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An Assessment and Evaluation of Acidic Cleaning Methods on Unglazed Terracotta Using Accelerated Weathering Test Protocols

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Abstract

According to the published literature, there has been very little quantitative evaluation of the short or long-term effects of cleaning terra cotta, other than visual assessment where success is pronounced by the degree of soiling removed.

Very little work (only 3% of our literature review) has attempted to measure the effects on terra cotta of various cleaning methods.

Nevertheless, today, still 80% of terracotta cleaning relies on chemical products, the majority acid-based.

This research evaluates the effects of acidic cleaners on unglazed terracotta to verify the potential for damage by accelerated weathering testing. This investigation continues previous studies (Matero et. al. 1996) where findings showed that by using hydrofluoric acid-based commercial cleaning system, an increased porosity of unglazed terra cotta resulted. The questions remains whether this physical alteration will lead to accelerated weathering and material damage.

In the first phase of this research a Literature Review of past and current cleaning of terra cotta was completed, together with a survey of professionals involved in terra cotta restoration. In the second phase, two commercial chemical cleaners are being tested in two applications on new unglazed red and tan terracotta samples: Prosoco Heavy Duty Restoration cleaner based on HF (1:3), and Prosoco Enviro Klean based on Ammonium Bi-fluoride (generally applied as a concentrate). These are now undergoing accelerated weathering based on the Rilem salt test (V.1B) and a QUV weatherometer (ASTM G154-12) to access the effects of acid cleaning on performance.

Several methods of assessment were used to evaluate the tiles before and after testing: optical microscopy, scanning electron microscopy, porosity by liquid nitrogen immersion, color change, and texture mapping imaging.

By examining physical changes and their response to accelerated weathering across two typical terra cotta clay bodies, it is hoped that better cleaning methods will be considered in practice and parameters to measure potential damage as well as cleaning efficacy become established.

Keywords
terra cotta, terracotta, cleaning, chemical, soiling

Disciplines
Architectural Engineering | Architectural Technology | Historic Preservation and Conservation | Materials Chemistry

Comments
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AN ASSESSMENT AND EVALUATION OF ACIDIC CLEANING METHODS ON UNGLAZED TERRACOTTA USING ACCELERATED WEATHERING TEST PROTOCOLS

Irene Matteini

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1.0 Introduction

Motivated by a personal interest and by the opportunity to contribute to the IIC Architectural Ceramics Conference in March 2014[1], I decided to focus my research on terracotta, and more specifically on cleaning, which has been a major concern for architectural terracotta since its re-introduction in the 19th century. Despite the relevance of the problem for the increasing number of soiled historical buildings worldwide, the published literature suggests that very little quantitative evaluation of the short or long-term effects or performance of cleaned terracotta has occurred. Instead, success has been pronounced almost exclusively by the degree of soiling removed, frequently by chemical means. According to David Boyer, president and CEO of ProSoCo, chemical products still account for 80% of all terracotta cleanings in the United States[2]. Unfortunately very little work has been done to measure and evaluate the effects of these cleaners on terra cotta before and after treatment[3]. Matero demonstrated that by using hydrofluoric acid (HF)-based commercial cleaner specifically designed for masonry, increased porosity and potentially increased permeability of the terracotta occurred.

While, no research has yet proven that this increased porosity is deleterious to the durability of the terra cotta and will cause accelerated weathering, the potential relationship between porosity, water permeability, and deterioration is a well know phenomenon for many porous building materials.

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[1] IIC Architectural Ceramics in the 21st Century: Design and Preservation of Contemporary and Historic Architecture at MIT in March 2014. I co-authored a paper on Cleaning Terracotta with Prof. Frank Matero and Prof. Reza Vatankhah.

[2] David Boyer-personal communication February 2014.

[3] Matero et al., An Approach to the Evaluation of Cleaning Methods for Unglazed Architectural Terracotta in the USA, from Architectural Ceramics : their history, manufacture and conservation: a joint symposium of English Heritage and the United Kingdom Institute for Conservation, 22-25 September 1994, edited by Jeanne Marie Teutonico , London: James & James, pages 57-88, 1996.

Therefore, this investigation assesses and evaluates the effects of acidic cleaners on unglazed terracotta in order to verify the potential for accelerated weathering. Two commercial chemical cleaners were tested in two applications: ProSoCo Heavy Duty Restoration Cleaner, an aqueous hydrofluoric acid-based cleaner (1 part cleaner: 3 parts water by volume), and ProSoCo Enviro Klean, an aqueous ammonium bi-fluoride cleaner (generally applied as a concentrate), both as recommended by the manufacturer. The selection of these two products is related to their popularity in the restoration market by architects, conservators, and building contractors, as confirmed by a 2014 field survey and literature review. While hydrofluoric acid as a masonry cleaner has been popular since the early 1960's, with the introduction of ProSoCo's first chemical cleaner Boyer R1 and R2 Restoration Cleaner in 1962, ammonium bi-fluoride was only introduced in the beginning of 2000, when HF based cleaners began to be banned in major American cities due to problems related to acidic "drift" and the introduction of more restrictive environmental laws.

This research was organized in three phases:

In the first phase, a literature review[4] was completed, together with a survey of professionals involved in the restoration of terra cotta buildings: architects, conservators, building contractors and product manufacturers. This data was reported and a timeline was produced and presented at the IIC Architectural Ceramics Conference in March 2014.

In the second phase, new commercial terra cotta samples [5] were obtained and treated with the two above cleaners, artificially weathered and evaluated in terms of the following properties:

- Morphology and especially change in porosity by Scanning Electron Microscopy
- Change in porosity using Liquid Nitrogen Porosimetry
- Change in Surface Texture–by Texture Mapping Photography
- Visual & Color change using a Minolta Spectrophotometer

As part of the final phase of this project, accelerated weathering testing protocols were developed and executed. One set of samples was tested using the RILEM Salt Test (V.1B) for 3 weeks; and a second set of samples was tested for 6 weeks with a QV-Lab accelerated weathering tester (ASTM G54-12).

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[4] An earlier lit review prepared by the Architectural Conservation Laboratory (Matero, 2000) was updated till today. For more details see Chapter 2.

[5] Generously donated by Boston Valley Terra cotta.

During this research, several limitations were encountered:

- Limited amount of time for testing
- Use of only unglazed or slip glazed terra cotta
- Three cohorts per test were treated

1.2 Definitions

Terracotta[6]

An article of an artistic character, made of clay and burnt, or of a composition in which clay forms the chief substance. The clays are generally red, brown, buff, or a dull white. They may be mixed with manganese, ochres, and cobalt. Old stoneware, ground to a powder, and combined with the new clays, tends to prevent large lumps of clay from warping and twisting in the drying and burning. By mixtures of feldspar, ground glass, and other bodies with the clay, the fire partially vitrifies the mass, and renders it proof against the weather.

A term for architectural enrichments of brickwork of various designs and shapes. Terracotta requires a greater degree and a more regular distribution of heat during firing than are required for bricks. The vitrifying ingredients usually added to terracotta clays are pure white sand, old pottery, fire-bricks finely pulverized, and clay previously burned, termed ‘grog’.

A hard baked pottery, especially that which is used in architecture or in decorative art of large scale. It may be left with its natural brown surface unglazed and uncoloured, or it may be painted as was customary among Greeks, or it may be covered with a solid enamel of grave or brilliant colours.

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[6] Definitions from the Dictionary of Architectural Terra cotta prepared for English Heritage by The Architectural Conservation Laboratory, Graduate Program in Historic Preservation, and Graduate School of Fine Arts University of Pennsylvania.

A term which, in its broadest sense, includes both pottery and structural objects made of burned clay and having a porous body. The term architectural terracotta is usually applied to those clay products employed for structural decorative work which cannot be formed by machinery; they are moulded by hand.

An unglazed porous ceramic, sometimes with a coarse texture and often made of red-burning clay.

An earthenware body, unglazed, usually red, relatively coarse and porous, and low fired; sculptural or architectural articles made from such an earthenware body.

A moulded clay product made from clays mixed with additives, such as sand and pulverized fire clay. Terracotta is moulded block used in a structural or semi-structural context. The clay is hand-pressed into absorbent moulds to form hollow boxes within which there may be clay ‘webs’ or ‘straps’ to support the form prior to firing and to allow thorough firing of clay in the kiln. Blocks were usually dowelled, cramped and anchored to a substrate or frame by means of iron or steel fixings, accommodated by holes at the back of blocks.

A large block of pressed clay, typically buff or red in colour, and usually in the form of statues, garden ornaments or building materials.

An unglazed fired clay building block or moulded ornamental building components.

Fireskin [7]

It is an important protective surface for the weather-ability of terra cotta. The formation of the fire skin is related to the concentration of colloidal clay particles in the upper surface due to the suction of the plaster molds during drying. This enriched colloidal clay zone becomes denser during sintering in the kiln while firing and creates a hard durable protective layer.

Slip[8]

A clay and water mixture.

A fine-particle clay mixture with water that can be applied to the surface of a clay body to form a layer or coating, often burnished before firing. Also used as a general term for any suspension, as a slurry.

A fluid suspension of fine clay and water, used to coat a body before firing or poured into a mould to cast a piece.

A clay which, in its natural state, contains sufficient flux to be used for glazing.

A suspension of fine solid particles in water, used in casting ceramics in moulds or to coat pressed ware.

A suspension in water of clay and/or other ceramic materials; normally a deflocculant is added to disperse the particles and to prevent their settling out. In the whiteware industry, a slip is made either as a means of mixing the constituents of a body (in which case it is

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[7] See note 6

[8] See note 6

subsequently dewatered, e.g. by filter-pressing) or preparatory to casting. In vitreous enameling, a slip is used for application of the enamel to the ware by spraying or dipping.

The mechanism by which shear stress causes plastic deformation, by driving lines of dislocation across certain crystalline planes, the slip or glide planes.

Plaster of Paris

Typically the molds used for the manufacture of terra cotta were made of plaster of Paris, due to its quick set, low shrinkage, porous nature and ability to absorb a large quantity of moisture from the clay.

Hydrofluoric Acid (HF)

An aqueous solution of hydrogen fluoride that attacks silica and silicates and that was initially used in finishing and etching glass.

Ammonium Bi-Fluoride (ABF)

A colorless salt produced from ammonia and hydrogen fluoride. When dissolved in water, it becomes Hydrofluoric acid. The use of ammonia as a buffer allows Ammonium Bi-Fluoride to strongly attack silicates, even at low concentrations. Ammonium bi-fluoride is more difficult to control and requires more rinsing than Hydrofluoric acid cleaners. Furthermore, the use of Ammonium Bi-fluoride appears to be less predictable than a low percentage of Hydrofluoric acid due to the variable environmental conditions on site.

2.0 Literature review on cleaning terracotta[9]

2.1 Terracotta cleaning techniques overtime

By the end of the 19th century, terra cotta became the first choice for cladding in combination with steel skeleton construction in the United States; a very durable, light-weight and versatile material, it rapidly became the protagonist of the skylines of America's major cities.

Advertised in early publications such as the *Atlantic Terra cotta Company Magazine* in 1917, this material was described as very easy to clean, requiring only a scrubbing and washing with soap.[10]

According to the *Economist,* the white glazed terracotta of Burnham's new Reliance Building in Chicago was the future:[11]

> *This is innovation. It is indestructible and as hard and as smooth as any porcelain ware. It will be washed by every rainstorm and may if necessary be scrubbed like a dinner plate.*

Eventually with the proliferation of factories and automobiles, urban pollution increased dramatically, and consequently terra cotta buildings rapidly soiled and blackened. Inevitably, cleaning became a major issue and challenged claims of terracotta's resistance to soiling.

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[9] This part of the research was co-authored by Matero, Matteini and Vatankha and presented at the Architectural Ceramic Conference in Boston at MIT in March 2014.

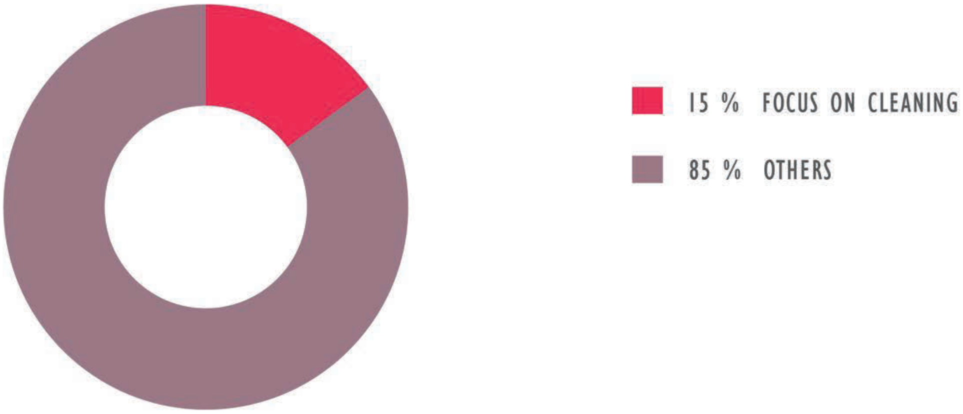
[10] Atlantic Terracotta Company, Spring Cleaning, *Atlantic Terra cotta Magazine*, vol.3 number 8 (1916). This publication documents the cleaning of the Woolworth Building in New York; this building was cleaned twice: first in 1916 only three years after its construction and then in 1932 by using a soap wash, Gold Dust with sharp sand. The company recommended cleaning glazed terra cotta with commercial detergents such as Gold Dust or Old Dutch which contained pumicite. Unglazed terra cotta was to be cleaned instead with "a little" muriatic acid (1 qt. to 4 gal.).

[11] *Economist*, XII (August 1894):206.

Figure 1: Sapolio Advertisement Poster. Source: Neil Harris, *Building Lives*, 1999

Overtime a vast array of cleaning techniques have been performed on terracotta buildings in the attempt to remove soiling: from the earliest techniques of steam cleaning, "sand-blasting," and soap to the introduction of the first commercial restoration specialty cleaning products in the 1960s. Later more targeted techniques including a range of chemical and micro-abrasive methods have been developed including laser ablation.[12]

The first phase of this research was the updating of an earlier literature review on the conservation of architectural terra cotta[13] together with a survey of professional practices in cleaning terra cotta buildings in the United States by polling architects, artists, engineers, conservators, contractors, and product manufacturers. [14]After updating the bibliography, the total number of publications (books, conference proceedings, journal articles, and standards) numbered 567 spanning from 1893-2014. Only 85 or 15% of the published material addressed the subjects of soiling and cleaning.



Graph 1: Terracotta Bibliography 2014

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[12] Larson, John, et al, The use of laser energy for cleaning architectural terracotta decoration, Architectural Ceramics-a joint symposium of English Heritage and the United Kingdom Institute for Conservation, (22-25 September 1994). Starting in 1994, the first experimentations with laser on terracotta were conducted at the Victoria Albert Hall in London.

[13] The first step of our research was to update the literature review (Matero et al. 2000); previously composed of 477 publications ranging from 1890- 1990's, today it contains 567 publications ranging from 1890's-2014. Available at: http://www.conlab.org/acl/initiatives/TerraCottaBibliography.pdf

[14] The survey was completed by using two different methods: 1) an on-line link with 10 questions, with anonymous answers (https://www.surveymonkey.com/s/S9HXDN2); 2) phone interviews completed during the months of January and March 2014. (More informative data were collected through phone interviews).

Within these 85 entries, 27 publications are represented as case studies (32%), followed by 23 publications describing specific cleaning methods (27%) which account for more than half of the sources found (59%). Hybrid publications addressing two or more of the above subjects in some degree of detail (25%) are next in representation followed by a very low percentage of research on soiling (7%), performance standards (6%), and finally evaluation of cleaning before or after treatment (3%).[15] As anticipated, this data clearly shows the scarcity of research on understanding the nature of soiling on terracotta and the effects of various cleaning methods despite the long observed problem of soiling on terracotta buildings. Few exceptions are Moynehan[16]et al. and Hall.[17]Similarly, evaluation before and after treatment surprisingly represents a very small percentage as well.

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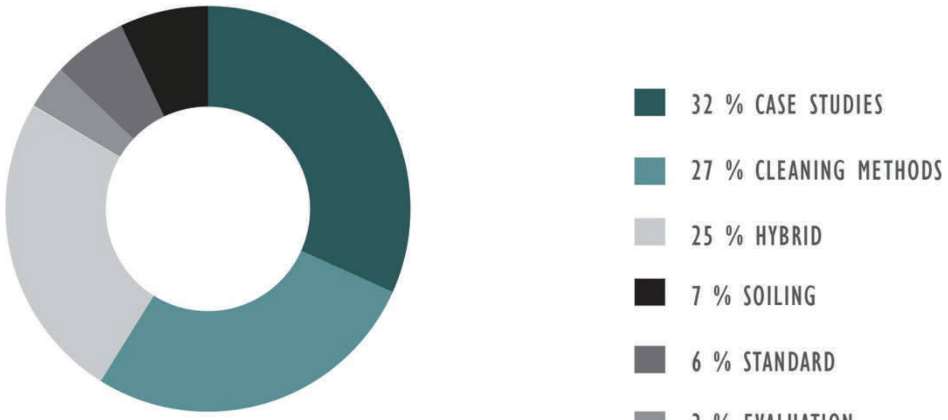
[15] From Matero, Matteini and Vatankhah, Cleaning Terra Cotta: Recent Trends in Technical Research and Practice, under publication.
See Definitions:
Case studies: published reports on the conservation of specific buildings and sites.
Cleaning methods: publication includes detailed descriptions of cleaning methods used on site or is focused specifically on testing and evaluating one or more cleaning methods
Hybrid: publication addresses two or more of the above subjects in some degree of detail.
Soiling: publication includes detailed discussion of the characterization and analysis of terra cotta soiling or is focused specifically on soiling mechanisms
Standards: publication includes or is devoted to the description or development of test standards for terra cotta, especially cleaning.
Evaluation: publication includes or is devoted to the assessment of cleaning methods for terra cotta either in the lab or field or both.

[16] Moynehan, C. R et al., Surface analysis of architectural terracotta including new and soiled examples, and pieces treated with a hydrofluoric acid-based cleaning solution, Journal of Architectural Conservation, 1(1), (1995):56-69.

[17] Hall, Matthew R., The Tenaciously Bonded Black Soiling unique to Architectural Terracotta on Historic Buildings: its composition, distribution and mechanisms of adhesion, Dissertation-Degree of BSc Building Surveying, Sheffield Hallam University, UK, (2003).

[17] Hall, Matthew R., Characterization of irreversible black soiling layer formation on historic unglazed terracotta substrates using analytical scanning electron microscopy (SEM) with energy dispersive X-RAY (EDX) analysis, International Journal of Architectural Heritage, number 5,(2011): 172–187.



Graph 2: Categories within the Cleaning Terracotta Bibliography

The literature survey suggests little is known about the mechanisms of soiling and even less about the effects of cleaning methods on the substrate. To chart trends and patterns, graphs and a timeline were created with the data collected from the literature review and the survey.

The first analysis presents the frequency of cleaning publications appearing overtime, showing a rapid escalation in publications from the 1960s to the 1980s. Two reasons are probably responsible for this: firstly, the general popularity in technical building preservation especially in the United States, and secondly the introduction and greater availability of commercial restoration cleaners during these years.[18]

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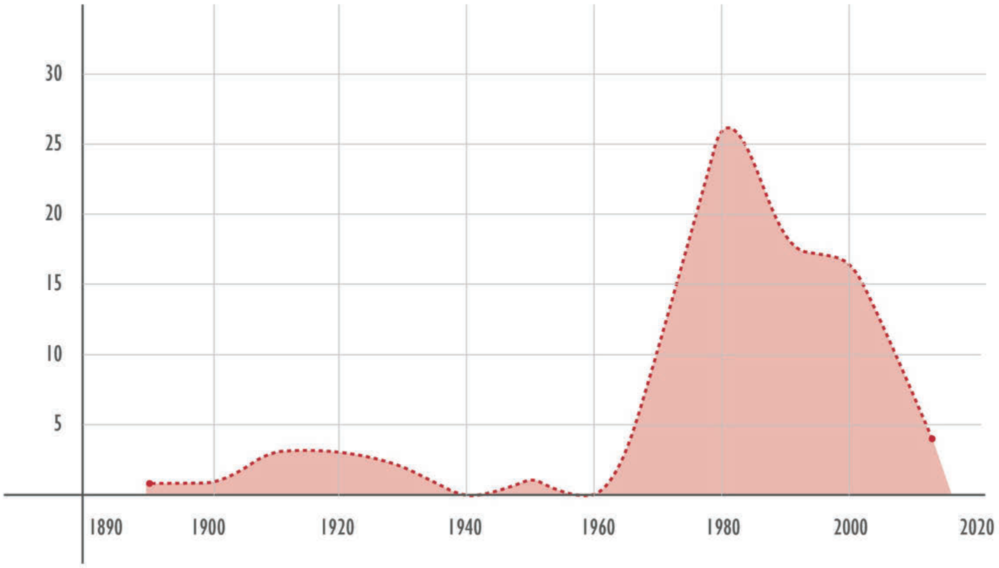
[18] In 1962, ProSoCo introduced its first chemical cleaning product marketed as a general purpose restoration cleaner called *Boyer's Restoration Cleaners R-1 and R-2*.



Graph 3: Cleaning Publication Overtime

By exploring the different cleaning techniques through the years, chemical, followed by mechanical methods, have remained the most popular according to the literature review, and also confirmed by the survey. Within the chemical methods, acidic cleaners lead at 44%, followed by alkaline cleaners at 24%, often in combination[19], and finally, detergents at 32%, also confirmed in practice by the survey. [20]

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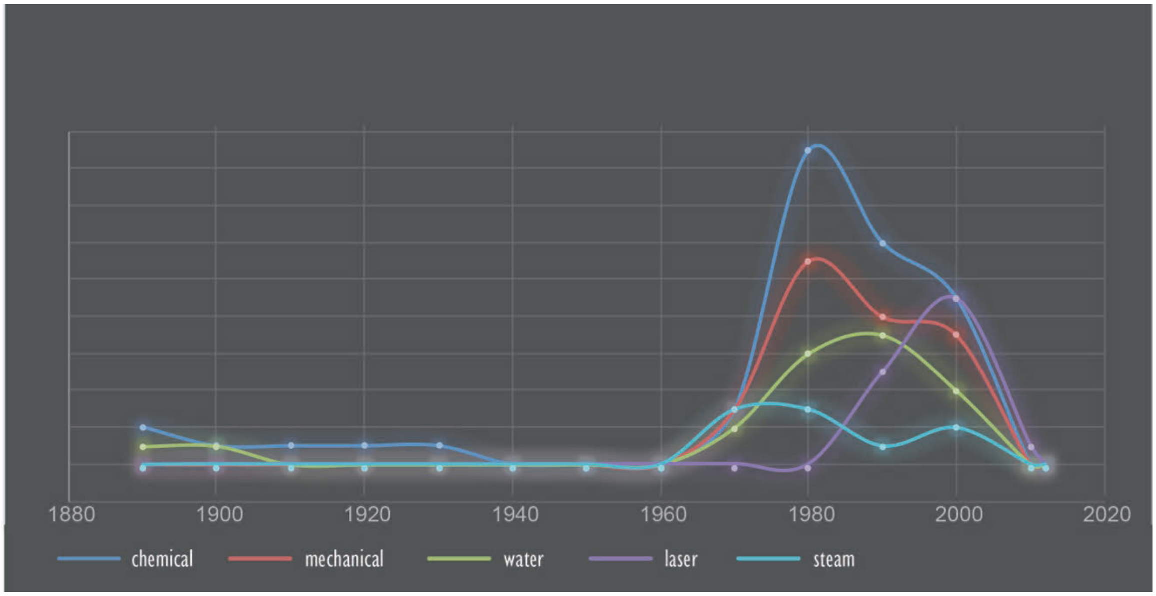
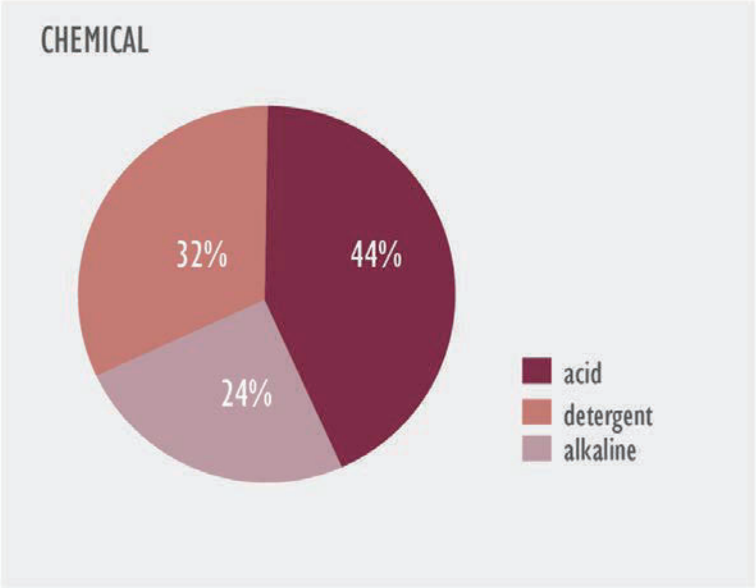
[19] Today, it is often used in combination consisting of an alkaline pre-wash acting as a surface degreaser, followed by the acidic cleaner which also functions as an after-wash to neutralize the high ph. A recent example of a large scale cleaning project that used this method is the Milwaukee City Hall, completed in 2008.

[20] From Matero, Matteini and Vatankhah, Cleaning Terra Cotta: Recent Trends in Technical Research and Practice, under publication.



Graph 4: Cleaning techniques overtime.



Graph 5: Different chemical cleaning products commonly used accordingly to the Literature Review and Survey.

Beginning in the early 1980's, more sophisticated micro-abrasive techniques were introduced such as Thoman-Hanry Gommage[21], Jos, Rotec Quintex[22], and Sponge-Jet[23], together with the rise of laser cleaning[24] with its first application on terracotta in 1994 at the Victoria Albert Hall in London. Additionally, the introduction of tighter environmental safety controls also encouraged the launch of these newer techniques in the market.[25]At the same time, the use of steam, as one of the oldest techniques, shows an oscillation of popularity in response to problems related to the misuse of chemical and mechanical systems.[26] In the last ten years, again chemical cleaning has shown a similar level of interest.[27]

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[21] *Façade Gommage* is a proprietary technique developed in France by Thoman-Hanry in the late 1970's. Initially, it was only performed by the company which eliminated inconsistencies in the results and guaranteed quality control. Consequently, it only arrived in the United States in the mid-1990s. This system involves the use of fine glass aggregate 10 to 50 microns in diameter at a very low-pressure. The glass and soiling debris are then collected in a glass chamber (*cabine*) to control pollution. From: Slaton, Deborah et al., Cleaning historic façade-choose a method that's kind to the substrate, *The Construction Specifier*, (July 1994): 55-61.

[22] The Jos System was initially developed in Europe, and arrived in Canada at the end of the 1980's. In 1988 Mark Sherman, head of the North America Jos Distribution, introduced a new nozzle called QUINTEK ROTEC®VORTEX Nozzle and founded Quintex Corporation, separating from Jos. The ROTEC®VORTEX cleaning system is a rotating wet jet micro-abrasive process. Gino Varalli, from Dan Lepore and Sons Co., stated that today Jos is no longer available in the United States-personal communication May, 2014.

[23] Introduced in 1994, Sponge-Jet is a micro-abrasive system that uses synthetic sponge-encased media. Sponge-Jet reported that the number of applications for terra cotta cleaning have increased in the past few years, mainly on the east coast. Ted Valoria, president of Sponge-Jet, personal communication, February 2014.

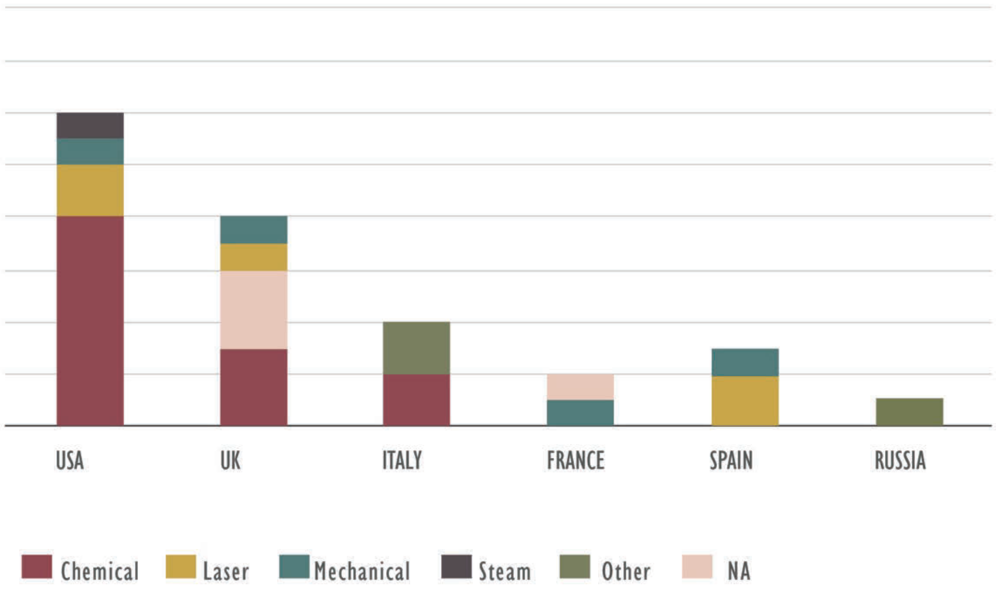
[24] In the United States, the use of laser is still limited due to cost of equipment and application knowledge. In Europe, the European Standard Committee is developing a standard for the use of laser for cleaning heritage buildings. CEN/TC 346 *Conservation of cultural heritage - Cleaning of porous inorganic materials - Laser cleaning techniques for cultural heritage.* (under review)

[25] By the end of 1970's, the use of chemicals increased exponentially, consequently OSHA and EPA began introducing regulations on the use and disposal of chemicals. In 1972, EPA introduced the Clean Water Act; followed by HAZCOM, OSHA's first training for handling chemicals in 1994, which became mandatory as of December 2013. Furthermore, by the end of the 1990s, major metropolitan areas started to ban the use of HF cleaning formulations due to the reported damage to adjacent surfaces from wind drift as well as reports of substrate damage.

[26] Steam remained popular during the mid-twentieth century. A good case studies of terracotta steam cleaning is the West Virginia Capitol in Charleston, 1979. The terracotta ornamentation was cleaned by using a high-pressure steam of 250 psi. Rogers, Anne and Doyle Wilhite, Exterior restoration of the West Virginia State Capitol: cleaning and structural stabilization procedures, Technology and Conservation, 4(1):14-17, (1979).

[27] ProSoCo stated that hydrofluoric acid still accounts for more than 80% of the restoration cleaning products sold. From David Boyer-personal communication, February 2014.

By looking at case studies, preferred cleaning methods vary from country to country as shown in the graph below.[28] Indeed, the United States presents the most diverse array of cleaning techniques used.



Graph 6: Cleaning techniques by country

Other interesting data were collected from ProSoCo's regional representatives, which illustrate how the use of different chemical products varies across the United States. In the Northeast the market promotes the use of more HF-based chemical cleaners, mainly due to the presence of more heavily soiled buildings, while in the West and Mid-West, low/no acidic products are used due to less pollution-related soot deposition and stricter environmental laws (especially in California), and ultimately in the Southeast region which shows a higher use of biocidal treatments given its climate.

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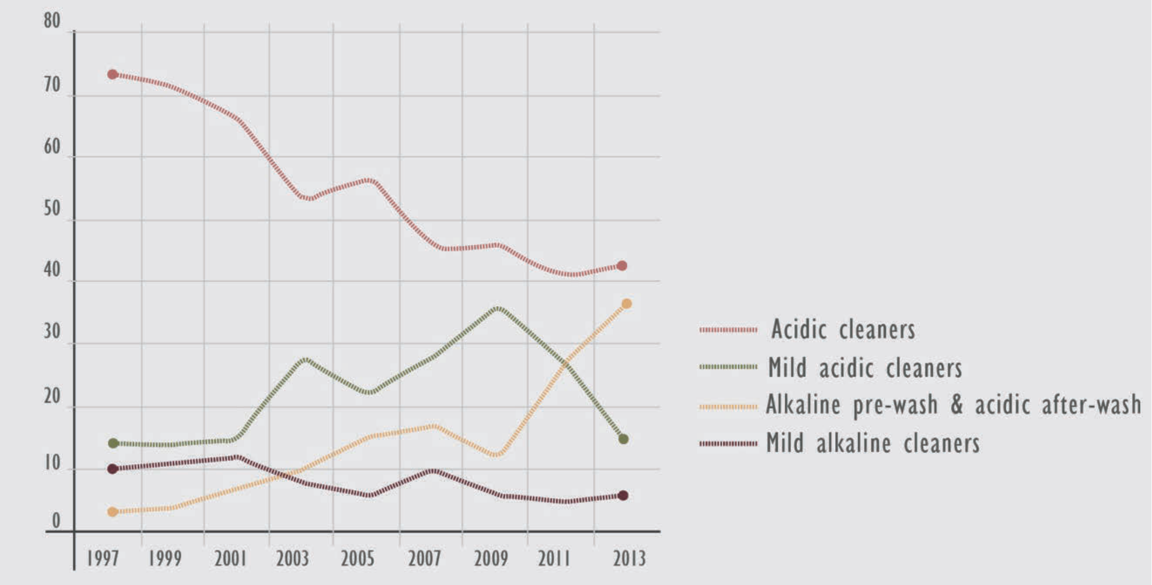
[28] The total number of Case Studies in our bibliography is 27 publications (32%): United States (11), United Kingdom (7), Italy (4), Spain (2), France (2), and Russia (1).

Graph 7: United States regional map of ProSoCo products. Data generously provided by ProSoCo.

Since 1997, ProSoCo has reported a clear trend in the decline of higher concentration HF-based cleaners (3%-7%) in favor of lower bi-fluoride cleaners (0.3%) as shown in the graph below. [29]



Graph 8: Chemical Cleaner Market Trends. Data generously provided by ProSoCo.

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[29] David Boyer-Personal communication, February 2014.

A review of case studies shows a very small percentage of before and after treatment assessment. This is not a surprise, and indeed very regrettable since cleaning is not a one-time operation: attention to the substrate, color changes, and pH changes on the surface should be recorded before and after treatment in order to correctly assess and evaluate the cleaning methods, and consequently learn from for future treatments. The most common evaluation methods use optical and scanning electron microscopy of samples removed and in situ pH strips. Only few case studies show the use of a spectrophotometer to determine color changes, indeed disappointing since color is an important physical property for terra cotta.[30]

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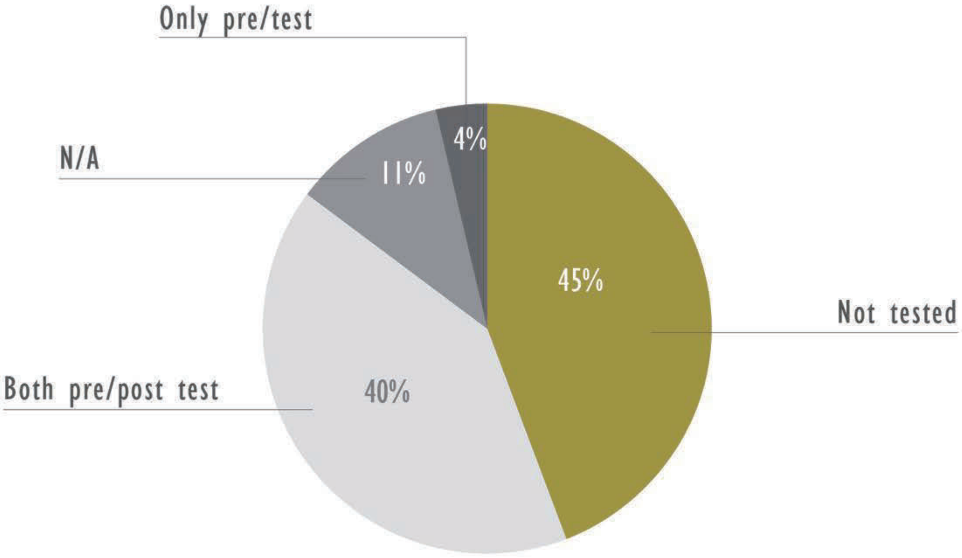
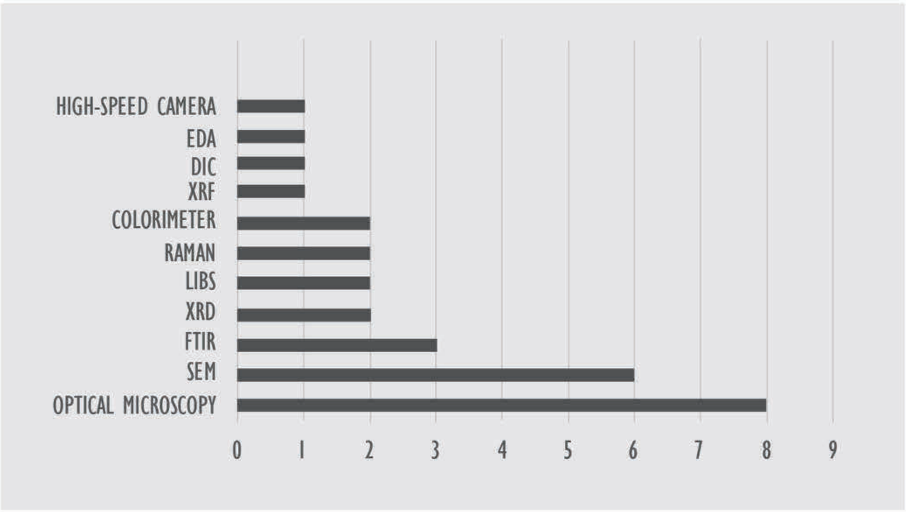
[30] Oujjaa, Mohamed et al., Laser cleaning of terracotta decorations of the portal of Palos of the Cathedral of Seville, Journal of Cultural Heritage, 4(6): 321-327, 2005.





Graph 9: Pre-Post treatment test data. The first pie chart represents the percentages of pre and post treatment tests based on literature review and survey. The second graph shows the most common technique used for pre and post-test.

2.2 Review of cleaning methods

According to the literature review and professional survey, the most common techniques used for cleaning masonry buildings and in particular for terracotta have been recently reconsidered.

Water washing is one of the oldest, gentlest and least expensive techniques used to clean buildings. This method can be delivered as soaking, intermittent water-spray, and pressure washings at low (20-100 psi) or high pressure (100-600 psi). It is particularly effective if the soiling or the dirt is not chemically bonded to the surface and is soluble in water. Importantly, frequent water washings are generally not effective to clean terracotta, since the soiling is not water-soluble and the substrate not sensitive to slightly acidic water.

Steam is another water based method and one of the oldest techniques as well. This method occurs in two steps: first, the heat from the steam softens the dirt layer, which then is mechanically removed with low-pressure washing. Overtime, this technique has varied in its popularity, mainly due to safety hazards reported with the use of hot steam, and the introduction of environmental health and safety laws in the use of chemical and mechanical systems.[31]

Detergents are defined as synthetic organic compounds that are chemically different from soaps[32]. They are generally composed of polar and non-polar ends. The polar-end allows the detergent to be soluble in water, and the non-polar to be soluble in grease. Therefore, the grease becomes attached to the non–polar ends, and then later is pulled into the solution.

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[31] See graph on Cleaning Techniques Overtime on page 14.

[32] From Matero, Matteini and Vatankhah, Cleaning Terra Cotta: Recent Trends in Technical Research and Practice, under publication. Soaps have the same general properties as detergents but are formed from alkaline salts of an organic acid. Soaps are generally not utilized in architectural conservation since they are rendered insoluble by calcium ions often present in masonry materials and hard water.

Often, chelating and complexing agents are added to improve its effectiveness. There are four different types of detergents, depending on their electrically charged groups: anionic (electrically negative hydrophobic ions), cationic (electrically positive hydrophobic ions), non-ionic (electrically neutral), and amphoteric (either positive or negative depending on the pH.) Non-ionic detergents are preferred for cleaning masonry because of their wetting properties, which can easily remove the dirt. Generally, the detergent is applied to the surface by using a non-metallic soft bristle brush; once the detergent is applied, the surface is thoroughly washed to avoid any remnant, which could possibly attract dirt again- due to its ionic nature.

Chelating Agents contain polar groups which are capable of breaking insoluble metallic bonds and form a soluble complex that can be removed with water. In conservation, EDTA (ethylene diaminotetra-acetic-acid) is one of the most popular chelating agents used. Due to the long dwell-time that reaction from solid soiling takes to pass into a liquid state through hydration, EDTA and other common chelating agents are generally formulated to contain a filler or a gel, which helps it to stay in place preventing further spread and contamination.

Acidic Cleaners are aqueous solutions that chemically attack and directly affect the interface between the soiling and the substrate[33]. The most common acids found in acidic cleaners are: hydrofluoric acid (HF), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3). Hydrofluoric acid is the first choice between acidic cleaners for siliceous masonry including terracotta. It attacks and dissolves silicates, and eventually removes the dirt by loss of surface. When using this acid, dilution and dwell time are

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[33] From Matero, Matteini and Vatankhah, Cleaning Terra Cotta: Recent Trends in Technical Research and Practice, under publication.

extremely important in order to control and avoid damage to the masonry surface.[34] The first commercial chemical cleaner for exterior restoration applications in the United States was developed by Jerry Boyer in 1962 and marketed as *R-1 and R2 Boyer Restoration Cleaner.* In the same year, this product was used to clean the Los Angeles City Hall[35].

BOYER'S RESTORATION CLEANERS

remove dirt and carbon atmospheric stains from all types of masonry surfaces.

WITH simple cold water rinse
WITHOUT special equipment
WITHOUT yellowing or discoloration

By the manufacturer of
SURE KLEAN Masonry Cleaning Products

BOYER'S RESTORATION CLEANERS

Instructions for use**

MASK ALL WINDOWS, aluminum, steel surfaces and areas not to be cleaned, using BOYER'S ACID-STOP*** Masking Agent.

**COMPLETE INSTRUCTIONS are attached to each container. Both products should be thoroughly tested on all surfaces to determine the more effective and best compound for your specific masonry cleaning job.

BOYER'S Restoration Cleaners, by the manufacturer of SURE KLEAN Masonry Cleaning Products, are packaged in 1 and 5-gallon containers and in 30 and 55-gallon drums.

1. APPLY UNDILUTED BOYER'S RESTORATION CLEANER, using liberally.
2. LET STAND ONE TO TWO MINUTES and then reapply solution.
3. RINSE WITH FRESH WATER at normal 50 to 60 pound pressure.
4. STEP BACK AND ADMIRE the sparkling clean masonry surface!

Figure 2: ProSoCo advertisemnt of the first commercial chemical cleaner introduced in the United States in 1962. Courtesy of ProSoCo.

By the late 1960's a new line of chemical cleaners evolved from R1 and R2: R1 became *Sure Klean Duty Restoration Cleaner* and R2 became *Sure Klean Heavy Duty Restoration Cleaner*, respectively containing from 3% to 7 % hydrofluoric acid; this formula became very popular throughout the 1970's. In the following years, due to the increased and uncontrolled use of acidic cleaners and a few highly visible large-scale projects, visible damage was reported[36], and stricter safety controls and environmental laws were introduced.[37] Consequently the first two-part formulations, based on an alkaline pre-wash

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[34] HF must be avoided for calcareous masonry materials as they are highly reactive to acids.
[35] David Boyer-Personal communication, February 2014.
[36] Ashurst, Nicola, Cleaning historic buildings*,* Donhead Publishing Ltd, London (1994).
Ashurst describes the "perceived" large scale damage reported on the Natural History Museum in London, as a result of the misuse of an HF based cleaner (1970's).
[37] See note 25.

which helps to break down the oily hydrophobic pollution layer followed by a neutralizing acidic after-wash, began to be tested. The Reliance Building in Chicago is one of the first large scale case studies that marked this shift in 1995[38].Throughout the 1990's, several major metropolitan areas in the United States began to ban the use of HF cleaning formulations, mainly due to the reported damage to the substrate and environmental drift.[39]

Under these circumstances, ProSoCo introduced two new products in April 2000 based on ammonium bi-fluoride and marketed as *EnviroKlean Restoration Cleaner*, and *EnviroKlean Säfe Restorer* in June 2006. Ammonium bi-fluoride is a salt that once dissolved in water, forms hydrofluoric acid. Ammonium bi-fluoride ions strongly attack terra cotta's silicate minerals due to the presence of ammonia; thus allowing use of a lower concentration; however due to its limited control, abundant rinsing is required. [40] At present, ProSoCo states that formulations that contain hydrofluoric acid still account for more than 80% of the restoration cleaning products sold.[41]

Alkaline Cleaners consist of a detergent (or surfactant) and an alkali salt, commonly sodium hydroxide or potassium hydroxide. Alkaline cleaners attack and saponify oily, greasy particulate films and can be used on carbonate materials as limestone, marble or sandstone, which are generally highly reactive to any acids. Indeed, sodium hydroxide can introduce sodium ions into the masonry, and if not properly neutralized, can cause destructive

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[38] Kelley, Stephen J., Office buildings of the Chicago School: the restoration of the Reliance Building, ICOMOS Germany, Munich, Vol. 24, and (date unknown):62-68.

[39] David Boyer-personal communication, February 2014.

[40] With ABF is still an open-question on its application and assessment; for this reason, two set of the samples were treated with *Enviro klean Restoration Cleaner*.

[41] David Boyer, personal communication-February 2014.

efflorescence. Therefore, alkaline salts are commonly used as a two-part system with an alkaline pre-wash, followed by an acidic after-wash.

Mechanical methods were introduced for the first time as "*sand blasting*" at the Philadelphia Centennial in 1876[42]. Since its early days, this technique has seen great improvements with the introduction of newer and more sophisticated methods[43], which allow control of the pressure, particle shape and size, and whether dispensed as a wet or dry system. Despite its improvement and advancement in technology, a question of "*control*" still remains open today[44] [45]; since this system removes soiling by abrasion, it is still very difficult to determine at a macroscopic level when it is affecting the substrate. Consequently due to its fragile glaze and slip layers on the surface, this technique is generally not recommended for fired materials such as brick and terracotta.[46]

Laser ablation with its first application on terracotta at the Victoria Albert Hall in London in 1994, laser ablation is the only technique that has minimum contact with the surface of the material and the substrate. Based on the use of short pulses of high peak power of laser radiation, this technique can rapidly heat and vaporize minuscule portions of the dark pollution material from the surface. Advancement in this technology is occurring at a very fast rate with fiber optics and smaller portable equipment already available. Despite the fact

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[42] Congressional Serial Set, *House Documents vol.128*, Government Printing Office, (1913). "The sand-blast in America was exhibited at the Philadelphia Centennial in 1876. The past 36 years have been spent in constant effort by the American Manufacturer to demonstrate the adaptability of sand blast to metal and other cleaning, over old methods."

[43] For info on newer mechanical systems: see note 22, 23, and 24.

[44] Grimmer, Anne E., Dangers of abrasive cleaning to historic buildings, NPS Preservation Briefs, (1979).

[45] Fidler, John, The conservation of architectural terracotta and faience, ASCHB Transactions, volume 6, (1981):3-16.

[46] Glance, Richard A., Terracotta: rehabilitation of a courthouse dome, APT Bulletin. XVII (2), (1985):39-45.
In this case study, wet sandblasting was used to remove multiple coatings from the terracotta. Ultimately, the glaze was completely removed, and this method dismissed.

that laser cleaning is still not controlled by standards nor practitioners certified [47] in the United States, large-scale buildings have been cleaned as reported by Dajnowsky et al[48] in 2009. At the same time, Gaspar et al. have completed an evaluation study of different cleaning techniques including laser ablation on numerous materials. No changes or adverse effect were observed with the laser. [49]

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[47] See note 24.

[48] Dajnowski, Andrzej et al., The use of lasers for cleaning large architectural structures, APT Bulletin, 40-no. 1,(2009): 13-23. This publication includes several large scale projects entirely cleaned with laser. An example for terra cotta is the laser cleaning of the polychrome cornices of terra cotta at the Philadelphia Museum of Art.

[49] Gaspar, Pedro et al., A topographical assessment and comparison of conservation cleaning treatments, Journal of Cultural Heritage, 4, (2003):203-302. Evaluations were completed with methods such as SEM.

2.3 Conclusions

As suggested by the literature review and the survey of current practice, our knowledge on terra cotta soiling and cleaning is very limited. The vast array of cleaning techniques, generally applied to terracotta buildings, comes directly from lessons learned from stone masonry, with little consideration of the differences between the two materials and their soiling mechanisms. Indeed, the tenacious nature of soiling on terracotta still leaves many open-questions, since very little work has been done over the years beginning with McIntyre's seminal publication in 1929.[50]Research begun in the late 1990's is only now receiving renewed attention.[51]

Today, cleaning is simply evaluated by the "look" and the level of soiling removed. Knowledge about the effects of various treatments is almost none, since very little evaluation of pre and post treatments is normally conducted, as reported from the literature review and the survey; additionally, very rarely work is evaluated after completion or exposure to weather.

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[50] McIntyre, W.A., Investigations into the Durability of Architectural Terra Cotta. Special Report 12. London: Department of Scientific and Industrial Research, Building Research Station, 1929.

[51] See note 3

Figure 3: Before and after cleaning of the Henry Cole Wing in London, 2010. This building was cleaned by using a chemical gel formulation, and then rinsed with steam. Source: www.buildingconservation.com

Undeniably, long and short term effects of cleaning treatments have not been studied; consequently, if we accept the conclusions formulated by Historic Scotland in 2003 on the consequences of past cleaning on stone masonry[52], methodologies to study the cumulative results of past and current cleaning on terra cotta buildings should be developed, and pre and post treatment testing should become standard practice amongst professionals. Regardless of this result, today a shift in thinking is occurring from remedial to preventive conservation, with a more proactive attitude on how we can reduce repetitious conservation treatments such as cleaning, regardless of how safe they are to the building.[53]

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[52] Maxwell, Robert Gordon University, 2003, IX.

[53] Matero, Matteini and Vatankhah, Cleaning Terra Cotta: Recent Trends in Technical Research and Practice, in publication.

3.0 Petrographic analysis of terracotta test coupons

3.1 Sample preparation

Two thin-sections of a newly made red and tan terra cotta (RBV.01 and TBV.01) for the testing program were prepared by The National Petrographic Service Inc.[54] They were embedded in blue dyed-epoxy and covered by a cover-slip to facilitate the observations. The analysis was conducted with a Zeiss Optical Microscope at the Ceramic Laboratory of the Penn Museum at the University of Pennsylvania with the assistance of Dr. Marie-Claude Boileau.

3.2 Petrographic analysis

Samples RBV.01 and TBV.01 are both unglazed and hand-pressed tiles made by the Boston Valley Terracotta Company (BVT). They are of a homogeneous fine-grained texture and a tan and dark-gray brown color. The fine fraction is mainly characterized by dominant quartz, few pyroxene minerals, opaque, and very rare mica flakes. The coarse fraction is composed of small to medium quartz inclusions, two different types of grog intentionally added, and pyroxene minerals, also added as a temper, visible from their sorting and crystal shapes. The optical inactivity of the groundmass, the cracks in the quartz inclusions, and the dissolution of calcium carbonate suggest that these tiles were well fired. According to the manufacturer, the firing was a typical cone 3-4 firing at 2100 degrees F approx. for 72-96 hours.[55]

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[54] The samples were cut from left-over tiles with the use of a tile clipper, and then ship to the National Petrographic Service Laboratory in Texas.

[55] Info generously provided by Tricia Herby from Boston Valley Terra cotta.

In this fabric group, there are two types of grog, added as temper: Type 1 is moderately-sorted and characterized by subangular and subrounded inclusions of a sand size with a dark-brown groundmass, with small quartz inclusions. Only few of the grog inclusions display a glaze.

Type 2 is moderately sorted, and composed of subangular and subrounded inclusions, characterized by a very fine brown texture with visible quartz and opaque inclusions. Several of the grog inclusions have a glaze. The pyroxene minerals, which represent 25 % of the coarse fraction, are moderately-well sorted and composed of elongated, angular and subangular crystals; Due to their sorting and shape, it is clear that these minerals were added to the mix as temper as well. The clays are generally sourced from Ohio, Pennsylvania or California. According to BVT the tan terra cotta is the most commonly used type for their glazed restoration material while the red is used less frequently.

The tiles are unglazed, with no presence of a slip-layer on top. During the preparation, they were hand slicked using a plastic tool after being released from the mold and cut to the size of 6x6 inches. [56]

These tiles were hand-pressed. This is revealed by the preferred orientation of the vughs (voids) with the wall of the tile, together with visible directional signs observed on the groundmass with the stereoscope.

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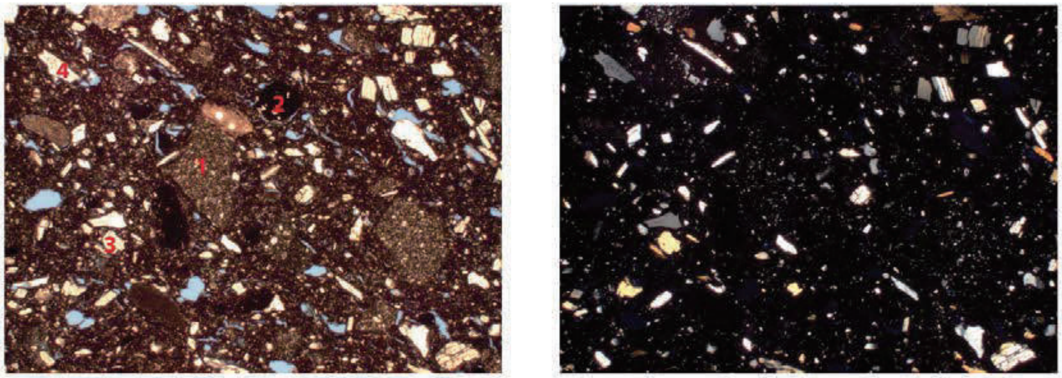
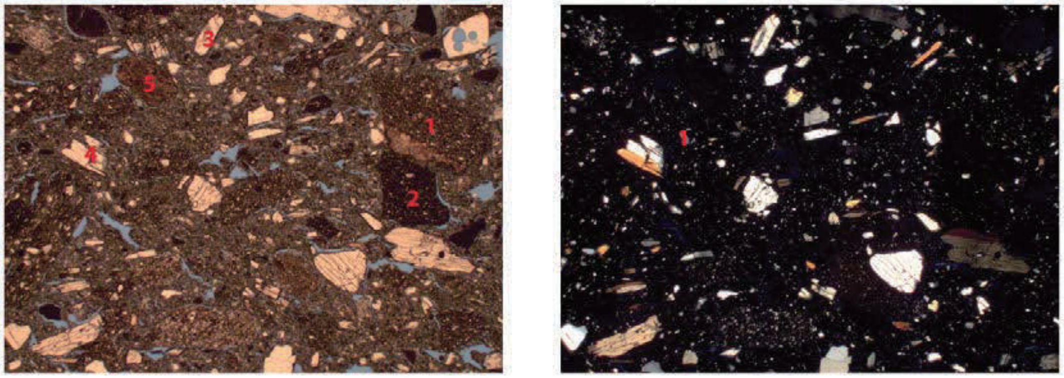
[56] See note 55.



Red Sample 25X-PPL: 1) Type grog 1 with glaze on top, 2) Type grog 2, 3) Pyroxene minerals, 4) Quartz

Red Sample 25X-XPL



Tan Sample 25X-PPL: 1) Type grog 1 with glaze on top, 2) Type grog 2, 3) Quartz, 4) Pyroxene minerals, 5) Claystone fragment

Tan Sample 25X-XPL

Figure 4: Optical microscope photos of samples.

3.2 Petrographic description of fabric group

SAMPLE: TBV.01

Geology: According to the information provided by BVT, clays are generally sorted from Ohio, Pennsylvania and California.

Fabric group 1

Microstructure

Low to medium porosity is visible, characterized by few macro elongated voids, very few macro vughs, and rare meso vesicle voids. The voids do not show any presence of burnt organics. The voids located close to the wall show a preferred orientation with it, as an indicator of hand-pressing technique.

Groundmass

This sample presents a homogeneous texture, optically inactive. In PPL, the groundmass presents a light-brown color, and in XPL appears as dark-red brown color.

This sample is unglazed, with the natural fire-skin finished surface and no presence of a slip layer on top. Additionally, few grog inclusions are located close to the surface. The surface was finished by simply using a plastic tool.

Inclusions

c:f:v0.125 mm = ca. 35:56:9. The inclusions are moderately sorted, < 1.40 mm.

<u>Fine Fraction (<0.125 mm)</u>

Very dominant Quartz

Few	Pyroxene
Very Few	Opaque
Very Rare	Yellowish-brown mineral (?), mica flakes

Coarse Fraction (>0.125 mm)

Frequent

Quartz: Equant and elongate, sr, a and sa. <1.40 mm, mode 0.84 mm, moderately sorted. In XPL, it shows the typical quartz extinction. Several grains present cracks, which are due to the change in their crystalline shape that occurs at 573 degree.

Common

Brown grog: Equant and elongate, sa and sr. < 1.24 mm, mode 1.00 mm. Moderately-poorly sorted, it presents a very fine grained texture of a light-brown color, with fine quartz and opaque inclusions. Several of the grog inclusions present a glaze on top. Visible elongated voids around few inclusions show signs of shrinkage.

Pyroxene: Elongate, sa and a. < 1.40 mm, mode 0.68 mm, moderately-sorted. In PPL, it appears colorless, with high-relief. No sign of pleochorism. In XPL, it presents a simple twinning, and birefringence of first order of color interference. Due to their size and sorting, pyroxene was added as a temper.

Very few

Dark brown grog: Equant and elongate, sr and sa. < 1.24 mm, mode 0.80mm. This grog type is poorly sorted, with a fine dark brown groundmass, composed of fine quartz inclusions. Several of the inclusions present voids around them, probably due to shrinkage during drying. One inclusion present a glaze on top, which appeared very weathered.

Rare

Opaque: Equant, sr and r. < 0.24 mm, mode 0.20 mm, well-sorted. In XPL, with the use of the condenser, they show sign of red color as iron concentration.

Rock fragment (claystone-shale?): Equant and elongate, sa and a. < 0.76 mm, mode 0.44 mm, moderately sorted. In PPL, they present a uniform dark-brown texture, no visible presence of inclusions. In XPL, they appear of a dark-brown.

SAMPLE: RBV.01

Geology: According to the information provided by BVT, clays are generally sorted from Ohio, Pennsylvania and California.

Fabric group 1

Microstructure

This sample shows a low to medium porosity, characterized by few macro vughs, and rare meso vesicles, and meso elongated voids. Many of the elongated voids show a preferred orientation with the surface of the tile. No burnt organics visible in the voids.

Groundmass

Moderately heterogeneous texture, with no optical activity. In PPL, it appears of a dark-brown color, and in XPL shows a dark-red brown color. This sample is unglazed, with the natural fire-skin finished surface and no presence of a slip layer on top. The surface was finished by simply using a plastic tool.

Inclusions

c:f:v0.125 mm = ca. 40:51:9. The inclusions are moderately sorted, < 1.60 mm.

Fine Fraction (<0.125 mm)

Very dominant	Quartz
Few	Pyroxene
Rare	Opaque
Very rare	Yellowish-brown mineral (?), Mica flakes

Coarse Fraction (>0.125 mm)

Frequent

Quartz: Equant and elongate, sr, a and sa. < 0.96 mm, mode 0.68 mm, moderately sorted. Several grains show cracks, which are due to the change in its crystalline shape that happens at 573 degree. In XPL, it presents the typical quartz extinction.

Common

Brown grog: Equant and elongate, sa and sr. < 1.36 mm, mode 0.84 mm. Moderately well-sorted. In PPL, it shows a light brown fine grained texture with fine quartz and opaque inclusions. Several grog inclusions present a glaze on top.

Few

Pyroxene: Elongate and equant, a and sa. < 0.68 mm, mode 0.48 mm, moderately sorted. In PPL, it appears colorless, one cleavage, and medium-high relief. In XPL, it presents a simple twinning, and first order of birefringence color. Due to its sorting and shape, it was added as a temper.

Very few

Opaque: Equant, r and sr. < 0.30 mm, mode 0.20 mm, moderately sorted.

Dark-brown grog: Equant and elongate, sr, sa and r. < 1.40 mm, mode 0.64 mm, moderately-well sorted. In PPL, it shows dark brown fine grained texture, composed of medium quartz inclusions. Few inclusions present a glaze on top, which appeared very weathered.

Rare

Yellowish-brown mineral (?): Equant and elongate, sr, r and sa. < 1.00 mm, mode 0.24 mm, moderately sorted. In PPL, it presents a yellowish-brown color, with medium-high relief. In XPL, it presents an orange-brown color similar to PPL, parallel extinction and simple twinning. Several grains appear very weathered. One inclusion shows a rhomboid shape.

Very rare

Rock fragment (claystone-shale?): Elongate, sr. < 1.60 mm, mode 1.12 mm. Only few inclusions are visible. In PPL, it shows a brown color, in XPL dark-gray with no optical activity present.

Light-gray grog: Equant and elongate, r and sr. < 1.2 mm, poorly sorted. It shows a light-gray brown fine texture with quartz, opaque, and mica inclusions visible. The mica inclusions could be chlorite (?).

Dissolution of calcium carbonate: Equant and sr. < 1.2 mm.

4.0 Accelerated weathering protocols

4.1 Durability and service life

Durability is defined as: *The ability of a building and its parts to perform its required function over a period of time and under the influence of an agent.*[57] It is a fundamental property of building materials and a major contributing factor when considering the following issues:[58]

- Estimation of service life
- Specification benchmarks
- Quality control
- Disputes

Building materials are affected by different factors, which are responsible for their performance and weathering. Weathering is a natural process that all materials experience over time and is defined as *the totality of irreversible chemical and physical alterations that may occur within a material in a course of time.*[59] For the case of terracotta, below are listed the major factors that influence its durability and service life (not related to installation):

- Composition and fabrication methods: type of clays, fireskin, surface finish such as unglazed, glazed, or englobe, fabrication methods such as hand-pressed or extruded.

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[57] BS 7543: 1992. Guide to durability of buildings and building elements, products and components. British Standards Institution, London, revised in 2003.

[58] A. J. Lewry and L. F. E. Crewdson, Approaches to testing the durability of materials used in the construction and maintenance of buildings, Construction and Building Materials 1994 Volume 8 Number 4

[59] As defined in the German Standard DIN 50 035.

- Previous treatments and maintenance: How many times the terracotta was cleaned? What treatments? Any maintenance work?
- Environmental factors such as soiling, temperature and moisture, marine environment etc.

An interest in developing methods for predicting the service life of building materials has been widely explored as early as Antiquity with Roman architect Marcus Vitruvius Pollio describing a two-year weather test for building stones.[60] In the last forty years, ASTM, RILEM and other major institutions have been developing committees exclusively dedicated to this topic. [61]

Unfortunately, as suggested by Lewry and Crewdson[62]: *Some guidance to the development of durability tests now exists, but the application of these to the needs of industry has yet to be fully implemented*.

Furthermore, more shortcomings related to durability testing are: [63]

- There is still no established correlation between laboratory testing and outdoor performance.
- Provisions are not made to take into account different applications.

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[60] Vitruvius in The Ten Books on Architecture, Dover Publications, New York, 1960, p. 50 (translated by H. Morgan).

[61] RILEM 140-TSLICIB W80 Committee and ASTM E6.22 Committee on Durability Performance of Building Constructions in 1974.

[62] See note 58

[63] Geoffrey Frohnsdorff and L. W. Masters, The Meaning of Durability and Durability Prediction, in Durability of Building Materials and Components, Proceedings on the first international Conference, ASTM STP 691

4.2 Selection of accelerated testing protocols

Despite the limitations and shortcomings associated with durability testing protocols, for this project accelerated weathering tests were chosen over field and outdoor testing mainly for the following reasons:[64]

- The conditions are well controlled. Outdoor conditions are too variable and cannot be controlled.
- More precise detection instruments are available.
- The environment is clean, so contamination can be eliminated or accurately controlled.
- Small samples can be used; waste can be minimized; cost per experiment can be minimized; less labor is needed than in field testing.
- Limited amount of time for testing. Simultaneous experiments can be carried out giving faster and more results.
- Samples exposed to outdoor weathering can become contaminated and consequently unsuitable for instrumental analysis.

Based on the weathering agents that commonly affect terracotta and its durability, the instrumentation available at the Architectural Conservation Laboratory, and the limited testing time for this project, two accelerated testing protocols were selected: RILEM VB Salt Test and ASTM G154:12 Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials.

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[64] George Wypych, Handbook of Material Weathering, ChemTec Publishing, Chapter 7, 2013.

4.3 Rilem VB Salt Test

The pressure generated by salt crystal growth in confined spaces in porous building materials such as terracotta, brick, and stone is fully acknowledged to be a major cause of damage and an important factor in their durability.[65] Sodium sulfate is the salt of choice to perform accelerated weathering testing, mainly for two reasons:

- Availability: in modern buildings, highways and civil work, soluble salts as sodium and calcium sulfates are commonly released by Portland cement.
- Its destructive nature: sodium sulfate is very damaging because it undergoes a high degree of volume change when hydrated.[66]

The testing protocol selected for this project is RILEM VB Salt Test[67]

The RILEM test consists of 15 cycles of 2 hour immersion in a 10% solution of sodium sulfate. For fifteen days, a daily cycle was completed which included: two hours of immersion, followed by 19 hours oven-dried at 60 degree Celsius and then cooling within 3 hours.

The test was run on 32 samples: one representative set of 6 cohorts for each product and application.

The 10% solution of sodium sulfate was prepared in the lab prior to starting the cycling. After completing 15 cycles, the samples were immersed for 7 days in tap water; and the water regularly changed.

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[65] Goudie and Viles, 1997; Doehne, 2002

[66] R.U. Cooke, Salt weathering in deserts, Proc Geol Assoc London 92, pp. 1 ± 16, 1981

[67] Standard available in the appendix.

Figure 5: Two hours immersion of the samples during salt test

4.4 Weatherometer

This method is based on the fact that temperature, ultra violet radiation, and water are the primary environmental agents of natural weathering. By delivering these stresses in a compressed period of time, it should be possible to observe weathering responses that correlate to normal exposure. As suggested by Grossman, when considering accelerated weathering it is important to establish a balance between the different stresses.[68] In this apparatus, samples are alternatively exposed to ultraviolet cycles of 8 hours at 60 degrees Celsius, followed by a condensation cycle of 4 hours at 50 degrees Celsius which include a 25 minute water spray cycle at the beginning of each condensation cycle.[69] This was completed for six weeks for a total of 1008 hours.

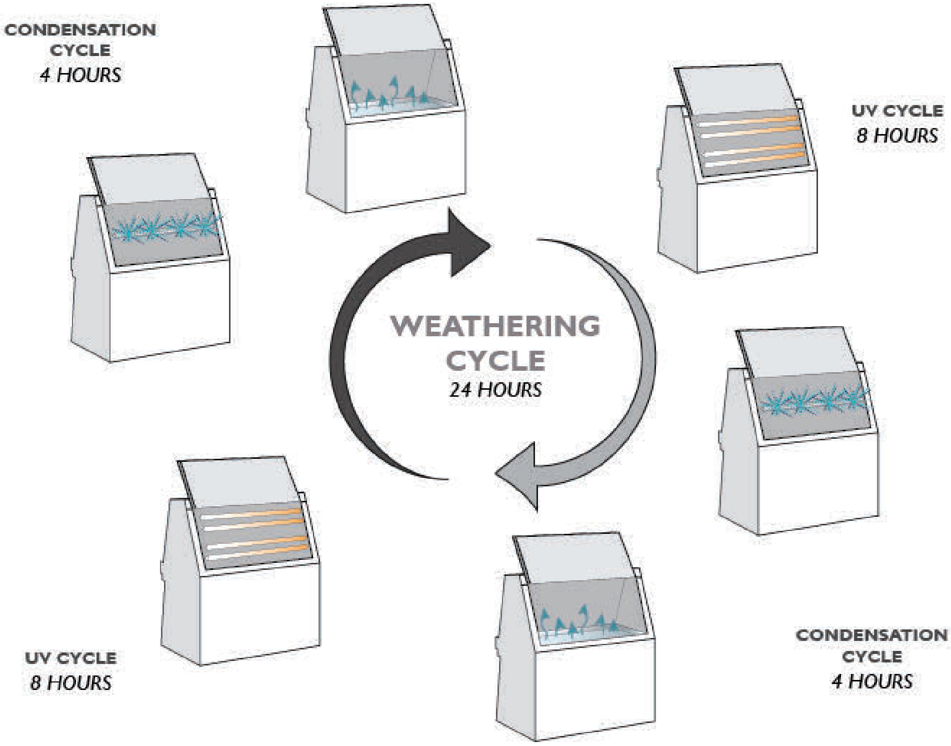

Figure 6: Scheme representing one day of the weathering cycle

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[68] George W. Grossman, Correlation of Laboratory to Natural Weathering, The Q-Lab Company publication, 2011
[69] This Standard is available in the appendix.

The total number of samples run in the machine was 32. The samples were placed in the middle area of each sample holder, to correspond with the position of the nozzle sprays for optimal exposure. The space left was filled with unused tiles to prevent heat loss, and water leakage.

The samples were kept in place by stainless steel clips. Due to the presence of large window areas close to the machine, the external temperature varied a few degrees up and down during each cycle.

All the UV lamps did not reach the set point of irradiance of 0.89 recommended by the standard. Consequently, the samples were rotated once a week, to allow a uniform exposure.

Figure 7: Samples were only displayed in the center area for a better exposure inside the weatherometer

4.4.1 Ultraviolet stress as sunlight

Light energy is transmitted in units called photons, whose energy is inversely proportional to their wavelength. The typical radiation that the sun emits is below 242 nm. At this wavelength, the energy is high enough to dissociate oxygen and create ozone. Consequently, ozone is a highly effective UV absorber, absorbing all solar radiation below 290 nm. According to the European weathering literature, the UV spectrum is divided into three ranges: UVA with wavelengths between 400nm and 315nm, followed by UVB ranging from 315nm - 290nm range, and ultimately UVC that includes the solar radiation below 290nm, which never reaches the earth's surface. Understanding this classification is crucial when choosing UV lamps for this test.[70]

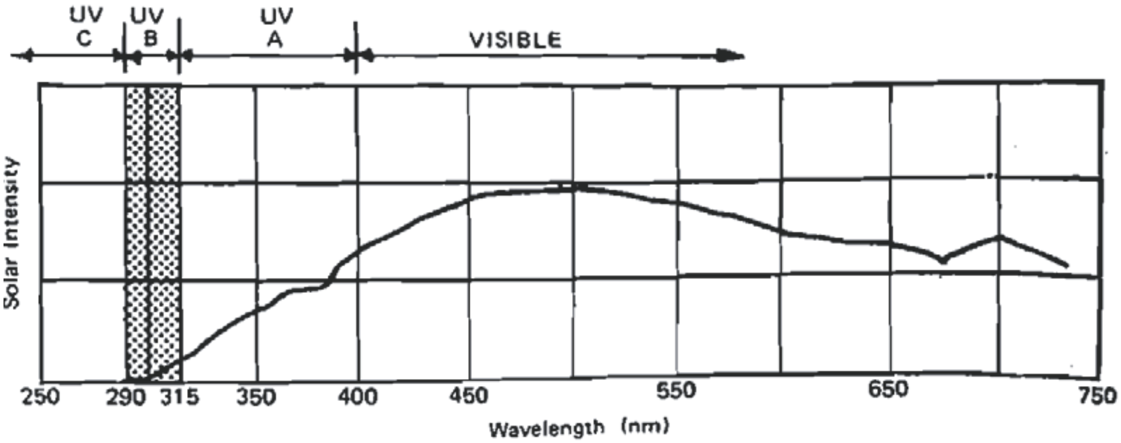

Figure 8: UV Lights Spectrum Source: George W. Grossman, Division and classification of solar ultraviolet spectrum, Correlation of Laboratory to Natural Weathering, Presented at the 20th Cleveland Society for Coatings Technology Symposium. Case Western Reserve University. Cleveland. Ohio. March 1 1, 1977. 26200 First Street. Cleveland, Ohio 44145.

UV Lamps were first introduced in 1970. UVA-340, which was selected for this test, was introduced in 1987 in order to achieve a better correlation with natural weathering. This

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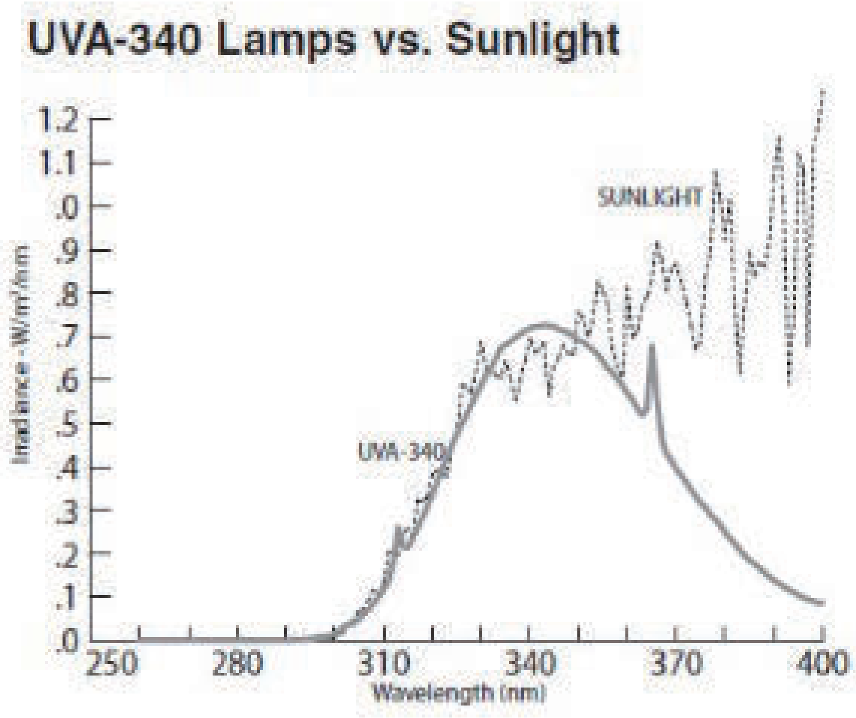
[70] See note 69.

lamp type delivers the best possible simulation of sunlight in the critical short wavelength region from 365 nm down to the solar cutoff of 295 nm, with its peak emission at 340 nm.

UVA lamps offer a better correlation with actual outdoor weathering, but they do not degrade materials as fast as UVB lamps.



Graph 10: UVA-340 Lamps vs. Sunlight graph. Source: Technical Bulletin Lu-8160, Q-lab, 2012

Furthermore, this apparatus is provided with a Solar Eye Controller, which is used to monitor the intensity of the radiation of each set of lamps. As recommended by the ASTM standard, the irradiance set-point is 0.89 w/m2, where 0.68 w/m2 is equivalent to noon summer sunlight.

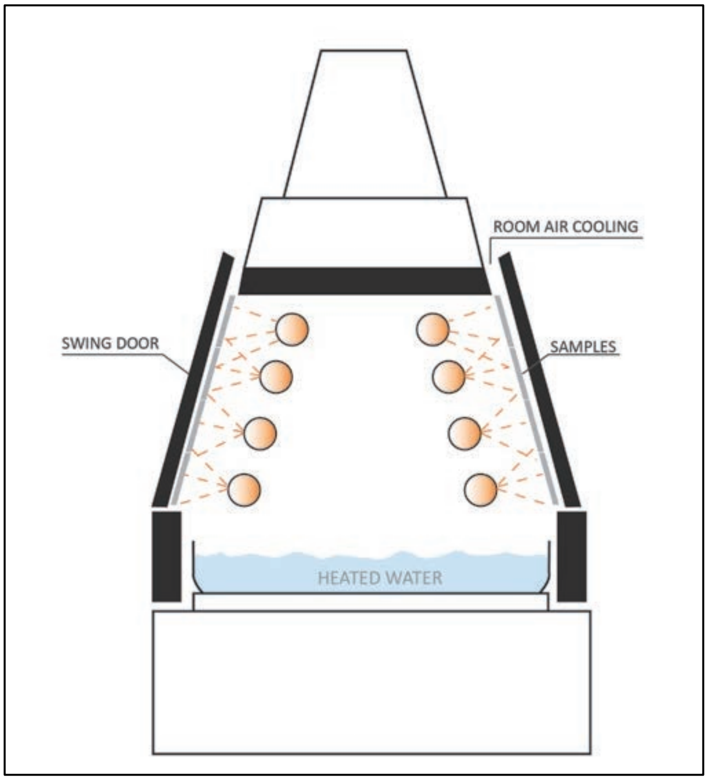


Figure 9: Operational diagram of UV lamps inside the machine

4.4.2 Water as rain and condensation

Water in all its states as liquid, gas, and aerosol can result in a wide variety of cycles varying from one location to another, and from one climate zone to another. For instance, during a summer day in the Mediterranean zone, it can rain for only 15 minutes, while in the Monsoon region it can rain for several days without interruption.

It therefore becomes more difficult to reproduce these varied conditions with laboratory testing. Studies done in 1963 by the Cleveland Society for Coatings Technology led to the introduction of the Cleveland Condensation Tester. The Cleveland apparatus simply relies on the use of water to produce rain and condensation, together with ambient room air used as a cooling influence. Through this study, different cycles where tested: from long cycles of 20 hours at 40°C to shorter cycles of 4 hours at higher temperature. It was established that by using higher temperature, the rate of permeation and the rate of oxidation reaction increased. As a result, a 4 hour cycle at 50 degree Celsius simulates a 14 hour cycle at 20 degrees Celsius. The cycle that was ultimately selected for this research was composed of a 4 hour condensation cycle at 50 degrees Celsius initiated by a 25 minute water-spray cycle. At the beginning of every condensation cycle, a 25 minute cold water-spray quickly cools the sample, and consequently produces a thermal shock effect. Due to the large amount of water needed to run the spray per minute, the water-spray was kept under 30 minutes, also recommended by the standard.[71]

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[71] The pressure required to run the spray is 7 liters per minute. For limitations and constraints, tap water was used.

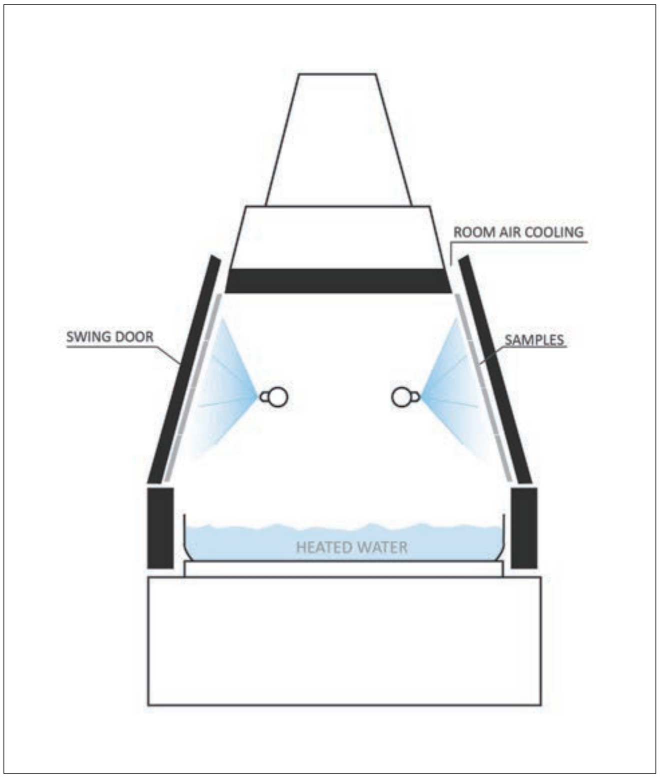

Figure 10: Operational diagram of the water spray inside the machine

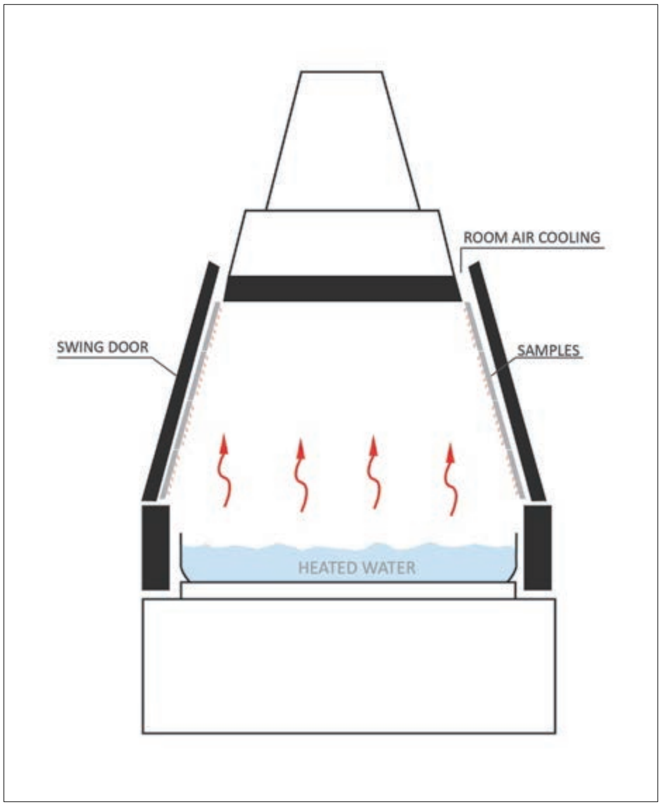

Figure 11: Operational diagram of condensation cycle inside the machine

4.4.3 Temperature control

Temperature has a strong impact on the rates of chemical and physical reactions; consequently it is an important variable on accelerated aging methods. In this apparatus, the chamber temperature could not reach above 50-60 degrees Celsius. Consequently, the highest temperature was 60 degrees Celsius used during UV cycling. The sample holder racks are also another aid in maintaining a uniform temperature within the chamber, in particular because the air that is mixed and supplied by the blower into the chamber, is additionally mixed by the sample racks. Another important consideration in controlling the temperature variable is the specimen's own physical characteristics, especially the influence of sample color on the temperature. For example: darker colored samples will absorb more energy than lighter colored or more reflective samples.

4.4.4 Other observations

Ultimately, when considering the use of a weatherometer, the following needs to be considered:

Benefits

- Fluorescent devices are commonly available in testing facilities, and are inexpensive.
- The apparatus is very easy to operate, and requires limited supervision.
- The sample holder can be easily moved and rotated to allow all the samples to have a uniform exposure during the different cycles.

Disadvantages

- Inability to fully simulate outdoor conditions – no correlation available.
- The relative humidity is not controlled.
- The temperature depends exclusively on the chamber temperature. Consequently, the color of the sample does not influence its temperature as it would outdoors.
- For condensation: Samples in this machine are exposed to hot water vapor which condenses on the sample surface (typically for 1/3 of exposure time) which is intended to simulate exposure to nighttime condensation. This is not a proper simulation since at night both the sample and the water vapor are cold. On the other hand, condensation of hot vapor on the surface of a heated sample is obviously much more severe than natural conditions.
- Fluorescent lamp UVA-340 delivers only a portion of the UV spectrum and does not emit either visible or infrared radiation.

5.0 Methodology

5.1 Sample acquisition and preparation

Boston Valley Terracotta in Buffalo generously donated the samples for this research[72]. The tiles provided were 6”x 6”x½”, unglazed and hand-pressed terracotta of two different colors: red and tan. For the purpose of our testing, each tile was subsequently cut into 4 smaller samples of 3”x 3” using a Felker diamond blade wet stone saw in the Fabrication Laboratory at the School of Design of the University of Pennsylvania.

Figure 12: Cutting samples in the fab lab

Each set was composed of four samples of 3” x 3”, which came from the same tile and contained one control and three cohorts.

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[72] On the 20th of May 2014, Professor Frank Matero, Professor Reza Vatankhah and I travelled to Buffalo. We visited the Boston Valley Terracotta Facility and collected the samples.

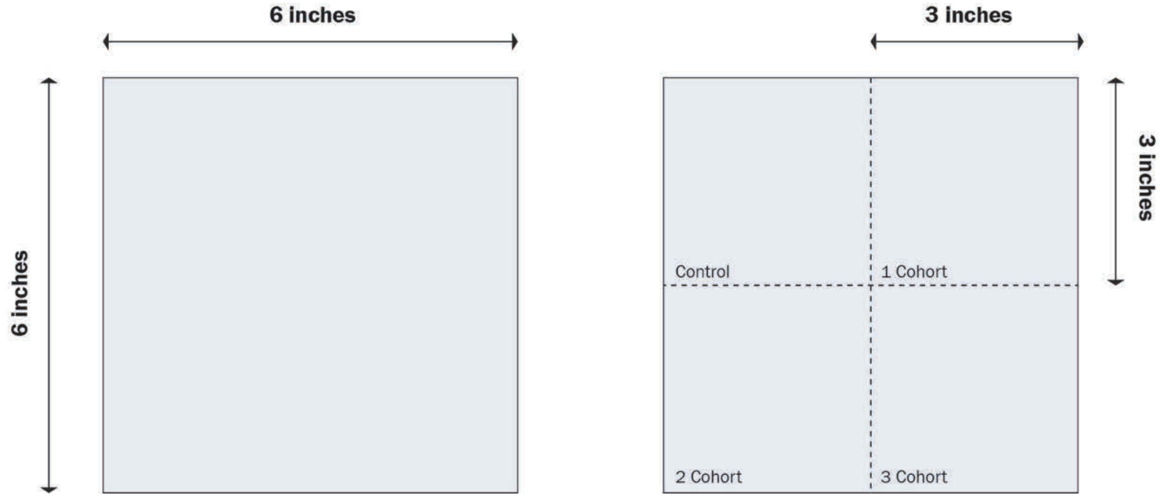

Figure 13: Diagram showing a sample set

The labeling system was organized according to the products used for the treatment (A/B), the color of the tile (R/T), number of applications (1/2/3), and cohort number (01/02/03). All the samples were carefully labeled on their verso with an indelible black ink pen.

After all samples were labeled, a layout was drawn in AUTOCAD to easily organize the samples and to use as a background for all photography.

Figure 14: Sample set treated with one application of ProSoCo Heavy Duty Restoration Cleaner

Figure 15: Sample set treated with two application of ProSoCo Heavy Duty Restoration Cleaner

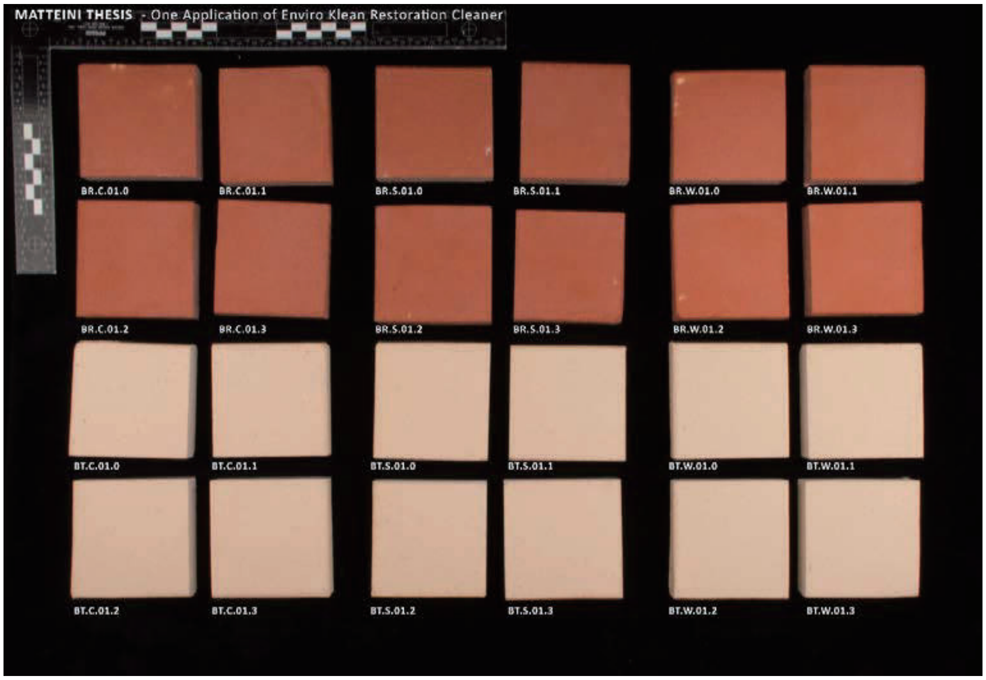

Figure 16: Sample set treated with one application of ProSoCo Enviro Klean Restoration Cleaner

Figure 17: Sample set treated with two applications of ProSoCo Enviro Klean Restoration Cleaner

5.2 Acid treatment

The tiles were treated with two different commercial acid based cleaning products in two applications: ProSoco *Sure Klean Heavy Duty Restoration Cleaner* based on hydrofluoric acid, and ProSoco *Enviro Klean Restoration Cleaner* based on ammonium bi-fluoride. According to the Material Safety Data Sheet provided by ProSoCo, *Heavy Duty Restoration Cleaner* is mainly composed of Hydroxyacetic Acid, Hydrofluoric Acid (3ppm), Nonionic Surfactant, Phosphoric Acid (1 mg/m3), and Citric Acid. While *Enviro Klean Restoration Cleaner* contains Hydroxyacetic Acid, Ammonium Bi-fluoride (2.5 mg (F)/m3), Betaine Derivative, and Amine Oxide. [73]

The treatment was completed in the Architectural Conservation Laboratory, and overseen by the Environmenal Health and Radiation Safety Department (EHRS) of the University of Pennsylvania. Although the concentration of hydrofluoric acid was very low, the water used for rinsing and wetting the samples was collected for disposal by EHRS and personal safety procedures were followed including a facial mask shield, nitrile gloves and an apron for acid protection.

For both products, manufacturer's instructions were followed.

Heavy Duty Restoration Cleaner was diluted 1 part cleaner to 3 parts water by volume and applied with a dwell time of 5 minutes, the maximum time recommended by the manufacturer. *Enviro Klean Restoration Cleaner* was applied as a concentrate, with a dwell time of 20 minutes, the maximum time recommended by the manufacturer.

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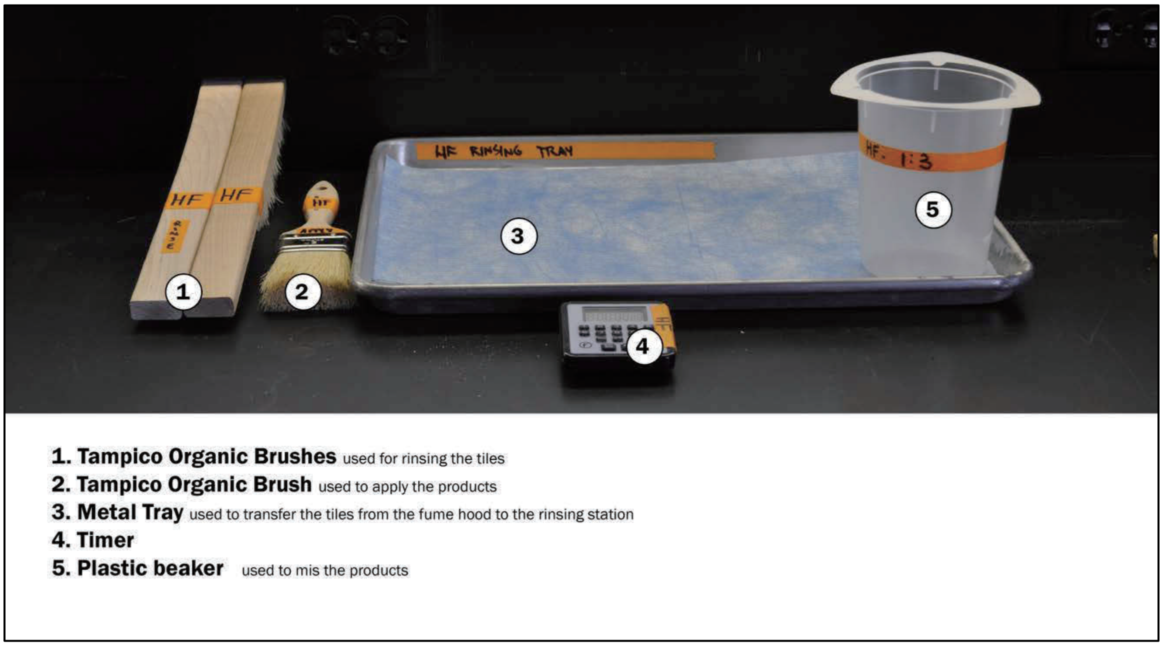
[73] These data are provided in the Material Safety Data Sheets - included in the appendix for both products.

Consequently, the treatment included several steps:

- First, the samples were pre-wetted with a water spray[74]
- Then, the product was applied by using a Tampico organic brush
- Lastly, the samples were carefully rinsed with the aid of a Tampico organic scrub-brush for 2 minutes
- The samples were then allowed to air-dry for twenty-four hours

The second application was directly reapplied after the first; samples were wetted again before re-applying the product.



1. Tampico Organic Brushes used for rinsing the tiles
2. Tampico Organic Brush used to apply the products
3. Metal Tray used to transfer the tiles from the fume hood to the rinsing station
4. Timer
5. Plastic beaker used to mis the products

Figure 18: Tools used for the acid treatment

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[74] Since our research does not focus on the analysis of chemical residues on the surface, tap water was used to wet and rinse the samples.

Figure 19: Irene applying chemical cleaner on samples

5.3 Evaluation method

Several methods were used to evaluate and quantify the samples before and after running accelerated weathering tests.

5.3.1 Texture mapping

In order to measure changes in the texture and surface profile of the tiles, several methods were investigated, and ultimately camera texture mapping was selected. Confocal Microscopy was tried at the Penn Medical School and a 3d-Profilometer at the Singh Nanotechnology Center. With both instruments, only a small area approximately 3 mm x 3mm could be scanned at a time. Due to the large number of samples and the limited amount of time available, and the variability of surface, these methods were not selected for evaluation.

Instead another technique was investigated by using a SLR digital camera with raking illumination, suggested by Joseph Elliott. Conveniently, this system produced excellent images, able to show the profile and texture of the samples.

The equipment used included: a camera stand, two Maglite quartz halogen raking lights set at an angle of 30 degrees within 7 inches distance from the sample and a SLR Camera Nikon 500D. Several camera settings were tried and ultimately an aperture of F/8 with a time 1/60, and 1/40 and ISO 200 were selected. A scale card was placed on the left side of each tile as a reference. After photographing all the samples, the files were opened as raw files in Photoshop CS 6, and then edited: lens correction applied, contrast increased, and image conversion to black and white. The use of black and white helped emphasize the surface texture and the profile of each tile.

By using this system, qualitative visual evaluation was completed in a reasonable amount of time. The resolution of the pictures was 300 dpi, with a pixel quantity between 11.6 M - 12.6 M. This technique provided exclusively comparative qualitative data. Few limitations were encountered along the way: the camera station was not built in and fixed, but prepared as needed. This allowed for small errors and the challenges with the light settings. Also, very limited studies are available on this technique.[75]

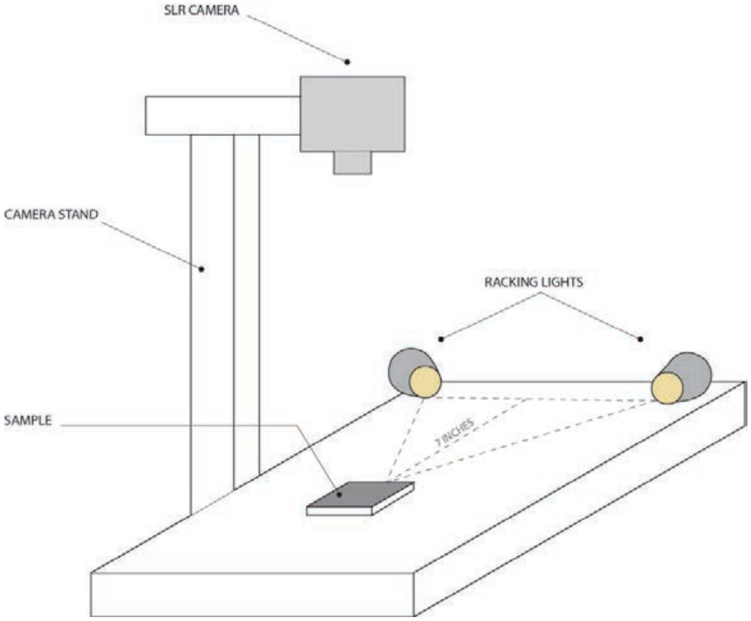

Figure 20: Camera station setting

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[75] C. A. Grissom, A. E. Charola and M. J. Wachowiak, Measuring Surface Roughness on Stone: Back to Basics, Studies in Conservation, Vol. 45, No. 2, pp. 73-84, 2000

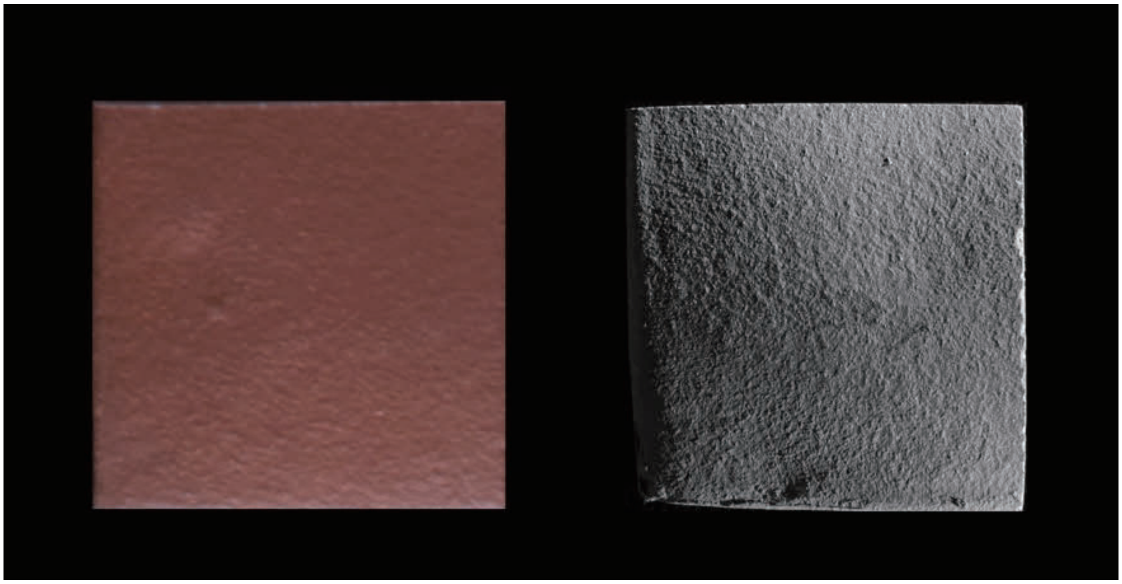

Figure 21: Early test with texture mapping photography

5.3.2 Scanning electron microscope

In order to evaluate changes in the morphology of the surface and surface cross section, Scanning Electron Microscopy was completed before and after accelerated weathering.

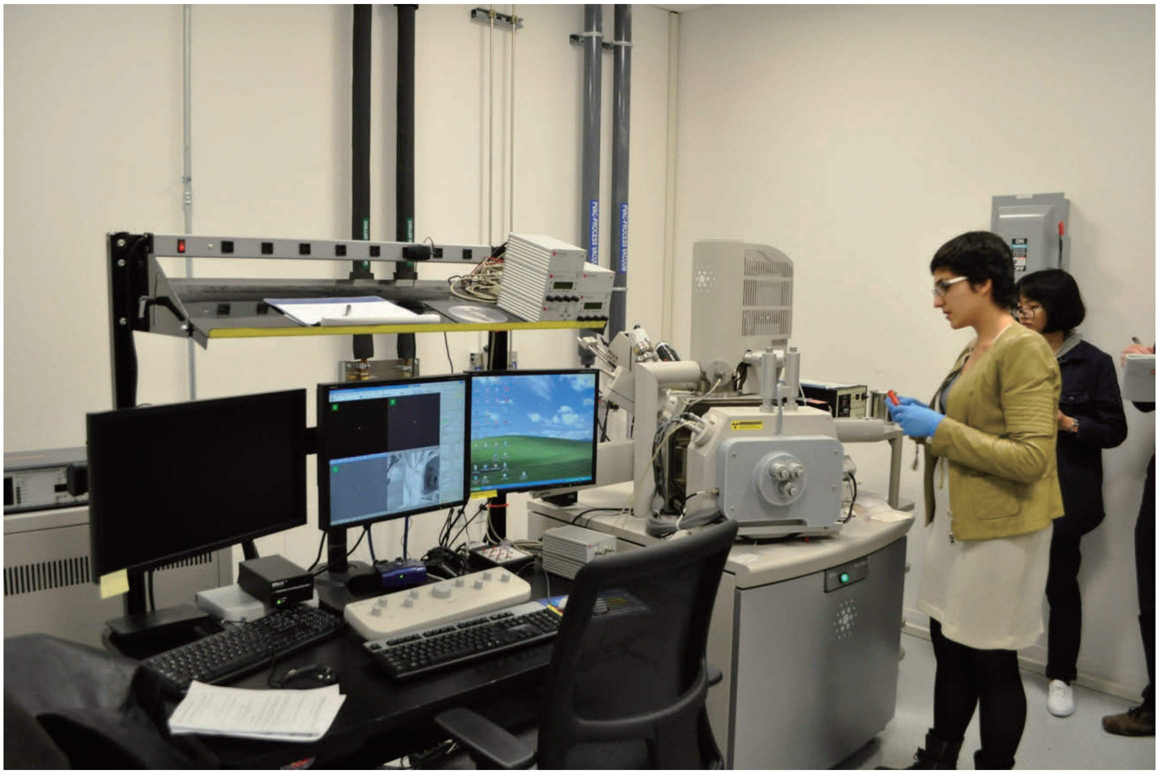

Figure 22: Session at the Scanning Electron Microscope at the Nanotechnology Center

A total number of 18 samples was analyzed: Cohort 1 from each sample set, and one control for each color.[76] The Scanning Electron Microscope used was a FEI 500 QUANTA located at the Nanotechnology Center of the University of Pennsylvania.

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[76] This facility was used for over 10 hrs.

The settings used for were: magnification 1000X and 2500X, high-voltage of 20.00 kW, spot area 3, and chamber pressure of 1.00 Torr. The samples were not coated.

5.3.3 Spectrophotometer

To evaluate any changes in color, a CM2500D Konica Minolta Spectrophotometer was used. All 96 tiles were recorded, and the data elaborated by using the C18 Minolta Software before and after accelerated weathering. The data were recorded based on the CIELAB Color System with D65 as the standard setting for daylight-recommended by Minolta. Before carrying out any readings, the instrument was calibrated for zero and white body. The reading for each tile was taken in the center of the sample. For each set, the control was used as a target and the cohorts as samples.

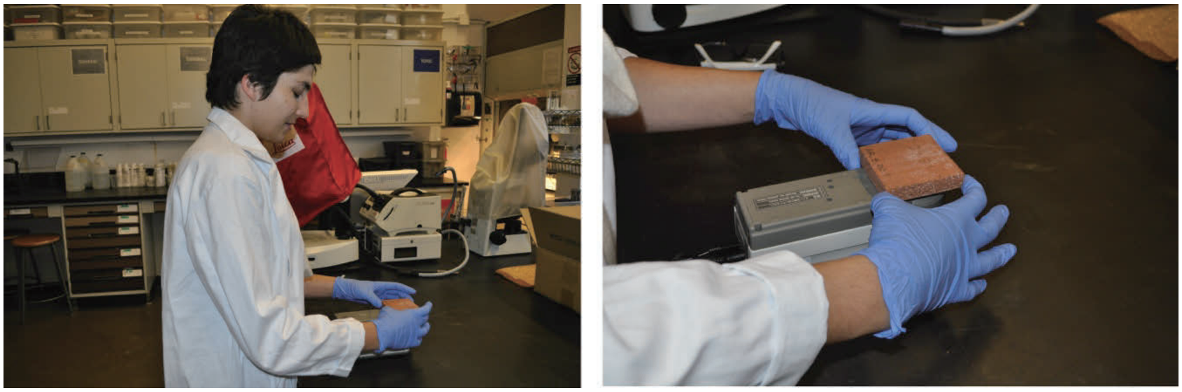
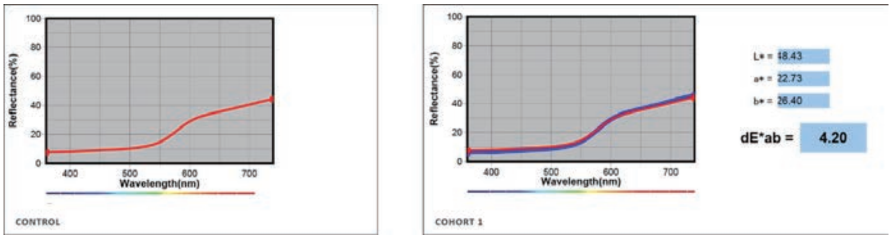


Figure 23: Irene completing a reading on a red tile with the Minolta Spectrophotometer.

The data for each sample was converted into a PDF and then inserted in a layout with all the other data.



Graph 11: Data obtained comparing the target or control with one cohort after running the salt test. Data produced by C18 Minolta software

5.3.4 Porosity

Liquid Nitrogen was used to measure porosity. This method is based on the liquid immersion technique ASTM C830 [77] and proved useful as applied to cultural material (ceramic sherds) at the University of Las Vegas.[78]

Porosity is t calculated by: $P=\frac{W-D}{W-S}X\ 100$

This experiment was conducted at the Penn Chemistry Department with the assistance of lab director Simon Berritt. The equipment used included: a Sartorius electronic balance with an under-hook, metal wire for hanging the tile, and a Dewar flask for the liquid nitrogen. To determine the best immersion times, tests were conducted based on 5 minute increments for a 30 minute period. In the end, the best immersion time was 10 minutes.

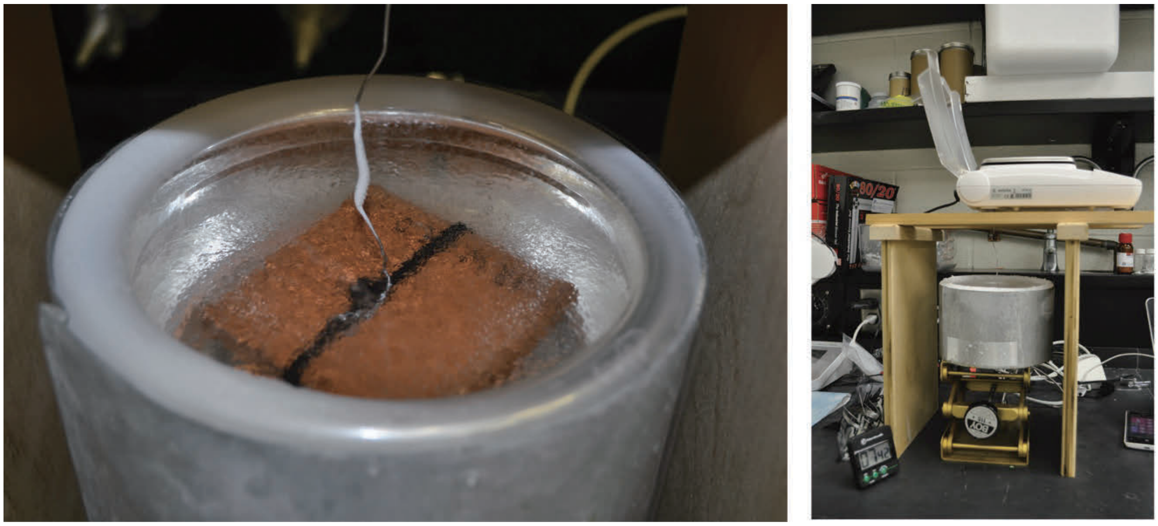


Figure 24: Completing the Liquid Nitrogen Test at the chemistry department

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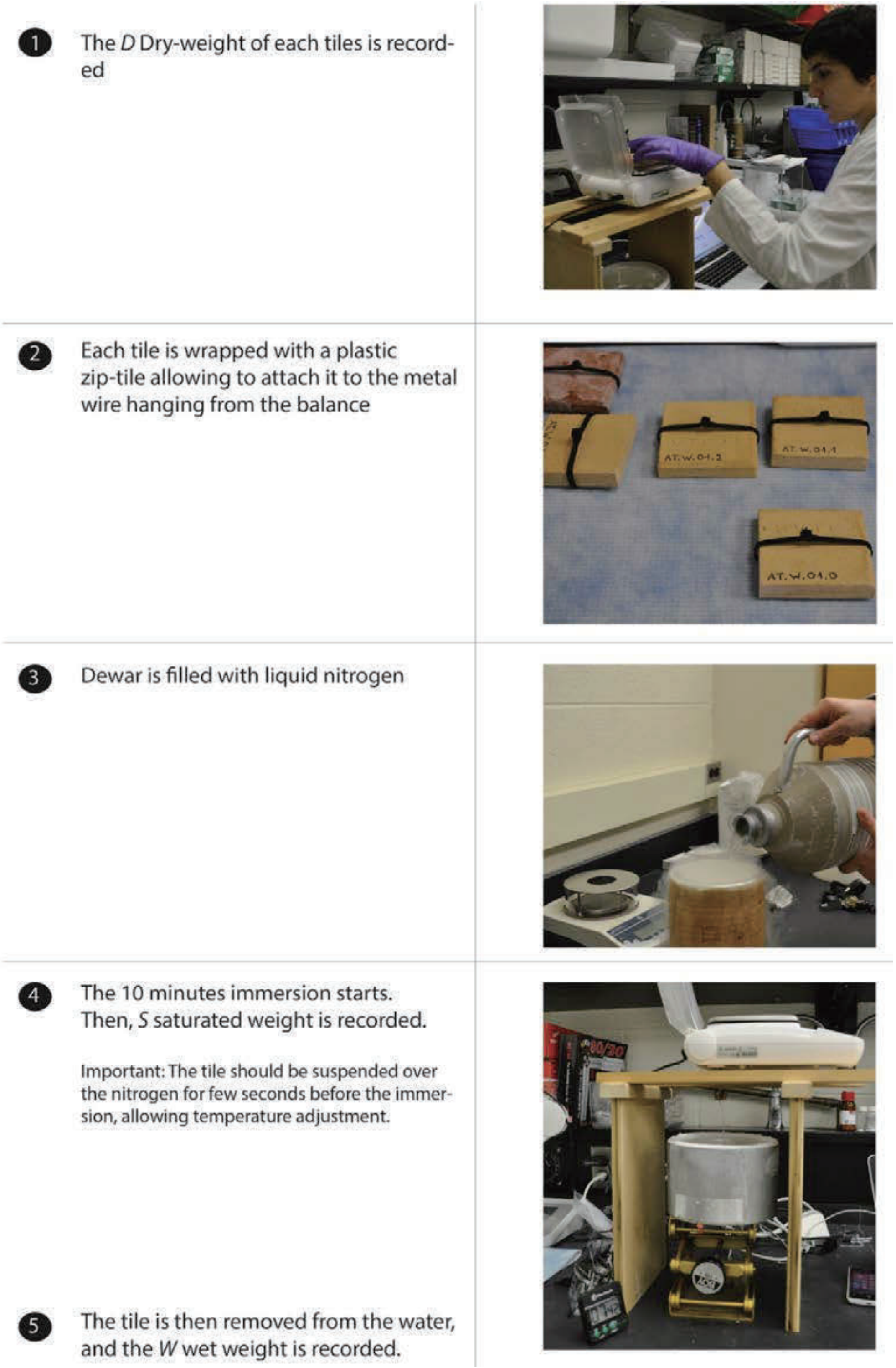
[77] American Society for Testing and Materials, C830-00: standard test methods for apparent porosity, liquid absorption, apparent specific gravity and bulk density of refractory shapes by vacuum pressure, ASTM Annual Book of Standards, Volume 15.01: Refractories; Activated Carbon; Advanced Ceramics (2002)

[78] Karen G. Harry, Allen Johnson, A non-destructive technique for measuring ceramic porosity using liquid nitrogen, Journal of Archaeological Science 31 (2004)

Below, the experiment is illustrated step by step:



① The *D* Dry-weight of each tiles is recorded

② Each tile is wrapped with a plastic zip-tile allowing to attach it to the metal wire hanging from the balance

③ Dewar is filled with liquid nitrogen

④ The 10 minutes immersion starts. Then, *S* saturated weight is recorded.

Important: The tile should be suspended over the nitrogen for few seconds before the immersion, allowing temperature adjustment.

⑤ The tile is then removed from the water, and the *W* wet weight is recorded.

Figure 25: Diagram showing the liquid nitrogen experiment step by step

Different methods are commonly used for measuring porosity of ceramic material and are organized into two major groups: methods that rely on impregnation of a gas or a liquid such as mercury porosimetry, and other methods that rely on direct observation of the pores. [79]

The first category is based on the quantification of the volume of the open pores, while the second relies on the quantification of open and close pores.

Within the first category, ASTM C830-00 liquid impregnation[80], and ASTM C20-00 water absorption test[81] are the most common techniques used to measure porosity in ceramic material.

Amongst the second category, several direct observation techniques have been developed overtime such as the direct microscopic examination of thin-sections, and x-radiography.[82]

The liquid nitrogen technique follows under the liquid impregnation method, where open pore volume is determined by calculating the amount of liquid nitrogen adsorbed by the open pores. There are several advantages to using liquid nitrogen for porosity measurements: it is very affordable, easy and quick to use as well as being more accurate than water based measurements and less toxic than mercury porosimetry. It evacuates on

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[79] Karen G. Harry, Allen Johnson, A non-destructive technique for measuring ceramic porosity using liquid nitrogen, Journal of Archaeological Science 31, 2004.

[80] American Society for Testing and Materials, C830-00: standard test methods for apparent porosity, liquid absorption, apparent specific gravity and bulk density of refractory shapes by vacuum pressure, ASTM Annual Book of Standards, Volume 15.01: Refractories; Activated Carbon; Advanced Ceramics (2002) 141e145.

[81] American Society for Testing and Materials, C20-00: standard test methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water, ASTM Annual Book of Standards, Volume 15.01: Refractories; Activated Carbon; Advanced Ceramics (2002) 6e8.

[82] A. Pierret, C.J. Moran, L.M. Bresson, Calibration and visualization of wall-thickness and porosity distributions of ceramics using x-radiography and image processing, Journal of Archaeological Science 23: 419e428, 1996.

its own, so there is no need to physically remove it from the tile as in the case of mercury, or a need for a vacuum.[83]

One of the critical aspects of using liquid nitrogen is that it evaporates very rapidly, requiring immediate measurement of the wet weight (WW) after removing the tile from the liquid. For this reason, a moving stage was used.

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[83] E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances, I. computations from nitrogen isotherms, Journal of the American Chemical Society 73: 373e380, 1951.

6.0 Results and discussions

6.1 Statistical analysis

Statistical analysis was conducted before and after accelerated weathering testing. Average, mean, standard deviation and t-test were calculated.

The t-test was completed in order to provide a better comparison between the same groups of data before and after, the two products and the two applications. T-test indicates: *whether or not the difference between two groups' averages most likely reflects a "real" difference in the population from which the groups were sampled.*[84]

$$t = \frac{\bar{x}_1 - \bar{x}_2 - \Delta}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

Where $\bar{x}_1$ and $\bar{x}_2$ are the means of the two samples, Δ is the hypothesized difference between the population means (0 if testing for equal means), s_1 and s_2 are the standard deviations of the two samples, and n_1 and n_2 are the sizes of the two samples. [85]

Calculations were completed with Microsoft Excel using built-in T-TEST (array1, array2, tails, type) function. Where:

Array 1: The first data set.

Array 2: The second data set.

Tails: Specifies the number of distribution tails. If tails = 1, T.TEST uses the one-tailed distribution. If tails = 2, T.TEST uses the two-tailed distribution.

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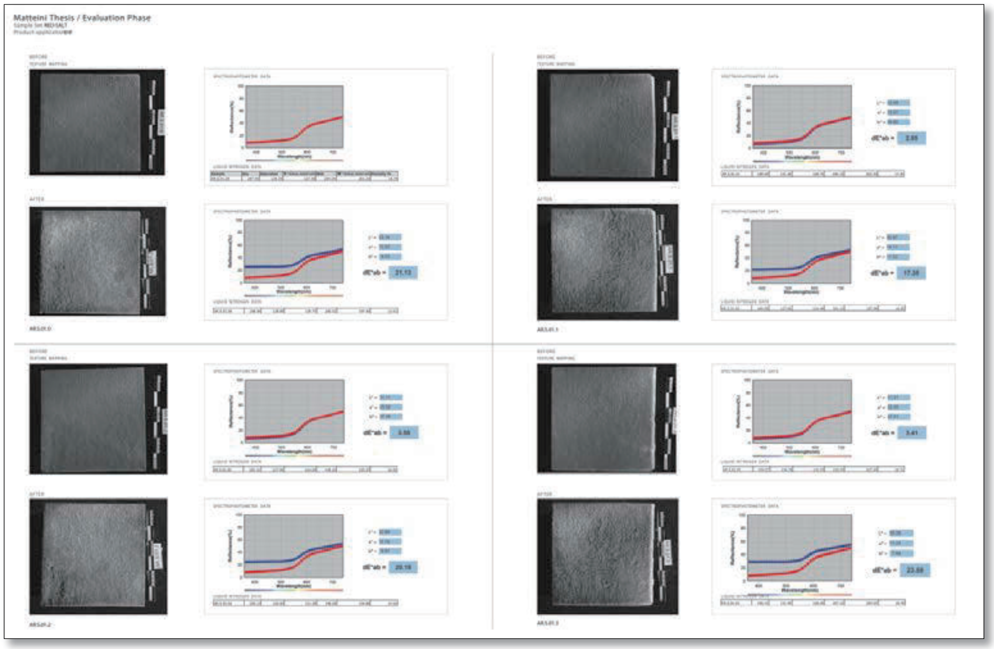
[84] http://docs.statwing.com/examples-and-definitions/t-test/statistical-significance/

[85] Excel Master Series, *t-Tests in Excel - The Excel Statistical Master*, Mark Harmon MBA, 2011

Type: The kind of t-Test to perform. 1 for Paired, 2 for Two-sample equal variance (homoscedastic), and 3 for Two-sample unequal variance (heteroscedastic).
All the results are shown in the appendix.

6.2 Display data

A layout for displaying data was developed with Adobe InDesignCS6 in an 11” x 17” page, and before and after data of one set of samples presented. The page is divided in four quadrants: top left for the control and the other three quadrants for the cohorts. This allowed for easily comparison, between data from texture mapping photography, liquid nitrogen porosity calculations, and spectrophotometer color measurements. For the Scanning Electron micrographs, since only one tile per set was evaluated,[86] different layouts were created. All the data are shown in the appendix.



Matteini Thesis / Evaluation Phase

Figure 26: Example of a layout developed to display data

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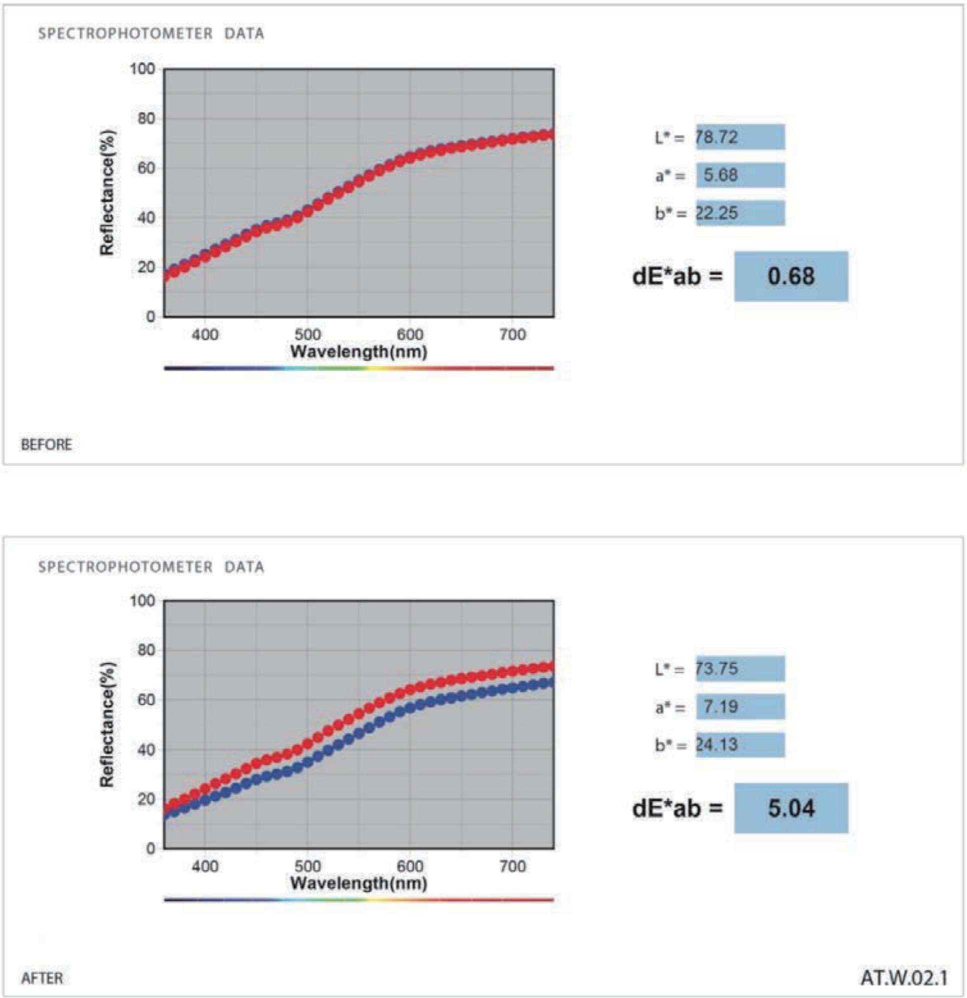
[86] Due to the limited amount of time and budget available only cohort 1 from each set was evaluated

6.3 Color measurement

Color measurements were collected from all the samples, before and after accelerated weathering testing. While small color variations occurred across the whole sample population, only a few sets of samples showed significant difference accordingly to the t-test and statistical analysis.

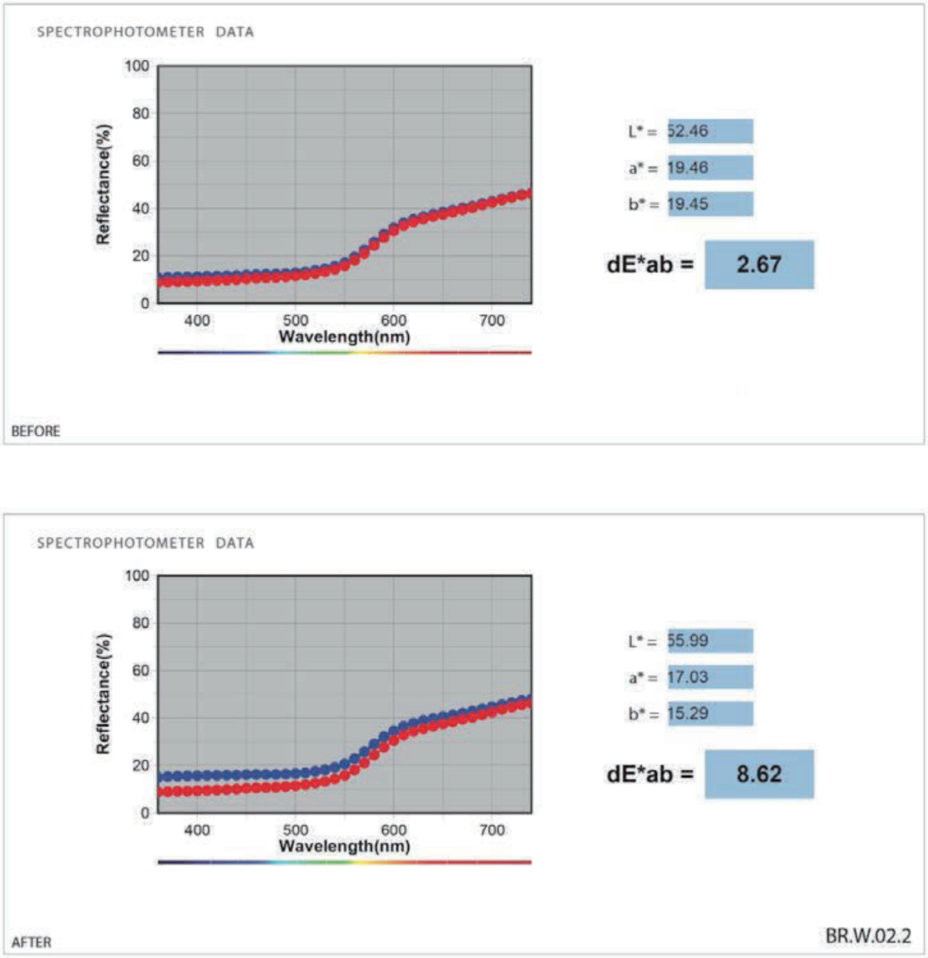
The tan samples treated with HF and ABF, all displayed significant color changes after accelerated weathering tests.



Graph 12: Comparing a tan sample treated with two applications of HF after running the weatherometer for 6 weeks.

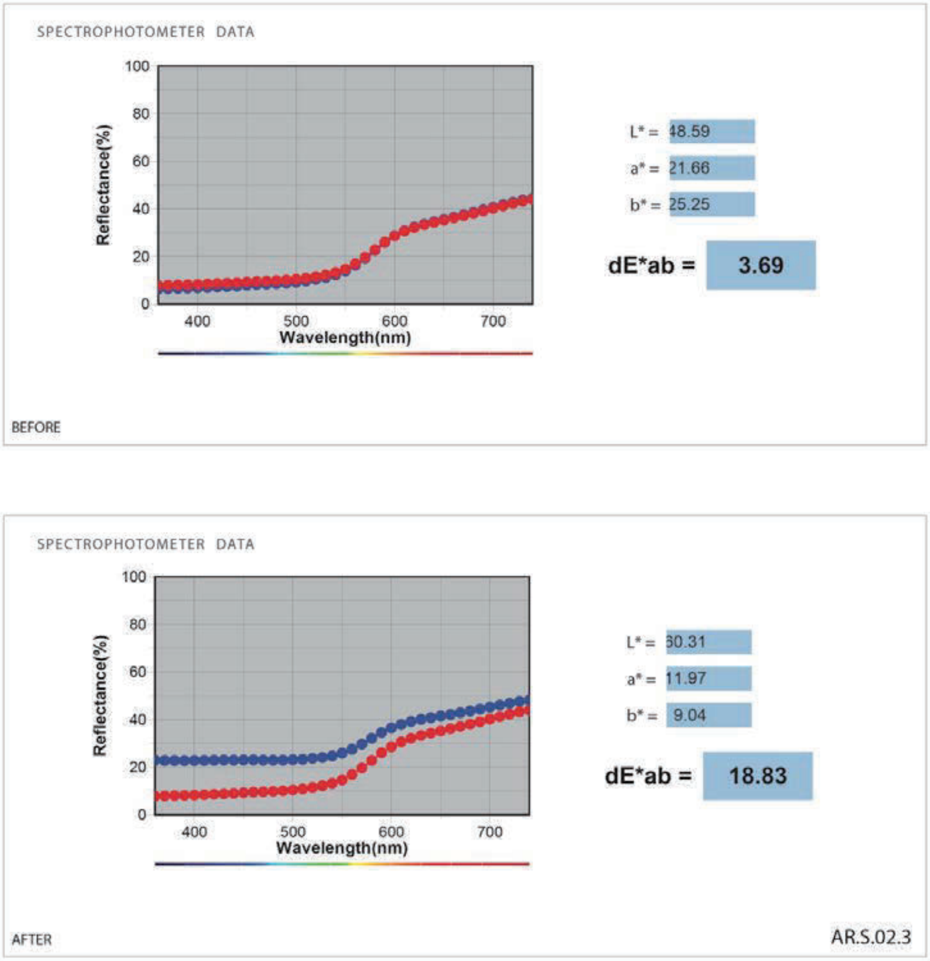
Conversely, the red samples showed changes in very few sets:

- Red samples treated with HF only showed color differences after the salt test, as abundant salt deposits remained on the surface.
- Red samples treated with ABF showed important color changes after completing both salt and weatherometer tests.



Graph 13: Comparing a red samples treated with two applications of ABF after running the weatherometer with the control

In general, the readings of the samples used for the salt test were severely affected by the deposits left on the surface, as visible in the example below:



L* = 48.59
a* = 21.66
b* = 25.25
dE*ab = 3.69

L* = 60.31
a* = 11.97
b* = 9.04
dE*ab = 18.83

Graph 14: Comparing a red sample treated with two application of HF after running the salt test with the control

The tan samples appear to be more susceptible to acid cleaning and especially AB cleaning showing greater variations. Additionally, the T-test was used to compare data amongst the two different products and applications. After running the two accelerated weathering tests, ABF in both applications showed greater color changes than HF applications. This could be very well attributed to the precipitation of fluoride salts from the prolonged dwell time of ABF in gel form, and is applied as a concentrate for a max dwell time of 20 minutes. Conversely, HF is diluted 1:3 with a maximum dwell time of 5 minutes. This raises a question on the application of ABF, and its dwell time.

6.4 Scanning electron microscopy

Observations made by Scanning Electron Microscopy include:

- Visible changes in pore structure: The microstructure of the pores was severely altered, in particular on the samples treated with HF before and after the salt test. As shown below, irregular and interconnected pores are visible in the images from AR.S.01.1-a red sample treated with 1 HF. Fractures around pores are also visible. Salt is mainly responsible for the change in the microstructure, since it crystallizes in the pores.

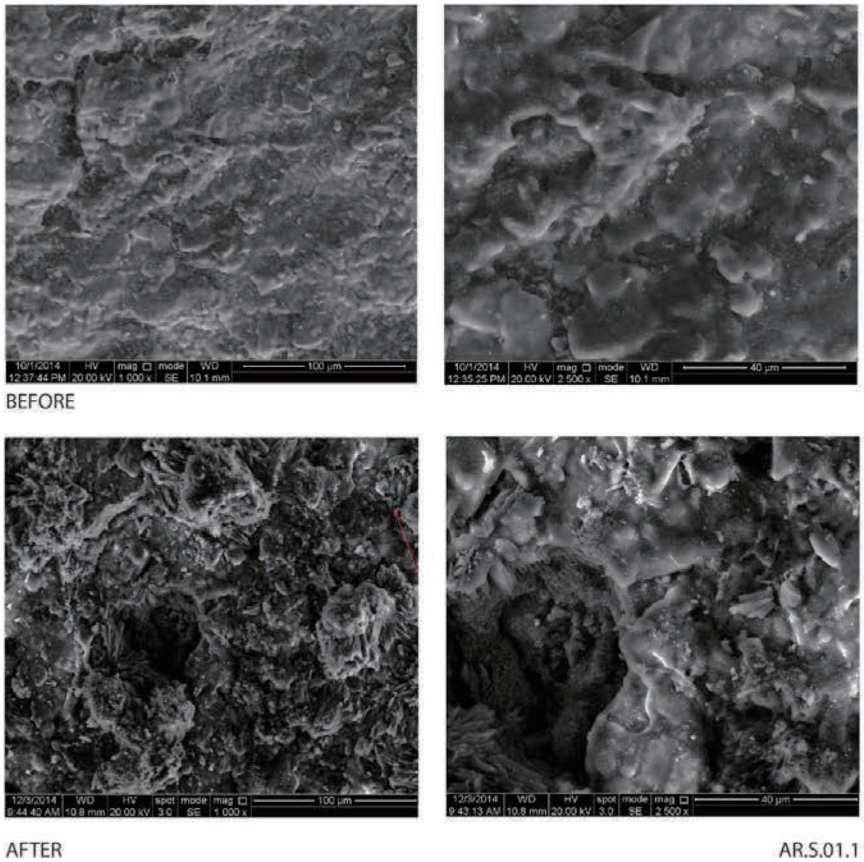
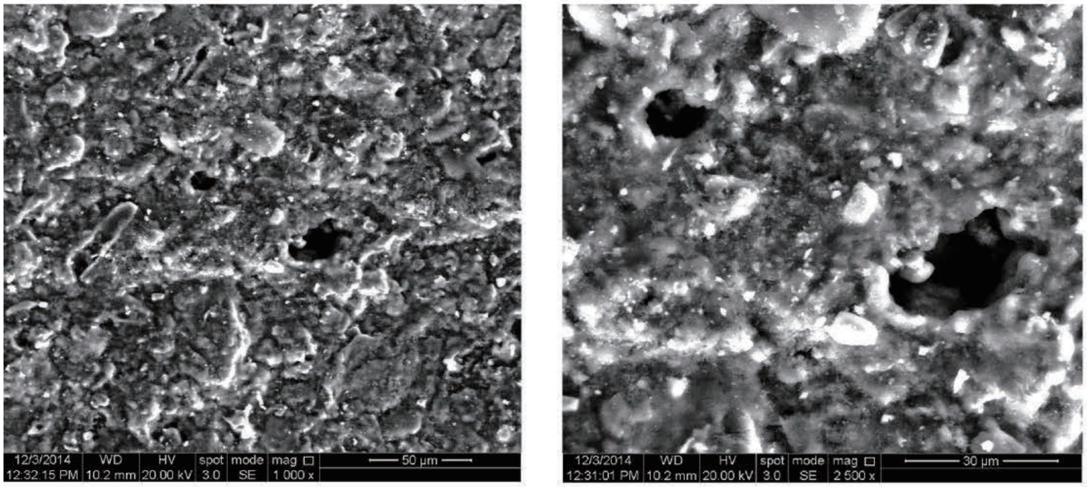


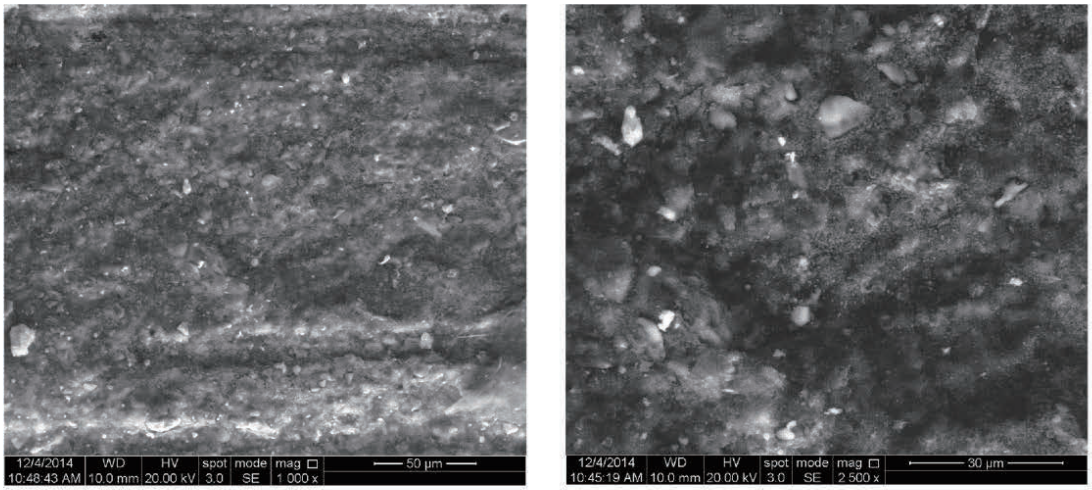
Figure 27: Red sample treated with one application of HF before and after running the salt test. Changes in the pore structure are clearly visible (Left side magnification 1000X, right side 2500X)

- Chemical stressing: Signs of chemical erosion are visible on the dense matrix of the terracotta. After running both accelerated testing protocols, it appears that the chemical erosion is more evident on the samples treated with HF compared to the samples treated with ABF, as shown in the pictures below.



AR.W.02.1

Figure 28: Red sample treated with two applications of HF after six weeks accelerated weathering. Visible change of the matrix of the terracotta, (Left side magnification 1000X, right side 2500X)



BT.W.02.1

Figure 29: Tan sample treated with two applications of ABF after accelerated weathering. Minimal chemical alteration is visible. By comparing with the two images above, HF strongly alters the surface. (Left side magnification 1000X, right side 2500X)

- Submicron layer deposits: In all the samples treated with ABF, submicron deposits were noticed on the images collected after the treatment, before running the weathering tests.

  EDS and XRD were conducted on sample BR.C.01.1 and on the submicron particles. With EDS, residual fluorine was detected, and with XRD, calcium fluoride. Previous studies (Poirier et al., 2009)[87] also reported the presence of fluoride deposits after treating glaze ceramic tile with ABF.

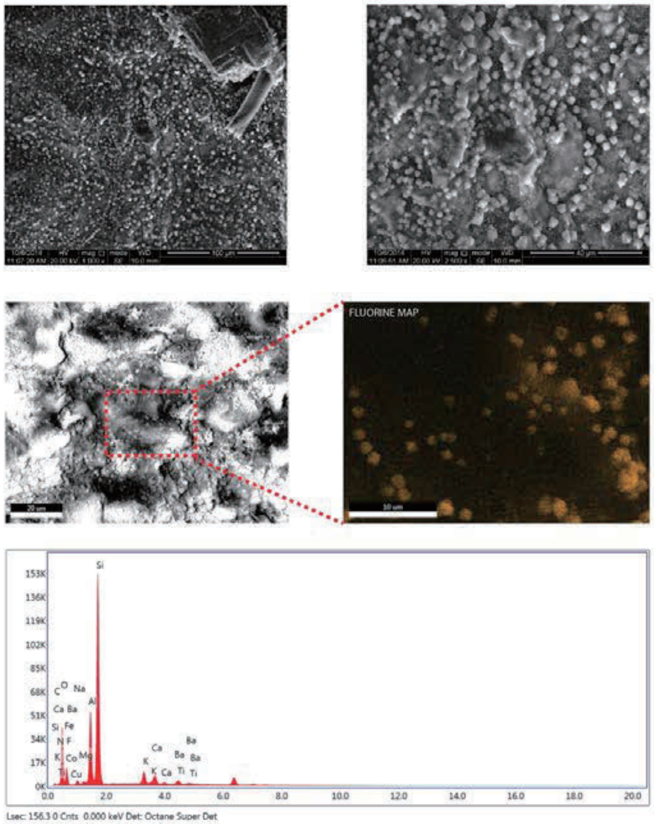


Figure 30: EDS Mapping Results from BR.C.01.1 show presence of residual fluoride.

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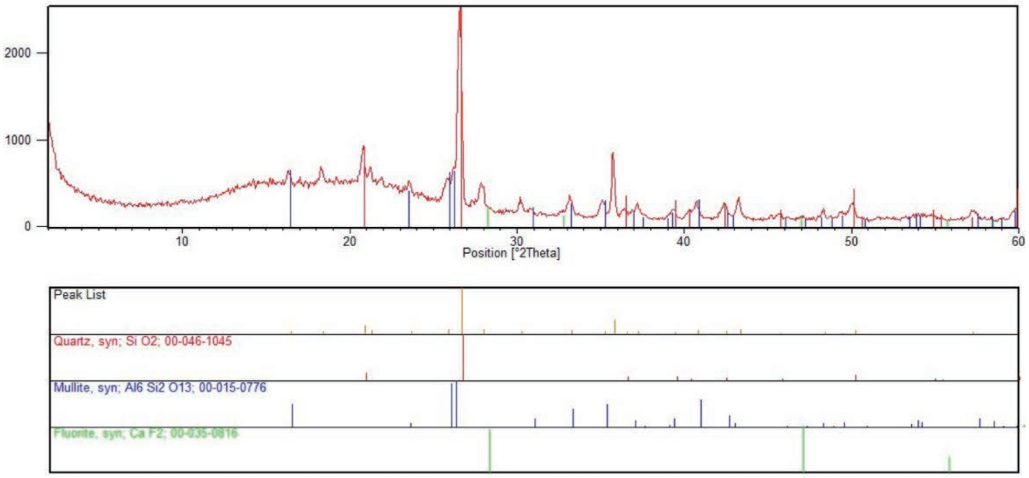
[87] Patrice Poirier et al., The impact of chemical treatments on the wear, gloss, roughness, maintenance, and slipperiness of glazed ceramic tiles, Journal of Environmental Health Research, On-line peer-reviewed Journal, Volume 9:2, 2009. http://www.cieh.org/jehr/impact_of_chemical_treatments_on_glazed_ceramic_tiles.html



Graph 15: XRD spectra from BR.C.01.1 show presence of calcium fluoride

As fluorine is not part of the clay composition of the samples, this strongly suggests that fluorine was deposited by ABF (NH4HF2). After running accelerated weathering tests, physical erosion occurred, and the majority of the particles were removed. [88]

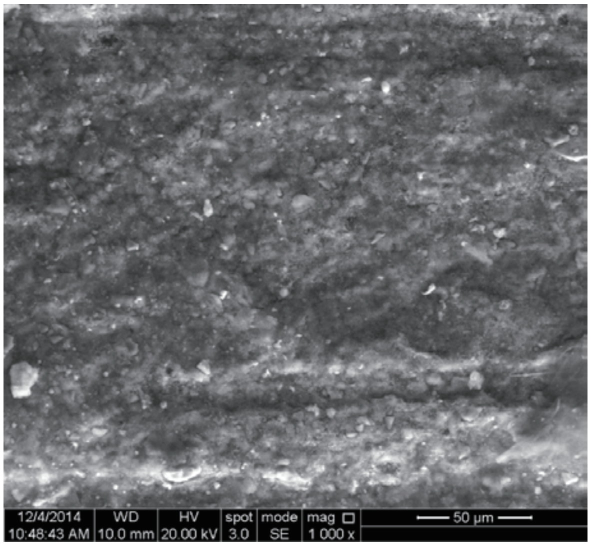


Figure 31: Submicron particles were not present after weathering for six weeks on a sample treated with ABF

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[88] Even after running the weatherometer, a small amount of particles were noticed. It is hard to see in this image due to the lower resolution.

Fluoride ions have a high affinity to certain elements such as calcium and silicon. Furthermore, they form an insoluble precipitate with calcium and lower plasma calcium. [89] This also explains why the deposits remained, after applying ABF although the tiles were well rinsed and the color lightened due to the masking effect of the precipitate.

- Salt crystallization: Another interesting observation was noticed on the tan samples treated with ABF. Despite the fact that the tiles were immersed for seven days in water after running the salt test, and additionally boiled for 5 hours in distilled water, dense and tenacious salt crystals remained strongly bonded to the surface.

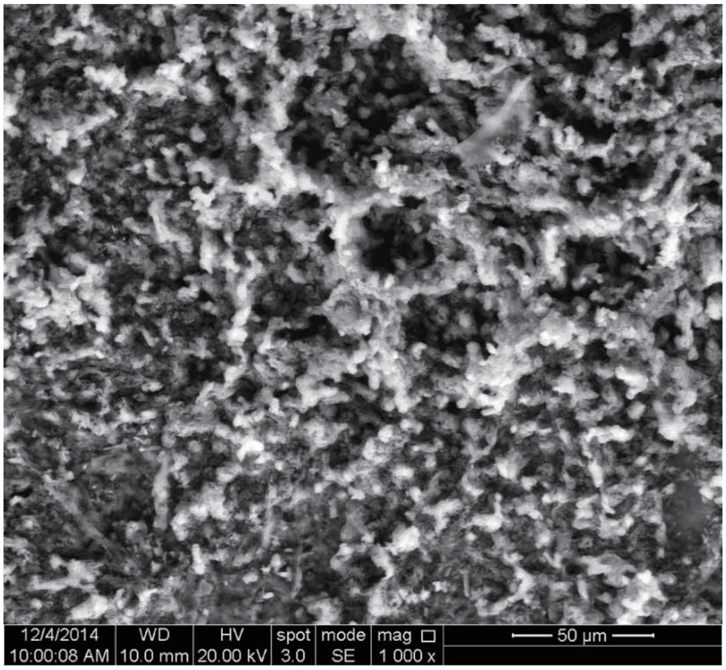

Figure 32: SEM micrograph showing the tenacious salt crystals on a tan sample treated with one application of ABF, after rinsing the sample for seven days and boiling for five hours

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[89] Jeff Prystupa, Fluorine-A current literature review. An NRC and ATSDR based review of safety standards for exposure to fluorine and fluorides, Toxicology Mechanisms and Methods, 2011; 21(2): 103–170, 2011

6.5 Liquid nitrogen porosity

The liquid nitrogen test was performed on all of the samples before and after accelerated weathering tests. As a general trend, porosity appeared to decrease amongst the sample population. Accordingly to the t-test, several observations were noticed:

- Within the red and tan samples treated with HF, only the tan shows a significant difference in porosity after running both the salt and the weatherometer tests.
- The samples treated with ABF do not show a significant difference in porosity between the two applications and color.
- By comparing data between the two products ABF and HF, it is evident that the samples treated with HF show more important and significant changes in porosity than the samples treated with ABF, particularly noticeable amongst the tan samples.

After performing the liquid nitrogen test on the samples used for the salt test, we noticed that a large amount of salt was still trapped in the pores, despite the seven-day water immersion. Consequently, the tiles were boiled in distilled water for five hours, accordingly to the ASTM C37-2014.[90] After drying, the samples still showed residues on the surface and on the side. Therefore, the liquid nitrogen was not performed again, and the pore structure studied with the Scanning Electron Microscope.

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[90] ASTM C37-14: Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products, Ceramic Tiles, and Glass Tiles.

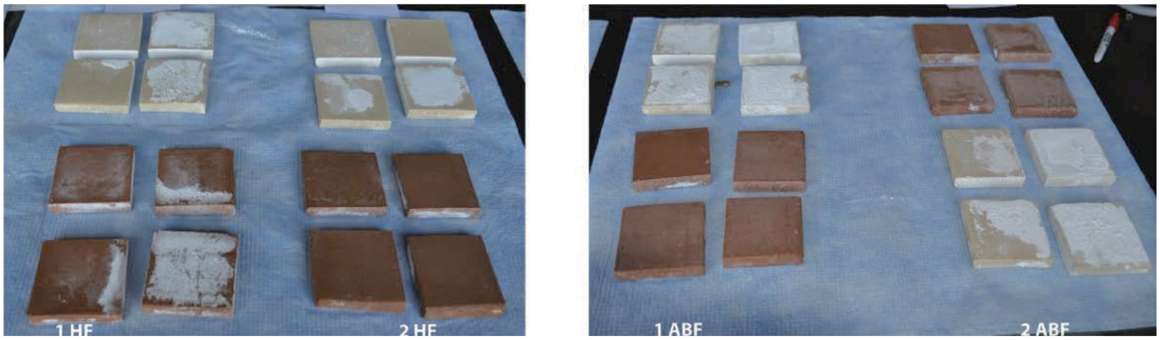

Figure 33: Salt is still visible on the samples after the 5 hours boiling

As a final note, after running the weathering tests, all the samples showed a small increase in weight, and decrease in porosity. Aside from the samples that were used for the salt test, this could possibly be attributed to the formation of colloidal silico-fluorides blocking the pores on the surface, as noticed in a previous study (Conahan, 1999).[91]

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[91] Heather Conahan, An assessment of the effects of hydrofluoric acid based cleaner on unglazed architectural terracotta, Thesis Dissertation, Historic Preservation Department, University of Pennsylvania, 1999. In this research, Conahan noticed a decrease in porosity after treating her samples with Hydrofluoric acid based cleaner, and associated as well to deposits of colloidal silicofluoride. (p. 58)

6.6 Texture mapping photography

Qualitative data were obtained from the texture mapping photographs.

As a general trend, all the tiles showed increased roughness, due to accelerated weathering and chemical erosion from the treatments.

In particular, the samples treated with HF showed more significant changes in texture than the samples treated with ABF. Amongst the two accelerated weathering tests, salt was responsible for more severe changes to the texture compared to the weatherometer, which showed very minimal changes. After rinsing and boiling the tiles, crystalline deposits were still visible on the surface, especially on the samples treated with HF.

In the following pages, several representative examples are shown. All the photographs are available in the appendix.

As a final note, data obtained with this technique were inconclusive due to the macro-scale of the pictures, the inexperience with this technique, and the facility limitations encountered along the way.

This technique has the potential to be very powerful, as previously tested by Charola et al. in 2000[92]. Furthermore, improvements should be made to the camera station. It should be built in and fixed. Additional experimentation should be completed with the lighting settings.

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[92] C.A. Grissom, A.E. Charola and M.J. Wachowiak, Measuring surface roughness on stone: back to basics, Studies in Conservation 45:73-84, 2000

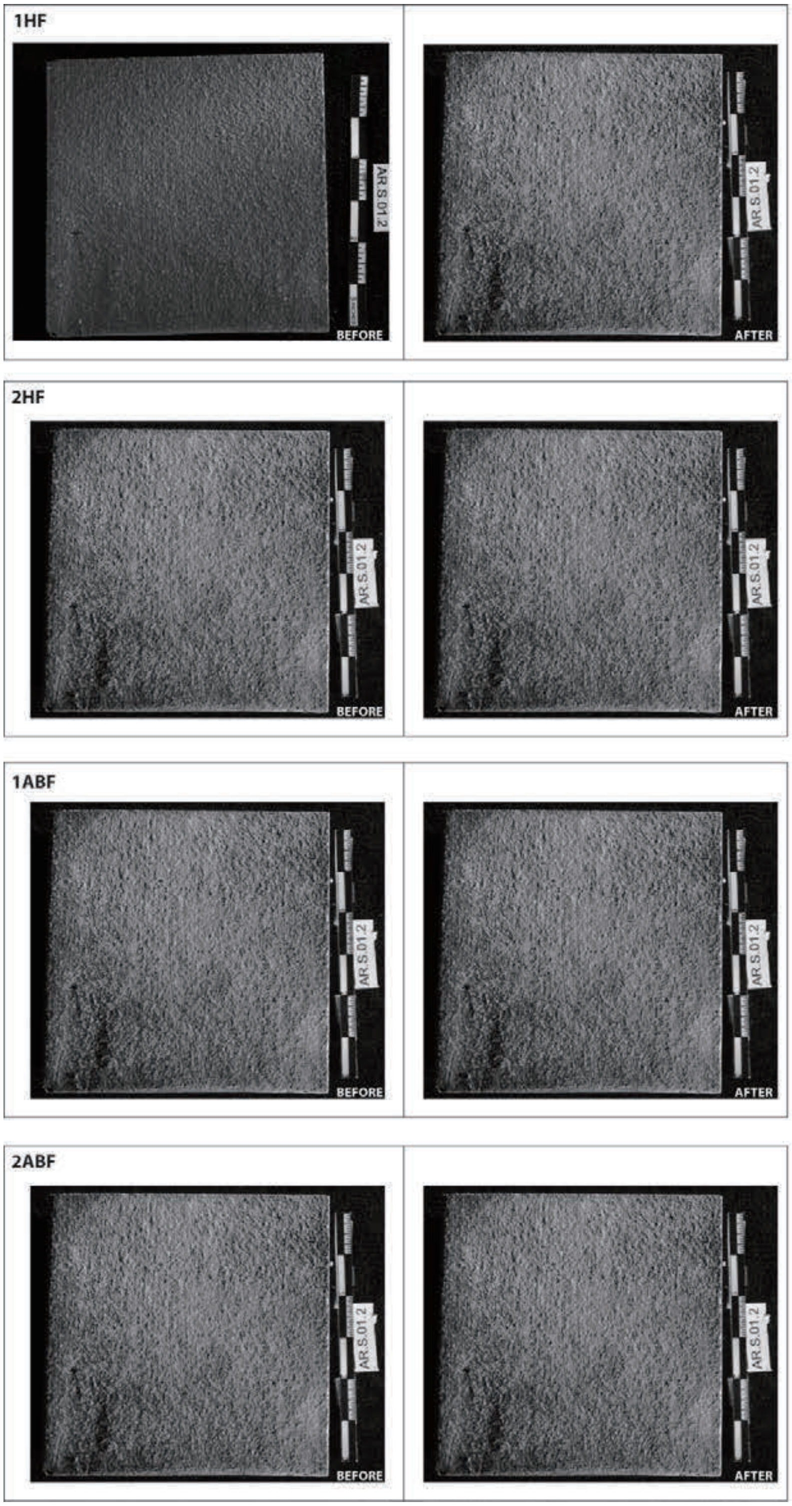

Figure 34: Examples of before and after texture mapping photos.

6.7 Conclusions

Based on previous research (Matero et al., 1996), this work proposed to assess and evaluate the effects of acidic cleaners on unglazed terracotta and to verify the potential for damage by accelerated weathering testing.

As a result of our findings, the following observations can be made on the effects of acidic cleaners on unglazed terracotta, and their relation to its weathering. Introduced in early 2000, Ammonium Bi-Fluoride was presented as a less aggressive delivery of HF. Consequently, ABF treated samples did show reduced alteration of the microstructure compared to HF treated terra cotta. However, the variations in color were significant, which represent an important physical property of terra cotta. Due to the long dwell time thorough rinsing is recommended after applying this product. The formation of submicron particles of calcium fluorides does not appear to adhere strongly to the surface; the samples will eventually restore to their initial surface properties, once the ABF treatment weathers. Consequently, as stated by Pourier[93]: *ABF solutions more resemble cleaning solutions than chemical treatments.*

Indeed, for HF cleaners the case is different. Widely in use since the early 1960's with the first product introduced by ProSoCo in 1962, HF based cleaners show irreversible changes to the microstructure of the pores as previously observed (Matero et. al, 1996). Furthermore, signs of physico-chemical erosion on the samples treated with HF were significant, including increase in surface roughness. After running the weatherometer test, EDS was conducted on samples treated with HF AT.W.01.1 and AT.W.02.1, and it was

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[93] Patrice Poirier et al., The impact of chemical treatments on the wear, gloss, roughness, maintenance, and slipperiness of glazed ceramic tiles, Journal of Environmental Health Research, On-line peer-reviewed Journal, Volume 9:2, 2009. http://www.cieh.org/jehr/impact_of_chemical_treatments_on_glazed_ceramic_tiles.html

noticed that the chemical composition of the tile was not altered. Nonetheless, further analysis with FTIR should be conducted in order to study the possibilities of deposits of colloidal silico-fluorides on the surface. No significant color variations were observed with HF. In conclusion, this testing protocol attempted to examine the weathering vulnerability of unglazed red and tan terracotta. Today, the results strongly suggests that the heavy duty cleaner not only enlarged the pores, but cause the terracotta to be further altered by the salt crystallization test. This suggested for an increase vulnerability as a result of the cleaning. Conversely, the Enviro Klean product based on ammonium bi-fluoride neither enlarged the pore structure after cleaning or after the salt crystallization test. Below, all the results are summarized in tables organized by type, products and applications, according to color change, porosity and surface texture.

Table 1: Red Samples Salt Test

	Red Samples-Salt Test		
	Color Change	**Porosity**	**Surface Texture**
1 HF	**Significant changes** Average Δe: before 3.28 and after 20.38. Statistically significant. (99.07 %)	**Significant changes** Average porosity decreased: before 17.33 % and after 11.92 %. Statistically not significant. (92.65 %). SEM shows changes in the pores structures.	**Significant changes** were noticed in the texture-Increased roughness and chemical erosions from the treatment was visible.
2 HF	**Significant changes** Average Δe: before 3.42 and after 14.36. Statistically significant. (96.36 %)	**Significant changes** Average porosity decreased: before 11.44 % and after 7.45 %. Statistically not significant. (87.40 %). SEM shows changes in the pores structures.	
1 ABF	**No Significant changes** Average Δe: before 1.84 and after 1.66 Statistically not significant. (17.14 %)	**Significant changes** Average porosity decreased: before 11.11 % and after 6.48 %. Statistically significant. (98.08 %)	**No Significant changes** were noticed in the texture.
2 ABF	**No Significant changes** Average Δe: before 4.61 and after 5.23 Statistically not significant. (17.49 %)	**No significant changes** Average porosity decreased: before 10.48 % and after 6.86 %. Statistically not significant. (78.99 %)	

Table 2: Red Samples Weatherometer

	Red Samples-Weatherometer		
	Color Change	**Porosity**	**Surface Texture**
1 HF	**No significant changes** Average Δe: before 3.49 and after 4.04. Statistically not significant. (66.59%)	**No significant changes** Average porosity decreased: before 12.79 % and after 6.47 %. Statistically not significant. (89.78%)	**No Significant changes** were noticed in the texture.
2 HF	**No significant changes** Average Δe: before 2.38 and after 3.34. Statistically not significant. (58.71%)	**No significant changes** Average porosity decreased: before 16.66 % and after 11.19%. Statistically not significant. (94.12%).	
1 ABF	**Significant changes** Average Δe: before 1.80 and after 4.04. Statistically significant. (97.91 %)	**No significant changes** Average porosity decreased: before 15.31 % and after 13.01%. Statistically not significant. (49.73%). SEM shows changes in the pores structures.	**No Significant changes** were noticed in the texture.
2 ABF	**Significant changes** Average Δe: before 2.31 and after 7.89. Statistically significant. (99.59 %)	**No significant changes** Average porosity decreased: before 11.50 % and after 10.41%. Statistically not significant. (19.44%)	

Table 3: Tan Samples Salt Test

	Tan Samples-Salt Test		
	Color Change	**Porosity**	**Surface Texture**
1 HF	**Significant changes** Average Δe: before 0.40 and after 4.27. Statistically significant. (97.46 %)	**Significant changes** Average porosity decreased: before 17.65 % and after 9.91 %. Statistically significant. (98.82 %). SEM shows changes in the pores structures.	**Significant changes** were noticed in the texture- Increased roughness and chemical erosions from the treatment was visible.
2 HF	**Significant changes** Average Δe: before 0.29 and after 8.47. Statistically significant. (98.73 %)	**Significant changes** Average porosity decreased: before 18.00 % and after 9.91%. Statistically significant. (98.12 %). SEM shows changes in the pores structures.)	
1 ABF	**No Significant changes** Average Δe: before 1.44 and after 2.04 Statistically not significant. (78.92 %)	**No significant changes** Average porosity decreased: before 15.24 % and after 10.84 %. Statistically not significant. (62.72 %)	**No Significant changes** were noticed in the texture.
2 ABF	**No Significant changes** Average Δe: before 1.63 and after 1.27 Statistically not significant. (58.56 %)	**No significant changes** Average porosity decreased: before 15.03 % and after 12.85 %. Statistically not significant. (79.60 %)	

Table 4: Tan Samples Weatherometer

	Tan Samples-Weatherometer		
	Color Change	**Porosity**	**Surface Texture**
1 HF	**Significant changes** Average Δe: before 0.98, after 4.76. Statistically significant. (97.61 %)	**Significant changes** Average porosity decreased: before 18.85 % and after 6.98 %. Statistically significant. (99.07%)	**No Significant changes** were noticed in the texture.
2 HF	**Significant changes** Average Δe: before 0.71, after 3.88. Statistically significant. (95.87 %)	**Significant changes** Average porosity decreased: before 16.88 % and after 8.34 %. Statistically significant. (95.16%).	
1 ABF	**No significant changes** Average Δe: before 1.22 and after 2.23. Statistically not significant. (82.94 %)	**No significant changes** Average porosity decreased: before 15.89 % and after 14.15 %. Statistically not significant. (63.37%)	**No Significant changes** were noticed in the texture.
2 ABF	**Significant changes** Average Δe: before 2.67 and after 5.55. Statistically significant. (99.07 %)	**No significant changes** Average porosity decreased: before 14.17 % and after 12.85 %. Statistically not significant. (79.60%)	

Furthermore, as previously noticed by Hupa et al., (2005)[94], when a surface is eroded, it becomes more difficult to clean. As observed, ABF leaves submicron particles on the surface and HF leaves irreversible changes in surface roughness and changes to the internal pore network. This increased roughness (i.e., surface area) will eventually cause greater soiling of the surface, which will result in the need for more frequent cleaning in the future, and probably more physico-chemical erosion of the terra cotta if HF cleaners are used. It is important to emphasize that these data and observations were obtained only on unglazed terracotta samples provided by one manufacturer, with limited amount of time available for running accelerated weathering tests. This research should be continued and extended, and further considerations should be taken:

- Additional exploration of quantification methods should be done, especially on the study of surface texture change.
- Texture mapping techniques should be further explored using polynominal mapping techniques. Samples should be coated for the Scanning Electron Microscope, in order to obtain higher quality images and to reach higher magnification.
- Longer time for weathering cycles is recommended.
- This research should also be extended to samples that have been previously weathered and soiled, possibly of historical terracotta. This will allow studying the interaction between soiling and substrate, which still leaves open questions as reported from the literature review.
- Chemical analysis of surface residues should be conducted.

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[94] Hupa L, Bergman R, Fröberg L, Vane-Tempest S, Hupa M, Kronberg, Pesonen Leinonen, E, Sjöberg, A M (2005), Chemical resistance and clean ability of glazed surfaces. Surface Science, 584, 113-118, 2005

7.0 Appendix

7.1 Material and Data sheet

MATERIAL SAFETY DATA SHEET
PROSOCO, Inc.

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME AND ADDRESS:	PROSOCO, Inc. 3741 Greenway Circle Lawrence, KS 66046	**EMERGENCY TELEPHONE NUMBERS:**	
		8:00 AM – 5:00 PM CST Monday-Friday:	785-865-4200
		NON-BUSINESS HOURS (INFOTRAC):	800/535-5053
PRODUCT TRADE NAME:	**Sure Klean® Heavy Duty Restoration Cleaner**		

II HAZARDOUS INGREDIENTS

CHEMICAL NAME	(COMMON NAME)	CAS NO.	NFPA CODE	ACGIH TLV/TWA	OHSA PEL/TWA
Glycolic Acid	(Hydroxyacetic Acid)	79-14-1	3,0,0,-	Not listed	Not listed
Hydrofluoric Acid	(Hydrogen Fluoride)	7664-39-3	4,0,1,-	3 ppm	3ppm
Nonionic Surfactant	(Nonionic Surfactant)	*	3,1,0,-	Not listed	Not listed
Orthophosphoric Acid	(Phosphoric Acid)	7664-38-2	3,0,1,-	1 mg/m^3	1 mg/m^3
B-Hydroxy-Tricarboxylic Acid, 2 Hydroxy	(Citric Acid)	77-92-9	Unknown	Not listed	Not listed

* Exact chemical identity withheld as Trade Secret pursuant to OSHA regulations.

III PHYSICAL DATA

	BOILING POINT (°F)	VAPOR PRESSURE (mm Hg)	VAPOR DENSITY (Air = 1)	EVAPORATION RATE (Butyl Acetate = 1)
Glycolic Acid	234°F	17.5 (68°F)	1.7	N/A
Hydrofluoric Acid	224°F	27 (70°F)	2.21 @ 70°F	N/A
Nonionic surfactant	360°F	< 0.01 (36°F)	> 1	< 0.01
Orthophosphoric Acid	243°F	0.0285 (36°F)	N/A	N/A
B-Hydroxy-Tricarboxylic Acid, 2 Hydroxy	> 212°F	N/A	N/A	< 1

	SPECIFIC GRAVITY	SOLIBILITY IN WATER	APPEARANCE AND ODOR
Heavy Duty Restoration Cleaner	1.132	Complete	Clear liquid with irritating odor.

IV FIRE AND EXPLOSION HAZARD DATA

EMERGENCY OVERVIEW

Sure Klean® Heavy Duty Restoration Cleaner is a highly corrosive material that may cause damage to skin, eyes and mucous membranes. Burns from this product may not be immediately painful or evident. Exposures to large skin areas may be fatal. Wear proper safety equipment to avoid exposure. Wash immediately after exposure. Exposures require fluoride specific treatment.

FLASH POINT (METHOD): Not applicable.

FLAMMABLE LIMITS: No applicable information found.

EXTINGUISHING MEDIA: No applicable information found.

SPECIAL FIRE FIGHTING PROCEDURES: Wear NIOSH/MSHA approved self-contained breathing apparatus with a full face piece operated in pressure demand or other positive pressure mode and full body protective clothing when fighting fires. Generates heat upon addition of water with possible spattering. Water may be used to keep fire-exposed containers cool until fire is out. Water or foam may cause frothing which can be violent and endanger the life of the fire fighter, especially if sprayed into containers of hot, burning liquid.

UNUSUAL FIRE AND EXPLOSION HAZARDS: Reacts with most metals to release hydrogen gas which can form explosive mixtures with air. Flammable and explosive mixtures are unlikely except in poorly ventilated or confined areas.

V HEALTH HAZARD DATA

PRIMARY ROUTES OF EXPOSURE: Skin, eyes, inhalation.

CARCINOGEN INFORMATION: Not listed (OSHA, IARC, NTP).

MEDICAL CONDITIONS AGGRAVATED BY OVEREXPOSURE: No applicable information found.

EFFECTS OF OVER EXPOSURE: Causes severe damage to eyes. Causes burns to skin. Breathing of mist or dust can damage nasal and respiratory passages. Swallowing results in damage to mucous membranes and deep tissue; can result in death on penetration to vital areas. Bronchitis, pulmonary edema and chemical pneumonitis may occur from inhalation of vapors or mists.

EYE CONTACT: Liquid or concentrated vapors can cause eye irritation, severe burns and permanent damage.

SKIN CONTACT: Vapors, mists and liquid are corrosive to the skin. Vapors will irritate the skin. Liquid and mists will burn the skin. Prolonged liquid contact will burn or destroy surrounding tissue. Exposure to large skin areas can cause potentially fatal hypocalcaemia. Burns from this product may be delayed as long as 24 hours after initial exposure.

INHALATION: Vapors and mists are corrosive to the nose, throat, and mucous membranes. Bronchitis, pulmonary edema, and chemical pneumonitis may occur. Irritation, coughing, chest pain, and difficulty in breathing may occur with brief exposure. Prolonged exposure may result in more severe irritation and tissue damage.

INGESTION: Vapors, mists, and liquid are corrosive to the mouth and throat. Swallowing the liquid burns the tissues, causes abdominal pain, nausea, vomiting and collapse. Ingestion can cause death.

EMERGENCY AND FIRST AID PROCEDURES:

EYE CONTACT: Irrigate eyes for 15-30 minutes with water, keeping eyelids apart and away from eyeballs during irrigation. Get medical attention immediately, preferably an eye specialist. If a physician is not immediately available, apply 1 or 2 drops of 0.5% Pontocaine® Hydrochloride solution followed by a second irrigation for 15 minutes. Do not use the solution described for skin treatment.

Irrigate with 1% calcium gluconate in normal saline for 1 to 2 hours to prevent or lessen corneal damage.

SKIN CONTACT: Immediately place under a safety shower or wash the burned area with a water hose. Remove all contaminated clothing while washing continuously. Keep washing with large amounts of water for 15 to 20 minutes. After washing, the burned area should be immersed in a solution of 0.13% Zephiran® Chloride. If immersion is not practical, towels should be soaked with the above solution and used as compresses for the burned area. The compresses should be changed every 2 minutes and continue until pain is relieved, up to 4 to 6 hours. Alternatively, 2.5% calcium gluconate gel may be promptly and continuously massaged into the burned area until the pain is relieved. Seek medical attention immediately for all burns.

INHALATION: Immediately remove to fresh air. If breathing is difficult, give oxygen. If not breathing, give artificial respiration, but NOT mouth-to-mouth.

INGESTION: Drink large amounts of water to dilute. **DO NOT** induce vomiting. Several glasses of milk or several ounces of milk of magnesia may be given for their soothing effect. Seek medical attention.

NOTE TO PHYSICIAN: For larger burns, if pain is not relieved by soaking in Zephiran® or by calcium gluconate gel, inject sterile 5% aqueous calcium gluconate solution subcutaneously beneath, around, and in the burned area. Initially use no more than 0.5 cc per square centimeter and do not distort appearance of skin. If pain is not completely relieved, additional treatment is indicated. (5% calcium gluconate solution may be prepared by mixing equal parts of 10% calcium gluconate solution with normal saline. For burns of large skin areas, (greater than 25 square inches), for ingestion and for significant inhalation exposure, severe systemic effects may occur. Monitor and correct for hypocalcemia, cardiac arrhythmias, hypomagnesemia and hyperkalemia. In some cases renal dialysis may be indicated. For certain burns, especially of the digits, use of intra-arterial calcium gluconate may be indicated. Use of local anesthetics is not recommend, as effectiveness of treatment is indicated by cessation of pain.

VI REACTIVITY DATA

STABILITY: Stable.

CONDITIONS TO AVOID: Contact with strong bases (alkali), can cause violent reaction generating large amounts of heat. Avoid heat, sparks, or open flame.

INCOMPATIBILITY (MATERIALS TO AVOID): Alkaline materials, metals, oxidizing materials, cyanides, sulfides, combustible materials, organic peroxides, strong reducing agents, carbides, chlorates, nitrates, picrates, fulminates and reducing materials.

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS: Carbon monoxide, carbon dioxide, hydrogen when in contact with metal. May release sulfur dioxide, hydrogen cyanide, or hydrogen sulfide.

VII SPILL OR LEAK PROCEDURES

SPILL, LEAK, WASTE DISPOSAL PROCEDURES: Provide adequate ventilation. Evacuate immediate area where concentrated fumes are present. Cleanup personnel must wear proper protective equipment. Contain spilled material with dikes, etc., and prevent runoff into ground and surface waters or into sewers.

Dilute spilled product with water to reduce fuming during cleanup work and from reaction with neutralizing substances. Spills and leaks should be neutralized by pouring dry soda ash or lime over the affected area to absorb as much liquid as possible. Allow powdered material to remain on spill for five to ten minutes and flush thoroughly with water. Neutralized material, both liquid and solid, must be recovered for proper disposal.

WASTE DISPOSAL METHODS: Recovered solids or liquids may be disposed of in a permitted waste management facility. Neutralized materials may be discharged to a sanitary sewer with approval of the receiving treatment plant. Typical pH range of 6-10 is generally considered appropriate for discharge. Consult federal, state, and/or local authorities for approved procedure. For additional information regarding handling and disposal of rinse-water, please review Technical Bulletin 200-CW "Controlled Handling of Cleaning Wastewater". Empty containers must be triple rinsed before disposal in a permitted sanitary landfill. Check local restrictions.

VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION: If you notice irritation or if air monitoring indicates concentrations above the TLV for hydrogen fluoride, wear a NIOSH approved half-mask respirator with acid vapor cartridges. Exposures to phosphoric acid above its TLV is unlikely because of its low vapor pressure. Supplied air is required for phosphoric acid exposures in excess of the TLV. A dust/mist respirator should be worn to avoid exposure to mists generated during application or removal of this product.

VENTILATION: Provide sufficient general and/or local exhaust ventilation to maintain exposure below the TLV.

PROTECTIVE CLOTHING: Wear acid-resistant neoprene or PVC rain suit and rubber boots with protective pants outside.

PROTECTIVE GLOVES: Rubber gloves with gauntlets.

EYE PROTECTION: Chemical splash goggles and/or full face shield. Do not wear contact lenses because they may contribute to the severity of an eye injury.

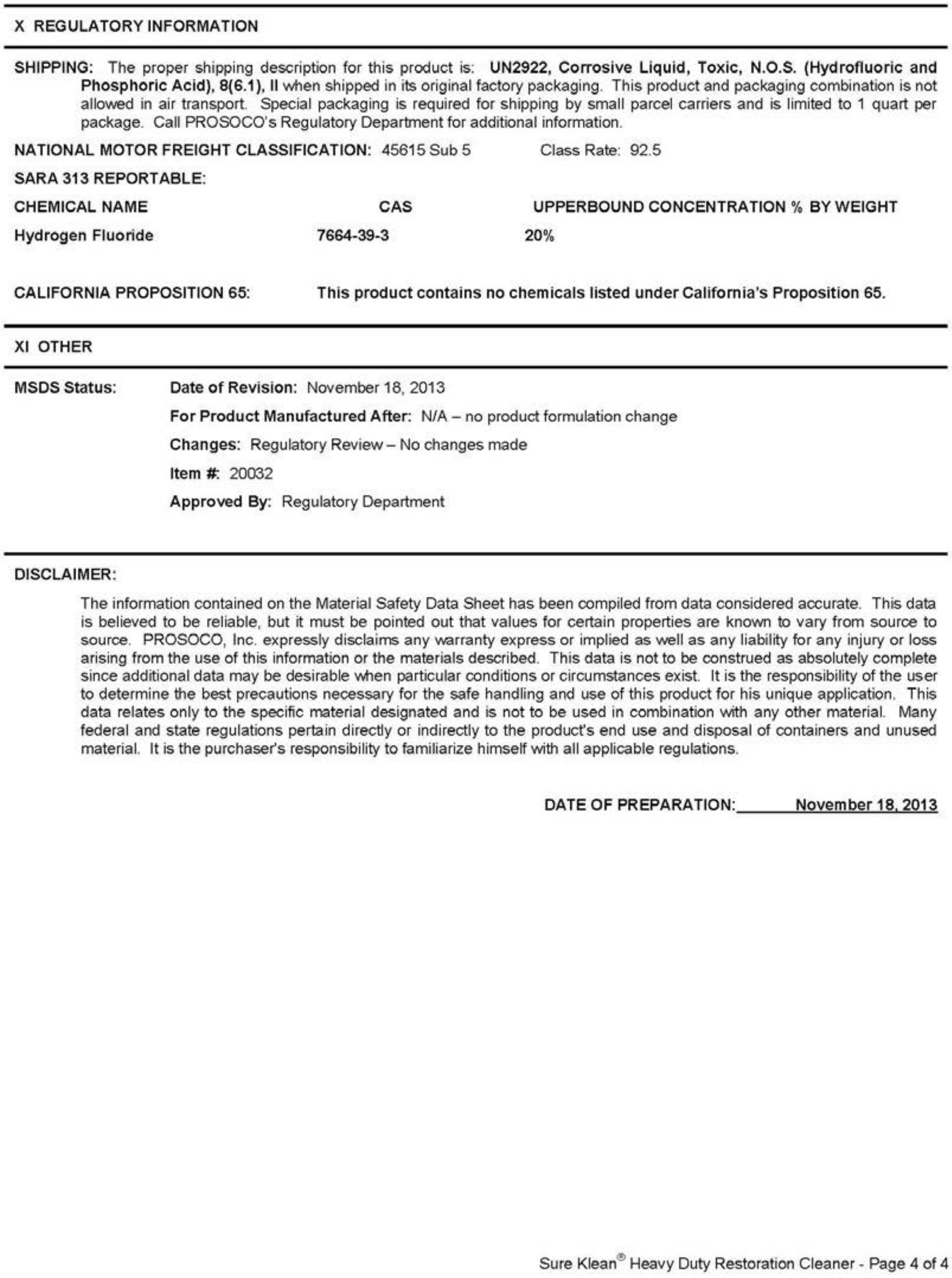
OTHER PROTECTIVE EQUIPMENT: An eyewash and safety shower should be nearby and ready for use.

IX SPECIAL PRECAUTIONS

WORK PRACTICES: Proper work practices and planning should be utilized to avoid contact with workers, passersby, and non-masonry surfaces. Do not atomize during application. Beware of wind drift. Wind-drift hazards may be diminished by pre-rinsing with low-pressure water before pressure washing. Divert pedestrian traffic around work areas. See the Product Data sheet and label for specific precautions to be taken during use. Smoking, eating and drinking should be discouraged during the use of this product. Wash hands after handling or use.

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE: Use proper safety equipment (see section VIII) when handling. Store in a cool, well-ventilated area. Separate from oxidizing agents, nitric acid, alkalis, chlorates, sulfides, etc. (see section VI). Store in proper acid-resistant containers such as rubber-lined steel, glass, or plastic. Emptied containers retain product residues (vapor, liquid, and/or solid). All hazard precautions given in this data sheet must be observed.

OTHER PRECAUTIONS: Do not get in eyes, on skin or on clothing. Can cause injury or blindness. Avoid breathing mist or vapor. Provide ventilation sufficient to limit employee exposure below OSHA permissible limit. Do not take internally. Wash thoroughly after handling. Empty containers should be treated as if they were full.



X REGULATORY INFORMATION

SHIPPING: The proper shipping description for this product is: **UN2922, Corrosive Liquid, Toxic, N.O.S. (Hydrofluoric and Phosphoric Acid), 8(6.1), II** when shipped in its original factory packaging. This product and packaging combination is not allowed in air transport. Special packaging is required for shipping by small parcel carriers and is limited to 1 quart per package. Call PROSOCO's Regulatory Department for additional information.

NATIONAL MOTOR FREIGHT CLASSIFICATION: 45615 Sub 5 Class Rate: 92.5

SARA 313 REPORTABLE:

CHEMICAL NAME	**CAS**	**UPPERBOUND CONCENTRATION % BY WEIGHT**
Hydrogen Fluoride	**7664-39-3**	**20%**

CALIFORNIA PROPOSITION 65: **This product contains no chemicals listed under California's Proposition 65.**

XI OTHER

MSDS Status: **Date of Revision:** November 18, 2013

For Product Manufactured After: N/A – no product formulation change

Changes: Regulatory Review – No changes made

Item #: 20032

Approved By: Regulatory Department

DISCLAIMER:

The information contained on the Material Safety Data Sheet has been compiled from data considered accurate. This data is believed to be reliable, but it must be pointed out that values for certain properties are known to vary from source to source. PROSOCO, Inc. expressly disclaims any warranty express or implied as well as any liability for any injury or loss arising from the use of this information or the materials described. This data is not to be construed as absolutely complete since additional data may be desirable when particular conditions or circumstances exist. It is the responsibility of the user to determine the best precautions necessary for the safe handling and use of this product for his unique application. This data relates only to the specific material designated and is not to be used in combination with any other material. Many federal and state regulations pertain directly or indirectly to the product's end use and disposal of containers and unused material. It is the purchaser's responsibility to familiarize himself with all applicable regulations.

DATE OF PREPARATION: **November 18, 2013**

MATERIAL SAFETY DATA SHEET
PROSOCO, Inc.

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME AND ADDRESS:	PROSOCO, Inc. 3741 Greenway Circle Lawrence, KS 66046	**EMERGENCY TELEPHONE NUMBERS:** **8:00 AM – 5:00 PM CST Monday-Friday:** **NON-BUSINESS HOURS (INFOTRAC):**	 785/865-4200 800/535-5053

PRODUCT TRADE NAME: **Enviro Klean® EK Restoration Cleaner**

II HAZARDOUS INGREDIENTS

CHEMICAL NAME	(COMMON NAME)	CAS NO.	NFPA CODE	ACGIH TLV/TWA	OSHA PEL/TWA
Glycolic Acid	(Hydroxyacetic Acid)	79-14-1	3,0,0,-	Not listed	Not listed
Ammonium Bifluoride	(Ammonium Difluoride)	1341-49-7	3,0,2,-	2.5 mg(F)/m3	2.5 mg(F)/m3
Cocoamido Betaine	Betaine Derivative	61789-40-0	1,1,0,-	Not listed	Not listed
Lauryl Dimethyl Amine Oxide	Amine Oxide	1643-20-5	1,1,0,-	Not listed	Not listed

III PHYSICAL DATA

	BOILING POINT (°F)	VAPOR PRESSURE (mm Hg)	VAPOR DENSITY (Air = 1)	EVAPORATION RATE (Butyl Acetate = 1)
Glycolic Acid	212°F	17.5 (68°F)	N/D	N/D
Ammonium Bifluoride	464°F	N/A	N/A	N/A
Cocoamido Betaine	212°F	N/D	<1	< ethyl ether (estimated)
Lauryl Dimethyl Amine Oxide	212°F	N/D	<1	< ethyl ether (estimated)

	SPECIFIC GRAVITY	pH	SOLUBILITY IN WATER	APPEARANCE AND ODOR
EK Restoration Cleaner	1.06	5.5	Complete	Clear amber liquid, mild odor

IV FIRE AND EXPLOSION HAZARD DATA

EMERGENCY OVERVIEW

Danger! Enviro Klean® EK Restoration Cleaner may be fatal if swallowed. Product affects respiratory system, heart, skeleton, circulatory system, central nervous system and kidneys. Causes irritation and burns to skin, eyes and respiratory tract. Irritation and burn effects may be delayed. Harmful if absorbed through skin. Near neutral pH of the product limits initial acute injuries, however, untreated exposures may cause fluoride type burns. Large-scale contacts or ingestion may cause systemic fluoride poisoning. Avoid atomizing during application. Contact with metals in poorly ventilated spaces may generate dangerous concentrations of hydrogen gas.

FLASH POINT (METHOD): no data

FLAMMABLE LIMITS: No applicable information found.

EXTINGUISHING MEDIA: As appropriate for combustibles in area.

SPECIAL FIRE FIGHTING PROCEDURES: Wear NIOSH/MSHA approved self-contained breathing apparatus with a full face piece operated in pressure demand or other positive pressure mode and full body protective clothing when fighting fires. Toxic emissions may be released if this product is involved in a fire.

UNUSUAL FIRE AND EXPLOSION HAZARDS: Contact with metal may evolve flammable hydrogen gas. Hydrogen fluoride gas and ammonia may be released if product is involved in a fire.

V HEALTH HAZARD DATA

PRIMARY ROUTES OF EXPOSURE: Skin, eyes, inhalation.

CARCINOGEN INFORMATION: Not listed (OSHA, IARC, NTP).

EFFECTS OF OVER EXPOSURE: Causes severe damage to eyes. Causes burns to skin. Breathing of mist can damage nasal and respiratory passages. Swallowing results in damage to mucous membranes and deep tissue; can result in death on penetration to vital areas. Bronchitis, pulmonary edema and chemical pneumonitis may occur from inhalation of vapors or mists. This product can cause fluoride poisoning.

EYE CONTACT: May be extremely irritating with possible burnsto eye tissue and permanent eye damage may result. Eye contact may also cause eye corrosion with corneal or conjunctival ulceration.

SKIN CONTACT: Prolonged or incidental contact can causes irritation, burns,and ulceration to the skin. Effects may not appear immediately.

INHALATION: Vapors and mists may cause irritation and burns to respiratory tract, symptoms may include coughing, sore throat, and labored breathing. May be absorbed through inhalation of mist, symptoms may parallel those from ingestion exposure. Irritation and burning effects may not appear immediately.

INGESTION: May cause salivation, nausea, vomiting, diarrhea, and abdominal pain, followed by symptoms of weakness, tremors shallow respiration, carpopedal spasm, convulsions, and coma. May cause brain and kidney damage. Affects heart and circulatory system. Death may be caused by respiratory paralysis.

CHRONIC EXPOSURE: Chronic exposure may cause mottling of teeth and bone damage (osteosclerosis) and fluorosis. Symptoms of fluorosis include brittle bones, weight loss, anemia, calcified ligaments, general ill health and joint stiffness.

AGGRAVATION OF PRE-EXISTING CONDITIONS: Populations that appear to be at risk from the effects of fluoride are individuals that suffer from diabetes insipidus or some forms of renal impairment.

EMERGENCY AND FIRST AID PROCEDURES: First aid procedures should be pre-planned for fluoride compound emergencies.

EYE CONTACT: Immediately flush eyes with gentle but large stream of water for at least 15 minutes, lifting lower and upper eyelids occasionally. GET MEDICAL ATTENTION IMMEDIATELY- Preferably an eye specialist. Irrigate with 1% calcium gluconate in normal saline for 1-2 hours.

SKIN CONTACT: Immediately flush skin with large amounts of water for a minimum of 15 minutes. Remove contaminated clothing and shoes. Wash clothing before re-use. Promptly apply a 2.5% calcium gluconate gel and continuously massage into the skin until pain is relieved. Symptoms of exposure may not show up immediately. CALL A PHYSICIAN IMMEDIATELY.

INHALATION: If suffering inhalation symptoms such as mouth or respiratory irritation remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. CALL A PHYSICIAN IMMEDIATELY.

INGESTION: DO NOT INDUCE VOMITTING. Administer milk, chewable calcium carbonate tablets or milk of magnesia. Never give anything by mouth to an unconscious person. CALL A PHYSICIAN IMMEDIATELY.

NOTE TO PHYSICIAN: Treat as appropriate for symptoms of fluoride exposure and monitor for systemic fluoride poisoning. Symptoms may be delayed up to 24 hours. For ingestion and exposures over large areas of skin, system effects (hypocalcaemia and hypomagnesia) may occur. Monitor and correct for hypocalcaemia, cardiac arrhythmias, hypomagnesemia and hyperkalemia.

VI REACTIVITY DATA

STABILITY: stable under ordinary conditions of use and storage.

CONDITIONS TO AVOID: Extreme temperatures, as well as contact with strong acids and strong bases.

INCOMPATIBILITY (MATERIALS TO AVOID): Reacts with acids to liberate hydrogen fluoride and base to liberate ammonia. Will corrode glass, cement, and most metals.

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS: Emits toxic fumes of hydrogen fluoride, nitric oxides, and ammonia when heated to decomposition. Upon contact with metal, this material may release hydrogen gas.

HAZARDOUS POLYMERIZATION: Will not occur.

VII SPILL OR LEAK PROCEDURES

SPILL, LEAK, WASTE DISPOSAL PROCEDURES: Provide adequate ventilation. Evacuate immediate area where concentrated fumes are present. Clean up personnel must wear proper protective equipment. Contain spilled material with dikes, etc., and prevent runoff into ground and surface waters or into sewers.

Spills and leaks should be diluted with copious quantities of water and neutralized by adding dry soda ash or lime over the affected area to adjust pH as needed. Allow powdered material to remain on spill for five to ten minutes and flush thoroughly with water. Neutralized material, both liquid and solid, should be recovered for proper disposal.

WASTE DISPOSAL METHODS: Neutralized materials may be discharged to a sanitary sewer with approval of local sewerage authorities. Product as supplied has a pH of 5.5 and meets pretreatment standards in most regions, although minor pH adjustment may be required depending on local restrictions. The primary active ingredient, ammonium bifluoride, is commonly used as an additive source of fluoride in drinking water supplies. Recovered solids or liquids may be sent to a licensed reclaimer or disposed of in a permitted waste management facility. Consult federal, state, and/or local authorities for approved procedure.

NOTE: Empty containers must be triple rinsed with water before disposal in a sanitary landfill. Neutralize rinse water before disposal.

VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION: The ingredients in this product have low vapor pressures and are not likely to contribute to airborne exposures unless heated or atomized. Some ammonia may be liberated during the product dwell time on the substrate. If the exposure limit for fluoride is exceeded, a NIOSH approved half-mask respirator with acid gas cartridges may be worn for up to ten times the exposure limit. For ammonia, use a half-mask respirator with ammonia specific cartridges. For emergencies or instances where the exposure levels are not known, use a full-face piece positive-pressure, air-supplied respirator. Use a NIOSH approved dust/mist respirator whenever mists are present to avoid respiratory tract exposure. **NOTE:** Fluoride is considered to have good warning properties and has odor and irritation thresholds below 1 ppm in air.

VENTILATION: A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

PROTECTIVE CLOTHING: Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact.

PROTECTIVE GLOVES: Rubber or neoprene gloves.

EYE PROTECTION: Use chemical splash resistant safety goggles and/or full-face shield. Maintain eye wash fountain and quick-drench facilities in work area.

OTHER PROTECTIVE EQUIPMENT: An eyewash and safety shower should be nearby and ready for use.

IX SPECIAL PRECAUTIONS

WORK PRACTICES: Proper work practices and planning should be utilized to avoid contact with workers, passersby, and non-masonry surfaces. Application equipment should be of acid resistant construction. Do not atomize during application. Beware of wind drift. Pre-rinsing with low pressure prior to pressure washing helps minimize wind drift concerns. See the Product Data sheet and label for specific precautions to be taken during use. Smoking, eating and drinking should be prohibited during the use of this product. Wash hands before breaks and at the end of a shift. Do not alter, dilute or use the product for purposes other than specified.

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE: Keep in tightly closed container. Store in cool, dry ventilated area. Protect against physical damage. Separate from acids and alkalis. Do not store in metal containers, as contact with moisture and metal at the same time may release flammable hydrogen gas. Containers of this material may be hazardous when empty since they retain product residues; observe all warnings and precautions listed for the product.

OTHER PRECAUTIONS: Do not get in eyes, on skin or on clothing. Can cause injury or blindness. Avoid breathing mist or vapor. Provide ventilation sufficient to limit employee exposure below OSHA permissible limit. Do not take internally. Wash thoroughly after handling. Empty containers should be treated as if they were full.

X REGULATORY INFORMATION

SHIPPING: This product carries the proper shipping description **UN2922, Corrosive Liquid, Toxic, N.O.S. (Ammonium Bifluoride And Hydroxyacetic Acid), 8(6.1), III** in domestic or international shipment.

NATIONAL MOTOR FREIGHT CLASSIFICATION: NMFC #: 45615 Sub 5 Class Rate: 92.5

SARA 313 REPORTABLE:

CHEMICAL NAME	CAS	UPPERBOUND CONCENTRATION % BY WEIGHT
Not applicable		

CALIFORNIA PROPOSITION 65: Contains no chemicals listed under California's Proposition 65.

XI OTHER

MSDS Status: **Date of Revision:** June 25, 2013

For Product Manufactured After: N/A – no change in formulation.

Changes: Updated "Appearance and Odor" in Section III. Product is a liquid, not a gel.

Item #: 41006

Approved By: Regulatory Department

DISCLAIMER:

The information contained on the Material Safety Data Sheet has been compiled from data considered accurate. This data is believed to be reliable, but it must be pointed out that values for certain properties are known to vary from source to source. PROSOCO, Inc. expressly disclaims any warranty express or implied as well as any liability for any injury or loss arising from the use of this information or the materials described. This data is not to be construed as absolutely complete since additional data may be desirable when particular conditions or circumstances exist. It is the responsibility of the user to determine the best precautions necessary for the safe handling and use of this product for his unique application. This data relates only to the specific material designated and is not to be used in combination with any other material. Many federal and state regulations pertain directly or indirectly to the product's end use and disposal of containers and unused material. It is the purchaser's responsibility to familiarize himself with all applicable regulations.

DATE OF PREPARATION: **June 25, 2013**

7.2 Rilem VB Salt Test

TEST Nº V.1b

CRYSTALLISATION TEST BY TOTAL IMMERSION
(FOR TREATED STONE)

1.- DEFINITION OF MEASURED PROPERTY

Resistance to a test that closely simulates the crystallisation phenomena occuring under natural environmental conditions.

2.- AIM

The destruction effect of sodium sulphate, filling the pore space of porous material, is used in the test : it is based on the volume increase during recrystallisation from Na_2SO_4 to $Na_2SO_4 \cdot 10\ H_2O$ in water solution at a temperature of 32.7°C.

3.- APPLICATION

Crystallisation test by total immersion is a laboratory test preferable for stone samples treated by impregnation.

This is a accelerated weathering test to assess the resistance to weathering agents, especially to damage caused by salts, of impregnated stones in comparison with the same kind of stone without impregnation. The test is also useful for showing the behaviour during weathering of the contact zone between the impregnated surface layer and the mass of the stone not reached by the impregnation.

4.- TEST METHOD

4.1 - Sample preparation

4.1.1. Number and dimensions of samples

A representative number of stone specimens for every type of impregnation under test and of reference specimens without impregnation of the same kind of stone have to be prepared. Cube with 50 mm sides should be used as standard size. If samples of other (larger) dimensions (for example : when the impregnation zone is very deep) are used, this has to be recorded in the test report.

4.1.2. Method of impregnation

For cases that the impregnation material under test is applied to the stone specimens in the laboratory the following method of impregnation should be used : the dry test cubes are impregnated on their four vertical planes for example by brushing. In cases of stones with bedding, the bedding has to be orientated vertically, i.e. two of the impregnated cube planes are parallel and two are across the bedding. The impregnation of the cubes on only four sides, leaving the bottom and top free of impregnation, guarantees the same degree of salt soaking for all test specimens, independent of the hydrophobic or highly pre-filling properties of the impregnation under test. It also imitates the conditions in impregnated facades, where soluble salts are present in the walls, attacking the impregnated surface from behind.

The test procedure should not be started sooner than four weeks after impregnation.

4.1;3. Drying of samples

The samples are dried at 60° ± 5°Ctill constant mass. The constant mass is reached when the difference between two successive weighings (at a time interval of 24 h) is not more than 0.1 % of the mass of the sample, determined with an accuracy of 0.01% of this mass. The samples are cooled at room temperature.

The drying temperature of 60° C ± 5° C is chosen instead of a higher one in order to avoid deterioration of the organic materials used to treat the stone.

4.2 - Test Procedure

During the test procedure cycles of soaking the samples in salt solution and drying them are repeated. A test cycle consists of :

- immersion in 10 % Na_2SO_4 solution for 2 hours
- drying on a preheated oven at 60° C for 19 hours*
- cooling to 20°C within 3 hours
- control weighing after every second cycle

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* in the case of very fine grained stones, a longer drying period may be necessary.

The test cycle is repeated 15 times or until a nearly complete destruction of the samples is achieved. After the final cycle, the salt is removed from the samples by 7 day immersion in often renewed tap water. The samples then are dried at 60° C to constant weight for determination of the final weight at 20°C.

5.- EXPRESSION AND INTERPRETATION OF RESULTS

The relative resistance of the samples is expressed as their loss of weight after 15 test cycles or as the number of cycles required for their complete destruction. The loss of weight of the samples is calculated as the difference between their initial weight and their final weight as a percentage of their initial weight.

More informative in particular is the process of the sample destruction during the test. It can be recorded in diagrams; the loss of weight of the specimens after every weight - controlled cycle expressed as a percentage of their initial weight is plotted against the respective number of the test cycles. Results obtained in separate test series can only be compared if the sample dimensions and the drying and soaking temperature have been the same. An additionnal visual and photographic recording of the kind of damages of the samples during the test, especially of damages in the impregnation zones and in the interface to the unimpregnated part of the stone (for example the flaking off of the impregnation zone) can be used as important hints to assess the behaviour of the different impregnations applied to stone materials under test.

7.3 ASTM G54:2012

Designation: G154 − 12a

Standard Practice for
Operating Fluorescent Ultraviolet (UV) Lamp Apparatus for Exposure of Nonmetallic Materials[1]

This standard is issued under the fixed designation G154; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This practice covers the basic principles and operating procedures for using fluorescent UV light, and water apparatus intended to reproduce the weathering effects that occur when materials are exposed to sunlight (either direct or through window glass) and moisture as rain or dew in actual usage. This practice is limited to the procedures for obtaining, measuring, and controlling conditions of exposure. A number of exposure procedures are listed in an appendix; however, this practice does not specify the exposure conditions best suited for the material to be tested.

NOTE 1—Practice G151 describes performance criteria for all exposure devices that use laboratory light sources. This practice replaces Practice G53, which describes very specific designs for devices used for fluorescent UV exposures. The apparatus described in Practice G53 is covered by this practice.

1.2 Test specimens are exposed to fluorescent UV light under controlled environmental conditions. Different types of fluorescent UV light sources are described.

1.3 Specimen preparation and evaluation of the results are covered in ASTM methods or specifications for specific materials. General guidance is given in Practice G151 and ISO 4892-1. More specific information about methods for determining the change in properties after exposure and reporting these results is described in ISO 4582.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.6 This standard is technically similar to ISO 4892-3 and ISO DIS 11507.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3980 Practice for Interlaboratory Testing of Paint and Related Materials (Withdrawn 1998)[3]

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

G53 Practice for Operating Light-and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials (Withdrawn 2000)[3]

G113 Terminology Relating to Natural and Artificial Weathering Tests of Nonmetallic Materials

G151 Practice for Exposing Nonmetallic Materials in Accelerated Test Devices that Use Laboratory Light Sources

2.2 *CIE Standard:*

CIE-Publ. No. 85: Recommendations for the Integrated Irradiance and the Spectral Distribution of Simulated Solar Radiation for Testing Purposes[4]

2.3 *ISO Standards:*

ISO 4582 Plastics—Determination of the Changes of Colour and Variations in Properties After Exposure to Daylight Under Glass, Natural Weathering or Artificial Light[5]

ISO 4892-1 Plastics—Methods of Exposure to Laboratory Light Sources, Part 1, Guidance[5]

ISO 4892-3 Plastics—Methods of Exposure to Laboratory Light Sources, Part 3, Fluorescent UV lamps[5]

ISO DIS 11507 Paint and Varnishes—Exposure of Coatings to Artificial Weathering in Apparatus—Exposure to Fluorescent Ultraviolet and Condensation Apparatus[5]

3. Terminology

3.1 *Definitions*—The definitions given in Terminology G113 are applicable to this practice.

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[1] This practice is under the jurisdiction of ASTM Committee G03 on Weathering and Durabilityand is the direct responsibility of Subcommittee G03.03 on Simulated and Controlled Exposure Tests.

Current edition approved Dec. 15, 2012. Published December 2012. Originally approved in 1997. Last previous edition approved in 2006 as G154 – 06. DOI: 10.1520/G0154-12a.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from Secretary, U.S. National Committee, CIE, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899.

[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

***A Summary of Changes section appears at the end of this standard**

3.2 *Definitions of Terms Specific to This Standard*—As used in this practice, the term *sunlight* is identical to the terms *daylight* and *solar irradiance, global* as they are defined in Terminology G113.

3.2.1 *Fluorescent Ultraviolet (UV) Apparatus*—An apparatus for performing exposure tests using fluorescent UV lamps as the light source.

4. Summary of Practice

4.1 Specimens are exposed to repetitive cycles of light and moisture under controlled environmental conditions.

4.1.1 Moisture is usually produced by condensation of water vapor onto the test specimen or by spraying the specimens with demineralized/deionized water.

4.2 The exposure condition may be varied by selection of:

4.2.1 The fluorescent lamp,

4.2.2 The lamp's irradiance level,

4.2.3 The type of moisture exposure,

4.2.4 The timing of the light and moisture exposure,

4.2.5 The temperature of light exposure, and

4.2.6 The temperature of moisture exposure, and

4.2.7 The timing of a light/dark cycle.

4.3 Comparison of results obtained from specimens exposed in same model of apparatus should not be made unless reproducibility has been established among devices for the material to be tested.

4.4 Comparison of results obtained from specimens exposed in different models of apparatus should not be made unless correlation has been established among devices for the material to be tested.

5. Significance and Use

5.1 The use of this apparatus is intended to induce property changes associated with the end use conditions, including the effects of the UV portion of sunlight, moisture, and heat. These exposures may include a means to introduce moisture to the test specimen. Exposures are not intended to simulate the deterioration caused by localized weather phenomena, such as atmospheric pollution, biological attack, and saltwater exposure. Alternatively, the exposure may simulate the effects of sunlight through window glass. Typically, these exposures would include moisture in the form of condensing humidity.

NOTE 2—**Caution:** Refer to Practice G151 for full cautionary guidance applicable to all laboratory weathering devices.

5.2 Variation in results may be expected when operating conditions are varied within the accepted limits of this practice. Therefore, no reference shall be made to results from the use of this practice unless accompanied by a report detailing the specific operating conditions in conformance with the Section 10.

5.2.1 It is recommended that a similar material of known performance (a control) be exposed simultaneously with the test specimen to provide a standard for comparative purposes. It is recommended that at least three replicates of each material evaluated be exposed in each test to allow for statistical evaluation of results.

6. Apparatus

6.1 *Laboratory Light Source*—The light source shall be fluorescent UV lamps. A variety of fluorescent UV lamps can be used for this procedure. Differences in lamp intensity or spectrum may cause significant differences in test results. A detailed description of the type(s) of lamp(s) used should be stated in detail in the test report. The particular testing application determines which lamp should be used. See Appendix X1 for lamp application guidelines.

NOTE 3—Do not mix different types of lamps. Mixing different types of lamps in a fluorescent UV light apparatus may produce major inconsistencies in the light falling on the samples, unless the apparatus has been specifically designed to ensure a uniform spectral distribution.

NOTE 4—Many fluorescent lamps age significantly with extended use. Follow the apparatus manufacturer's instructions on the procedure necessary to maintain desired irradiance (1,2).

6.1.1 Actual irradiance levels at the test specimen surface may vary due to the type or manufacturer of the lamp used, or both, the age of the lamps, the distance to the lamp array, and the air temperature within the chamber and the ambient laboratory temperature. Consequently, the use of a radiometer to monitor and control the radiant energy is recommended.

6.1.2 Several factors can affect the spectral power distribution of fluorescent UV lamps:

6.1.2.1 Aging of the glass used in some types of lamps can result in changes in transmission. Aging of glass can result in a significant reduction in the short wavelength UV emission of some lamp types,

6.1.2.2 Accumulation of dirt or other residue on lamps can affect irradiance,

6.1.2.3 Thickness of glass used for lamp tube can have large effects on the amount of short wavelength UV radiation transmitted, and

6.1.2.4 Uniformity and durability of phosphor coating.

6.1.3 *Spectral Irradiance:*

NOTE 5—Fluorescent UVA lamps are available with a choice of spectral power distributions that vary significantly. The more common may be identified as UVA-340 and UVA-351. These numbers represent the characteristic nominal wavelength (in nm) of peak emission for each of these lamp types. The actual peak emissions are at 343 and 350 nm, respectively.

6.1.3.1 *Spectral Irradiance of UVA-340 Lamps for Daylight UV*—The spectral power distribution of UVA-340 fluorescent lamps shall comply with the requirements specified in Table 1.

NOTE 6—The main application for UVA-340 lamps is for simulation of the short and middle UV wavelength region of daylight.

6.1.3.2 *Spectral Irradiance of UVA-351 Lamps for Daylight UV Behind Window Glass*—The spectral power distribution of UVA-351 lamp for Daylight UV behind Window Glass shall comply with the requirements specified in Table 2.

NOTE 7—The main application for UVA-351 lamps is for simulation of the short and middle UV wavelength region of daylight which has been filtered through window glass (3).

6.1.3.3 *Spectral Irradiance of UVB-313 Lamps*—The spectral power distribution of UVB-313 fluorescent lamps shall comply with the requirements specified in Table 3.

NOTE 8—Fluorescent UVB lamps have the spectral distribution of

TABLE 1 Relative Ultraviolet Spectral Power Distribution Specification for Fluorescent UVA-340 Lamps for Daylight UV[A,B]

Spectral Bandpass Wavelength λ in nm	Minimum Percent[C]	Benchmark Solar Radiation Percent[D,E,F]	Maximum Percent[C]
$\lambda < 290$			0.01
$290 \le \lambda \le 320$	5.9	5.8	9.3
$320 < \lambda \le 360$	60.9	40.0	65.5
$360 < \lambda \le 400$	26.5	54.2	32.8

[A] Data in Table 1 are the irradiance in the given bandpass expressed as a percentage of the total irradiance from 290 to 400 nm. The manufacturer is responsible for determining conformance to Table 1. Annex A1 states how to determine relative spectral irradiance.

[B] The data in Table 1 are based on the rectangular integration of 65 spectral power distributions for fluorescent UV devices operating with UVA 340 lamps of various lots and ages. The spectral power distribution data is for lamps within the aging recommendations of the device manufacturer. The minimum and maximum data are at least the three sigma limits from the mean for all measurements.

[C] The minimum and maximum columns will not necessarily sum to 100 % because they represent the minimum and maximum for the data used. For any individual spectral power distribution, the calculated percentage for the bandpasses in Table 1 will sum to 100 %. For any individual fluorescent UVA-340 lamp, the calculated percentage in each bandpass must fall within the minimum and maximum limits of Table 1. Test results can be expected to differ between exposures using devices with fluorescent UVA-340 lamps in which the spectral power distributions differ by as much as that allowed by the tolerances. Contact the manufacturer of the fluorescent UV devices for specific spectral power distribution data for the fluorescent UVA-340 lamp used.

[D] The benchmark solar radiation data is defined in ASTM G177 and is for atmospheric conditions and altitude chosen to maximize the fraction of short wavelength solar UV. While this data is provided for comparison purposes only, it is desirable for the laboratory accelerated light source to provide a spectrum that is a close match to the benchmark solar spectrum.

[E] Previous versions of this standard used solar radiation data from Table 4 of CIE Publication Number 85. See Appendix X3 for more information comparing the solar radiation data used in this standard with that for CIE 85 Table 4.

[F] For the benchmark daylight spectrum, the UV irradiance (290 to 400 nm) is 9.8 % and the visible irradiance (400 to 800 nm) is 90.2 % expressed as a percentage of the total irradiance from 290 to 800 nm. Because the primary emission of fluorescent UV lamps is concentrated in the 300 to 400 nm bandpass, there are limited data available for visible light emissions of fluorescent UV lamps.

TABLE 2 Relative Spectral Power Distribution Specification for Fluorescent UVA-351 Lamps for Daylight UV Behind Window Glass[A,B]

Spectral Bandpass Wavelength λ in nm	Minimum Percent[C]	Window Glass Filtered Daylight Percent[D,E,F]	Maximum Percent[C]
$\lambda < 300$		0.0	0.2
$300 \le \lambda \le 320$	1.1	≤ 0.5	3.3
$320 < \lambda \le 360$	60.5	34.2	66.8
$360 < \lambda \le 400$	30.0	65.3	38.0

[A] Data in Table 2 are the irradiance in the given bandpass expressed as a percentage of the total irradiance from 300 to 400 nm. The manufacturer is responsible for determining conformance to Table 1. Annex A1 states how to determine relative spectral irradiance.

[B] The data in Table 2 are based on the rectangular integration of 21 spectral power distributions for fluorescent UV devices operating with UVA 351 lamps of various lots and ages. The spectral power distribution data is for lamps within the aging recommendations of the device manufacturer. The minimum and maximum data are at least the three sigma limits from the mean for all measurements.

[C] The minimum and maximum columns will not necessarily sum to 100 % because they represent the minimum and maximum for the data used. For any individual spectral power distribution, the calculated percentage for the bandpasses in Table 2 will sum to 100 %. For any individual fluorescent UV device operating with UVA 351 lamps, the calculated percentage in each bandpass must fall within the minimum and maximum limits of Table 2. Test results can be expected to differ between exposures using fluorescent UV devices in which the spectral power distributions differ by as much as that allowed by the tolerances. Contact the manufacturer of the fluorescent UV devices for specific spectral power distribution data for the lamps used.

[D] The window glass filtered solar radiation data is for a solar spectrum with atmospheric conditions and altitude chosen to maximize the fraction of short wavelength solar UV (defined in ASTM G177) that has been filtered by window glass. The glass transmission is the average for a series of single strength window glasses tested as part of a research study for ASTM Subcommittee G3.02.[6] While this data is provided for comparison purposes only, it is desirable for the laboratory accelerated light source to provide a spectrum that is a close match to this benchmark window glass filtered solar spectrum.

[E] Previous versions of this standard used window glass filtered solar radiation data based on Table 4 of CIE Publication Number 85. See Appendix X3 for more information comparing the solar radiation data used in the standard with that for CIE 85 Table 4.

[F] For the benchmark window glass filtered solar spectrum, the UV irradiance (300 to 400 nm) is 8.2 % and the visible irradiance (400 to 800 nm) is 91.8 % expressed as a percentage of the total irradiance from 300 to 800 nm. Because the primary emission of fluorescent UV lamps is concentrated in the 300 to 400 nm bandpass, there are limited data available for visible light emissions of fluorescent UV lamps.

radiation peaking near the 313-nm mercury line. They emit significant amounts of radiation below 300 nm, the nominal cut on wavelength of global solar radiation, that may result in aging processes not occurring outdoors. Use of this lamp is not recommended for sunlight simulation. See Table 3.

6.2 *Test Chamber*—The design of the test chamber may vary, but it should be constructed from corrosion resistant material and, in addition to the radiant source, may provide for means of controlling temperature and relative humidity. When required, provision shall be made for the spraying of water on the test specimen for the formation of condensate on the exposed face of the specimen or for the immersion of the test specimen in water.

6.2.1 The radiant source(s) shall be located with respect to the specimens such that the uniformity of irradiance at the specimen face complies with the requirements in Practice G151.

6.2.2 Lamp replacement, lamp rotation, and specimen repositioning may be required to obtain uniform exposure of all specimens to UV radiation and temperature. Follow manufacturer's recommendation for lamp replacement and rotation.

6.3 *Instrument Calibration*—To ensure standardization and accuracy, the instruments associated with the exposure apparatus (for example, timers, thermometers, wet bulb sensors, dry bulb sensors, humidity sensors, UV sensors, and radiometers) require periodic calibration to ensure repeatability of test results. Whenever possible, calibration should be traceable to national or international standards. Calibration schedule and procedure should be in accordance with manufacturer's instructions.

6.4 *Radiometer*—The use of a radiometer to monitor and control the amount of radiant energy received at the sample is recommended. If a radiometer is used, it shall comply with the requirements in Practice G151.

6.5 *Thermometer*—Either insulated or un-insulated black or white panel thermometers may be used. The un-insulated thermometers may be made of either steel or aluminum. Thermometers shall conform to the descriptions found in Practice G151.

6.5.1 The thermometer shall be mounted on the specimen rack so that its surface is in the same relative position and subjected to the same influences as the test specimens.

TABLE 3 Relative Spectral Power Distribution Specification for Fluorescent UVB 313 lamps[A,B]

Spectral Bandpass Wavelength λ in nm	Minimum Percent[C]	Benchmark Solar Radiation Percent[D,E,F]	Maximum Percent[C]
$\lambda < 290$	1.3		5.4
$290 \leq \lambda \leq 320$	47.8	5.8	65.9
$320 < \lambda \leq 360$	26.9	40.0	43.9
$360 < \lambda \leq 400$	1.7	54.2	7.2

[A] Data in Table 3 are the irradiance in the given bandpass expressed as a percentage of the total irradiance from 250 to 400 nm. The manufacturer is responsible for determining conformance to Table 3. Annex A1 states how to determine relative spectral irradiance.

[B] The data in Table 3 are based on the rectangular integration of 44 spectral power distributions for fluorescent UV devices operating with UVB 313 lamps of various lots and ages. The spectral power distribution data is for lamps within the aging recommendations of the device manufacturer. The minimum and maximum data are at least the three sigma limits from the mean for all measurements.

[C] The minimum and maximum columns will not necessarily sum to 100 % because they represent the minimum and maximum for the data used. For any individual spectral power distribution, the calculated percentage for the bandpasses in Table 3 will sum to 100 %. For any individual UVB 313 lamp, the calculated percentage in each bandpass must fall within the minimum and maximum limits of Table 3. Test results can be expected to differ between exposures conducted in fluorescent UV devices using UVB 313 lamps in which the spectral power distributions differ by as much as that allowed by the tolerances. Contact the manufacturer of the fluorescent UV device for specific spectral power distribution data for the device operated with the UVB 313 lamp used.

[D] The benchmark solar radiation data is defined in ASTM G177 and is for atmospheric conditions and altitude chosen to maximize the fraction of short wavelengthsolar UV. This data is provided for comparison purposes only.

[E] Previous versions of this standard used solar radiation data from Table 4 of CIE Publication Number 85. See Appendix X3 for more information comparing the solar radiation data used in this standard with that for CIE 85 Table 4.

[F] For the benchmark solar spectrum, the UV irradiance (290 to 400 nm) is 9.8 % and the visible irradiance (400 to 800 nm) is 90.2 % expressed as a percentage of the total irradiance from 290 to 800 nm. Because the primary emission of fluorescent UV lamps is concentrated in the 300 to 400 nm bandpass, there are limited data available for visible light emissions of fluorescent UV lamps.

6.5.2 Some specifications may require chamber air temperature control. Positioning and calibration of chamber air temperature sensors shall be in accordance with the descriptions found in Practice G151.

NOTE 9—Typically, these devices control by black panel temperature only.

6.6 *Moisture*—The test specimens may be exposed to moisture in the form of water spray, condensation, or high humidity.

6.6.1 *Water Spray*—The test chamber may be equipped with a means to introduce intermittent water spray onto the test specimens under specified conditions. The spray shall be uniformly distributed over the samples. The spray system shall be made from corrosion resistant materials that do not contaminate the water used.

6.6.1.1 *Spray Water Quality*—Spray water shall have a conductivity below 5 µS/cm, contain less than 1-ppm solids, and leave no observable stains or deposits on the specimens. Very low levels of silica in spray water can cause significant deposits on the surface of test specimens. Care should be taken to keep silica levels below 0.1 ppm. In addition to distillation, a combination of deionization and reverse osmosis can effectively produce water of the required quality. The pH of the water used should be reported. See Practice G151 for detailed water quality instructions.

6.6.2 *Condensation*—The test chamber may be equipped with a means to cause condensation to form on the exposed face of the test specimen. Typically, water vapor shall be generated by heating water and filling the chamber with hot vapor, which then is made to condense on the test specimens.

6.6.3 *Relative Humidity*—The test chamber may be equipped with a means to measure and control the relative humidity. Such instruments shall be shielded from the lamp radiation.

6.7 *Specimen Holders*—Holders for test specimens shall be made from corrosion resistant materials that will not affect the test results. Corrosion resistant alloys of aluminium or stainless steel have been found acceptable. Brass, steel, or copper shall not be used in the vicinity of the test specimens.

6.8 *Apparatus to Assess Changes in Properties*—Use the apparatus required by the ASTM or other standard that describes determination of the property or properties being monitored.

7. Test Specimen

7.1 Refer to Practice G151.

8. Test Conditions

8.1 Any exposure conditions may be used as long as the exact conditions are detailed in the report. Appendix X2 shows some representative exposure conditions. These are not necessarily preferred and no recommendation is implied. These conditions are provided for reference only.

9. Procedure

9.1 Identify each test specimen by suitable indelible marking, but not on areas used in testing.

9.2 Determine which property of the test specimens will be evaluated. Prior to exposing the specimens, quantify the appropriate properties in accordance with recognized ASTM or international standards. If required (for example, destructive testing), use unexposed file specimens to quantify the property. See ISO 4582 for detailed guidance.

9.3 *Mounting of Test Specimens*—Attach the specimens to the specimen holders in the equipment in such a manner that the specimens are not subject to any applied stress. To assure uniform exposure conditions, fill all of the spaces, using blank panels of corrosion resistant material if necessary.

NOTE 10—Evaluation of color and appearance changes of exposed materials shall be made based on comparisons to unexposed specimens of the same material which have been stored in the dark. Masking or shielding the face of test specimens with an opaque cover for the purpose of showing the effects of exposure on one panel is not recommended. Misleading results may be obtained by this method, since the masked portion of the specimen is still exposed to temperature and humidity that in many cases will affect results.

9.4 *Exposure to Test Conditions*—Program the selected test conditions to operate continuously throughout the required number of repetitive cycles. Maintain these conditions throughout the exposure. Interruptions to service the apparatus and to inspect specimens shall be minimized.

9.5 *Specimen Repositioning*—Periodic repositioning of the specimens during exposure is not necessary if the irradiance at the positions farthest from the center of the specimen area is at least 90 % of that measured at the center of the exposure area. Irradiance uniformity shall be determined in accordance with Practice G151.

9.5.1 If irradiance at positions farther from the center of the exposure area is between 70 and 90 % of that measured at the center, one of the following three techniques shall be used for specimen placement.

9.5.1.1 Periodically reposition specimens during the exposure period to ensure that each receives an equal amount of radiant exposure. The repositioning schedule shall be agreed upon by all interested parties.

9.5.1.2 Place specimens only in the exposure area where the irradiance is at least 90 % of the maximum irradiance.

9.5.1.3 To compensate for test variability randomly position replicate specimens within the exposure area which meets the irradiance uniformity requirements as defined in 9.5.1.

9.6 *Inspection*—If it is necessary to remove a test specimen for periodic inspection, take care not to handle or disturb the test surface. After inspection, the test specimen shall be returned to the test chamber with its test surface in the same orientation as previously tested.

9.7 *Apparatus Maintenance*—The test apparatus requires periodic maintenance to maintain uniform exposure conditions. Perform required maintenance and calibration in accordance with manufacturer's instructions.

9.8 Expose the test specimens for the specified period of exposure. See Practice G151 for further guidance.

9.9 At the end of the exposure, quantify the appropriate properties in accordance with recognized ASTM or international standards and report the results in conformance with Practice G151.

NOTE 11—Periods of exposure and evaluation of test results are addressed in Practice G151.

10. Report

10.1 The test report shall conform to Practice G151.

11. Precision and Bias

11.1 *Precision:*

11.1.1 The repeatability and reproducibility of results obtained in exposures conducted according to this practice will vary with the materials being tested, the material property being measured, and the specific test conditions and cycles that are used. In round-robin studies conducted by Subcommittee G03.03, the 60° gloss values of replicate PVC tape specimens exposed in different laboratories using identical test devices and exposure cycles showed significant variability (3). The variability shown in these round-robin studies restricts the use of "absolute specifications" such as requiring a specific property level after a specific exposure period (4,5).

11.1.2 If a standard or specification for general use requires a definite property level after a specific time or radiant exposure in an exposure test conducted according to this practice, the specified property level shall be based on results obtained in a round-robin that takes into consideration the variability due to the exposure and the test method used to measure the property of interest. The round-robin shall be conducted according to Practice E691 or Practice D3980 and shall include a statistically representative sample of all laboratories or organizations that would normally conduct the exposure and property measurement.

11.1.3 If a standard or specification for use between two or three parties requires a definite property level after a specific time or radiant exposure in an exposure test conducted according to this practice, the specified property level shall be based on statistical analysis of results from at least two separate, independent exposures in each laboratory. The design of the experiment used to determine the specification shall take into consideration the variability due to the exposure and the test method used to measure the property of interest.

11.1.4 The round-robin studies cited in 11.1.1 demonstrated that the gloss values for a series of materials could be ranked with a high level of reproducibility between laboratories. When reproducibility in results from an exposure test conducted according to this practice have not been established through round-robin testing, performance requirements for materials shall be specified in terms of comparison (ranked) to a control material. The control specimens shall be exposed simultaneously with the test specimen(s) in the same device. The specific control material used shall be agreed upon by the concerned parties. Expose replicates of the test specimen and the control specimen so that statistically significant performance differences can be determined.

11.2 *Bias*—Bias can not be determined because no acceptable standard weathering reference materials are available.

12. Keywords

12.1 accelerated; accelerated weathering; durability; exposure; fluorescent UV lamps; laboratory weathering; light; lightfastness; non-metallic materials; temperature; ultraviolet; weathering

ANNEX

A1. DETERMINING CONFORMANCE TO RELATIVE SPECTRAL POWER DISTRIBUTION TABLES

(Mandatory Information for Equipment Manufacturers)

A1.1 Conformance to the relative spectral power distribution tables is a design parameter for fluorescent UV device with the different lamps that can be used. Manufacturers of equipment claiming conformance to this standard shall determine conformance to the spectral power distribution tables for all fluorescent lamps provided, and provide information on maintenance procedures to minimize any spectral changes that may occur during normal use.

A1.2 The relative spectral power distribution data for this standard were developed using the rectangular integration technique. Eq A1.1 is used to determine the relative spectral irradiance using rectangular integration. Other integration techniques can be used to evaluate spectral power distribution data, but may give different results. When comparing relative spectral power distribution data to the spectral power distribution requirements of this standard, use the rectangular integration technique.

A1.3 To determine whether a specific fluorescent UV lamp for a fluorescent UV device meets the requirements of Table 1, Table 2, or Table 3, measure the spectral power distribution from 250 nm to 400 nm. Typically, this is done at 2 nm increments. If the manufacturer's spectral measurement equipment cannot measure wavelengths as low as 250 nm, the lowest measurement wavelength must be reported. The lowest wavelength measured shall be no greater than 270 nm. For determining conformance to the relative spectral irradiance requirements for a fluorescent UVB-313 lamp, measurement from 250 nm to 400 nm is required. The total irradiance in each wavelength bandpass is then summed and divided by the specified total UV irradiance according to Eq A1.1. Use of this equation requires that each spectral interval must be the same (for example, 2 nm) throughout the spectral region used.

$$I_R = \frac{\sum_{\lambda_i=A}^{\lambda_i=B} E_{\lambda_i}}{\sum_{\lambda_i=C}^{\lambda_i=400} E_{\lambda_i}} \times 100 \qquad \text{(A1.1)}$$

where:

I_R = relative irradiance in percent,
E = irradiance at wavelength λ_i (irradiance steps must be equal for all bandpasses),
A = lower wavelength of wavelength bandpass,
B = upper wavelength of wavelength bandpass,
C = lower wavelength of total UV bandpass used for calculating relative spectral irradiance (290 nm for UVA 340 lamps, 300 nm for UVA 351 lamps, or 250 nm for UVB 313 lamps), and
λ_i = wavelength at which irradiance was measured.

APPENDIXES

(Nonmandatory Information)

X1. APPLICATION GUIDELINES FOR TYPICAL FLUORESCENT UV LAMPS

X1.1 *General*:

X1.1.1 A variety of fluorescent UV lamps may be used in this practice. The lamps shown in this section are representative of their type. Other lamps, or combinations of lamps, may be used. The particular application determines which lamp should be used. The lamps discussed in this Appendix differ in the total amount of UV energy emitted and their wavelength spectrum. Differences in lamp energy or spectrum may cause significant differences in test results. A detailed description of the type(s) of lamp(s) used shall be stated in detail in the test report.

X1.1.2 All spectral power distributions (SPDs) shown in this section are representative only and are not meant to be used to calculate or estimate total radiant exposure for tests in fluorescent UV devices. Actual irradiance levels at the test specimen surface will vary due to the type and/or manufacturer of the lamp used, the age of the lamps, the distance to the lamp array, and the air temperature within the chamber.

Note X1.1—All SPDs in this appendix were measured using a spectroradiometer with a double grating monochromator (1-nm band pass) with a quartz cosine receptor. The fluorescent UV SPDs were measured at the sample plane in the center of the allowed sample area. SPDs for sunlight were measured in Phoenix, AZ at solar noon at the summer solstice with a clear sky, with the spectroradiometer on an equatorial follow-the-sum mount.

X1.2 *Simulations of Direct Solar UV Radiation Exposures*:

X1.2.1 *UVA-340 Lamps*—For simulations of direct solar UV radiation the UVA-340 lamp is recommended. Because UVA-340 lamps typically have little or no UV output below 300 nm (that is considered the "cut-on" wavelength for terrestrial sunlight), they usually do not degrade materials as rapidly as UVB lamps, but they may allow enhanced correlation with actual outdoor weathering. Tests using UVA-340 lamps have been found useful for comparing different nonmetallic materials such as polymers, textiles, and UV stabilizers. Fig. X1.1 illustrates the SPD of the UVA-340 lamp compared to noon, summer sunlight.

X1.2.2 *UVB-313 Lamps*—The UVB region (280 to 315 nm) includes the shortest wavelengths found in sunlight at the earth's surface and is responsible for considerable polymer damage. There are two commonly available types of UVB-313 lamps that meet the requirements of this document. These are known commercially as the UVB-313 and the FS-40. These lamps emit different amounts of total energy, but both peak at 313 nm and produce the same UV wavelengths in the same relative proportions. In tests using the same cycles and temperatures, shorter times to failure are typically observed when the lamp with higher UV irradiance is used. Furthermore, tests using the same cycles and temperatures with these two lamps may exhibit differences in ranking of materials due to difference in the proportion of UV to moisture and temperature.

NOTE X1.2—The Fig. X1.2 illustrates the difference between the lamps.

X1.2.2.1 All UVB-313 lamps emit UV below the normal sunlight cut-on. This short wavelength UV can produce rapid polymer degradation and often causes degradation by mechanisms that do not occur when materials are exposed to sunlight. This may lead to anomalous results. Fig. X1.2 shows the spectral power distribution (SPD) of typical UVB-313 lamps compared to the SPD of noon, summer sunlight.

X1.3 *Simulations of Exposures to Solar UV Radiation Through Window Glass*:

X1.3.1 *Filtering Effect of Glass*—Glass of any type acts as a filter on the sunlight spectrum (see Fig. X1.3). Ordinary glass is essentially transparent to light above about 370 nm. However, the filtering effect becomes more pronounced with decreasing wavelength. The shorter, more damaging UVB wavelengths are the most greatly affected. Window glass filters out most of the wavelengths below about 310 nm. For purposes of illustration, only one type of window glass is used in the accompanying graphs. Note that glass transmission characteristics will vary due to manufacturer, production lot, thickness, or other factors.

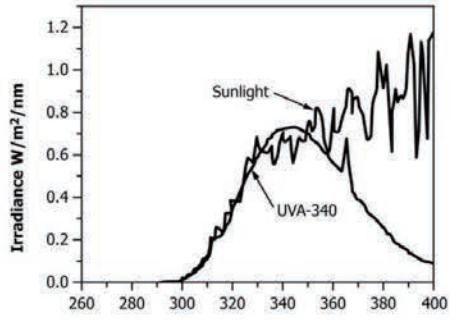

FIG. X1.1 Spectral Power Distributions of UVA-340 Lamp and Sunlight

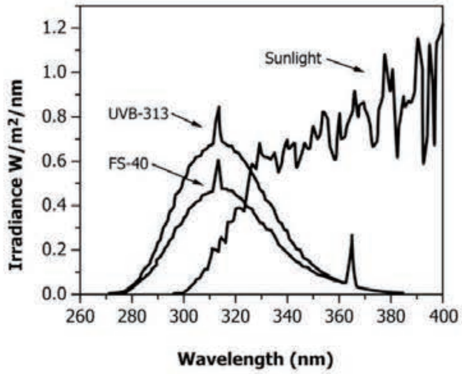

FIG. X1.2 Spectral Power Distributions of UVB Lamps and Sunlight

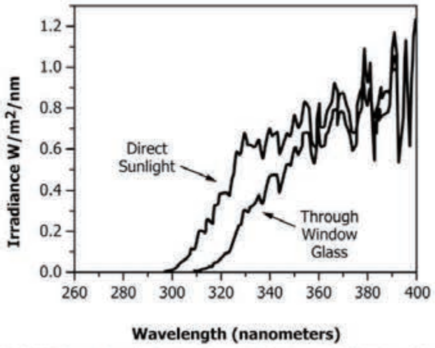

FIG. X1.3 Direct Sunlight and Sunlight Through Window Glass

X1.3.2 *UVA-351 Lamps*—For simulations of sunlight through window glass, UVA-351 lamps are recommended. The UVA-351 is used for these applications because the low end cut-on of this lamp is similar to that of direct sunlight which has been filtered through window glass (Fig. X1.4).

NOTE X1.3—UVB-313 lamps are not recommended for simulations of sunlight through window glass. Most of the emission of UVB-313 lamps is in the short wavelength UV that is filtered very efficiently by glass. Because of this, very little energy from this short wavelength region will reach materials in "behind glass" applications. This is because window glass filters out about 80 % of the energy from UVB-313 lamps, as shown in Fig. X1.5. As a result of filtering out these short wavelengths, its total effective energy is very limited. Further, because there is little longer wavelength energy, the glass-filtered UVB-313 is actually less severe than a UVA Lamp.

X1.4 *Simulations of Exposures Where Glass or Transparent Plastic Forms Part of the Test Specimen*:

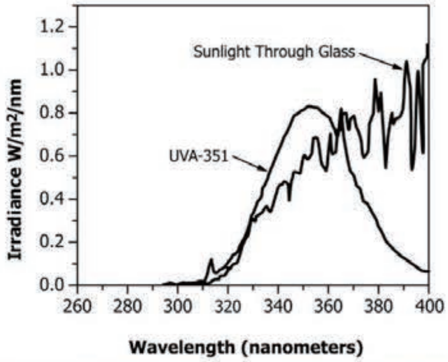

FIG. X1.4 Spectral Power Distributions of UVA-351 Lamp and Sunlight Through Window Glass

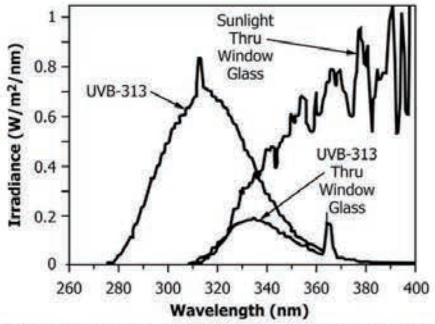

FIG. X1.5 Spectral Power Distributions of Unfiltered UVB-313 Lamp, UVB-313 Through Window Glass, and Sunlight Through Window Glass

X1.4.1 *UVA-340 Lamps*—In some instances (for example, window sealants), glass or transparent plastic is part of the test specimen itself and normally acts as a filter to the light source. In these special cases, the use of UVA-340 lamps is recommended since the glass or plastic will filter the spectrum of the lamp in the same way that it would filter sunlight. Fig. X1.6 compares the spectral power distribution of sunlight filtered through window glass to the spectral power distribution of the UVA-340 lamp, both unfiltered and filtered through window glass.

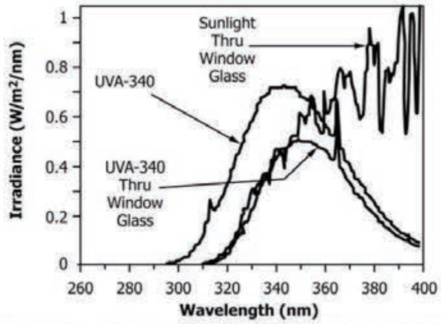

FIG. X1.6 Spectral Power Distributions of Unfiltered UVA-340 Lamp, UVA-340 Through Window Glass, and Sunlight Through Window Glass

NOTE X1.4—UBV-313 lamps are lamps not recommended for exposures where glass or transparent plastic forms part of the test specimen. See Note X1.3.

NOTE X1.5—UVA-351 lamps are not recommended for exposures where glass or transparent plastic forms part of the test specimen. This is because the UVA-351 has a special power distribution in the short wave UV region that is similar to sunlight that has already been filtered by window glass. As shown in Fig. X1.7, using this lamp through window glass or other transparent material further filters out the short wavelength UV and results in a spectrum that is deficient in the short wavelength UV.

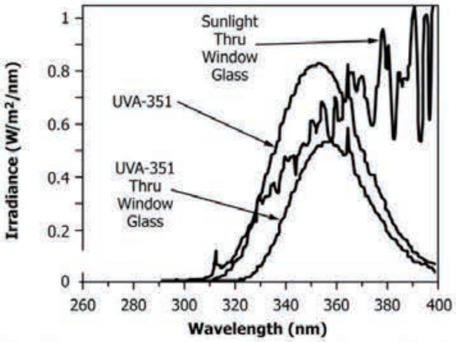

FIG. X1.7 Spectral Power Distributions of Unfiltered UVA-351 Lamp, UVA-351 Through Window Glass, and Sunlight Through Window Glass

X2. EXPOSURE CONDITIONS

X2.1 Any exposure conditions may be used, as long as the exact conditions are detailed in the report. Following are some representative exposure conditions. These are not necessarily preferred and no recommendation is implied. These conditions are provided for reference only (See Table X2.1).

NOTE X2.1—Cycle 1 is a commonly used exposure cycle for coatings and plastics. Cycle 2 has been widely used for coatings. Cycles 3 and 4 have been used for exterior automotive materials. Cycle 5 has been used for roofing materials. Cycle 6 has been used for high irradiance exposures of coatings and plastics. Cycle 7 has been used for thermal shock and for erosion testing of coatings for wood.

NOTE X2.2—When selecting programs of UV exposure followed by condensation, allow at least 2 h per interval to assure attainment of equilibrium.

NOTE X2.3—Surface temperature of specimens is an essential test quantity. Generally, degradation processes accelerate with increasing temperature. The specimen temperature permissible for the accelerated test depends on the material to be tested and on the aging criterion under consideration.

NOTE X2.4—Irradiance data shown is typical. Frequently, the irradiance is not controlled in this type of exposure device.

NOTE X2.5—The light output of fluorescent lamps is affected by the temperature of the air which surrounds the lamps. Consequently, in testers without feed-back-loop control of irradiance, the lamp output will decrease with increasing chamber temperature.

NOTE X2.6—Laboratory ambient temperature may have an effect on the light output of devices without feed-back-loop control of irradiance. Some fluorescent UV devices use laboratory ambient air to cool the lamps and thereby compensate for the drop in light output at higher exposure temperatures (see Note X2.5).

X2.2 For the most consistent results, it is recommended that apparatus without feed-back-loop control of irradiance be operated in an environment in which the ambient temperature is maintained between 18 and 27°C. Apparatus operated in ambient temperatures above or below this range may produce irradiances different from devices operated in the recommended manner.

NOTE X2.7—Fluorescent UV lamps emit relatively little infrared radiation when compared to xenon arc and carbon arc sources. In fluorescent UV apparatus, the primary heating of the specimen surface is by convection from heated air passing across the panel. Therefore, there is a minimal difference between the temperature of an insulated or uninsulated black or white panel thermometer, specimen surface, air in the test chamber, or different colored samples (3).

X2.3 For conversion of test cycles described in Practice G53 to test cycles described in Practice G154 see Table X2.2. For operational fluctuations see Table X2.3.

NOTE X2.8—Unless otherwise specified, operate the apparatus to maintain the operational fluctuations specified in Table X2.3 for the parameters in Table X2.1. If the actual operating conditions do not agree with the machine settings after the equipment has stabilized, discontinue the test and correct the cause of the disagreement before continuing.

TABLE X2.1 Common Exposure Conditions

Cycle	Lamp	Typical Irradiance	Approximate Wavelength	Exposure Cycle
1	UVA-340	0.89 W/m^2/nm	340 nm	8 h UV at 60 (±3) °C Black Panel Temperature; 4 h Condensation at 50 (±3) °C Black Panel Temperature
2	UVB-313	0.71 W/m^2/nm	310 nm	4 h UV at 60 (±3) °C Black Panel Temperature; 4 h Condensation at 50 (±3) °C Black Panel Temperature
3	UVB-313	0.49 W/m^2/nm	310 nm	8 h UV at 70 (± 3) °C Black Panel Temperature; 4 h Condensation at 50 (± 3) °C Black Panel Temperature
4	UVA-340	1.55 W/m^2/nm	340 nm	8 h UV at 70 (±3) °C Black Panel Temperature; 4 h Condensation at 50 (±3) °C Black Panel Temperature
5	UVB-313	0.62 W/m^2/nm	310 nm	20 h UV at 80 (±3) °C Black Panel Temperature; 4 h Condensation at 50 (±3) °C Black Panel Temperature
6	UVA-340	1.55 W/m^2/nm	340 nm	8 h UV at 60 (±3) °C Black Panel Temperature; 4 h Condensation at 50 (±3) °C Black Panel Temperature.
7	UVA-340	1.55 W/m^2/nm	340 nm	8 h UV at 60 (±3) °C Black Panel Temperature; 0.25 h water spray (no light), temperature not controlled; 3.75 h condensation at 50 (±3) °C Black Panel Temperature
8	UVB-313	28 W/m^2	270 to 700 nm	8 h UV at 70 (±3) °C Black Panel Temperature; 4 h Condensation at 50 (±3) °C Black Panel Temperature

TABLE X2.2 Conversion of Test Cycles Described in Practice G53 to Test Cycles Described in Practice G154

Practice G53 Test Cycle Description	Corresponding Test Cycle in Practice G154
Practice G53 describes one default cycle of 4 hours UV at 60°C, 4 hours condensation at 50°C. The default lamp for this and other cycles is the UVB lamps with peak emission at 313 nm, but fluorescent UVA lamps with peak emission at 343 nm or 351 nm may also be used.	Cycle 2 of Table X2.1 describes the Practice G53 default cycle using UVB-313 lamps.
Practice G53 indicated that a cycle of 8 hours UV and 4 hours condensation is widely used. Suggested temperatures during UV exposure were 50°C, 60°C, 70°C	Table X2.1 describes 6 specific exposure cycles that use 8 hours UV followed by 4 hours condensation. These cycles use either UVA-340 or UVB-313 lamps.

TABLE X2.3 Operational Fluctuations On Exposure Conditions

Parameter	Maximum Allowable Deviation from the Set Point at the Control Point Indicated by the Readout of the Calibrated Control Sensor During Equilibrium Operation
Black Panel Temperature	±2.5°C
Irradiance (monitored at 340 nm or monitored at 310 nm)	±.02 W/(m^2 • nm)
Irradiance (monitored at 270– 700 nm)	±0.5 W/m^2

X3. COMPARISON OF BENCHMARK SOLAR UV SPECTRUM AND CIE 85 TABLE 4 SOLAR SPECTRUM

X3.1 This standard uses a benchmark solar spectrum based on atmospheric conditions that provide for very high level of solar ultraviolet radiation. This benchmark solar spectrum is published in ASTM G177, Standard Tables for Reference Solar Ultraviolet Spectral Distributions: Hemispherical on 37 degree Tilted Surface. The solar spectrum is calculated using the SMARTS2 solar radiation model.[7,8,9] ASTM Adjunct ADJG0173, SMARTS2 Solar Radiation Model for Spectral Radiation provides the program and documentation for calculating solar spectral irradiance.

X3.2 Previous versions of this standard used CIE 85 Table 4[10] as the benchmark solar spectrum. Table X3.1 compares the basic atmospheric conditions used for the benchmark solar spectrum and the CIE 85 Table 4 solar spectrum.

TABLE X3.1 Comparison of Basic Atmospheric Conditions Used for Benchmark Solar Spectrum and CIE 85 Table 4 Solar Spectrum

Atmospheric Condition	Benchmark Solar Spectrum	CIE 85 Table 4 Solar Spectrum
Ozone (atm-cm)	0.30	0.34
Precipitable water vapor (cm)	0.57	1.42
Altitude (m)	2000	0
Tilt angle	37° facing Equator	0° (horizontal)
Air mass	1.05	1.00
Albedo (ground reflectance)	Light Soil wavelength dependent	Constant at 0.2
Aerosol extinction	Shettle & Fenn Rural (humidity dependent)	Equivalent to Linke Turbidity factor of about 2.8
Aerosol optical thickness at 500 nm	0.05	0.10

X3.3 Table X3.2 compares irradiance (calculated using rectangular integration) and relative irradiance for the benchmark solar spectrum and the CIE 85 Table 4 solar spectrum, in the bandpasses used in this standard.

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[7] Gueymard, C., "Parameterized Transmittance Model for Direct Beam and Circumsolar Spectral Irradiance," *Solar Energy*, Vol 71, No. 5, 2001, pp. 325-346.

[8] Gueymard, C. A., Myers, D., and Emery, K., "Proposed Reference Irradiance Spectra for Solar Energy Systems Testing," *Solar Energy*, Vol 73, No 6, 2002, pp. 443-467.

[9] Myers, D. R., Emery, K., and Gueymard, C., "Revising and Validating Spectral Irradiance Reference Standards for Photovoltaic Performance Evaluation," Transactions of the American Society of Mechanical Engineers, *Journal of Solar Energy Engineering*, Vol 126, pp 567–574, Feb. 2004.

[10] CIE-Publication Number 85: Recommendations for the Integrated Irradiance and the Spectral Distribution of Simulated Solar Radiation for Testing Purposes, 1st Edition, 1989 (Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036).

TABLE X3.2 Irradiance and Relative Irradiance Comparison for Benchmark Solar Spectrum and CIE 85 Table 4 Solar Spectrum

Bandpass	Benchmark Solar Spectrum	CIE 85Table 4 Solar Spectrum
	Irradiance (W/m^2) in stated bandpass	
$\lambda < 290$	0.000	0.000
$290 \leq \lambda \leq 320$	3.748	4.060
$320 < \lambda \leq 360$	25.661	28.450
$360 < \lambda \leq 400$	34.762	42.050
$290 \leq \lambda \leq 400$	64.171	74.560
$290 \leq \lambda \leq 800$	652.300	678.780
	Percent of 290 to 400 nm irradiance	
$\lambda < 290$	0.0 %	0.0 %
$290 < \lambda \leq 320$	5.8 %	5.4 %
$320 < \lambda \leq 360$	40.0 %	38.2 %
$360 < \lambda \leq 400$	54.2 %	56.4 %
	Percent of 290 to 800 nm irradiance	
$290 \leq \lambda \leq 400$	9.8 %	11.0 %

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(3) Ketola, W., Robbins, J. S., "UV Transmission of Single Strength Window Glass," *Accelerated and Outdoor Durability Testing of Organic Materials. ASTM STP 1202*. Warren D. Ketola and Douglas Grossman, Editors, American Society for Testing and Materials, 1993.

(4) Fischer, R. M., "Results of Round-Robin Studies of Light- and Water-Exposure Standard Practices," *Accelerated and Outdoor Durability Testing of Organic Materials, ASTM STP 1202*. Warren K. Ketola and Douglas Grossman, Editors, American Society for Testing and Materials, 1993.

(5) Fischer, R. M., and Ketola, W. D., "Surface Temperatures of Materials in Exterior Exposures and Artificial Accelerated Tests," *Accelerated and Outdoor Durability Testing of Organic Materials, ASTM STP 1202*. Warren K. Ketola and Douglas Grossman, Editors, American Society for Testing and Materials, 1993.

SUMMARY OF CHANGES

Committee G03 has identified the location of selected changes to this standard since the last issue (G154 – 06) that may impact the use of this standard.

(1) Added Ultraviolet (UV) Lamp and removed light from title

(2) Deleted note 1, for Table X.2.1 in Appendix X.2. The note documented differences in calibration for instruments from different manufacturers, due to an inaccuracy in one manufacturer's calibration process, while also provided guidance for users on how to address this issue in their tests.

(3) Added definition of Fluorescent Ultraviolet (UV) Apparatus to terminology, section 3.2.1

7.4 Statistical analysis and results

7.4.1 Liquid nitrogen results

Table 5: 1HF Liquid Nitrogen Results

Liquid Nitrogen Test				
1 HF	Before	After	P-Value	Difference%
Sample Red	Porosity %	Porosity %		
AR.C.01.00	11.75			
AR.C.01.01	7.96			
AR.C.01.02	15.97			
AR.C.01.03	11.36			
Mean	11.76			
Standard Dev	3.29			
AR.S.01.00	18.78	12.61		
AR.S.01.01	17.30	10.05		
AR.S.01.02	16.92	14.63	0.07	92.65
AR.S.01.03	16.31	10.40		
Mean	17.33	11.92		
Standard Dev	1.05	2.13		
AR.W.01.00	12.51	6.10		
AR.W.01.01	11.90	8.86		
AR.W.01.02	11.93	6.54	0.10	89.78
AR.W.01.03	14.82	4.40		
Mean	12.79	6.47		
Standard Dev	1.38	1.84		
Sample Tan	Porosity %	Porosity %	P-Value	Difference%
AT.C.01.00	14.35			
AT.C.01.01	15.94			
AT.C.01.02	17.00			
AT.C.01.03	18.00			
Mean	16.32			
Standard Dev	1.56			
AT.S.01.00	18.46	12.69		
AT.S.01.01	18.43	8.19		
AT.S.01.02	16.86	9.44	0.01	98.82
AT.S.01.03	16.84	9.31		
Mean	17.65	9.91		
Standard Dev	0.92	1.94		
AT.W.01.00	17.34	5.12		
AT.W.01.01	21.31	8.91		
AT.W.01.02	18.66	9.14	0.01	99.07
AT.W.01.03	18.07	4.75		
Mean	18.85	6.98		
Standard Dev	1.73	2.37		

Table 6: 2HF Liquid Nitrogen Results

Liquid Nitrogen Test				
2 HF	Before	After	P-Value	Difference%
Sample Red	Porosity %	Porosity %		
AR.C.02.00	14.68	14.68		
AR.C.02.01	11.60	11.60		
AR.C.02.02	14.70	14.70		
AR.C.02.03	12.16	12.16		
Mean	13.29	13.29		
Standard Dev	1.64	1.64		
AR.S.02.00	12.56	10.94		
AR.S.02.01	8.14	7.12		
AR.S.02.02	12.51	5.77	0.13	87.40
AR.S.02.03	12.57	5.96		
Mean	11.44	7.45		
Standard Dev	2.20	2.40		
AR.W.02.00	20.31	14.08		
AR.W.02.01	15.00	8.38		
AR.W.02.02	15.36	12.79	0.06	94.12
AR.W.02.03	15.97	9.51		
Mean	16.66	11.19		
Standard Dev	2.46	2.69		
Sample Tan	Porosity %	Porosity %		
AT.C.02.00	17.43	17.43		
AT.C.02.01	17.54	17.54		
AT.C.02.02	17.29	17.29		
AT.C.02.03	17.82	17.82		
Mean	17.52	17.52		
Standard Dev	0.22	0.22		
AT.S.02.00	17.35	11.10		
AT.S.02.01	16.73	8.57		
AT.S.02.02	17.81	10.88	0.02	98.12
AT.S.02.03	20.10	9.09		
Mean	18.00	9.91		
Standard Dev	1.47	1.27		
AT.W.02.00	16.40	7.44		
AT.W.02.01	17.12	5.17		
AT.W.02.02	17.68	12.32	0.05	95.16
AT.W.02.03	16.33	8.45		
Mean	16.88	8.34		
Standard Dev	0.64	2.98		

Table 7: 1 ABF Liquid Nitrogen Results

Liquid Nitrogen Test				
1 ABF	Before	After	P-Value	Difference%
Sample Red	Porosity %	Porosity %		
BR.C.01.00	13.96	13.96		
BR.C.01.01	12.19	12.19		
BR.C.01.02	9.48	9.48		
BR.C.01.03	9.60	9.60		
Mean	11.30	11.30		
Standard Dev	2.16	2.16		
BR.S.01.00	16.00	8.51		
BR.S.01.01	8.71	5.55		
BR.S.01.02	8.78	5.60	0.02	98.08
BR.S.01.03	10.97	6.25		
Mean	11.11	6.48		
Standard Dev	3.42	1.39		
BR.W.01.00	15.00	9.37		
BR.W.01.01	12.22	13.34		
BR.W.01.02	16.05	15.27	0.50	49.73
BR.W.01.03	17.96	14.04		
Mean	15.31	13.01		
Standard Dev	2.39	2.55		
Sample Tan	Porosity %	Porosity %		
BT.C.01.00	16.70	16.70		
BT.C.01.01	15.91	15.91		
BT.C.01.02	15.44	15.44		
BT.C.01.03	12.89	12.89		
Mean	15.23	15.23		
Standard Dev	1.65	1.65		
BT.S.01.00	16.93	12.67		
BT.S.01.01	17.68	5.94		
BT.S.01.02	9.91	11.56	0.37	62.72
BT.S.01.03	16.45	13.18		
Mean	15.24	10.84		
Standard Dev	3.59	3.33		
BT.W.01.00	17.43	13.05		
BT.W.01.01	16.23	15.07		
BT.W.01.02	15.11	15.67	0.37	63.37
BT.W.01.03	14.77	12.81		
Mean	15.89	14.15		
Standard Dev	1.20	1.43		

Table 8: 2 ABF Liquid Nitrogen Results

Liquid Nitrogen Test				
2ABF	Before	After	P-Value	Difference%
Sample Red	Porosity %	Porosity %		
BR.C.02.00	13.99	13.99		
BR.C.02.01	9.36	9.36		
BR.C.02.02	10.31	10.31		
BR.C.02.03	13.09	13.09		
Mean	11.69	11.69		
Standard Dev	2.21	2.21		
BR.S.02.00	12.65	8.11		
BR.S.02.01	6.77	7.07		
BR.S.02.02	11.01	6.25	0.21	78.99
BR.S.02.03	11.49	5.99		
Mean	10.48	6.86		
Standard Dev	2.57	0.96		
BR.W.02.00	14.94	8.97		
BR.W.02.01	12.19	8.96		
BR.W.02.02	9.67	12.25	0.81	19.44
BR.W.02.03	9.21	11.44		
Mean	11.50	10.41		
Standard Dev	2.64	1.70		
Sample Tan	Porosity %	Porosity %		
BT.C.02.00	18.35	18.35		
BT.C.02.01	19.73	19.73		
BT.C.02.02	16.25	16.25		
BT.C.02.03	18.63	18.63		
Mean	18.24	18.24		
Standard Dev	1.46	1.46		
BT.S.02.00	17.16	12.33		
BT.S.02.01	14.36	15.95		
BT.S.02.02	14.52	11.79	0.49	51.45
BT.S.02.03	14.08	11.70		
Mean	15.03	12.94		
Standard Dev	1.43	2.02		
BT.W.02.00	17.85	8.91		
BT.W.02.01	12.16	14.00		
BT.W.02.02	13.05	14.94	0.20	79.60
BT.W.02.03	13.64	13.55		
Mean	14.17	12.85		
Standard Dev	2.52	2.69		

Table 9: Comparison liquid nitrogen results-1HF versus 1ABF

Liquid Nitrogen Test	**1HF**		**1ABF**		**Delta HF**	**Delta ABF**
1HF versus 1 ABF	Before	After	Before	After		
Sample Red	Porosity %	Porosity %	Porosity %	Porosity %		
SALT	18.78	12.61	16.00	8.51	6.16	7.49
SALT 1	17.30	10.05	8.71	5.55	7.24	3.15
SALT 2	16.92	14.63	8.78	5.60	2.29	3.18
SALT 3	16.31	10.40	10.97	6.25	5.91	4.72
Mean	17.33	11.92	11.11	6.48	P-Value	Difference%
Standard Deviation	1.05	2.13	3.42	1.39	0.58	42.27
WEATHEROMETER	12.51	6.10	15.00	9.37	6.42	5.63
WEATHEROMETER 1	11.90	8.86	12.22	13.34	3.04	1.12
WEATHEROMETER 2	11.93	6.54	16.05	15.27	5.38	0.77
WEATHEROMETER 3	14.82	4.40	17.96	14.04	10.43	3.92
Mean	12.79	6.47	15.31	13.01	P-Value	Difference%
Standard Deviation	1.38	1.84	2.39	2.55	0.08	92.44
Sample Tan	Porosity %		Porosity %	Porosity %		
SALT	18.46	12.69	16.93	12.67	5.77	4.27
SALT 1	18.43	8.19	17.68	5.94	10.24	11.73
SALT 2	16.86	9.44	9.91	11.56	7.42	1.65
SALT 3	16.84	9.31	16.45	13.18	7.53	3.27
Mean	17.65	9.91	15.24	10.84	P-Value	Difference%
Standard Deviation	0.92	1.94	3.59	3.33	0.21	78.54
WEATHEROMETER	17.34	5.12	17.43	13.05	12.22	4.38
WEATHEROMETER 1	21.31	8.91	16.23	15.07	12.40	1.17
WEATHEROMETER 2	18.66	9.14	15.11	15.67	9.53	0.55
WEATHEROMETER 3	18.07	4.75	14.77	12.81	13.32	1.96
Mean	18.85	6.98	15.89	14.15	P-Value	Difference%
Standard Deviation	1.73	2.37	1.20		0.00	99.85

Table 10: Comparison liquid nitrogen results-2HF versus 2ABF

Liquid Nitrogen Test	**2HF**		**2ABF**		**Delta HF**	**Delta ABF**
2 HF versus 2 ABF	Before	After	Before	After		
Sample Red						
SALT	12.56	10.94	12.65	8.11	1.62	4.54
SALT 1	8.14	7.12	6.77	7.07	1.02	0.30
SALT 2	12.51	5.77	11.01	6.25	6.73	4.76
SALT 3	12.57	5.96	11.49	5.99	6.60	5.50
Mean	11.44	7.45	10.48	6.86	P-Value	Difference%
Standard Deviation	2.20	2.40	2.57	0.96	0.85	14.84
WEATHEROMETER	20.31	14.08	14.94	8.97	6.23	5.96
WEATHEROMETER 1	15.00	8.38	12.19	8.96	6.62	3.23
WEATHEROMETER 2	15.36	12.79	9.67	12.25	2.57	2.59
WEATHEROMETER 3	15.97	9.51	9.21	11.44	6.46	2.23
Mean	16.66	11.19	11.50	10.41	P-Value	Difference%
Standard Deviation	2.46	2.69	2.64	1.70	0.17	83.40
Sample Tan	Porosity %	Porosity %	Porosity %	Porosity %		
SALT	17.35	11.10	17.16	12.33	6.25	4.83
SALT 1	16.73	8.57	14.36	15.95	8.16	1.59
SALT 2	17.81	10.88	14.52	11.79	6.93	2.74
SALT 3	20.10	9.09	14.08	11.70	11.01	2.38
Mean	18.00	9.91	15.03	12.94	P-Value	Difference%
Standard Deviation	1.47	1.27	1.43	2.02	0.04	95.59
WEATHEROMETER	16.40	7.44	17.85	8.91	8.96	8.93
WEATHEROMETER 1	17.12	5.17	12.16	14.00	11.95	1.84
WEATHEROMETER 2	17.68	12.32	13.05	14.94	5.36	1.90
WEATHEROMETER 3	16.33	8.45	13.64	13.55	7.88	0.09
Mean	16.88	8.34	14.17	12.85	P-Value	Difference%
Standard Deviation	0.64	2.98	2.52	2.69	0.10	90.24

7.4.2 Spectrophotometer results

Table 11: 1HF Spectrophotometer results

Spectrophotometer				
1 HF				
Sample Red	**Before**	**After**	P-Value	Difference%
AR.C.01.00				
AR.C.01.01	4.20			
AR.C.01.02	3.87			
AR.C.01.03	2.22			
AR.S.01.00		21.13		
AR.S.01.01	2.85	17.35		
AR.S.01.02	3.58	20.19		
AR.S.01.03	3.41	23.59		
Mean	3.28	20.38		
Standard Dev	0.38	3.12	0.01	99.07
AR.W.01.00		0.93		
AR.W.01.01	3.61	3.73		
AR.W.01.02	3.30	4.73		
AR.W.01.03	3.55	3.66		
Mean	3.49	4.04		
Standard Dev	0.16	0.60	0.33	66.59
Sample Tan	**Before**	**After**	P-Value	Difference%
AT.C.01.00				
AT.C.01.01	0.77			
AT.C.01.02	0.55			
AT.C.01.03	0.95			
AT.S.01.00		8.05		
AT.S.01.01	0.10	3.53		
AT.S.01.02	0.56	5.67		
AT.S.01.03	0.53	3.60		
Mean	0.40	4.27		
Standard Dev	0.26	1.22	0.03	97.46
AT.W.01.00		1.29		
AT.W.01.01	0.80	3.39		
AT.W.01.02	1.13	5.48		
AT.W.01.03	1.01	5.41		
Mean	0.98	4.76		
Standard Dev	0.17	1.19	0.02	97.61

Table 12: 2HF Spectrophotometer results

Spectrophotometer				
2 HF				
Sample Red	**Before**	**After**	P-Value	Difference%
AR.C.02.00				
AR.C.02.01	1.80			
AR.C.02.02	2.17			
AR.C.02.03	1.17			
AR.S.02.00		0.60		
AR.S.02.01	2.38	10.43		
AR.S.02.02	4.18	13.82		
AR.S.02.03	3.69	18.83		
Mean	3.42	14.36		
Standard Dev	0.93	4.23	0.04	96.36
AR.W.02.00		1.94		
AR.W.02.01	2.46	3.20		
AR.W.02.02	1.41	4.09		
AR.W.02.03	3.26	2.72		
Mean	2.38	3.34		
Standard Dev	0.93	0.70	0.41	58.71
Sample Tan	**Before**	**After**	P-Value	Difference%
AT.C.02.00				
AT.C.02.01	0.27			
AT.C.02.02	0.51			
AT.C.02.03	0.49			
AT.S.02.00		9.55		
AT.S.02.01	0.26	8.19		
AT.S.02.02	0.39	7.09		
AT.S.02.03	0.23	10.12		
Mean	0.29	8.47		
Standard Dev	0.09	1.53	0.01	98.73
AT.W.02.00		4.87		
AT.W.02.01	0.68	5.04		
AT.W.02.02	0.71	2.77		
AT.W.02.03	0.75	3.84		
Mean	0.71	3.88		
Standard Dev	0.04	1.14	0.04	95.87

Table 13: 1 ABF Spectrophotometer results

Spectrophotometer				
1 ABF				
Sample Red	**Before**	**After**	P-Value	Difference%
BR.C.01.00				
BR.C.01.01	1.01			
BR.C.01.02	2.97			
BR.C.01.03	3.43			
BR.S.01.00		0.87		
BR.S.01.01	2.06	2.91		
BR.S.01.02	2.32	0.76		
BR.S.01.03	1.14	1.32		
Mean	1.84	1.66		
Standard Dev	0.62	1.12	0.83	17.14
BR.W.01.00		0.93		
BR.W.01.01	2.15	3.73		
BR.W.01.02	2.16	4.73		
BR.W.01.03	1.10	3.66		
Mean	1.80	4.04		
Standard Dev	0.61	0.60	0.02	97.91
Sample Tan	**Before**	**After**	P-Value	Difference%
BT.C.01.00				
BT.C.01.01	0.83			
BT.C.01.02	0.27			
BT.C.01.03	0.54			
Mean				
Standard Dev				
BT.S.01.00		0.62		
BT.S.01.01	1.72	2.15		
BT.S.01.02	1.21	1.34		
BT.S.01.03	1.40	2.63		
Mean	1.44	2.04		
Standard Dev	0.26	0.65	0.21	78.92
BT.W.01.00		1.39		
BT.W.01.01	0.88	2.82		
BT.W.01.02	1.47	1.82		
BT.W.01.03	1.31	2.04		
Mean	1.22	2.23		
Standard Dev	0.31	0.53	0.17	82.94

Table 14: 2 ABF Spectrophotometer results

Spectrophotometer				
2 ABF				
Sample Red	**Before**	**After**	P-Value	Difference%
BR.C.02.00				
BR.C.02.01	4.36			
BR.C.02.02	4.58			
BR.C.02.03	4.00			
BR.S.02.00		4.06		
BR.S.02.01	4.05	9.24		
BR.S.02.02	5.16	4.96		
BR.S.02.03	4.63	1.48		
Mean	4.61	5.23		
Standard Dev	0.56	3.89	0.83	17.49
BR.W.02.00		2.61		
BR.W.02.01	1.22	6.08		
BR.W.02.02	2.67	8.62		
BR.W.02.03	3.05	8.98		
Mean	2.31	7.89		
Standard Dev	0.97	1.58	0.00	99.59
Sample Tan	**Before**	**After**	P-Value	Difference%
BT.C.02.00				
BT.C.02.01	3.09			
BT.C.02.02	2.43			
BT.C.02.03	2.85			
BT.S.02.00		4.00		
BT.S.02.01	1.05	1.39		
BT.S.02.02	2.00	1.22		
BT.S.02.03	1.84	1.20		
Mean	1.63	1.27		
Standard Dev	0.51	0.10	0.41	58.56
BT.W.02.00		5.33		
BT.W.02.01	2.56	5.06		
BT.W.02.02	2.72	5.44		
BT.W.02.03	2.72	6.15		
Mean	2.67	5.55		
Standard Dev	0.09	0.55	0.01	99.07

Table 15: Comparing spectrophotometer results between 1 HF and 1ABF

Spectrophotometer						
Red	**1 HF**		**1 ABF**			
Sample	**Before**	**After**	**Before**	**After**	**Delta HF**	**Delta ABF**
SALT RED		21.13		0.87		
SALT RED 1	2.85	17.35	2.06	2.91	14.50	0.85
SALT RED 2	3.58	20.19	2.32	0.76	16.61	1.56
SALT RED 3	3.41	23.59	1.14	1.32	20.18	0.18
Mean	3.28	20.38	1.84	1.66	P-Value	Difference%
Standard Dev	0.38	3.12	0.62	1.12	0.01	98.62
W. RED		0.93		0.93		
W. RED 1	3.61	3.73	2.15	3.73	0.12	1.58
W. RED 2	3.30	4.73	2.16	4.73	1.43	2.57
W. RED 3	3.55	3.66	1.10	3.66	0.11	2.56
Mean	3.49	4.04	1.80	4.04	P-Value	Difference%
Standard Dev	0.16	0.60	0.61	0.60	0.05	94.93
Sample	**Before**	**After**	**Before**	**After**	**Delta HF**	**Delta ABF**
SALT TAN		8.05		0.62		
SALT TAN 1	0.10	3.53	1.72	2.15	3.43	0.43
SALT TAN 2	0.56	5.67	1.21	1.34	5.11	0.13
SALT TAN 3	0.53	3.60	1.40	2.63	3.07	1.23
Mean	0.40	4.27	1.44	2.04	P-Value	Difference%
Standard Dev	0.26	1.22	0.26	0.65	0.07	92.97
W. TAN		1.29		1.39		
W. TAN 1	0.80	3.39	0.88	2.82	2.59	1.94
W. TAN 2	1.13	5.48	1.47	1.82	4.35	0.35
W. TAN 3	1.01	5.41	1.31	2.04	4.40	0.73
Mean	0.98	4.76	1.22	2.23	P-Value	Difference%
Standard Dev	0.17	1.19	0.31	0.53	0.12	87.86

Table 16: Comparing spectrophotometer results between 2 HF and 2 ABF

Spectrophotometer						
	2 HF		**2 ABF**			
Sample Red	**Before**	**After**	**Before**	**After**	**Delta HF**	**Delta ABF**
SALT RED		0.60		4.06		
SALT RED 1	2.38	10.43	4.05	9.24	8.05	5.19
SALT RED 2	4.18	13.82	5.16	4.96	9.64	0.20
SALT RED 3	3.69	18.83	4.63	1.48	15.14	3.15
Mean	3.42	14.36	4.61	5.23	P-Value	Difference%
Standard Dev	0.93	4.23	0.56	3.89	0.10	90.33
W. RED		1.94		2.61		
W. RED 1	2.46	3.20	1.22	6.08	0.74	4.86
W. RED 2	1.41	4.09	2.67	8.62	2.68	5.95
W. RED 3	3.26	2.72	3.05	8.98	0.54	5.93
Mean	2.38	3.34	2.31	7.89	P-Value	Difference%
Standard Dev	0.93	0.70	0.97	1.58	0.02	97.97
Sample Tan	**Before**	**After**	**Before**	**After**	**Delta HF**	**Delta ABF**
SALT TAN		9.55		4.00		
SALT TAN 1	0.26	8.19	1.05	1.39	7.93	0.34
SALT TAN 2	0.39	7.09	2.00	1.22	6.70	0.78
SALT TAN 3	0.23	10.12	1.84	1.20	9.89	0.64
Mean	0.29	8.47	1.63	1.27	P-Value	Difference%
Standard Dev	0.09	1.53	0.51	0.10	0.02	98.43
W. TAN		4.87		5.33		
W. TAN 1	0.68	5.04	2.56	5.06	4.36	2.50
W. TAN 2	0.71	2.77	2.72	5.44	2.06	2.72
W. TAN 3	0.75	3.84	2.72	6.15	3.09	3.43
Mean	0.71	3.88	2.67	5.55	P-Value	Difference%
Standard Dev	0.04	1.14	0.09	0.55	0.75	24.79

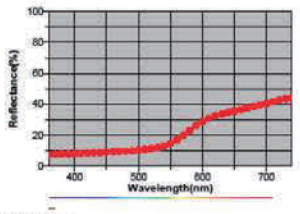
7.5 Layout data

Matteini Thesis / Evaluation Phase

Sample Set: **RED-CONTROL**
Product-application: **1HF**

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



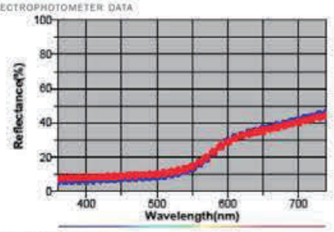
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
AR.C.01.00	189.89	130.00	127.23	201.00	198.23	11.75

AR.C.01.0

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 48.43
a* = 22.73
b* = 26.40

dE*ab = 4.20

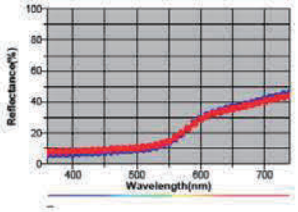
LIQUID NITROGEN DATA

AR.C.01.01	171.15	92.00	89.23	181.00	178.23	7.96

AR.C.01.1

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 48.70
a* = 22.48
b* = 26.21

dE*ab = 3.87

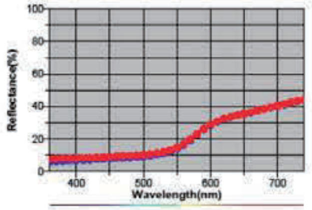
LIQUID NITROGEN DATA

AR.C.01.02	184.92	128.20	125.43	199.00	196.23	15.97

AR.C.01.2

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 48.67
a* = 21.46
b* = 24.81

dE*ab = 2.22

LIQUID NITROGEN DATA

AR.C.01.03	196.73	136.60	133.83	207.56	204.79	11.36

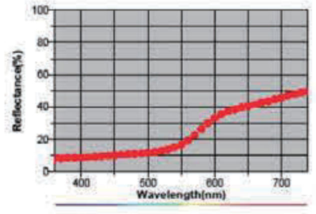
AR.C.01.3

Matteini Thesis / Evaluation Phase

Sample Set: RED-SALT
Product-application: 1HF

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA

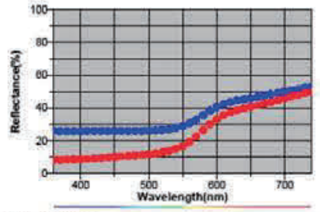


LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
AR.S.01.00	187.40	130.35	127.58	204.00	201.23	18.78

AFTER

SPECTROPHOTOMETER DATA



L* = 53.14
a* = 12.22
b* = 9.03

dE*ab = 21.13

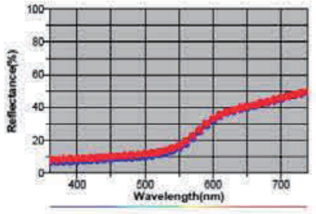
LIQUID NITROGEN DATA

AR.S.01.00	188.36	128.85	125.73	200.52	197.40	12.61

AR.S.01.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



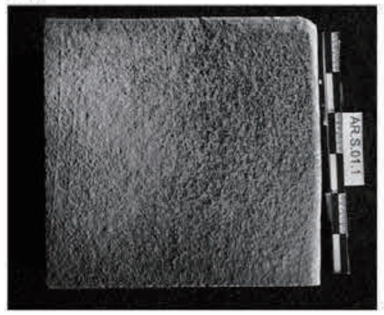
L* = 50.98
a* = 23.07
b* = 26.60

dE*ab = 2.85

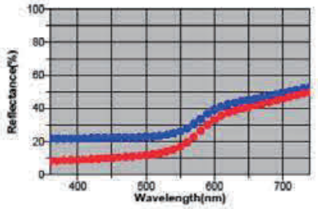
LIQUID NITROGEN DATA

AR.S.01.01	189.60	131.50	128.73	205.10	202.33	17.30

AFTER



SPECTROPHOTOMETER DATA



L* = 50.97
a* = 14.11
b* = 11.52

dE*ab = 17.35

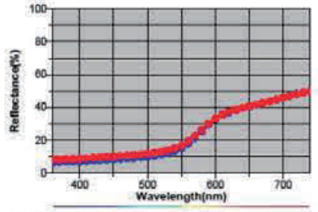
LIQUID NITROGEN DATA

AR.S.01.01	190.59	127.60	124.48	201.10	197.98	10.05

AR.S.01.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



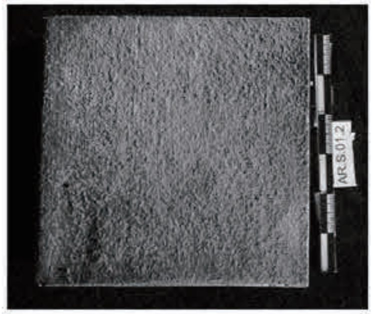
L* = 51.11
a* = 23.32
b* = 27.46

dE*ab = 3.58

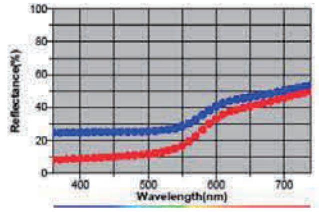
LIQUID NITROGEN DATA

AR.S.01.02	183.31	127.06	124.29	198.10	195.33	16.92

AFTER



SPECTROPHOTOMETER DATA



L* = 52.89
a* = 12.78
b* = 9.81

dE*ab = 20.19

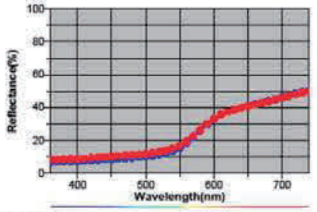
LIQUID NITROGEN DATA

AR.S.01.02	184.13	124.50	121.38	198.00	194.88	14.63

AR.S.01.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



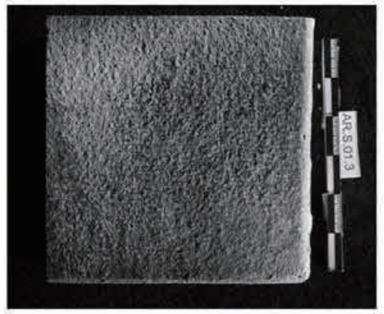
L* = 51.31
a* = 23.35
b* = 27.31

dE*ab = 3.41

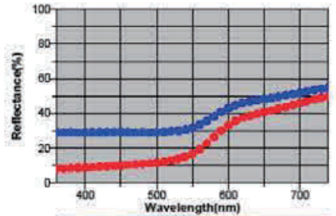
LIQUID NITROGEN DATA

AR.S.01.03	194.97	134.70	131.93	210.03	207.26	16.31

AFTER



SPECTROPHOTOMETER DATA



L* = 55.35
a* = 11.24
b* = 7.84

dE*ab = 23.59

LIQUID NITROGEN DATA

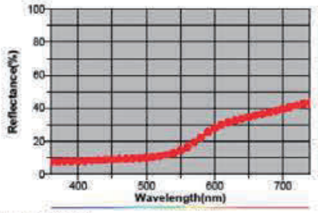
AR.S.01.03	196.15	131.40	128.28	207.15	204.03	10.40

AR.S.01.3

BEFORE

TEXTURE MAPPING

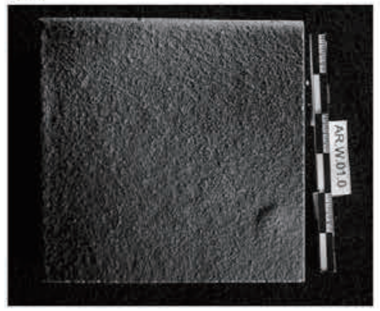
SPECTROPHOTOMETER DATA



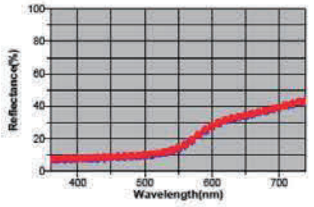
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wir	Wet	W *minus metal wir	Porosity %
AR.W.01.00	182.59	124.25	121.48	194.10	191.33	12.51

AFTER



SPECTROPHOTOMETER DATA



L* = 48.15
a* = 20.72
b* = 22.87

dE*ab = 0.93

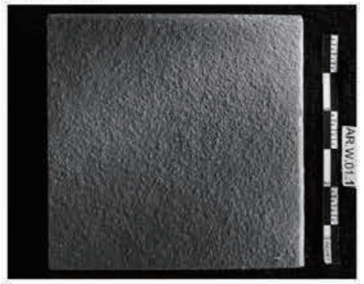
LIQUID NITROGEN DATA

AR.W.01.00	185.46	123.65	121.07	192.22	189.64	6.10

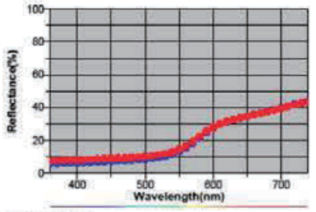
AR.W.01.0

BEFORE

TEXTURE MAPPING



SPECTROPHOTOMETER DATA



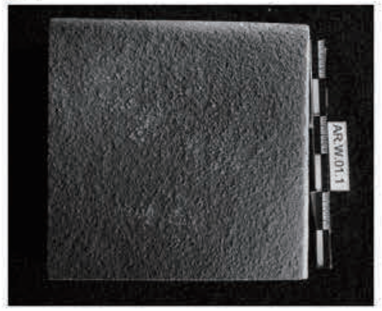
L* = 47.88
a* = 21.78
b* = 25.46

dE*ab = 3.61

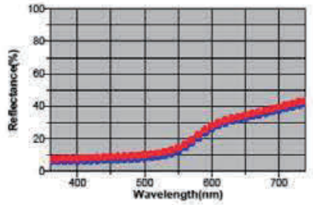
LIQUID NITROGEN DATA

AR.W.01.01	196.13	131.50	128.73	208.00	205.23	11.90

AFTER



SPECTROPHOTOMETER DATA



L* = 46.52
a* = 21.98
b* = 24.80

dE*ab = 3.73

LIQUID NITROGEN DATA

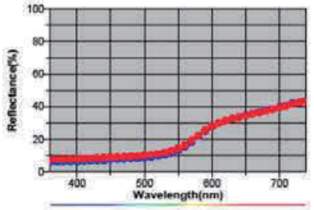
AR.W.01.01	199.60	132.00	129.42	209.00	206.42	8.86

AR.W.01.1

BEFORE

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 47.75
a* = 21.87
b* = 25.06

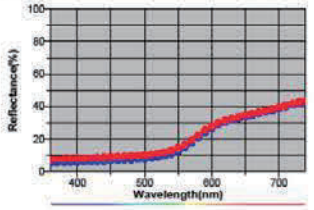
dE*ab = 3.30

LIQUID NITROGEN DATA

AR.W.01.02	197.95	132.20	129.43	210.00	207.23	11.93

AFTER

SPECTROPHOTOMETER DATA



L* = 46.68
a* = 22.61
b* = 25.90

dE*ab = 4.73

LIQUID NITROGEN DATA

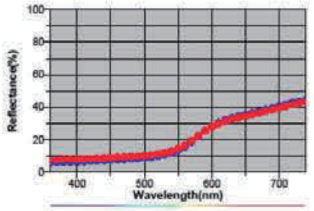
AR.W.01.02	201.58	132.90	130.32	209.15	206.57	6.54

AR.W.01.2

BEFORE

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



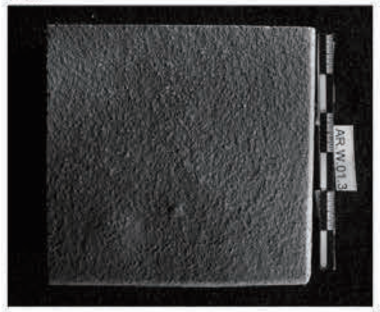
L* = 48.03
a* = 21.96
b* = 25.39

dE*ab = 3.55

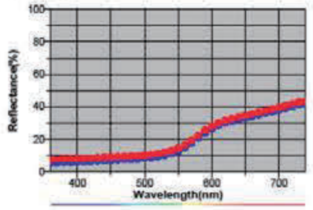
LIQUID NITROGEN DATA

AR.W.01.03	188.85	127.80	126.50	201.00	199.70	14.82

AFTER



SPECTROPHOTOMETER DATA



L* = 46.83
a* = 21.69
b* = 25.13

dE*ab = 3.66

LIQUID NITROGEN DATA

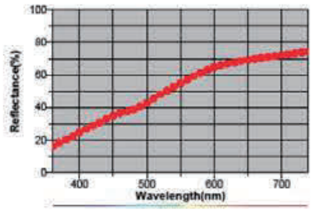
AR.W.01.03	192.21	135.85	133.27	197.50	194.92	4.40

AR.W.01.3

Sample Set: **TAN-NO TEST**
Product-application: **1HF**

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



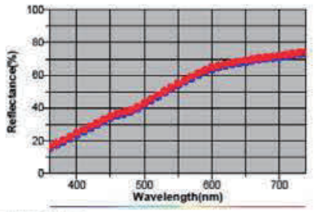
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
AT.C.01.00	188.81	128.80	126.03	202.10	199.33	14.35

AT.C.01.0

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 78.14
a* = 5.69
b* = 23.07

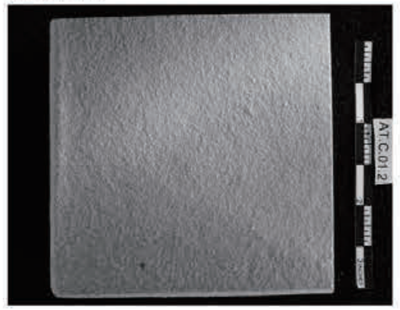
dE*ab = 0.77

LIQUID NITROGEN DATA

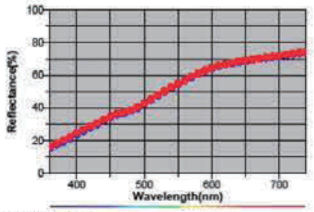
AT.C.01.01	197.12	135.50	132.73	212.10	209.33	15.94

AT.C.01.1

BEFORE
TEXTURE MAPPING



SPECTROPHOTOMETER DATA



L* = 78.47
a* = 5.71
b* = 23.04

dE*ab = 0.55

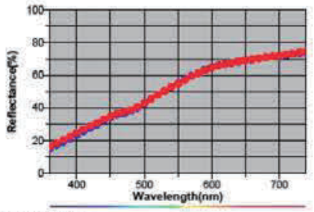
LIQUID NITROGEN DATA

AT.C.01.02	209.74	145.66	142.89	226.20	223.43	17.00

AT.C.01.2

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 78.71
a* = 5.54
b* = 23.47

dE*ab = 0.95

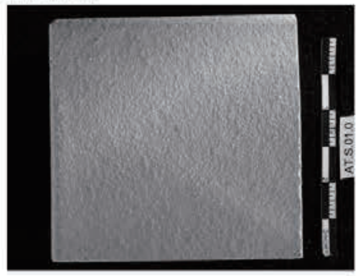
LIQUID NITROGEN DATA

AT.C.01.03	193.66	134.50	131.73	210.02	207.25	18.00

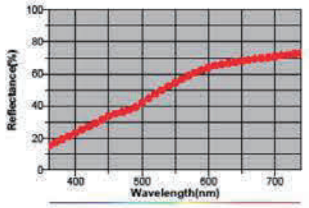
AT.C.01.3

Sample Set:**TAN-SALT**
Product-application:**1HF**

BEFORE
TEXTURE MAPPING



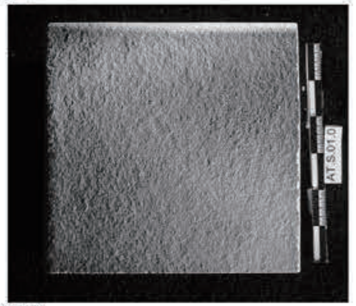
SPECTROPHOTOMETER DATA



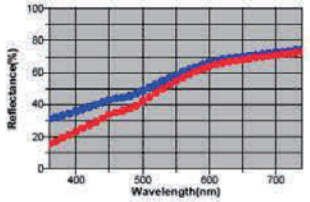
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wir	Wet	W *minus metal wir	Porosity %
AT.S.01.00	201.80	139.96	137.19	219.20	216.43	18.46

AFTER



SPECTROPHOTOMETER DATA



L* = 80.74
a* = 4.75
b* = 16.09

dE*ab = 8.05

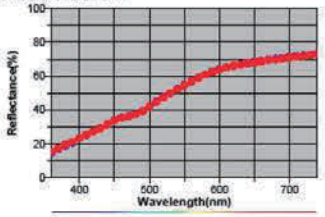
LIQUID NITROGEN DATA

AT.S.01.00	203.10	135.50	132.38	216.50	213.38	12.69

AT.S.01.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



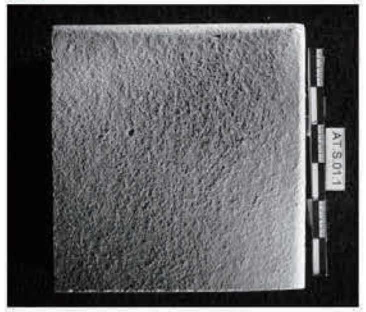
L* = 78.40
a* = 5.36
b* = 23.71

dE*ab = 0.10

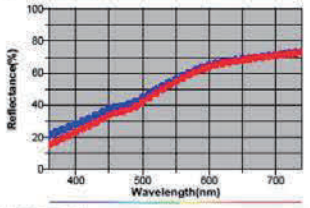
LIQUID NITROGEN DATA

AT.S.01.01	202.20	138.00	135.23	220.10	217.33	18.43

AFTER



SPECTROPHOTOMETER DATA



L* = 79.27
a* = 5.12
b* = 20.38

dE*ab = 3.53

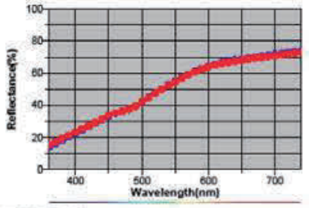
LIQUID NITROGEN DATA

AT.S.01.01	203.47	133.60	130.48	213.10	209.98	8.19

AT.S.01.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



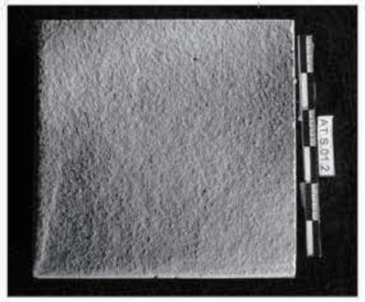
L* = 78.48
a* = 5.43
b* = 24.28

dE*ab = 0.56

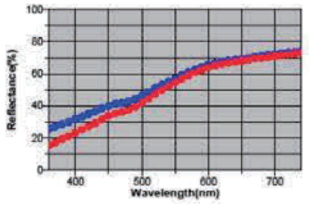
LIQUID NITROGEN DATA

AT.S.01.02	203.32	140.46	137.69	219.40	216.63	16.86

AFTER



SPECTROPHOTOMETER DATA



L* = 79.97
a* = 4.94
b* = 18.33

dE*ab = 5.67

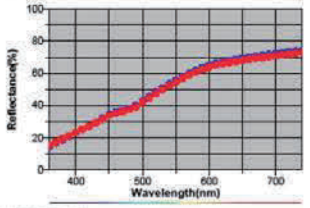
LIQUID NITROGEN DATA

AT.S.01.02	204.43	135.10	131.98	215.10	211.98	9.44

AT.S.01.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



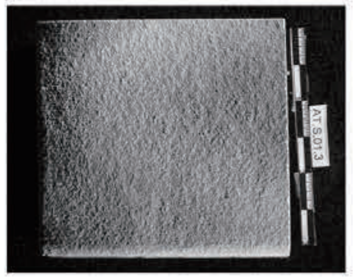
L* = 78.80
a* = 5.40
b* = 23.96

dE*ab = 0.53

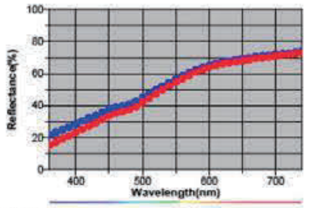
LIQUID NITROGEN DATA

AT.S.01.03	191.66	131.87	129.10	207.10	204.33	16.84

AFTER



SPECTROPHOTOMETER DATA



L* = 79.44
a* = 5.17
b* = 20.32

dE*ab = 3.60

LIQUID NITROGEN DATA

AT.S.01.03	192.80	126.83	123.71	203.01	199.89	9.31

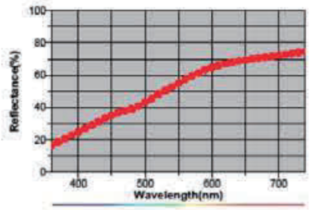
AT.S.01.3

Matteini Thesis / Evaluation Phase

Sample Set: **TAN-WEATHEROMETER**
Product-application: **1HF**

BEFORE
TEXTURE MAPPING

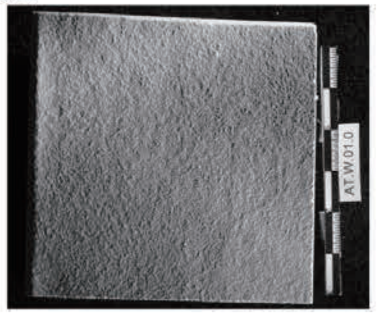
SPECTROPHOTOMETER DATA



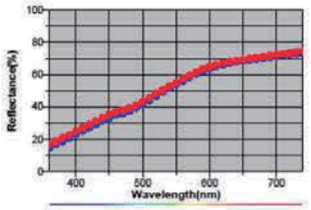
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
AT.W.01.00	196.08	134.85	133.55	210.5	209.20	17.34

AFTER



SPECTROPHOTOMETER DATA



L* = 78.18
a* = 5.03
b* = 23.47

dE*ab = 1.29

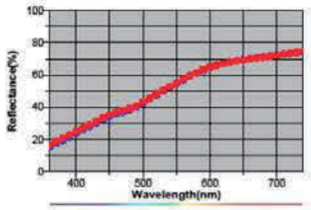
LIQUID NITROGEN DATA

AT.W.01.00	198.35	137.55	134.97	204.35	201.77	5.12

AT.W.01.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



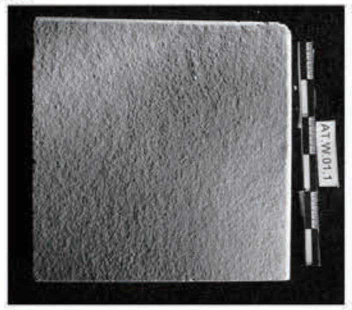
L* = 78.66
a* = 5.83
b* = 23.13

dE*ab = 0.80

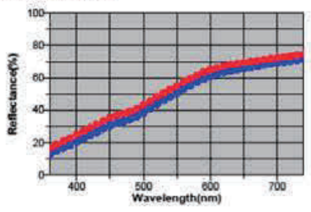
LIQUID NITROGEN DATA

AT.W.01.01	200.46	138.11	136.81	219	217.70	21.31

AFTER



SPECTROPHOTOMETER DATA



L* = 76.30
a* = 6.56
b* = 24.49

dE*ab = 3.39

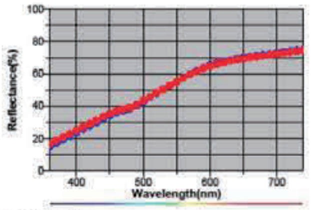
LIQUID NITROGEN DATA

AT.W.01.01	203.47	134.00	131.42	213.1	210.52	8.91

AT.W.01.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



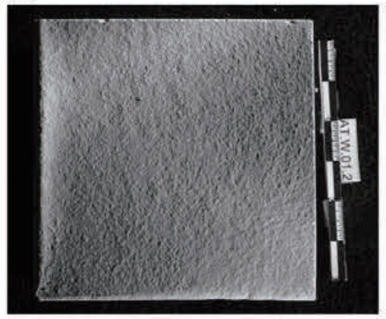
L* = 78.78
a* = 5.94
b* = 23.47

dE*ab = 1.13

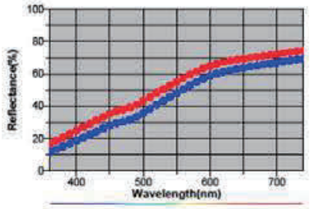
LIQUID NITROGEN DATA

AT.W.01.02	204.16	140.35	139.05	220.4	219.10	18.66

AFTER



SPECTROPHOTOMETER DATA



L* = 74.85
a* = 7.21
b* = 25.63

dE*ab = 5.48

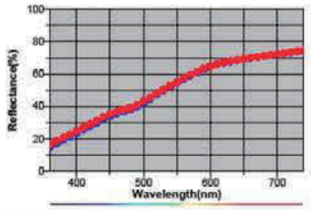
LIQUID NITROGEN DATA

AT.W.01.02	208.20	136.00	133.42	218.3	215.72	9.14

AT.W.01.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



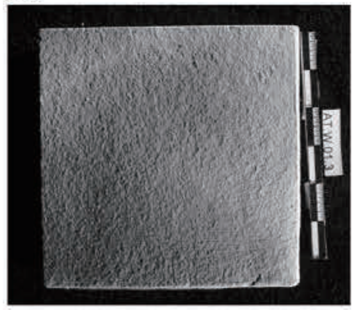
L* = 78.51
a* = 5.95
b* = 23.30

dE*ab = 1.01

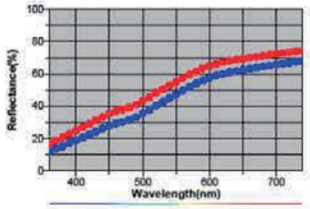
LIQUID NITROGEN DATA

AT.W.01.03	196.15	135.50	134.20	211.11	209.81	18.07

AFTER



SPECTROPHOTOMETER DATA



L* = 74.13
a* = 7.04
b* = 24.75

dE*ab = 5.41

LIQUID NITROGEN DATA

AT.W.01.03	200.81	130.00	127.42	207.05	204.47	4.75

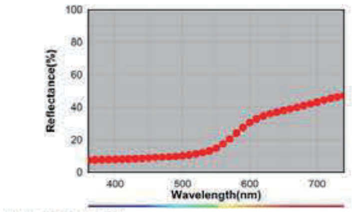
AT.W.01.3

Matteini Thesis / Evaluation Phase

Sample Set: **RED-NO TEST**
Product-application: **2HF**

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



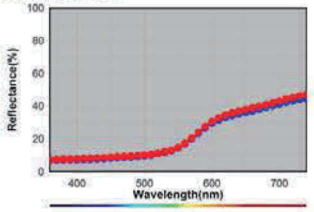
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
AR.C.02.00	187.35	129.35	126.58	200.58	197.81	14.68

AR.C.02.0

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 49.28
a* = 21.55
b* = 25.22

dE*ab = 1.17

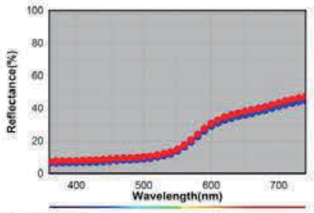
LIQUID NITROGEN DATA

AR.C.02.01	180.94	123.30	120.53	191.64	188.87	11.60

AR.C.02.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 48.51
a* = 22.37
b* = 26.12

dE*ab = 2.17

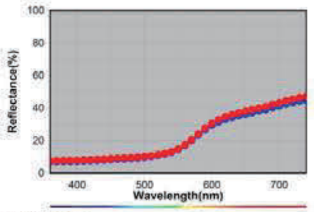
LIQUID NITROGEN DATA

AR.C.02.02	199.83	137.85	135.08	213.76	210.99	14.70

AR.C.02.2

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 49.28
a* = 21.55
b* = 25.22

dE*ab = 1.17

LIQUID NITROGEN DATA

AR.C.02.03	187.81	127.30	124.53	199.34	196.57	12.16

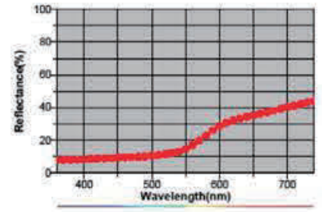
AR.C.02.3

Matteini Thesis / Evaluation Phase

Sample Set: **RED-SALT**
Product-application: **2HF**

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA

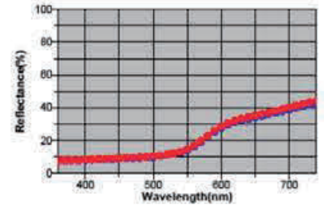


LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wir	Wet	W *minus metal wir	Porosity %
AR.S.02.00	186.21	127.93	125.16	197.75	194.98	12.56

AFTER

SPECTROPHOTOMETER DATA



L* = 48.78
a* = 20.07
b* = 21.88

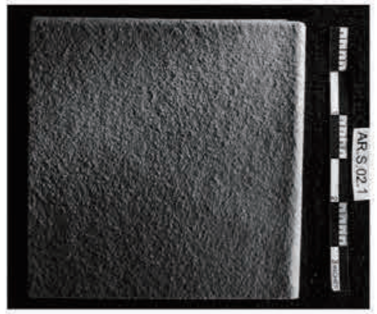
dE*ab = 0.60

LIQUID NITROGEN DATA

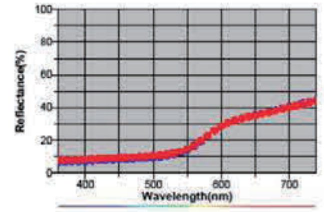
AR.S.02.00	187.09	126.00	122.88	198.10	194.98	10.94

AR.S.02.0

BEFORE
TEXTURE MAPPING



SPECTROPHOTOMETER DATA



L* = 48.81
a* = 21.09
b* = 24.09

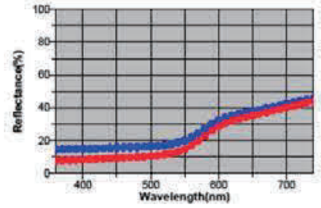
dE*ab = 2.38

LIQUID NITROGEN DATA

AR.S.02.01	178.52	120.45	117.79	186.56	183.90	8.14

AFTER

SPECTROPHOTOMETER DATA



L* = 54.87
a* = 15.52
b* = 14.42

dE*ab = 10.43

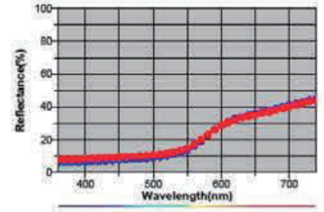
LIQUID NITROGEN DATA

AR.S.02.01	180.12	121.10	117.98	188.00	184.88	7.12

AR.S.02.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



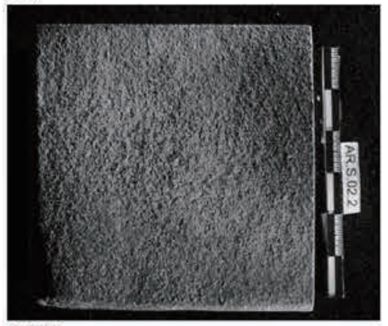
L* = 48.56
a* = 21.97
b* = 25.65

dE*ab = 4.18

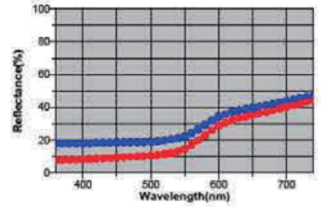
LIQUID NITROGEN DATA

AR.S.02.02	196.61	134.60	131.83	208.64	205.87	12.51

AFTER



SPECTROPHOTOMETER DATA



L* = 57.22
a* = 14.21
b* = 12.29

dE*ab = 13.82

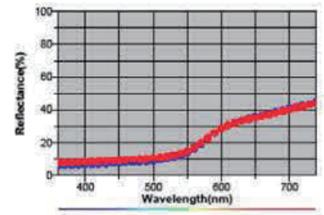
LIQUID NITROGEN DATA

AR.S.02.02	198.07	132.85	129.05	206.10	202.30	5.77

AR.S.02.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 48.59
a* = 21.66
b* = 25.25

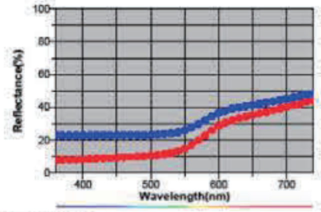
dE*ab = 3.69

LIQUID NITROGEN DATA

AR.S.02.03	191.63	130.60	127.83	203.57	200.80	12.57

AFTER

SPECTROPHOTOMETER DATA



L* = 50.31
a* = 11.97
b* = 9.04

dE*ab = 18.83

LIQUID NITROGEN DATA

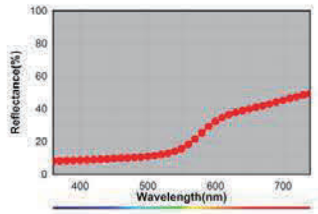
AR.S.02.03	193.89	129.71	125.91	202.00	198.20	5.96

AR.S.02.3

Sample Set: RED-WEATHEROMETER
Product-application: 2HF

BEFORE
TEXTURE MAPPING

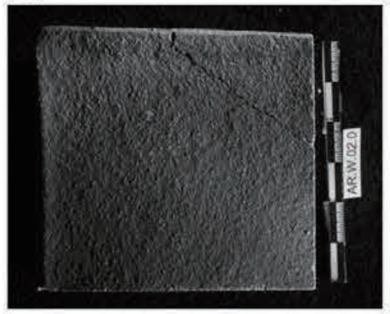
SPECTROPHOTOMETER DATA



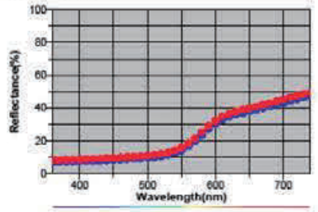
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wir	Wet	W *minus metal wir	Porosity %
AR.W.02.00	191.57	133.86	131.09	209.75	206.98	20.31

AFTER



SPECTROPHOTOMETER DATA



L* = 49.60
a* = 22.95
b* = 25.10

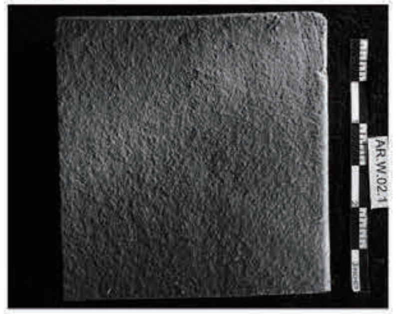
dE*ab = 1.94

LIQUID NITROGEN DATA

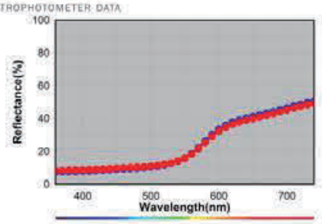
AR.W.02.00	193.75	131.00	127.59	208.00	204.59	14.08

AR.W.02.0

BEFORE
TEXTURE MAPPING



SPECTROPHOTOMETER DATA



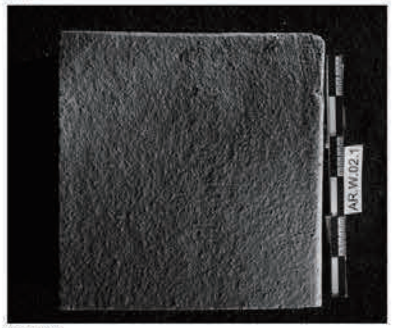
L* = 51.56
a* = 23.34
b* = 26.63

dE*ab = 2.46

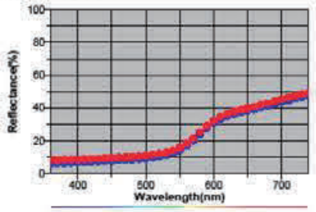
LIQUID NITROGEN DATA

AR.W.02.01	195.52	135.10	132.44	209.31	206.65	15.00

AFTER



SPECTROPHOTOMETER DATA



L* = 49.62
a* = 23.52
b* = 26.86

dE*ab = 3.20

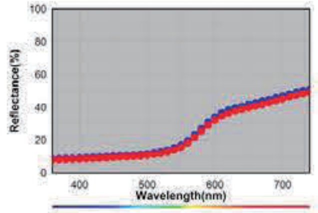
LIQUID NITROGEN DATA

AR.W.02.01	198.85	132.00	129.42	209.00	205.20	8.38

AR.W.02.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 52.69
a* = 22.31
b* = 24.68

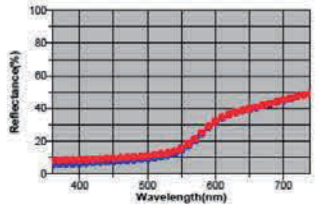
dE*ab = 1.41

LIQUID NITROGEN DATA

AR.W.02.02	209.17	144.68	142.02	224.02	221.36	15.36

AFTER

SPECTROPHOTOMETER DATA



L* = 50.20
a* = 23.81
b* = 28.05

dE*ab = 4.09

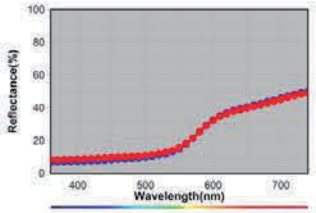
LIQUID NITROGEN DATA

AR.W.02.02	211.90	144.27	141.69	226.00	222.20	12.79

AR.W.02.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



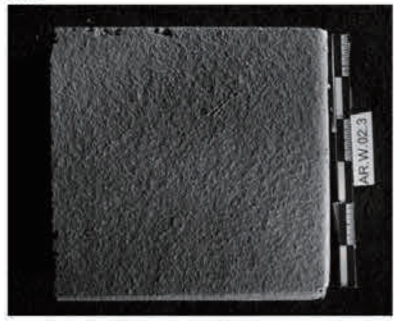
L* = 50.83
a* = 23.73
b* = 27.31

dE*ab = 3.26

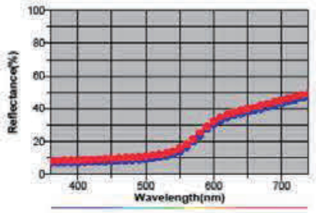
LIQUID NITROGEN DATA

AR.W.02.03	179.60	124.81	122.15	193.18	190.52	15.97

AFTER



SPECTROPHOTOMETER DATA



L* = 49.40
a* = 23.56
b* = 25.90

dE*ab = 2.72

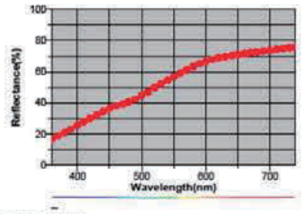
LIQUID NITROGEN DATA

AR.W.02.03	182.16	122.51	119.93	192.50	188.70	9.51

AR.W.02.3

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



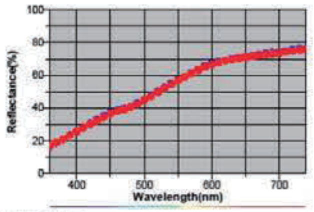
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
AT.C.02.00	202.99	140.75	138.09	219.35	216.69	17.43

AT.C.02.0

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 79.92
a* = 5.54
b* = 22.12

dE*ab = 0.27

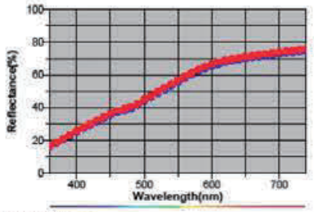
LIQUID NITROGEN DATA

AT.C.02.01	209.28	144.66	142.00	226.25	223.59	17.54

AT.C.02.1

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 79.24
a* = 5.58
b* = 22.34

dE*ab = 0.51

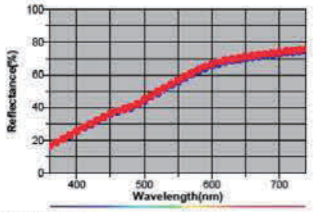
LIQUID NITROGEN DATA

AT.C.02.02	203.40	140.67	138.01	219.73	217.07	17.29

AT.C.02.2

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 79.33
a* = 5.55
b* = 22.08

dE*ab = 0.49

LIQUID NITROGEN DATA

AT.C.02.03	203.74	141.40	138.74	220.49	217.83	17.82

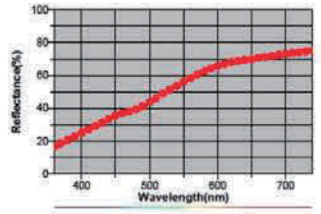
AT.C.02.3

Matteini Thesis / Evaluation Phase

Sample Set: **TAN-SALT**
Product-application: **2HF**

BEFORE
TEXTURE MAPPING

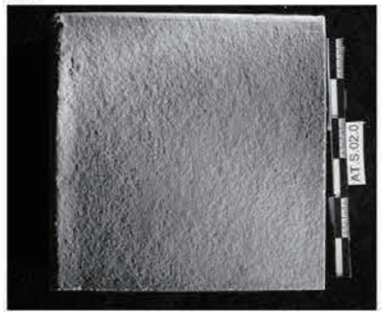
SPECTROPHOTOMETER DATA



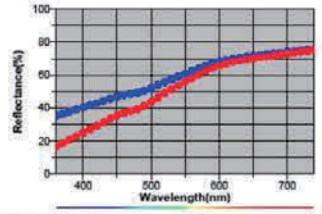
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
AT.S.02.00	205.37	141.50	138.84	222.00	219.34	17.35

AFTER



SPECTROPHOTOMETER DATA



L* = 82.12
a* = 4.31
b* = 13.80

dE*ab = 9.55

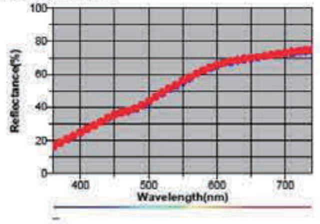
LIQUID NITROGEN DATA

AT.S.02.00	209.45	140.19	137.61	221.00	218.42	11.10

AT.S.02.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



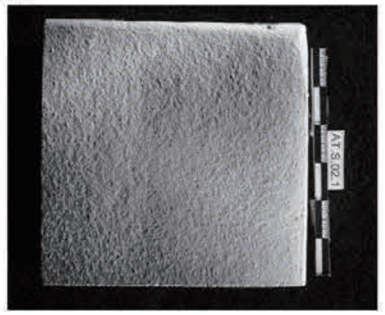
L* = 79.04
a* = 5.69
b* = 22.77

dE*ab = 0.26

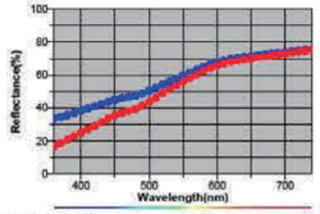
LIQUID NITROGEN DATA

AT.S.02.01	203.31	139.80	137.14	219.26	216.60	16.73

AFTER



SPECTROPHOTOMETER DATA



L* = 81.54
a* = 4.84
b* = 14.99

dE*ab = 8.19

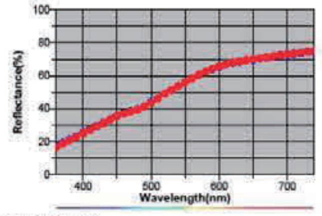
LIQUID NITROGEN DATA

AT.S.02.01	204.26	134.00	130.20	215.00	211.20	8.57

AT.S.02.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 79.27
a* = 5.52
b* = 22.43

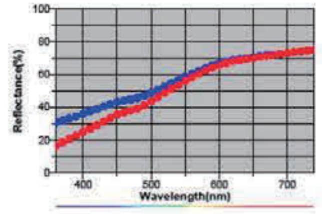
dE*ab = 0.39

LIQUID NITROGEN DATA

AT.S.02.02	205.45	142.20	139.54	222.39	219.73	17.81

AFTER

SPECTROPHOTOMETER DATA



L* = 80.85
a* = 5.00
b* = 15.94

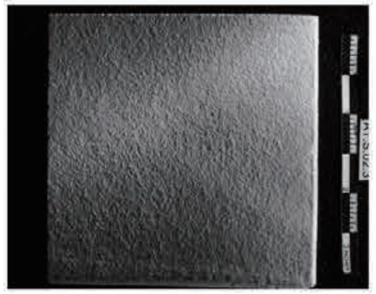
dE*ab = 7.09

LIQUID NITROGEN DATA

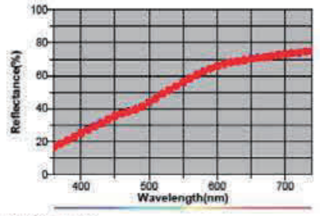
AT.S.02.02	206.44	138.50	134.70	219.00	215.20	10.88

AT.S.02.2

BEFORE
TEXTURE MAPPING



SPECTROPHOTOMETER DATA



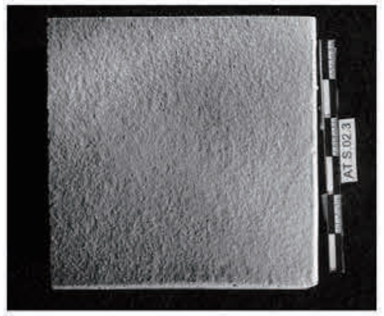
L* = 79.27
a* = 5.62
b* = 22.60

dE*ab = 0.23

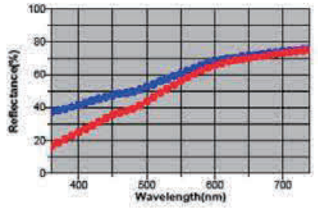
LIQUID NITROGEN DATA

AT.S.02.03	203.00	140.30	137.64	222.10	219.44	20.10

AFTER



SPECTROPHOTOMETER DATA



L* = 82.23
a* = 4.39
b* = 13.22

dE*ab = 10.12

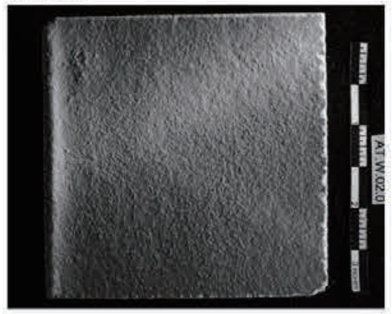
LIQUID NITROGEN DATA

AT.S.02.03	203.96	135.35	131.55	215.00	211.20	9.09

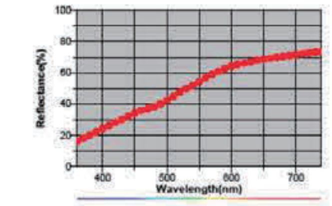
AT.S.02.3

Sample Set: **TAN-WEATHEROMETER**
Product-application: **2HF**

BEFORE
TEXTURE MAPPING



SPECTROPHOTOMETER DATA

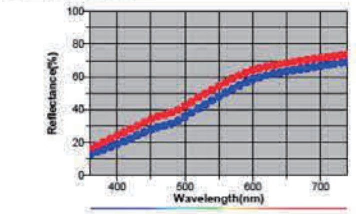


LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wir	Wet	W *minus metal wir	Porosity %
AT.W.02.00	213.98	147.85	145.19	230.13	227.47	16.40

AFTER

SPECTROPHOTOMETER DATA



L* = 74.53
a* = 7.11
b* = 25.46

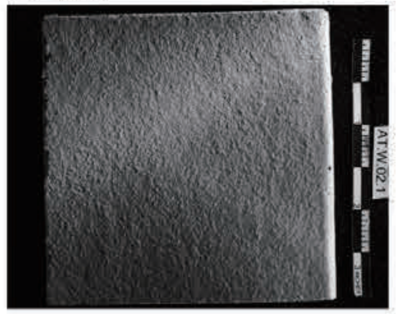
dE*ab = 4.87

LIQUID NITROGEN DATA

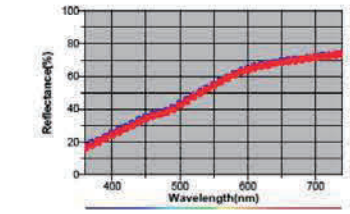
AT.W.02.00	217.35	143.78	141.20	226	223.47	7.44

AT.W.02.0

BEFORE
TEXTURE MAPPING



SPECTROPHOTOMETER DATA



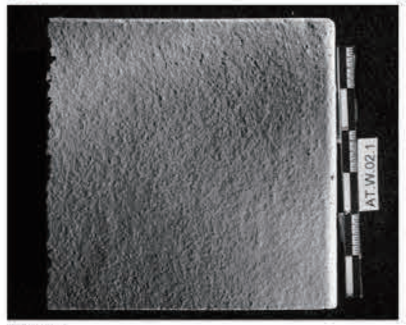
L* = 78.72
a* = 5.68
b* = 22.25

dE*ab = 0.68

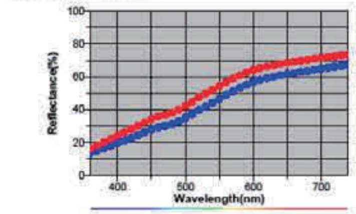
LIQUID NITROGEN DATA

AT.W.02.01	207.23	142.55	139.89	223.8	221.14	17.12

AFTER



SPECTROPHOTOMETER DATA



L* = 73.75
a* = 7.19
b* = 24.13

dE*ab = 5.04

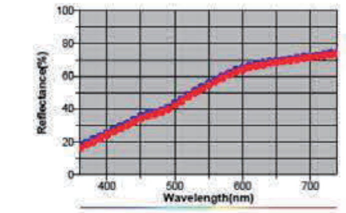
LIQUID NITROGEN DATA

AT.W.02.01	212.32	138.82	136.24	219	216.47	5.17

AT.W.02.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



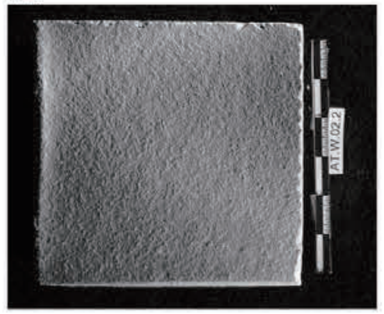
L* = 70.01
a* = 5.58
b* = 22.53

dE*ab = 0.71

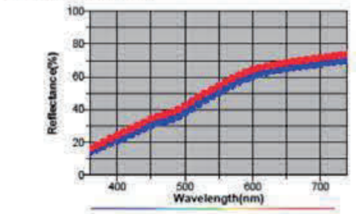
LIQUID NITROGEN DATA

AT.W.02.02	203.90	140.50	137.84	220.75	218.09	17.68

AFTER



SPECTROPHOTOMETER DATA



L* = 76.08
a* = 6.45
b* = 24.14

dE*ab = 2.77

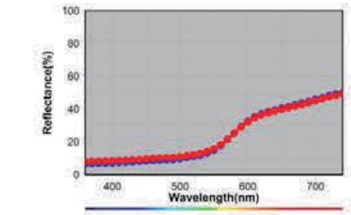
LIQUID NITROGEN DATA

AT.W.02.02	207.20	136.70	134.12	220	217.47	12.32

AT.W.02.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 50.83
a* = 23.73
b* = 27.31

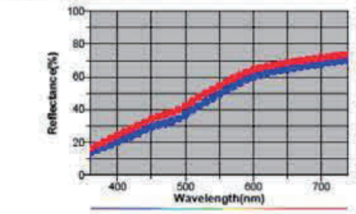
dE*ab = 3.26

LIQUID NITROGEN DATA

AT.W.02.03	199.55	137.80	135.14	214.78	212.12	16.33

AFTER

SPECTROPHOTOMETER DATA



L* = 75.48
a* = 6.97
b* = 24.99

dE*ab = 3.84

LIQUID NITROGEN DATA

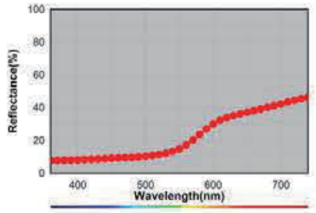
AT.W.02.03	201.92	133.50	130.92	211	208.47	8.45

AT.W.02.3

Sample Set: **RED-NO TEST**
Product-application: **1ABF**

TEXTURE MAPPING

SPECTROPHOTOMETER DATA

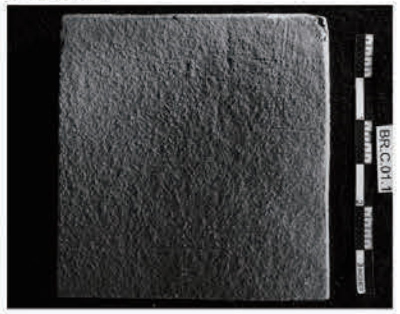


LIQUID NITROGEN DATA

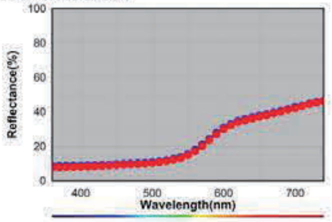
Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BR.C.01.00	184.64	126.88	124.22	197.10	194.44	13.96

BR.C.01.0

TEXTURE MAPPING



SPECTROPHOTOMETER DATA



L* = 50.62
a* = 21.24
b* = 22.96

dE*ab = 1.01

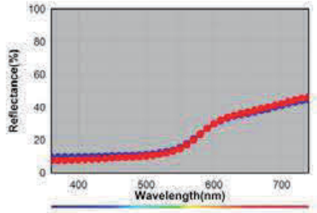
LIQUID NITROGEN DATA

BR.C.01.01	173.03	118.40	115.74	183.64	180.98	12.19

BR.C.01.1

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 50.34
a* = 20.37
b* = 20.81

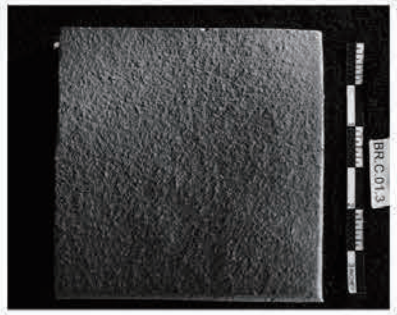
dE*ab = 2.97

LIQUID NITROGEN DATA

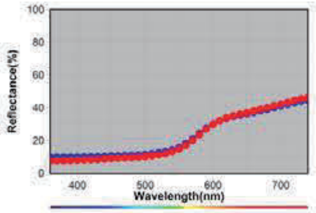
BR.C.01.02	196.47	133.10	130.75	205.70	203.35	9.48

BR.C.01.2

TEXTURE MAPPING



SPECTROPHOTOMETER DATA



L* = 50.72
a* = 20.00
b* = 20.56

dE*ab = 3.43

LIQUID NITROGEN DATA

BR.C.01.03	176.45	119.00	116.65	185.15	182.80	9.60

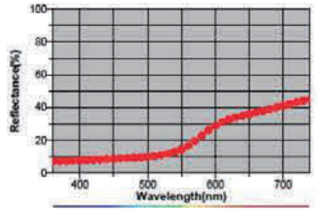
BR.C.01.3

Matteini Thesis / Evaluation Phase

Sample Set: RED-SALT
Product-application: 1ABF

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA

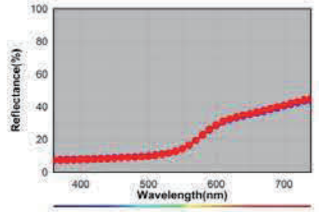


LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BR.S.01.00	198.44	136.17	133.82	213.10	210.75	16.00

AFTER

SPECTROPHOTOMETER DATA



L* = 49.09
a* = 20.77
b* = 22.83

dE*ab = 0.87

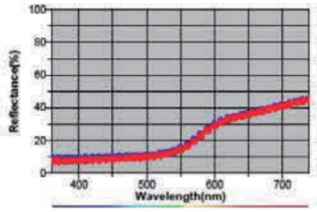
LIQUID NITROGEN DATA

BR.S.01.00	202.16	136.40	133.82	211.10	208.52	8.51

BR.S.01.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



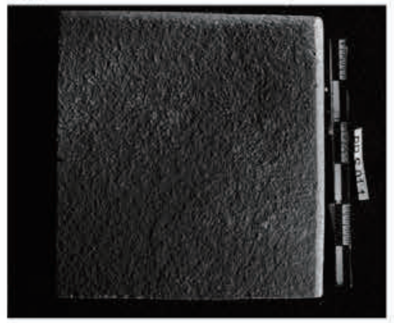
L* = 50.04
a* = 20.80
b* = 21.80

dE*ab = 2.06

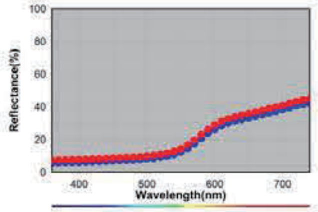
LIQUID NITROGEN DATA

BR.S.01.01	190.62	128.70	126.35	199.10	196.75	8.71

AFTER



SPECTROPHOTOMETER DATA



L* = 46.58
a* = 22.18
b* = 24.64

dE*ab = 2.91

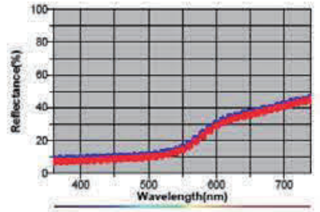
LIQUID NITROGEN DATA

BR.S.01.02	213.05	142.00	139.42	220.00	217.42	5.60

BR.S.01.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 50.68
a* = 20.49
b* = 22.04

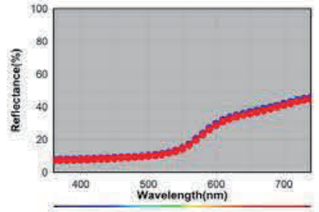
dE*ab = 2.32

LIQUID NITROGEN DATA

BR.S.01.02	207.72	139.30	136.95	216.88	214.53	8.78

AFTER

SPECTROPHOTOMETER DATA



L* = 49.82
a* = 21.33
b* = 23.45

dE*ab = 0.76

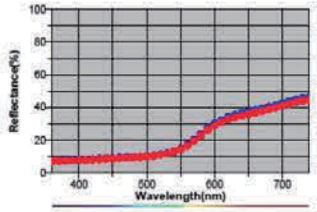
LIQUID NITROGEN DATA

BR.S.01.02	213.05	142.00	139.42	220.00	217.42	5.60

BR.S.01.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



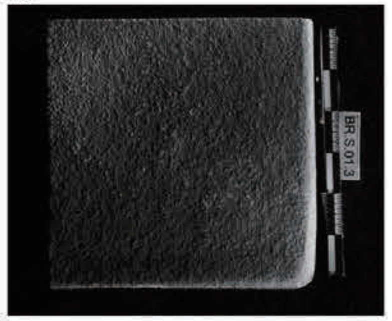
L* = 49.87
a* = 21.86
b* = 24.06

dE*ab = 1.14

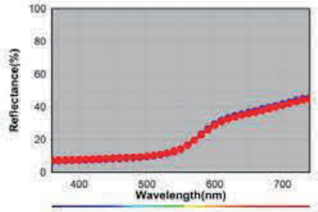
LIQUID NITROGEN DATA

BR.S.01.03	185.98	125.04	122.93	196.10	193.75	10.97

AFTER



SPECTROPHOTOMETER DATA



L* = 49.13
a* = 22.00
b* = 24.61

dE*ab = 1.32

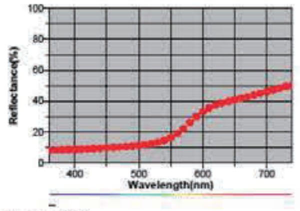
LIQUID NITROGEN DATA

BR.S.01.03	191.17	128.25	125.67	198.12	195.54	6.25

BR.S.01.3

BEFORE
TEXTURE MAPPING

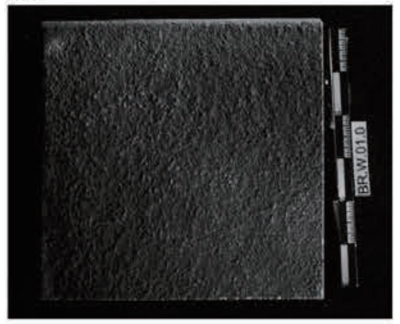
SPECTROPHOTOMETER DATA



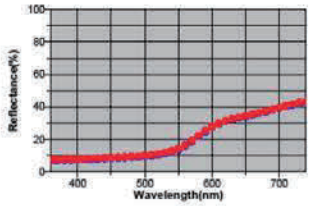
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BR.W.01.00	174.03	120.16	118.05	186.02	183.91	15.00

AFTER



SPECTROPHOTOMETER DATA



L* = 48.15
a* = 20.72
b* = 22.87

dE*ab = 0.93

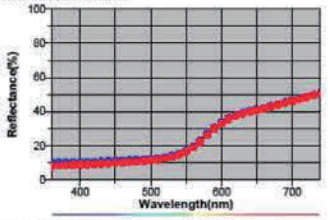
LIQUID NITROGEN DATA

BR.W.01.00	176.12	117.80	115.22	185.00	182.42	9.37

BR.W.01.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



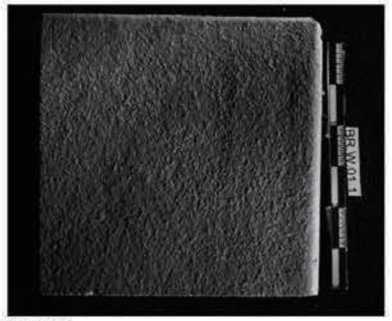
L* = 52.75
a* = 21.93
b* = 22.81

dE*ab = 2.15

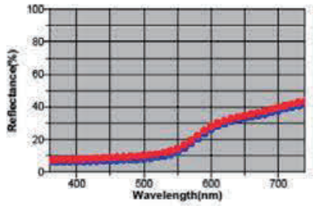
LIQUID NITROGEN DATA

BR.W.01.01	189.40	128.75	126.64	200.25	198.14	12.22

AFTER



SPECTROPHOTOMETER DATA



L* = 46.52
a* = 21.98
b* = 24.80

dE*ab = 3.73

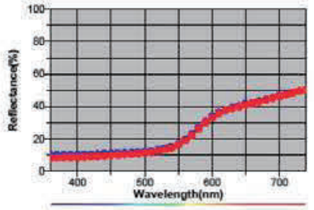
LIQUID NITROGEN DATA

BR.W.01.01	191.60	129.75	127.17	204.10	201.52	13.34

BR.W.01.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 52.67
a* = 22.12
b* = 22.76

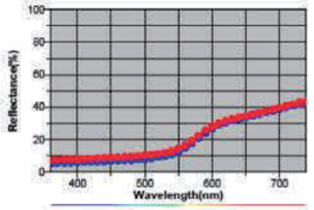
dE*ab = 2.16

LIQUID NITROGEN DATA

BR.W.01.02	183.26	124.00	121.89	197.10	194.99	16.05

AFTER

SPECTROPHOTOMETER DATA



L* = 46.68
a* = 22.61
b* = 25.90

dE*ab = 4.73

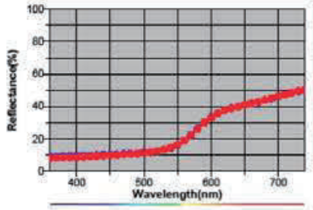
LIQUID NITROGEN DATA

BR.W.01.02	185.30	126.20	123.62	199.00	196.42	15.27

BR.W.01.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 52.10
a* = 22.54
b* = 23.78

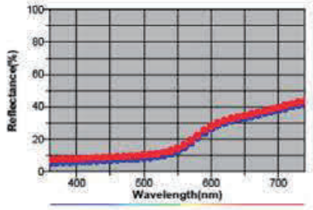
dE*ab = 1.10

LIQUID NITROGEN DATA

BR.W.01.03	186.35	126.15	124.04	202.10	199.99	17.96

AFTER

SPECTROPHOTOMETER DATA



L* = 46.83
a* = 21.69
b* = 25.13

dE*ab = 3.66

LIQUID NITROGEN DATA

BR.W.01.03	188.50	128.50	125.92	201.30	198.72	14.04

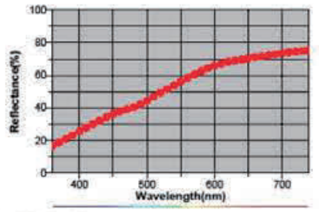
BR.W.01.3

Matteini Thesis / Evaluation Phase

Sample Set: TAN-NO TEST
Product-application: 1ABF

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



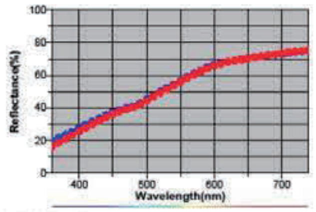
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BT.C.01.00	195.45	135.50	133.39	210.00	207.89	16.70

BT.C.01.0

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 79.65
a* = 5.59
b* = 21.14

dE*ab = 0.83

LIQUID NITROGEN DATA

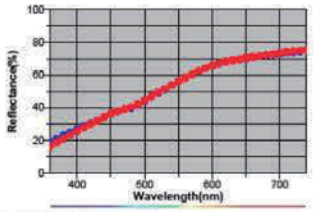
BT.C.01.01	192.09	131.30	129.19	206.10	203.99	15.91

BT.C.01.1

BEFORE

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 79.35
a* = 5.78
b* = 21.76

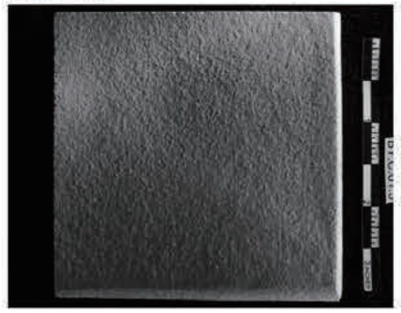
dE*ab = 0.27

LIQUID NITROGEN DATA

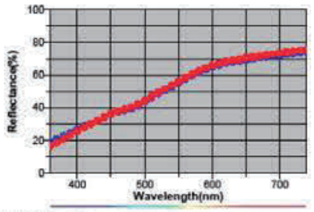
BT.C.01.02	204.11	138.70	136.59	218.55	216.44	15.44

BT.C.01.2

TEXTURE MAPPING



SPECTROPHOTOMETER DATA



L* = 79.03
a* = 5.76
b* = 21.57

dE*ab = 0.54

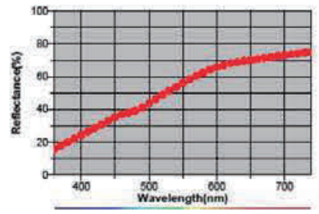
LIQUID NITROGEN DATA

BT.C.01.03	207.58	140.00	137.89	220.00	217.89	12.89

BT.C.01.3

BEFORE
TEXTURE MAPPING

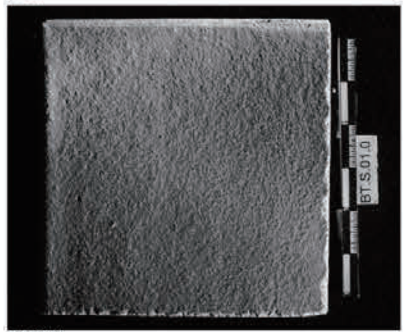
SPECTROPHOTOMETER DATA



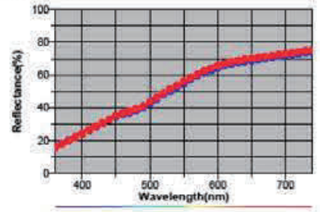
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BT.S.01.00	186.64	129.20	127.09	200.89	198.78	16.93

AFTER



SPECTROPHOTOMETER DATA



L* = 78.69
a* = 5.85
b* = 22.97

dE*ab = 0.62

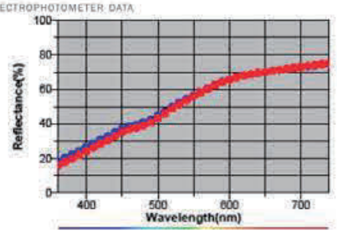
LIQUID NITROGEN DATA

BT.S.01.00	190.15	128.74	126.16	202.01	199.43	12.67

BT.S.01.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



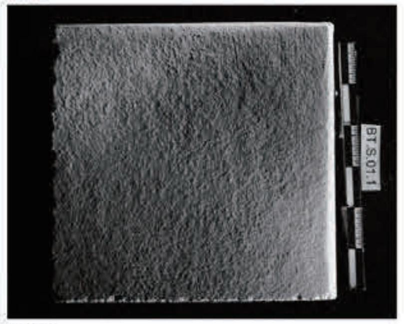
L* = 79.54
a* = 5.36
b* = 21.55

dE*ab = 1.72

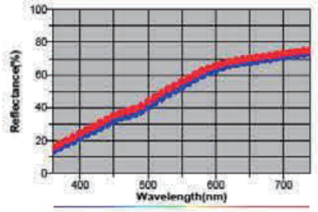
LIQUID NITROGEN DATA

BT.S.01.01	191.51	131.30	129.19	207.00	204.89	17.68

AFTER



SPECTROPHOTOMETER DATA



L* = 77.60
a* = 6.24
b* = 24.42

dE*ab = 2.15

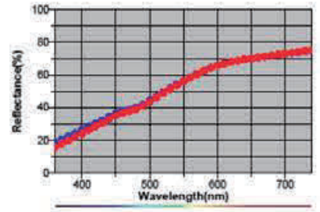
LIQUID NITROGEN DATA

BT.S.01.01	194.36	131.10	128.52	201.10	198.52	5.94

BT.S.01.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



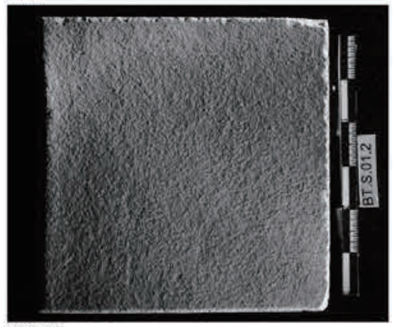
L* = 79.44
a* = 5.51
b* = 22.04

dE*ab = 1.21

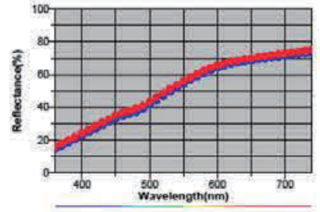
LIQUID NITROGEN DATA

BT.S.01.02	191.44	132.20	130.09	200.30	198.19	9.91

AFTER



SPECTROPHOTOMETER DATA



L* = 78.29
a* = 5.80
b* = 24.14

dE*ab = 1.34

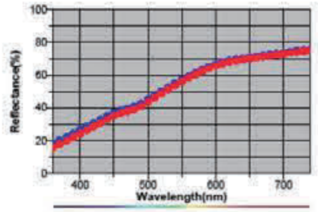
LIQUID NITROGEN DATA

BT.S.01.02	194.83	132.85	130.27	205.85	203.27	11.56

BT.S.01.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



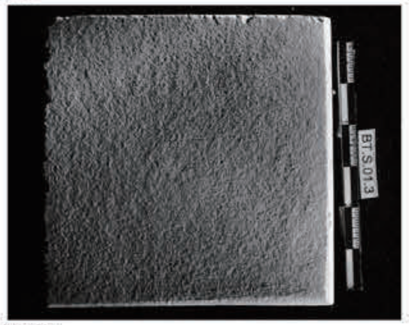
L* = 79.81
a* = 5.38
b* = 21.97

dE*ab = 1.40

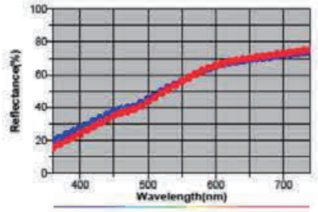
LIQUID NITROGEN DATA

BT.S.01.03	206.67	141.65	139.54	222.00	219.89	16.45

AFTER



SPECTROPHOTOMETER DATA



L* = 79.48
a* = 5.18
b* = 20.84

dE*ab = 2.63

LIQUID NITROGEN DATA

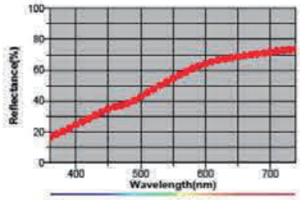
BT.S.01.03	209.96	143.00	140.42	223.10	220.52	13.18

BT.S.01.3

Sample Set: TAN-WEATHEROMETER
Product-application: 1ABF

BEFORE
TEXTURE MAPPING

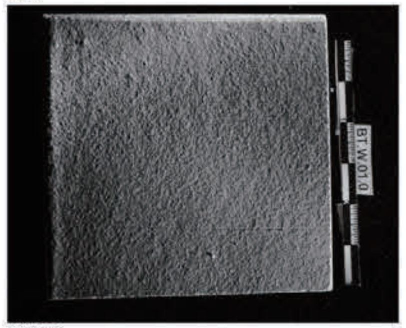
SPECTROPHOTOMETER DATA



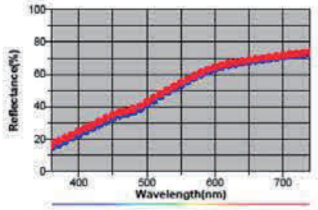
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BT.W.01.00	202.79	140.00	138.30	218.1	216.40	17.43

AFTER



SPECTROPHOTOMETER DATA



L* = 77.77
a* = 5.91
b* = 23.75

dE*ab = 1.39

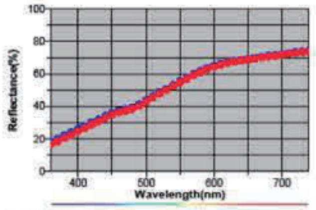
LIQUID NITROGEN DATA

BT.W.01.00	204.87	137.15	134.57	218	215.42	13.05

BT.W.01.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



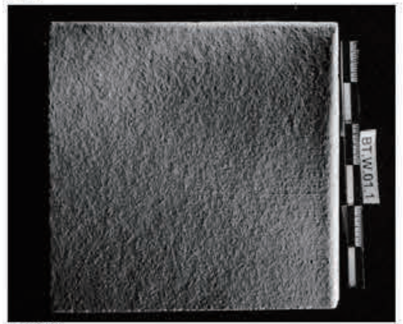
L* = 78.96
a* = 5.86
b* = 21.83

dE*ab = 0.88

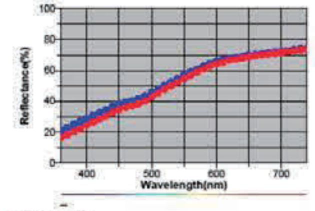
LIQUID NITROGEN DATA

BT.W.01.01	197.33	134.80	133.50	211	209.70	16.23

AFTER



SPECTROPHOTOMETER DATA



1.1 AFTER(11/24/2014 1:47
L* = 79.66
a* = 5.20
b* = 20.06

dE*ab = 2.82

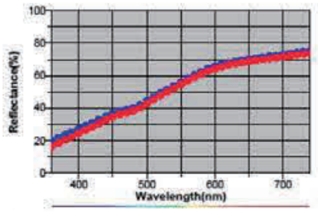
LIQUID NITROGEN DATA

BT.W.01.01	198.80	135.88	133.30	213	210.42	15.07

BT.W.01.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



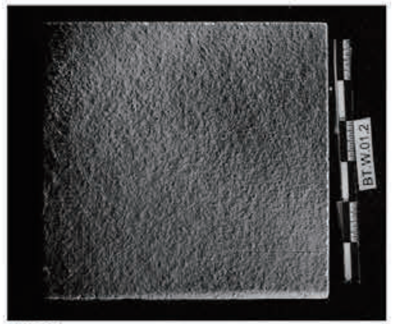
L* = 79.27
a* = 5.76
b* = 21.34

dE*ab = 1.47

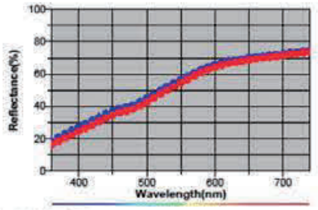
LIQUID NITROGEN DATA

BT.W.01.02	208.24	141.65	139.95	222.1	220.40	15.11

AFTER



SPECTROPHOTOMETER DATA



L* = 79.57
a* = 5.32
b* = 21.15

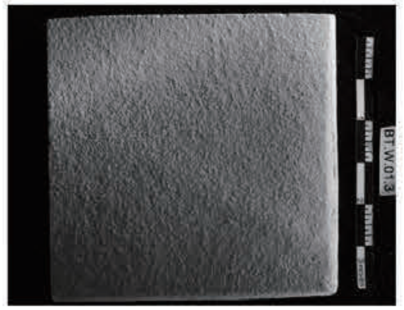
dE*ab = 1.82

LIQUID NITROGEN DATA

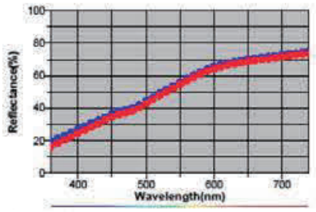
BT.W.01.02	210.40	142.35	139.77	226.1	223.52	15.67

BT.W.01.2

BEFORE
TEXTURE MAPPING



SPECTROPHOTOMETER DATA



L* = 79.23
a* = 5.67
b* = 21.49

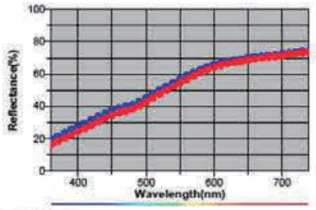
dE*ab = 1.31

LIQUID NITROGEN DATA

BT.W.01.03	201.34	136.50	135.20	214.1	212.80	14.77

AFTER

SPECTROPHOTOMETER DATA



L* = 79.63
a* = 5.23
b* = 20.95

dE*ab = 2.04

LIQUID NITROGEN DATA

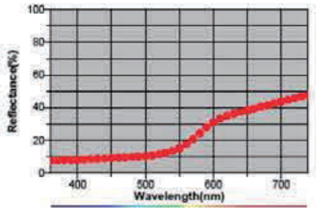
BT.W.01.03	203.30	137.00	134.42	216	213.42	12.81

BT.W.01.3

Sample Set: **RED-NO TEST**
Product-application: **2ABF**

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



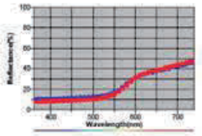
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BR.C.02.00	192.57	132.80	130.50	204.97	202.67	13.99

BR.C.02.0

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 51.88
a* = 20.21
b* = 20.82

dE*ab = 4.36

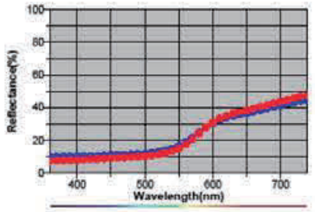
LIQUID NITROGEN DATA

BR.C.02.01	186.56	124.07	121.77	195.55	193.25	9.36

BR.C.02.1

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 51.25
a* = 19.52
b* = 20.68

dE*ab = 4.58

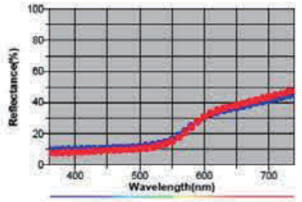
LIQUID NITROGEN DATA

BR.C.02.02	184.62	124.50	121.84	194.50	191.84	10.31

BR.C.02.2

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 51.14
a* = 19.90
b* = 21.10

dE*ab = 4.00

LIQUID NITROGEN DATA

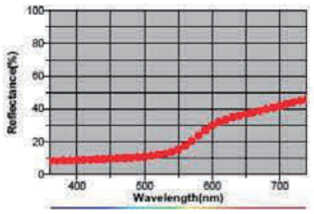
BR.C.02.03	174.85	116.50	113.84	186.70	184.04	13.09

BR.C.02.3

Sample Set: **RED-SALT**
Product-application: **2ABF**

BEFORE
TEXTURE MAPPING

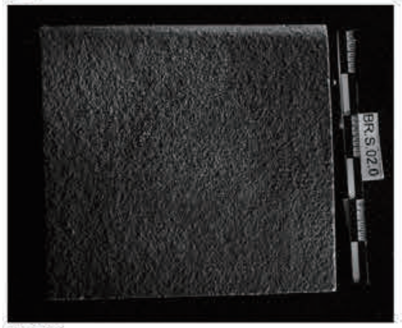
SPECTROPHOTOMETER DATA



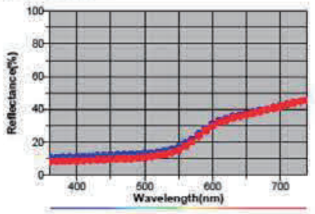
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BR.S.02.00	188.87	129.50	127.20	200.10	197.80	12.65

AFTER



SPECTROPHOTOMETER DATA



L* = 51.93
a* = 18.71
b* = 19.14

dE*ab = **4.06**

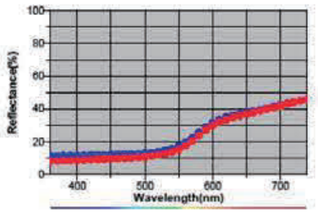
LIQUID NITROGEN DATA

BR.S.02.00	192.30	129.63	127.05	200.64	198.06	8.11

BR.S.02.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



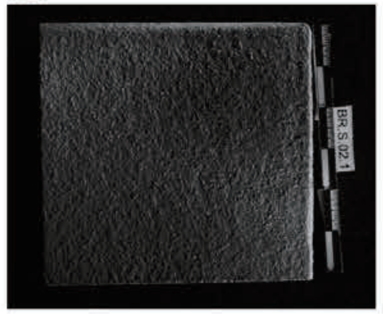
L* = 52.22
a* = 19.08
b* = 19.12

dE*ab = **4.05**

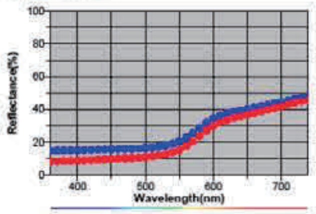
LIQUID NITROGEN DATA

BR.S.02.01	175.73	116.50	114.20	182.50	180.20	6.77

AFTER



SPECTROPHOTOMETER DATA



L* = 55.75
a* = 16.96
b* = 15.87

dE*ab = **9.24**

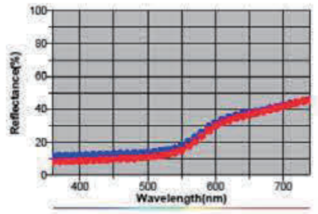
LIQUID NITROGEN DATA

BR.S.02.01	179.68	119.98	117.40	187.00	184.42	7.07

BR.S.02.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



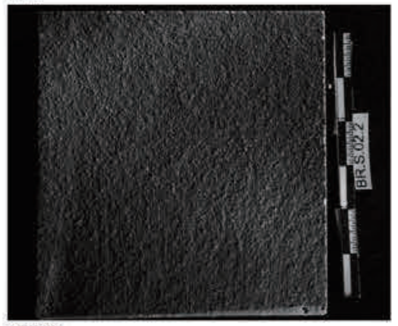
L* = 52.78
a* = 18.37
b* = 18.42

dE*ab = **5.16**

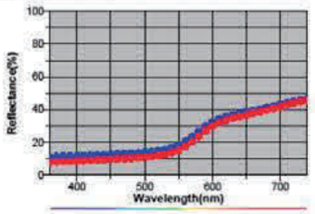
LIQUID NITROGEN DATA

BR.S.02.02	194.08	129.15	126.85	204.70	202.40	11.01

AFTER



SPECTROPHOTOMETER DATA



L* = 53.24
a* = 18.28
b* = 19.14

dE*ab = **4.96**

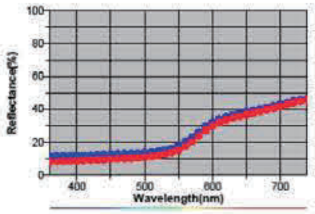
LIQUID NITROGEN DATA

BR.S.02.02	198.95	133.00	130.42	206.10	203.52	6.25

BR.S.02.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 52.87
a* = 18.79
b* = 18.96

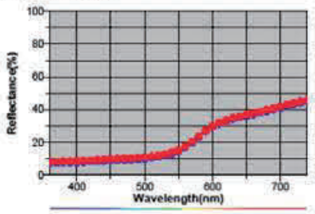
dE*ab = **4.63**

LIQUID NITROGEN DATA

BR.S.02.03	201.55	132.60	130.30	213.10	210.80	11.49

AFTER

SPECTROPHOTOMETER DATA



L* = 49.51
a* = 21.19
b* = 23.45

dE*ab = **1.48**

LIQUID NITROGEN DATA

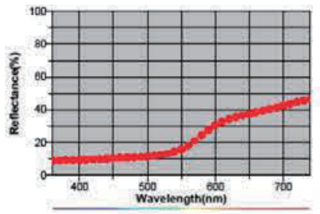
BR.S.02.03	207.03	137.26	134.68	214.22	211.64	5.99

BR.S.02.3

Matteini Thesis / Evaluation Phase
Sample Set: **RED-WEATHEROMETER**
Product-application: **2ABF**

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



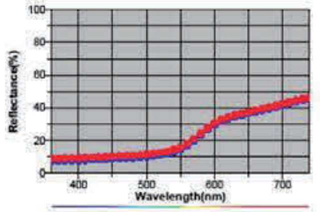
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BR.W.02.00	203.14	139.60	137.30	217.00	214.70	14.94

AFTER

BR.W.02.0

SPECTROPHOTOMETER DATA



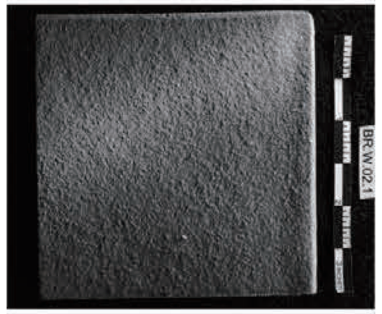
L* = 49.58
a* = 21.32
b* = 23.45

dE*ab = 2.61

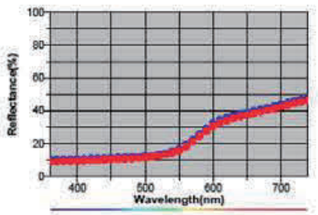
LIQUID NITROGEN DATA

BR.W.02.00	205.58	137.77	135.19	215.10	212.52	8.97

BEFORE
TEXTURE MAPPING



SPECTROPHOTOMETER DATA



L* = 52.05
a* = 20.61
b* = 21.11

dE*ab = 1.22

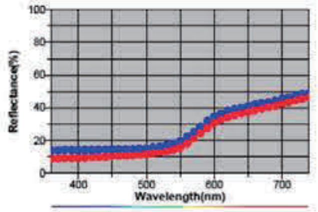
LIQUID NITROGEN DATA

BR.W.02.01	189.83	127.15	124.85	201.15	198.85	12.19

AFTER

BR.W.02.1

SPECTROPHOTOMETER DATA



L* = 56.12
a* = 18.59
b* = 17.40

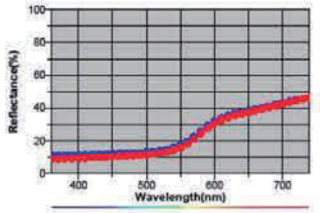
dE*ab = 6.08

LIQUID NITROGEN DATA

BR.W.02.01	191.98	129.10	126.52	201.00	198.42	8.96

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 52.46
a* = 19.46
b* = 19.45

dE*ab = 2.67

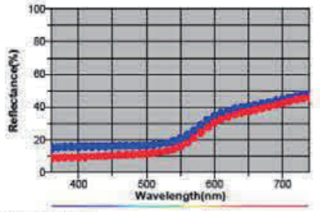
LIQUID NITROGEN DATA

BR.W.02.02	184.67	123.60	121.30	193.75	191.45	9.67

AFTER

BR.W.02.2

SPECTROPHOTOMETER DATA



L* = 55.99
a* = 17.03
b* = 15.29

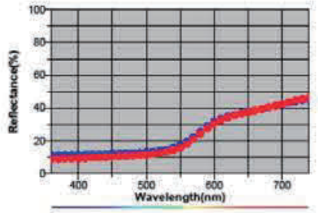
dE*ab = 8.62

LIQUID NITROGEN DATA

BR.W.02.02	186.66	125.80	123.22	198.10	195.52	12.25

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 52.30
a* = 19.09
b* = 19.03

dE*ab = 3.05

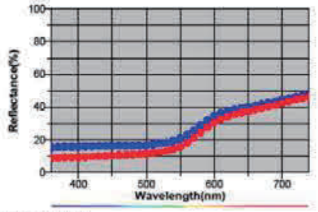
LIQUID NITROGEN DATA

BR.W.02.03	198.78	131.90	129.60	208.10	205.80	9.21

AFTER

BR.W.02.3

SPECTROPHOTOMETER DATA



L* = 55.99
a* = 16.75
b* = 14.95

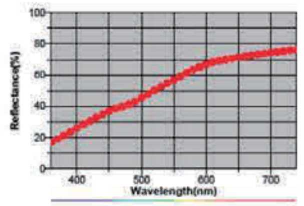
dE*ab = 8.98

LIQUID NITROGEN DATA

BR.W.02.03	199.80	134.87	132.29	211.10	208.52	11.44

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



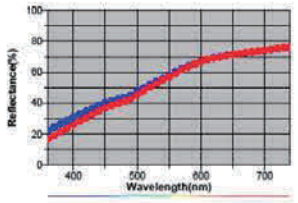
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BT.C.02.00	197.70	136.35	134.05	214.30	212.00	18.35

BT.C.02.0

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 80.57
a* = 5.27
b* = 18.97

dE*ab = 3.09

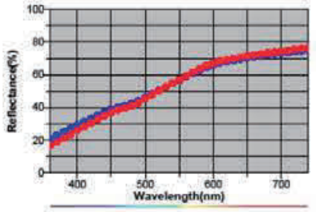
LIQUID NITROGEN DATA

BT.C.02.01	201.60	138.00	135.70	220.10	217.80	19.73

BT.C.02.1

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 79.85
a* = 5.46
b* = 19.57

dE*ab = 2.43

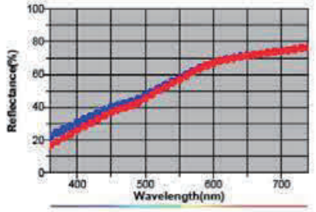
LIQUID NITROGEN DATA

BT.C.02.02	193.70	132.30	130.55	207.70	205.95	16.25

BT.C.02.2

TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 80.54
a* = 5.35
b* = 19.20

dE*ab = 2.85

LIQUID NITROGEN DATA

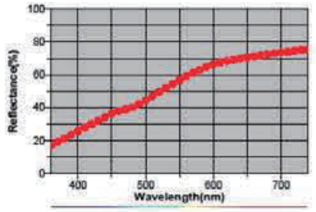
BT.C.02.03	180.77	123.66	121.91	196.00	194.25	18.63

BT.C.02.3

Sample Set: **TAN-SALT**
Product-application: **2ABF**

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA

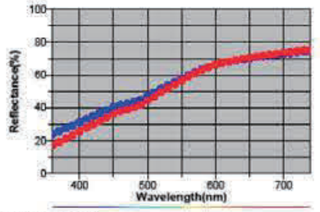


LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BT.S.02.00	197.28	135.95	134.20	212.10	210.35	17.16

AFTER

SPECTROPHOTOMETER DATA



L* = 80.34
a* = 4.93
b* = 18.42

dE*ab = 4.00

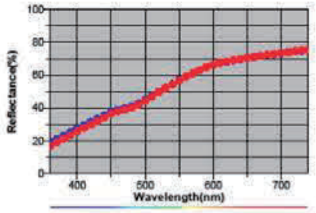
LIQUID NITROGEN DATA

BT.S.02.00	200.98	135.72	133.14	213.10	210.52	12.33

BT.S.02.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



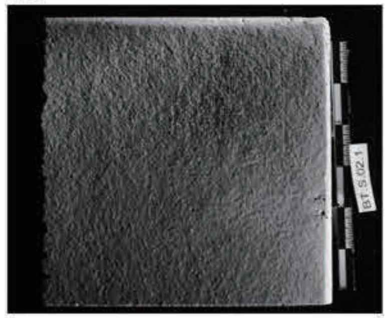
L* = 78.74
a* = 5.44
b* = 21.27

dE*ab = 1.05

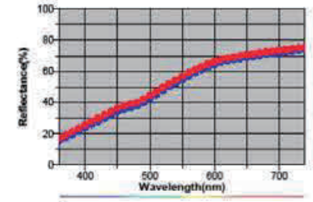
LIQUID NITROGEN DATA

BT.S.02.01	199.15	134.70	132.95	212.00	210.25	14.36

AFTER



SPECTROPHOTOMETER DATA



L* = 78.58
a* = 5.76
b* = 23.18

dE*ab = 1.39

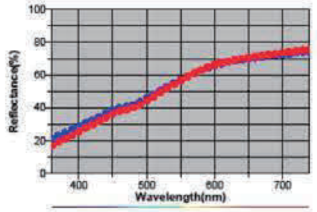
LIQUID NITROGEN DATA

BT.S.02.01	202.55	137.30	134.72	218.00	215.42	15.95

BT.S.02.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



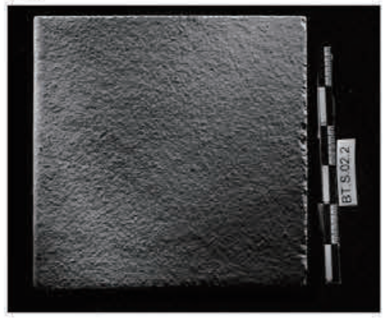
L* = 79.87
a* = 5.15
b* = 20.35

dE*ab = 2.00

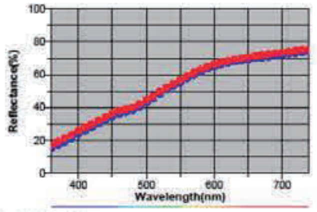
LIQUID NITROGEN DATA

BT.S.02.02	205.10	139.75	138.00	218.25	216.50	14.52

AFTER



SPECTROPHOTOMETER DATA



L* = 78.94
a* = 5.44
b* = 23.33

dE*ab = 1.22

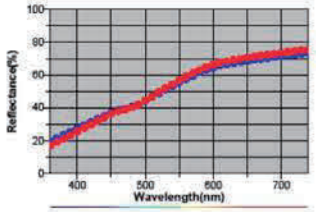
LIQUID NITROGEN DATA

BT.S.02.02	209.12	142.10	139.52	221.00	218.42	11.79

BT.S.02.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



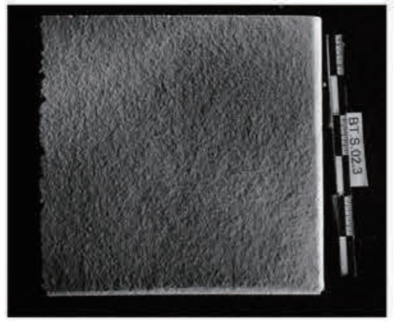
L* = 79.12
a* = 5.31
b* = 20.56

dE*ab = 1.84

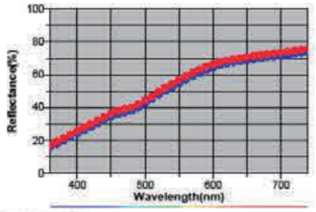
LIQUID NITROGEN DATA

BT.S.02.03	203.40	137.40	135.65	216.25	214.50	14.08

AFTER



SPECTROPHOTOMETER DATA



L* = 78.61
a* = 5.68
b* = 22.91

dE*ab = 1.20

LIQUID NITROGEN DATA

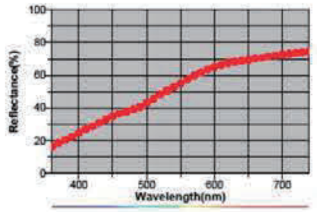
BT.S.02.03	208.04	139.80	137.22	220.00	217.42	11.70

BT.S.02.3

Sample Set: TAN-WEATHEROMETER
Product-application: 2ABF

BEFORE
TEXTURE MAPPING

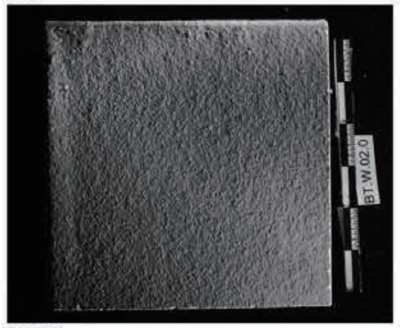
SPECTROPHOTOMETER DATA



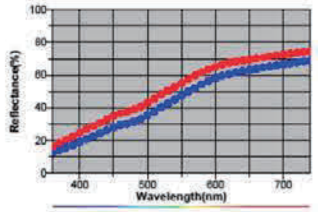
LIQUID NITROGEN DATA

Sample	Dry	Saturated	S *minus metal wire	Wet	W *minus metal wire	Porosity %
BT.W.02.00	193.53	133.50	131.75	208.7	206.95	17.85

AFTER



SPECTROPHOTOMETER DATA



L* = 74.32
a* = 7.33
b* = 25.05

dE*ab = 5.33

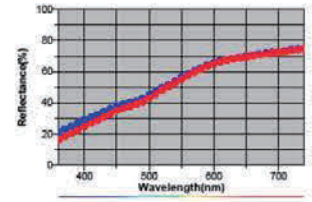
LIQUID NITROGEN DATA

BT.W.02.00	195.95	129.85	127.27	205.25	202.67	8.91

BT.W.02.0

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



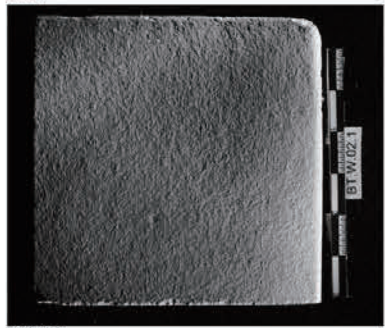
L* = 79.45
a* = 5.72
b* = 20.18

dE*ab = 2.56

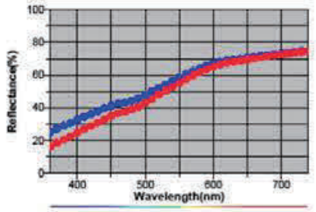
LIQUID NITROGEN DATA

BT.W.02.01	197.01	132.00	130.25	208	206.25	12.16

AFTER



SPECTROPHOTOMETER DATA



L* = 80.69
a* = 4.95
b* = 18.04

dE*ab = 5.06

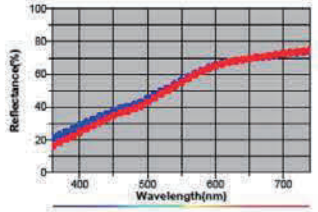
LIQUID NITROGEN DATA

BT.W.02.01	197.96	135.65	133.07	211.1	208.52	14.00

BT.W.02.1

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



L* = 79.37
a* = 5.57
b* = 20.02

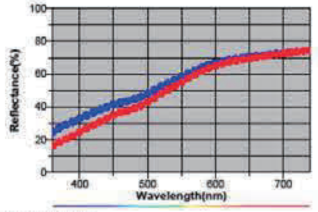
dE*ab = 2.72

LIQUID NITROGEN DATA

BT.W.02.02	196.63	132.60	130.85	208.25	206.50	13.05

AFTER

SPECTROPHOTOMETER DATA



L* = 80.73
a* = 4.80
b* = 17.67

dE*ab = 5.44

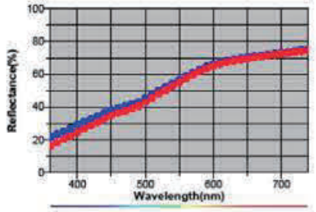
LIQUID NITROGEN DATA

BT.W.02.02	197.54	135.63	133.05	211.45	208.87	14.94

BT.W.02.2

BEFORE
TEXTURE MAPPING

SPECTROPHOTOMETER DATA



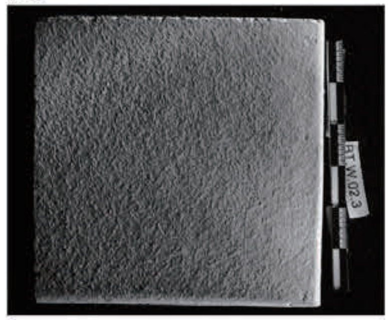
L* = 79.69
a* = 5.63
b* = 20.10

dE*ab = 2.72

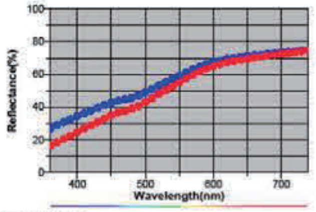
LIQUID NITROGEN DATA

BT.W.02.03	191.62	129.25	127.50	203.5	201.75	13.64

AFTER



SPECTROPHOTOMETER DATA



L* = 81.18
a* = 4.78
b* = 17.07

dE*ab = 6.15

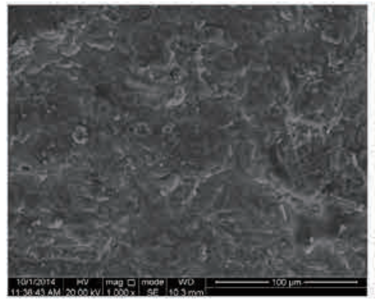
LIQUID NITROGEN DATA

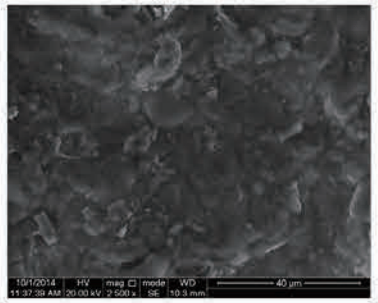
BT.W.02.03	193.18	130.44	127.86	206	203.42	13.55

BT.W.02.3

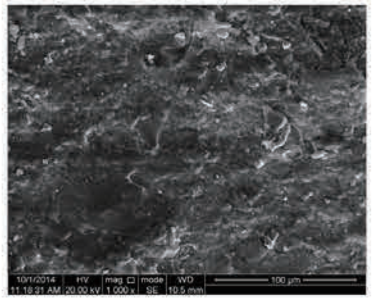
7.9 Scanning electron microscope

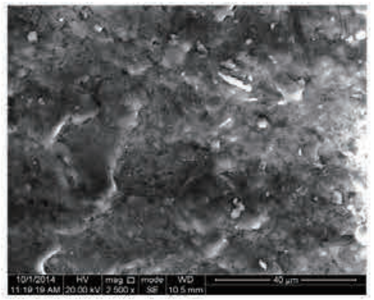
Sample Set: **TAN CONTROL**



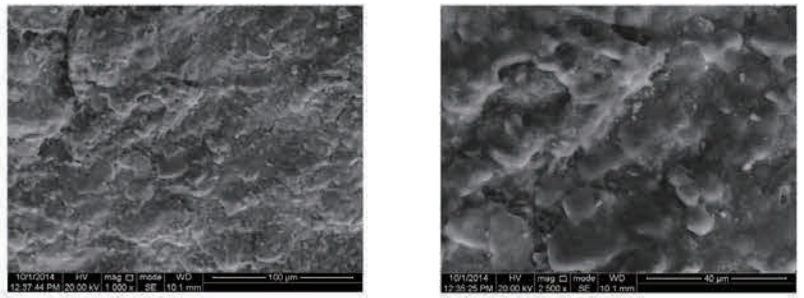


Sample Set: **TAN CONTROL**

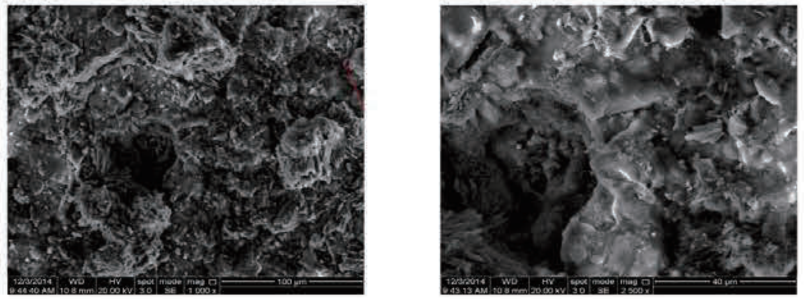




RED-SALT
1HF
BEFORE

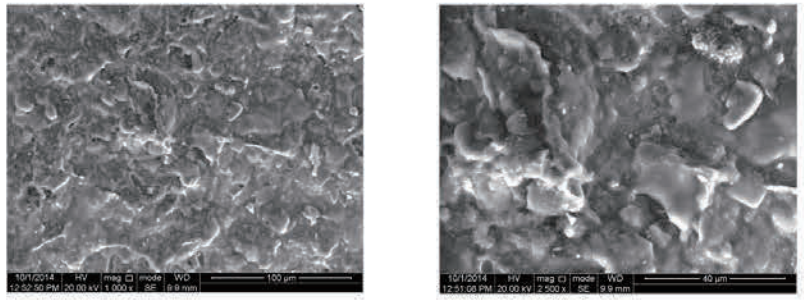


AFTER



AR.S.01.1

RED-WEATHEROMETER
1HF
BEFORE



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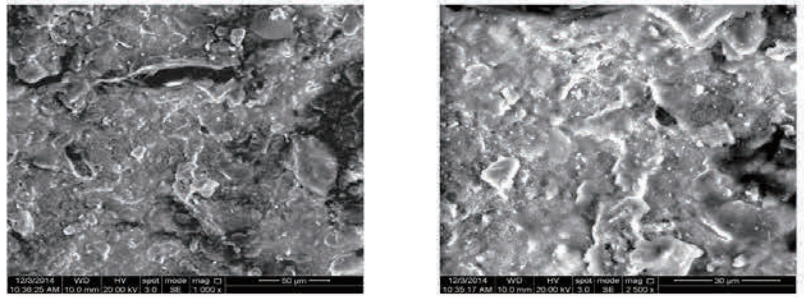

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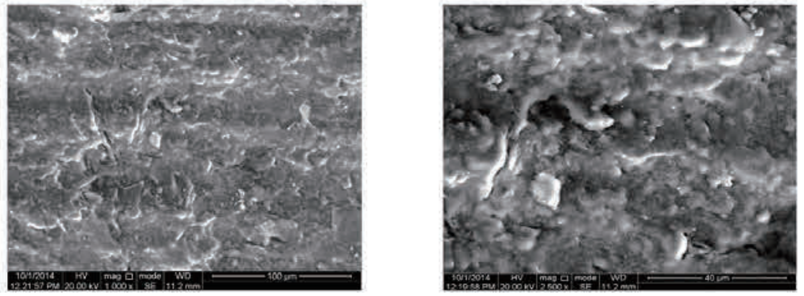

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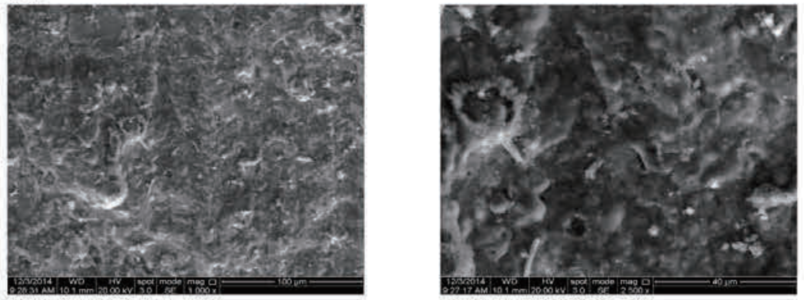

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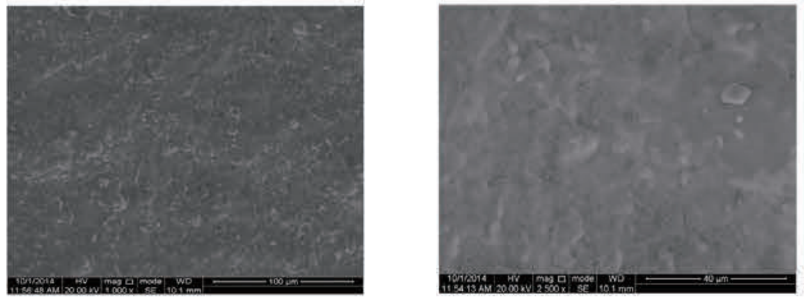

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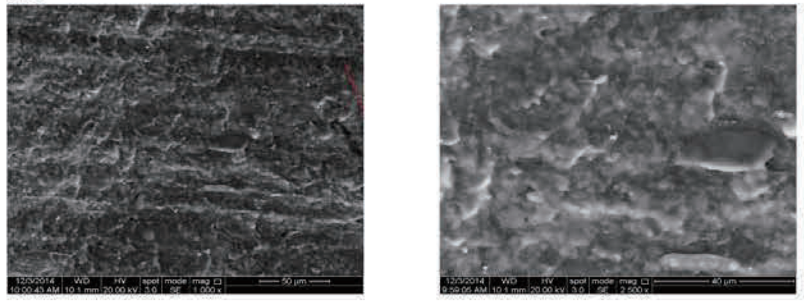

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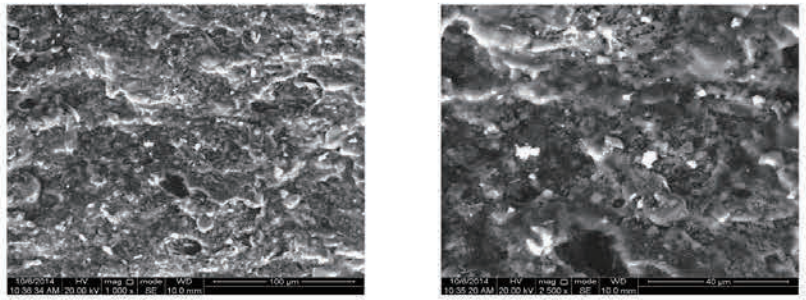

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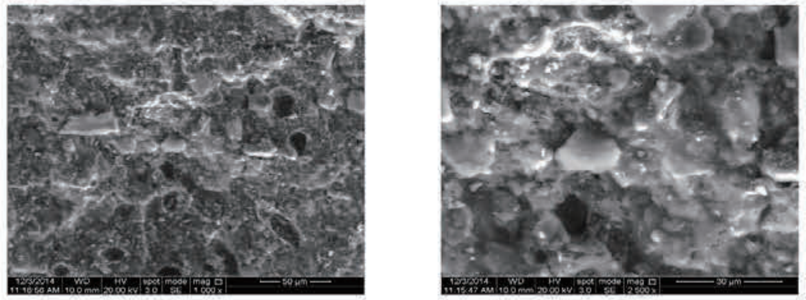

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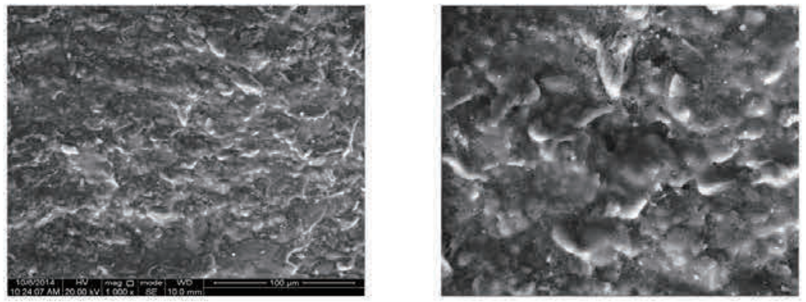

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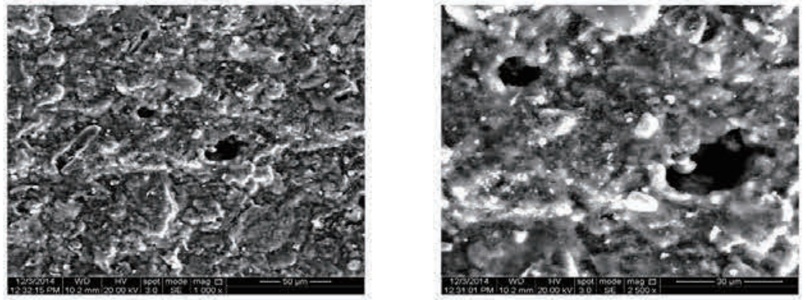

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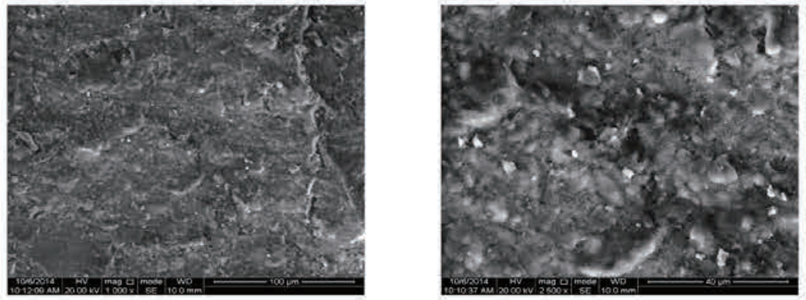

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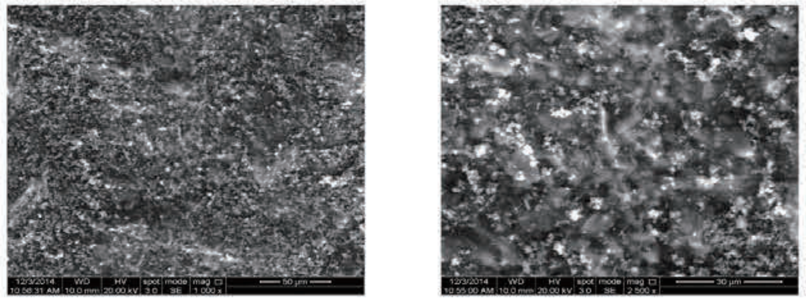

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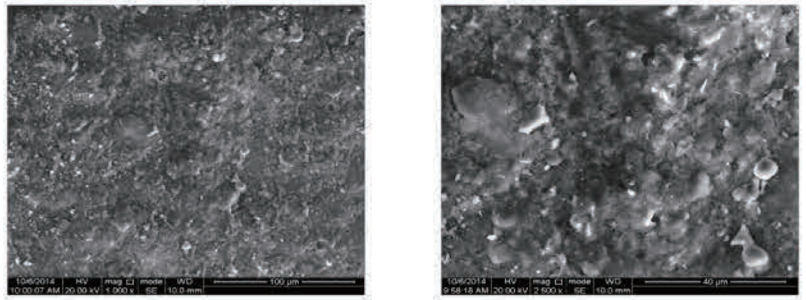

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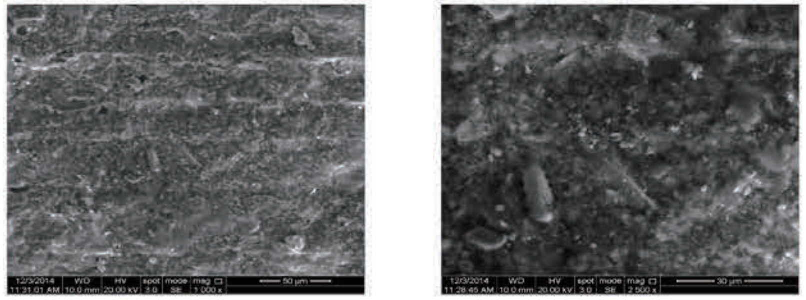

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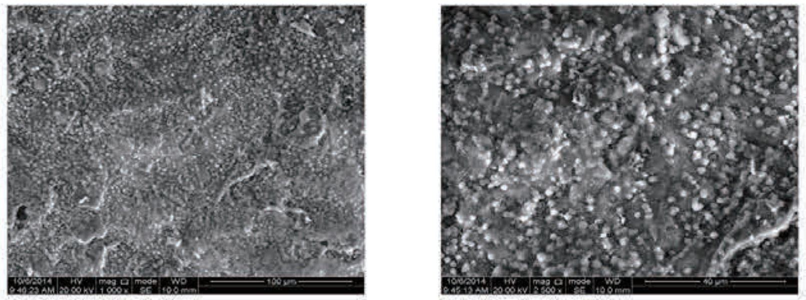

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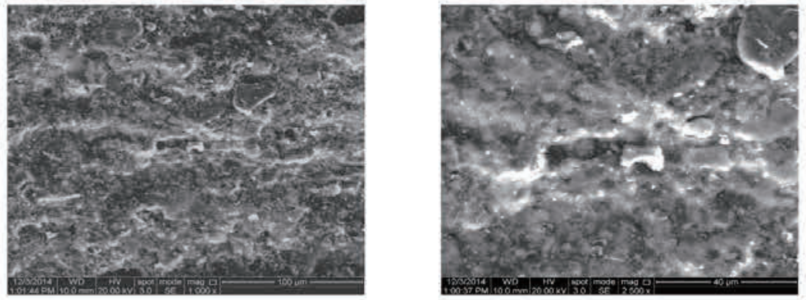

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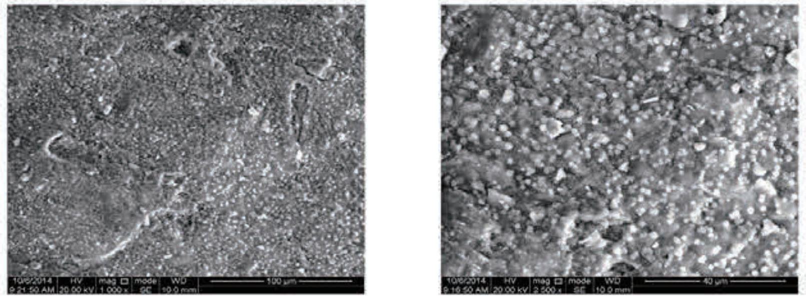

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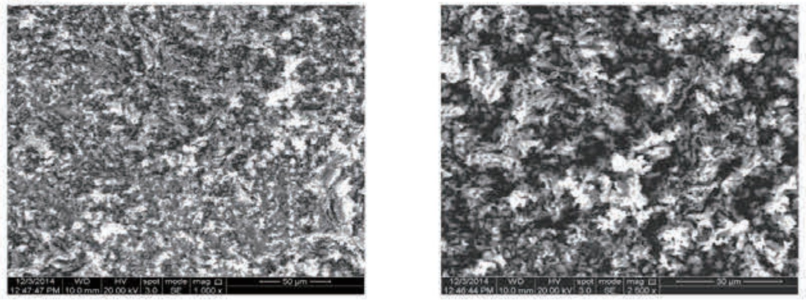

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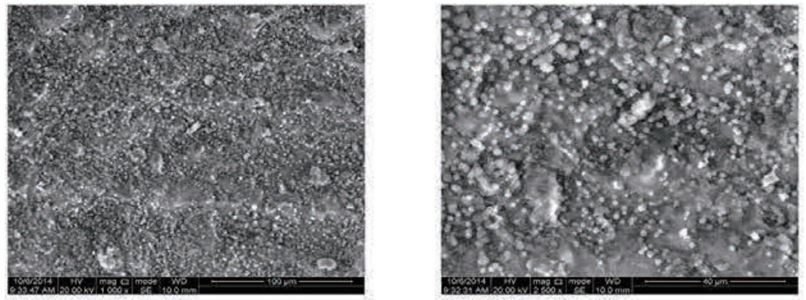

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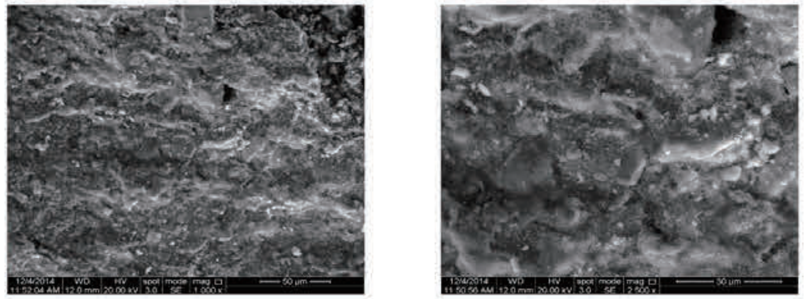

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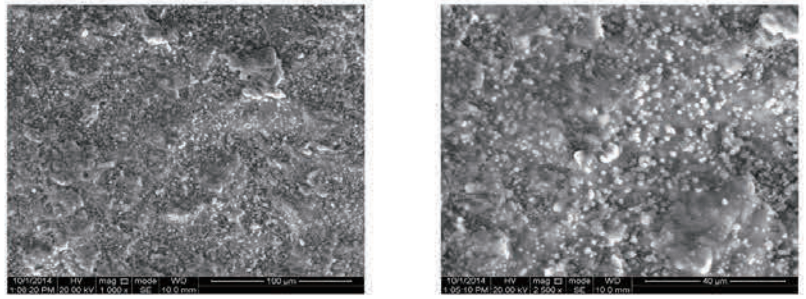

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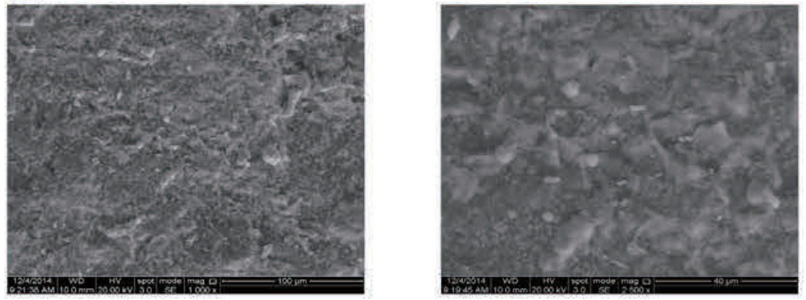

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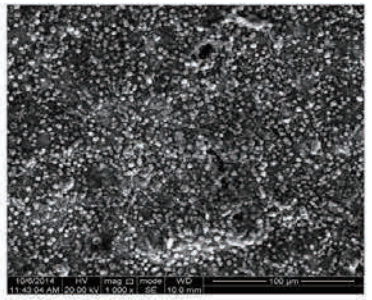

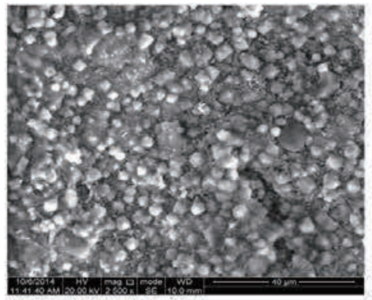

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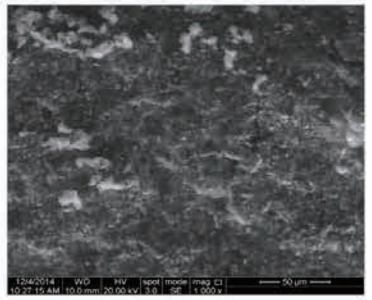

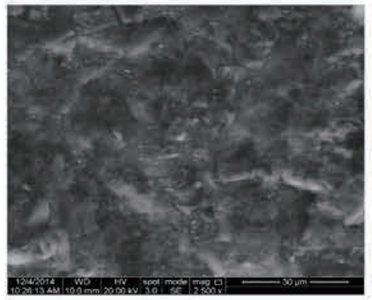

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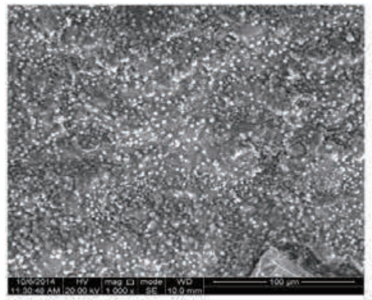

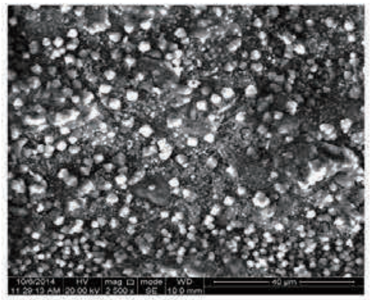

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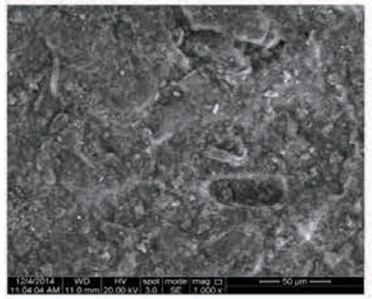

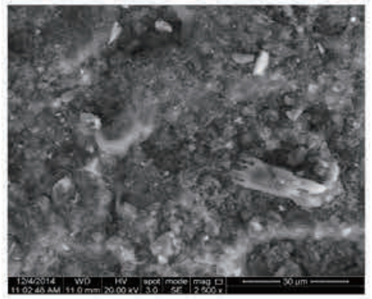

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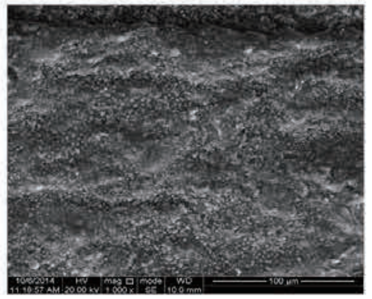

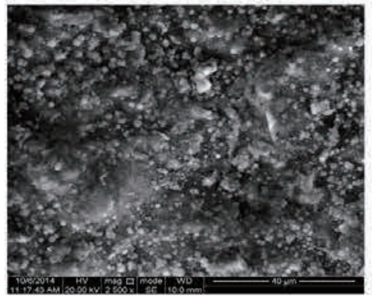

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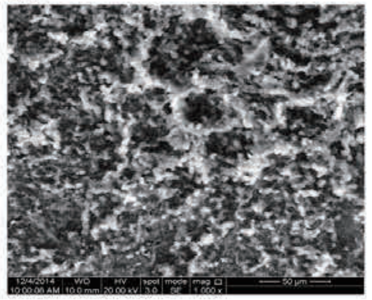

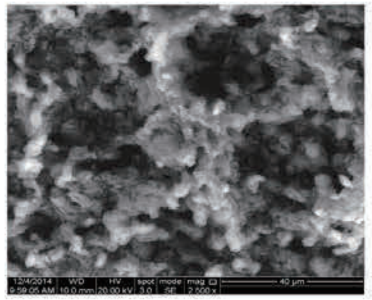

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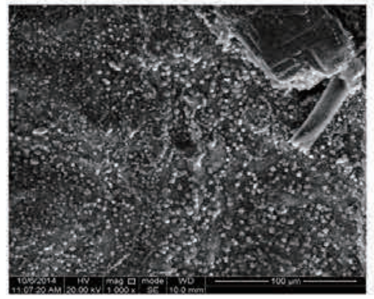

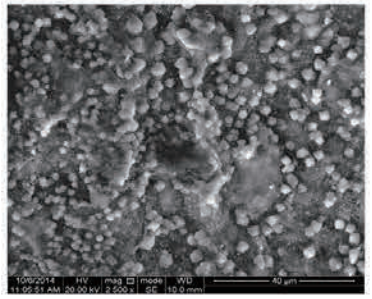

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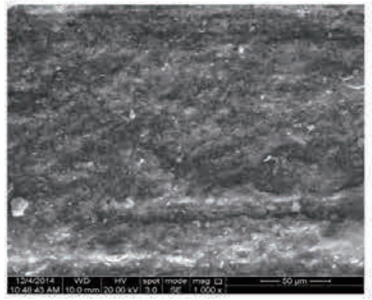

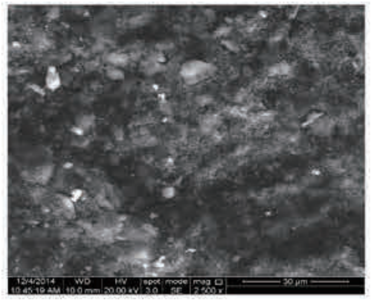

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