NATURAL STONES: 
DETERMINATION OF SENSITIVITY TO ACCIDENTAL STAINING

Key words: natural stones, stains, cleaning, test method

1 SCOPE
This Nordtest method describes a laboratory procedure for determining the sensitivity of natural stones when exposed to accidental staining. It contains a standardised procedure for the application of the stains, the cleaning and the assessment of the surface appearance after cleaning. It also covers the possibility to assess the efficiency of a surface treatment. Note that the method does not intend to present any de-staining technique!

2 FIELD OF APPLICATION
The method can be used to assess the suitability of any stone type for a specific application. Flooring and internal wall cladding are the most common fields of application.

3 REFERENCES
5. prEN12059: Natural stone products – Dimensional stone work – Requirements (June 2006).

4 DEFINITIONS
Surface finishing: The final surface texture applied to a stone during processing.
Surface treatment: The term implies that a chemical (including soap) has been used for protecting the surface by coating.
Impregnation: A chemical that penetrates the surface and has been used for protecting the stone.
Staining agent: The liquid used to produce stains on the surface of the stone.
D65: Reference for daylight according to CIE standard illuminants.
5 SAMPLING, DIMENSIONS AND PREPARATION

• The method of sampling shall be stated in the test report and shall be chosen so that the samples are representative of the batch to be tested.

• One sample set consists of three test specimens sized, minimum 300 mm by 100 mm (preferably 400 mm by 100 mm), thickness as in use (maximum 30 mm). Alternative dimensions can be used if different washing equipment is used.

• For material characterisation and comparison, the specimens shall have a “matt finished surface” (F 400 mesh, see ref. No. 6). Schist and slate are exceptions to this rule. They can be tested on natural cleft surface.

• For “object testing” the actual surface finishing to be used in the intended application shall be tested.

6 TEST METHOD

6.1 Principle

A defined set of staining agents is applied on a standardised stone surface. The mode of application is specified. The specimens are conditioned and washed with a standardised washing machine. The stones are dried and the possible remainders of the stains are assessed versus a text-based scale of categories. An alternative method by use of spectrophotometer is also described. However, the visual evaluation is the reference method.

6.2 Equipment

• Pipette, 0.10 – 1.00 ml

• Wet Abrasion Scrub Tester, Byk-Gardner, or equivalent according to ISO 11998 or ASTM D 2486. The machine (Figure 1) works with a sinus-shaped movement with a frequency of 35 cycles per minute, and amplitude of approximately 350 mm. The total weight of the scrubbing arm with dry cloth and its holder shall be 350 ± 35 g.

• Weights to achieve the specified load on the scrubbing arm

• Cleaning cloth

• Dimensions of the cloth 120 × 38 mm (may be different depending on the washing equipment)

• Thickness: 2 ± 0.5 mm at 23 °C / 50 % Rh

• Area weight: 300 ± 50 g/m² at 23 °C / 50 % Rh

• A thinner cloth may be used in layers to achieve the above stated properties

• At least 50 % viscose (regenerated cellulose fibres)

• At least 20% cotton.

Examples of cloths that fulfil these requirements are: Nordex Wizzo and Wettex.

• Holder for the cleaning cloth, e.g. wooden block (Figure 2). The scrubbing arm of the machine is equipped with e.g. a wooden block measuring 89 × 38 × 32 mm. The block holds a piece of cleaning cloth measuring 120 × 38 mm. 89 × 39 mm is the standard dimension of the scrubbing area of the brush in the standards mentioned above.

• Camera, preferably digital, for documentation of unstained and stained test specimens

• Daylight lamps for photography in correct light

• Stand for repeatable photography conditions

• Cleaning solution: Soft soap made from pine oil, 0.50 v%/ solution in water. E.g. Grumme Grön soft soap

• Hand spray pump for applying the cleaning solution

• Optional if a spectrophotometer shall be used for the evaluation: Spektrophotometer according to ISO 7724/1 with a measurement opening of ≥ 25 mm.

6.3 Testing environment

• The test specimens shall be placed in 23 ± 3 °C and 50 ± 5 % relative humidity during the entire stain exposure

• Daylight or artificial light D65 according to ISO/IEC 10526 is used during the photography and the evaluation.
6.4 Pre-conditioning and treatment of the samples

Marble and limestone shall be dried in 40 ± 3 °C for one week before the test. Other stone types shall be dried in 70 ± 5 °C for at least 24 hours. Commercially used stone products are sometimes impregnated in some way to make them easier to clean. The traditional treatment of carbonaceous stones is soft soap, which partially seals the pores and makes the surface a bit more hydrophobic. For standard test the stones shall be non-treated as a reference and one set treated with soft soap, e.g. Grumme Grön (Green), soft soap made from pine oil, 2.5 vol. % solution in water, or similar which is recommended by the Nordic Stone Industry federations.

Instruction for the treatment with soft soap:
- The solution is sprayed on with a hand-pumped spray can
- After 3 hours: The next layer is applied
- After another 21 hours: The excess shall be rinsed off under running water

The test specimens are kept in 23 ± 3 ºC and 50 ± 5 % relative humidity for a minimum 16 hours before applying the staining agents.

6.5 Test procedure and assessment of results

6.5.1 Documentation of the test specimens

Document the test specimens by digital photography before the stains are applied. Use daylight or artificial light D65 according to ISO/IEC 10526.

6.5.2 Stain agents to be used in the standard set:

The standard set of stain agents are: Red wine, Cooking oil, Instant coffee, Ketchup and Coca-Cola (or similar). The specifications are given in Enclosure 1.

It is also recommended to use blood, urine and blueberry soup.

Other products can be used and prepared according to instructions by the manufacturer or commissioner.

6.5.3 Staining procedure

To be able to make an objective assessment of resistance against staining, all samples have to be stained in the same way. The important factors for a visual assessment are that the stains have the same size and shape. This can be allowed to differ between different stain types but not between surfaces to be compared.

All staining shall be performed at 23 ± 3 °C and 50 ± 5 % relative humidity. This is important as the drying time of a water based stain depends on this. A dry stain cannot penetrate the stone and is therefore harmless. The samples shall remain in this atmosphere during the whole exposure time, usually 24 hours as a default value. Other time schedules may be used provided that the commissioner asks for it.

The diameter of the stains shall be approximately 35 mm. Most water based stains, like Coca-Cola, wine and coffee has the same surface properties and a suitable stain volume is 0.70 ml. This volume is also sufficient for ketchup which shall be spread out to the same size. A stain like oil has completely different surface properties and immediately floats out on most stone materials. To get a stain in the same size as for the water based products a volume of 0.15 ml is suitable. See Figures 3 and 4.

A very small amount of blood is needed. By pricking a finger with a needle and let it drip down on the sample surface, a quite suitable stain is obtained. The blood, usually, do not float out very much and the stains get a bit smaller than the above. There is no recommended volume.

Surface treated samples may need the staining agent to be spread out to reach the optimal 35 mm Ø.

Figure 3. Optimal sample size and stain pattern.

Figure 4. Stone specimens after staining with (from left to right); blood, cooking oil, Ketchup, urine, Coca Cola and coffee. Document the test specimens by photography after the 24 hours conditioning.
6.5.4 Washing procedure

- Gently remove possible liquid residues of the stains with dry paper.
- Apply the correct load to the washing arm, 350 ± 10 g (arm, cloth and cloth holder).
- Spray cleaning solution on the stains 4 minutes before the cleaning.
- Soak the cleaning cloth in cleaning solution.
- Mount the cleaning cloth and the holder to the scrubbing arm.
- The stained surfaces are then washed with a “Wet Abrasion Scrub Tester”.
- Ten cleaning cycles (10 strokes back and forth) shall be used in all tests.
- Rinse the surfaces with 150 ml water to remove residues of the cleaning solution.
- Condition the test specimens for 16 hours in 23 ± 3 ºC and 50 ± 5 % relative humidity before they are photographed and evaluated.

6.5.5 Evaluation of staining and defining the result

A text-based scale of grades is used. It is taken from ISO 4628/1, developed for visual assessment of degradation of painted surfaces.

0 unchanged, i.e. no perceptible change
1 very slight, i.e. just perceptible change
2 slight, i.e. clearly perceptible change
3 moderate, i.e. very clearly perceptible change
4 considerable, i.e. pronounced change
5 severe, i.e. intense change.

See Enclosure 2, with photos exemplifying the difference between the grades.

Etching effects (gloss change) from acidic staining agents is assessed separately. The same text-based scale of grades is used and the result is reported separately. The evaluation can be done in a reflecting light. Note that an etching effect is, in cases, also observed as a colour change. The use of a gloss meter is not recommended.

The visual assessment is to be performed in daylight or artificial light D65 according to ISO/IEC 10526.

The evaluation is performed by three persons individually. The three stains on each test specimen are evaluated as a group. Each stain type is evaluated separately. Present the mean value as an integral number (2, 2, 3 = 2). If the result of two evaluators differs more than one grade, the evaluators have to come to consensus by discussion.

OPTIONAL PROCEDURE

The use of a spectrophotometer to measure the colour change is optional. In this case, the colour is measured according to ISO 7724/1 with d/8 geometry. Since all stone surfaces have naturally shifting patterns, the largest possible measuring diameter, at least 25 mm, is used to obtain a representative average. The measured area is marked so that the exact same area is measured after staining as before staining. The difference in colour shall be expressed in CIE-Lab units, where \( \Delta L \) is the difference in lightness, \( \Delta a \) is the difference on the red/green-scale and \( \Delta b \) is the difference on the blue/yellow-scale. The average \( \Delta E \) can generally be used as the only evaluation result.

\[
\Delta E = \sqrt{\left(\Delta L\right)^2 + \left(\Delta a\right)^2 + \left(\Delta b\right)^2}
\]

Individual \( \Delta E \) differing more than 2 units for the 9 measurements/stains shall not be used for calculation of the results. A new mean value shall be calculated without the deviating \( \Delta E \).

6.6 Applicability

The method describes a standardised procedure for applying a defined set of stains, the cleaning procedure and the assessment of the colour changes. The method is thereby applicable for comparison of the relative staining sensitivity of different stone types. Other techniques for cleaning can, of course, be used in the actual application. It has then to be defined by the commissioner. The method is also suitable for assessment of the efficiency of different treatments.

6.7 Uncertainty

No inter-comparison trial has been performed between different laboratories. The repeatability is based on the fact that three different persons evaluate the changes by using 6 categories. The difference between the persons is maximum 1 category. If there is more than 1 scale deviation between any of the evaluators they shall discuss until consensus is reached.

6.8 Test report

The test report shall include the following information (when relevant)

a) Name and address of the testing laboratory
b) Identification number of the test report
c) Name and address of the organisation or the person who ordered the test
d) Purpose of the test
e) Method of sampling and other circumstances (date and person responsible for sampling)
f) Name and address of the manufacturer or the supplier of the tested object(s)
g) Name and other identification marks of the test specimens
h) Description of the test specimens
i) Date of supply of the test specimens
j) Date of test
k) Reference to this method
l) Condition of the test specimens (i.e. orientation of stone fabric in relation to the test object and the surface finishing)
m) Surface coating or impregnation if used
n) The staining agents used
o) Any deviations from the test method
p) Test result as defined in 6.5
q) Photographs of the stains
r) Statement about the uncertainty of measurement
s) Date and signature.

7 APPENDIX
1 Recipes of staining agents
2 Colour photos to facilitate the evaluation of staining.
ENCLOSURE 1. RECIPES OF STAINING AGENTS

- **Red wine**
  100% Cabernet Sauvignon, a world-wide spread grape
  One to two years old
  pH 3.0–4.0

- **Cooking oil**
  100% colza oil (rape-oil)
  without any colorants

- **Instant Coffee**
  Brewed and freeze-dried coffee powder
  1.50 g is solved in 100 ml hot (>80 °C) deionised water.
  Let cool down to about 23 °C before use

- **Ketchup**
  pH 3–4

- **Coca-Cola (“regular Coke”, not light or with modified taste)**
  A world wide spread product
  Brewed on licence by The Coca-Cola Company

- **Artificial urine**
  According to ASTM F1828 Annex A1:
  - Urea 25 g
  - Sodium chloride 9 g
  - Disodium hydrogen phosphate, anhydrate 2.5 g
  - Potassium dihydrogen phosphate, anhydrate 2.5 g
  - Ammonium chloride 3 g
  - Creatine 2 g
  - Sodium sulphite 3 g
  - Destilled water up to 1 l

- **Blood**
  No specification (fresh from laboratory personnel)

- **Blueberry soup**
  Commercially available in most Nordic countries.
  Prepare as defined on the package or use “Ekströms for coffee machines”. 10 g dry soup is solved in 50 ml hot deionised water. pH 3.0.
ENCLOSURE 2. COLOUR PHOTOS TO FACILITATE THE EVALUATION OF STAINING

The photos give examples of some common stones on the market. Depending on the type of staining agent and surface, it has been possible to visualise all grades of the evaluation scale from 0 to 5. Note, that, in some cases, it is difficult to display the difference between No. 3 and 4. The ultrabasite is also difficult to illustrate by photo since the stains are partly a change in colour and partly an effect of etching.

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Marble

Limestone

Ultrabasite

Schist
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