	13.94	10.34	12.88
Minimum (%)	0.55	1.18	–0.07	1.02
Standard deviation	2.06	3.11	2.23	2.93

A positive difference means that more water runs off the ordinary tiles than the self-cleaning tiles.

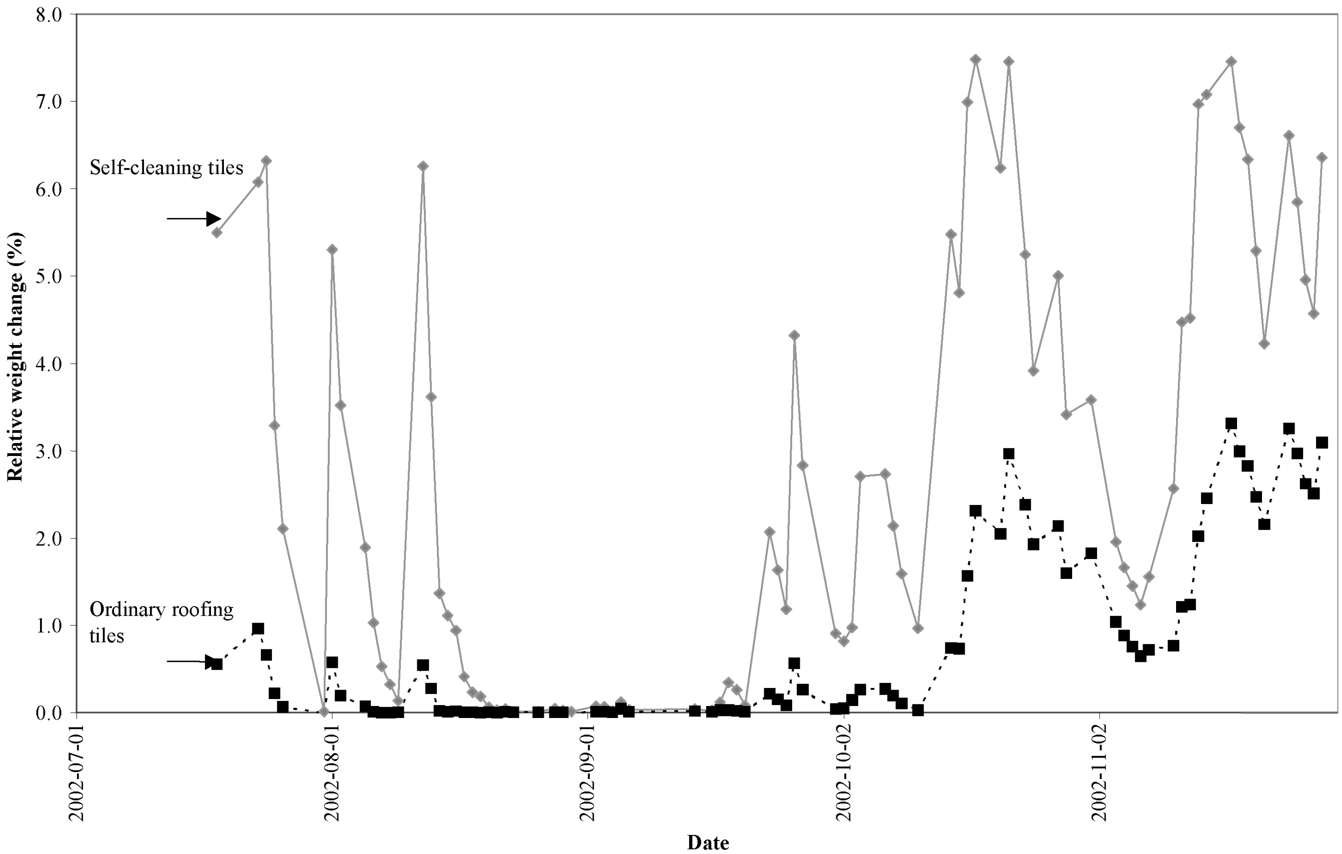

Figure 9 *Relative weight change of tiles exposed to natural weather. The two lines represent the average of the tiles in four different positions, a total of 16 tiles.*

where longer periods with rain occurred, and the tiles did not dry out between showers, the difference in the two tile types was smaller but still distinct; self-cleaning tiles took up as much as approximately 7.5% and ordinary tiles up to 3.9% of their weight. Frost or aging did not change this.

Material Testing

Tests in the laboratory were conducted under controlled conditions, but mostly on small samples of the tiles.

Freeze-Thaw Test. After the test, neither of the tile types showed any of the damage types described in the Danish Standard DS/EN 539-2 for test of frost resistance of clay roofing tiles (Danish Standard 2000); no additional cracks, scaling, or other surface damage was visible after the test. However, there was a slight weight loss in tiles with a surface treatment; the tiles lost 8-10 g (0.3- 0.4 ounces) each, while the ordinary tiles had a weight difference of less than 0.5 g (0.02 ounces).

Porosity. The porosity test did not show any statistically significant difference in the porosity of the two tile types; the results are listed in Table 2.

Pore Size Distribution. Traditional capillary uptake tests did not reveal any significant differences in the pore size of the two tile types. The pore size distribution as obtained with suction pressure is shown in Figure 10. The curves are not identical; self-cleaning tiles vary more than untreated tiles. Generally, ordinary tiles have larger pores than tiles with self-cleaning effect.

Table 2. Porosity of the Two Tile Types

	Ordinary Tiles	Self-Cleaning Tiles
Average	0.2308	0.2249
Minimum	0.2250	0.2243
Maximum	0.2349	0.2258
Standard deviation	0.0036	0.0005

Water Vapor Transmission. The results of the water vapor permeability test are given in Table 3. A statistical analysis showed that, at a 5% confidence level, there is a difference between the water vapor permeability of the two types. The self-cleaning tiles are the most permeable.

Chemical Composition of the Surface. The chemical composition determined by XPS is shown in Table 4.

SEM pictures did not show a surface treatment, and measurements with EDX did not show any difference in chem-

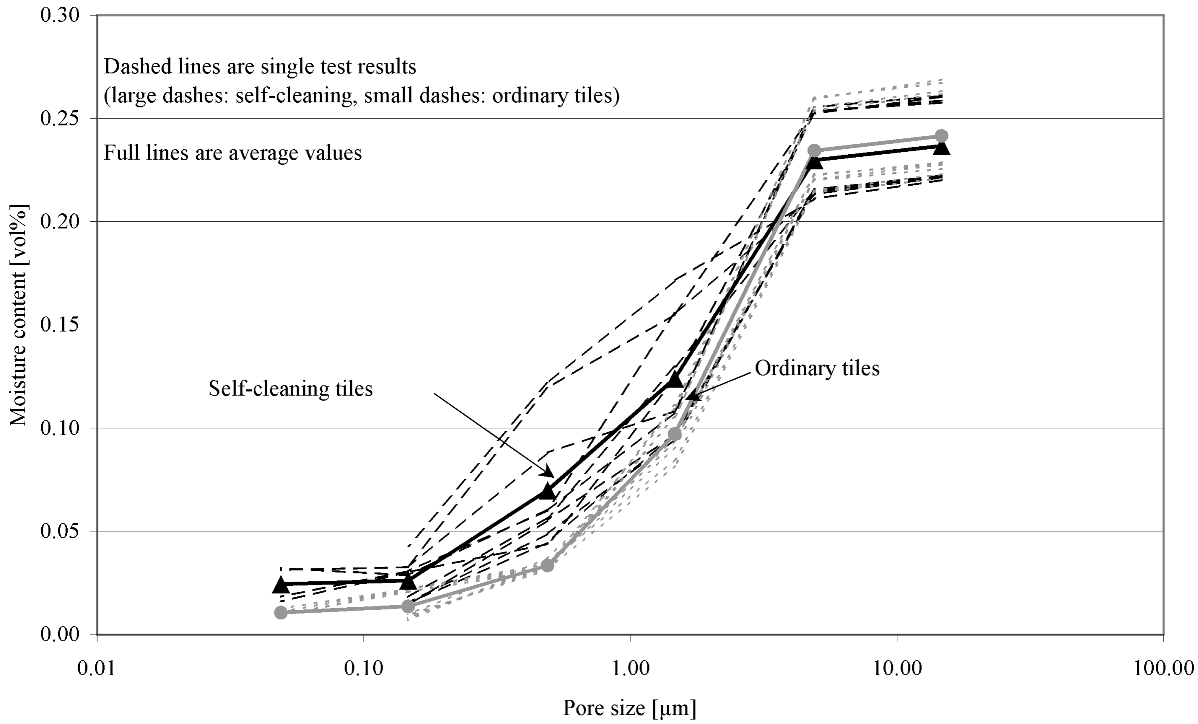

Figure 10 *Pore size distribution obtained by pressure plate measurements.*

Table 3. Water Vapor Permeability of the Two Tile Types

		Ordinary Tiles	Self-Cleaning Tiles
SI	Average (kg/[m s Pa])	2.41E-12	2.95E-12
	Standard deviation	3.38E-13	3.27E-13
IP	Average (perm in.)	1.65	2.02
	Standard deviation	0.232	0.224

Table 4. Chemical Composition of the Surface in % (by XPS)

	Ordinary Tiles	Self-Cleaning Tiles
Si	13.3	5.4
C	35.6	37.6
O	46.6	15.4
Ca	1.6	-
N	2.9	-
F	-	41.6

ical composition—neither through the cross section nor between the two tile types. Therefore, no penetration depth was measured. Simple experiments where water was sprayed on fresh fractions of treated tiles also did not show any penetration depth.

Topography. Although the SEM analysis on cross sections could indicate that there was no treatment on the surface of the self-cleaning tiles, SEM pictures of the surface (Figure 11) showed clear differences. The protrusions described in the patent for the effect (European Patent Office 1998b) are visible. Comparisons between new tiles and tiles exposed for two years did not show any difference in the topography.

DISCUSSION

Low surface free energy is important for hydrophobic treatments and for obtaining low adhesion; however, most porous building materials do not naturally have low surface energy—it is a property that must be obtained by applying a surface treatment. But the property can be lost, either because the treatment is covered or because it disappears with time. Paint can be a water and dirt repellent treatment, and it is generally accepted that paint has to be renewed. Other treatments are almost invisible, but they also have to be renewed. Before applying a treatment, the building owner therefore has to consider not only the initial costs of a treatment but also the maintenance costs and compare these to the gains.

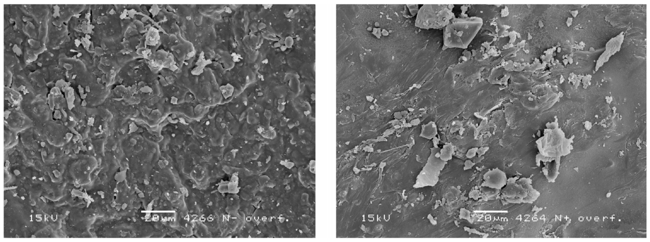

Figure 11 *SEM images of surfaces of new tiles. Left: ordinary tile. Right: self-cleaning tile. Bar equals 20 μm.*

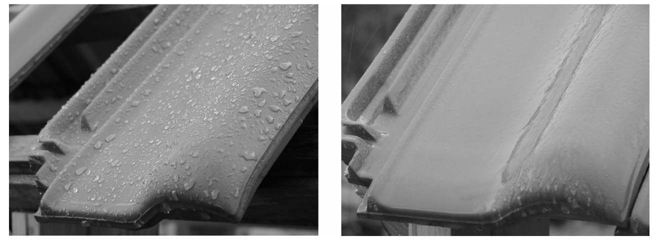

Figure 12 *Change in wetting behavior of tiles with self-cleaning effect. The pictures were taken one after the other. Left: a tile that has been exposed for ten days. Right: a tile that has been exposed for a year.*

The self-cleaning tiles used for the experiments were approximately 30% more expensive than ordinary tiles.

Moisture

Moisture is not always a problem, e.g., the ordinary roofing tile did not show any frost damage after the accelerated test. Neither did the self-cleaning tiles, although they took up more water.

Contact Angle. No contact angle measurements were made, but on new self-cleaning tiles, the water clearly formed beads while water was spread on the ordinary tiles. After one year, water formed films on both tile types. It seemed that at least in the beginning, the theoretical definition of hydrophobic behavior was fulfilled (contact angle > 90°). However, the practical definition—that moisture uptake should be reduced—was never fulfilled. The self-cleaning tiles were not hydrophobic from a practical point of view. The decreased water runoff at the treated tiles corroborates this.

This could make the investigations less interesting, but, at the same time, it underlines the difference between science and practice.

Measurements of contact angle were omitted because several researchers have reported (e.g., Houvenaghel and Carmeliet [2001]) that the contact angle is time dependent (changes within minutes) and that there is no correlation between contact angle and water uptake. From a practical point of view, measurements of the contact angle are therefore irrelevant or, in the worst case, misleading. Figure 12 shows how the wetting of the surface and, thereby, the contact angle changed in the experiment—from droplets on the new surface to a film after the tile had been exposed for one year.

Differences in the Tiles. That a supposedly hydrophobic treatment would result in an up to ten times increased water uptake seems unlikely, and the pore size distribution of the two tile types may indicate that the bulk material in the two types had different pore systems. The porosity was similar, but the self-cleaning tiles had a larger amount of small pores, which could explain a higher capillary activity. The tiles could have been made from different clay or burnt differently.

The Nature of the Treatment. As the bulk material was not similar, the influence of the treatment is difficult to determine, but it does seem odd that two materials with so little difference in chemical composition and pore size distribution react so differently to water exposure. That the SEM/EDX images did not show any chemical trace of a treatment does not mean that there was no treatment. XPS analysis showed clear differences and experiments with other treatments, which were applied by brush, showed that the preparation of the cross section could be responsible for the loss of information. The little available information on the treatment can be found in the patent, where it is described as siloxane. However, the XPS analysis showed a high content of fluorine, which indicates that a fluorinated polymer has been used. Theoretically, this should increase the hydrophobic behavior. The nature of this treatment has not been fully understood through these experiments.

Soiling

The Self-Cleaning Effect. If one has decided to use a self-cleaning material, it is because soiling is seen as a failure. Although the soiling was somewhat delayed by the treatment, the surface of the north-facing tiles could not be described as self-cleaning. Houses that had two-year-old roofs with the self-cleaning tiles but were located in areas with extensive biological growth—typical coastal areas—showed the same picture. In one case, even the south side was soiled, probably with environmental dirt (Møller 2003). The tiles with self-cleaning effect were not sufficiently self-cleaning.

Why was this particular self-cleaning method not effective on the roofing tiles if it works in the lotus flower? There can be different explanations:

- The tiles were not hydrophobic. If the contact angle is <90°, the extra hydrophobicity shown in Figure 5 will be lost. Instead, the protrusions will decrease the contact angle.
- The scale of the protrusions is larger than in the lotus flower, where there is a double system of protrusions (25 μm and 1-5 μm).
- The lotus flower can move in the wind or rain, pushing particles from the valleys between the large protrusions to the top of the protrusions where water can remove the particles.

- Large particles are generally washed off surfaces, hydrophobic or not, but a large part of the particles in the air are very small (see Figure 3); these particles would be trapped between the protrusions. The floating dust would not even be visible in Figure 4.

Temperature. It is unlikely that the extra water uptake in the self-cleaning tiles could explain some of the biological growth. Algae growth was only seen at north-facing tiles and more abundantly at tiles with steep slope; however, the water content in the tiles was independent of the orientation and slope—the only difference must therefore be the temperature. High temperatures, caused by direct sunlight at the south-facing tiles, or the low RH, which is a result of the high temperatures, must inhibit biological growth.

LED Technique. The LED technique was employed to get an objective measurement of soiling, which, at the same time, described the soiling more than just as discoloration in a very small area. Although only few areas were measured, the technique seemed to reveal soiling before it became visible to the naked eye. The method should be developed further, especially in a way that it can be used in-situ in a nondestructive way. If this is obtained, the method could be used to describe soiling over time in the future. As larger areas are measured, the measurement would be more reliable than the usual measurements with color meters.

CONCLUSION

It can be concluded that the tiles with self-cleaning effect that were used for the experiments

- were not hydrophobic, as the water uptake was higher than in ordinary tiles;
- were not self-cleaning, although the soiling was delayed by a few months;
- had a surface treatment that provided the surface with protrusions, approximately 25 μm in height and spacing and was probably a fluorinated polymer; and
- were of a different clay or burnt differently than the ordinary tiles, as the pore size distribution was slightly different but the chemical composition was similar.

It is unclear why the water uptake could be up to ten times higher in the supposedly hydrophobic tiles than in ordinary tiles, especially when a polymer was used that theoretically has the potential to create a more hydrophobic surface than more usual polymers. The higher water uptake did not influence the frost resistance of the tiles. The tiles tested here are no longer manufactured.

Although the surface of the tested tiles did not meet the expectations of water and dirt repellent surface treatments, some practical implications can be drawn:

- Low free surface energy of the agent is important, but contact angle and water uptake do not always correspond.
- Not one agent works for every surface; chemical composition and porosity of the material behind the surface are important.
- A hydrophobic treatment must be renewed from time to time.
- Aesthetics is important when considering soiling. It can be seen as a nuisance, or more positively as patina. However, after a while, soiling will dominate the expression of the building and become unacceptable.
- Soiling can be the reason for deterioration or protection of a surface, depending on the nature of the soiling.
- SEM images can show the surface of the tiles, but SEM/EDX is not useful in determining penetration depth.
- LED technique can be useful in describing soiling, but the method must be developed further so it can be used on the site.

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