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Exploiting New Silicon-Based Products for Conservation

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Abstract

In 2000-2001 a student’s thesis stimulated a research project and collaboration between ICCROM and CISTeC. Diverse characterization methods and laboratory weathering of some organosilane water-repellents revealed some important information. These and other results presented in the Congress: Silicates in Conservation 2002 made us aware of the great confusion that exists in the market regarding silicon-based products. One of the results was a market and bibliographical research; a CD was complied attempting to understand the different typologies of products, and to organize the companies that manufactured, supplied and formulated them. Currently, new silicon-based products found in the market are significantly diverse from one another: chemical structure (e.g. silicone resins or silanes), the polymerisation reactants (e.g. mixtures of polymerised products dispersed in solvent or monomer mixtures and dimers that polymerise in condensation), type of dispersion (as in water, e.g. micro-emulsions), methodology of application (e.g. nature of the support, environmental conditions) and of their chemical-physical behaviour (interaction with pollutants and solar radiation). A new market/bibliographical research was undertaken and was exploited by testing some of the new products found in the market. The present work considers a wider market and emphasizes quality control methods and optimisation of performance efficiency tests. For this reason standard methods were evaluated and selected or proposed. The experimental part of the 2003 research

is comprised of two parts: 1) Testing raw materials: the products (protectives and consolidants) 2) Applying the products on Carrara marble samples and testing them under a) artificial weathering conditions in comparison to b) natural weathering conditions by exposing them in the Colosseum and monitoring the environmental conditions. Although research is still in progress some significant information and results have been obtained.

1 Introduction

The present work came as a result of the further development of the work presented in the congress: Silicates in Conservative Treatments [1], which revealed the need for the in depth study of problems related to the identification and characterization of silicon-based products used in the field of conservation and restoration. This initial research led to the compilation of the CD-Rom Silicates in Conservation [2]; it gathers a bibliography specific to the use of silicon-based protectives and consolidants as well as related references on the chemical manufacturers, suppliers and formulators. ICCROM, following the release of the CD, accepted an intern under its 2004 Internship Programme to activate, in collaboration with CISTeC, a study named “Stone Cultural Heritage: Silicon-based Products in Conservation” [3], with the aim to broaden the information collected in the foregoing CD. The work carried out during the internship was developed through a series of laboratory and outdoor tests on diverse commercial products, and through the careful study of the technical and safety data sheets provided with each of these products.

This study tries to answer the needs and requests from many of the professionals within the field of conservation and restoration of cultural heritage to gain better knowledge on the nature, availability and behaviour of silicon-based protectives and consolidants for stone.

The objective of this paper is to expose the European market’s present situation; to illustrate the difficulties encountered while the research was performed; and, to propose specific interactions for improving communication between both sides of the market (chemical manufacturers and conservation community).

2 Work description

2.1 Identification of products

The first part consisted and was limited to the identification of products found in the market – but released by chemical manufacturers only. This limit was established due to the existing difficulties in finding all possible information referring to suppliers and formulators.

From the collected data, five chemical manufacturers specializing on silicones and silanes for treating building materials, whether modern or historic, were identified at a worldwide scale: Wacker, Degussa-Sivento Silanes, Degussa-Goldschmidt, Dow Corning, and Rhodia Silicones.

Among the products proposed by these manufacturers and from the available information, resulted that around 100 products are exclusively based on seventeen different main components.

Of the 100 products found, some only differed in their solvent type, while others only differed in the label used to market them in different countries [4]. Within a five-year period, many variations were registered in the trade names of some products: For example, Wacker OH changed to Wacker BS OH 100 and is now called Silres BS OH 100 while Rhodia Rhoximat 224

Table 1: Seventeen different compounds used as main components for protective or consolidant treatments

Main Component in Silicon-based Product	CAS Number
Potassium methyl silane triolate	31795-24-1
Silane (dimethoxy-dimethyl-silane)	1112-39-6
Silane (hexadecyl-trimethoxy-silane)	16415-12-6
Silane (tetraethoxy-silane)	78-10-4
Silane (tetramethoxy-silane)	681-84-5
Silane (triethoxy-(2-methylpropyl)-silane)	17980-47-1
Silane (triethoxy-octyl-silane)	2943-75-1
Silane (triethoxy-propyl-silane)	2550-02-9
Silane (triethoxy-(2,4,4-trimethylpentyl)-silane)	35435-21-3
Silane (trimethoxy-methyl-silane)	1185-55-3
Silane (trimethoxy-phenyl-silane)	2996-92-1
Silane (trimethoxy-propyl-silane)	1067-25-0
Silane (trimethoxy-(2,4,4-trimethylpentyl)-silane)	34396-03-7
Silicic acid, tetraethyl ether, hydrolyzed	68412-37-3
Silicic acid, tetra propyl ester	682-01-9
di-Me,(((3-((2-aminoethyl) amino) propyl) dimethoxy silyl) oxy) -terminated	71750-80-6
di-Me,(((3-((2-aminoethyl) amino) propyl) silydyne) tris (oxy))tris-,methoxy-terminated	67923-07-3

changed to Rhodorsil H224. Variations in the trade names of products also reflect modifications in the composition to adjust the product to standards on volatile organic contents (VOC) or type of catalyst. Many professionals within this field, who often do not have access to safety data sheets [5] or who do not read with particular attention, have continued to use a product without noticing changes in the composition. By eliminating the use of organic solvents many products have become 100 % concentrated or are waterborne, which in our field is not always ideal. In fact, chemical manufacturers are not the only responsible for this confusion. Suppliers and distributors – who often are not product specialists but marketing agents – do not completely fulfil their function as intermediaries between manufacturers and users.

It would be favourable to promote a better interaction between manufacturers and users because of the need to be informed about updates in production processes. This would help to avoid negative situations as those related to acrylic products: for example, with the disappearance of Primal AC 33 (by Rohm & Haas) from the market other chemical alternatives have arisen with names that evoke the “disappeared” product (as ACril 33). The problem lies when new products that follow are not always comparable in efficacy to the original one, which, as it is known, takes a certain number of years to correctly determine.

2.2 Selecting and testing

The second part of the research consisted in selecting and testing from two typologies of commercial products: protectives and consolidants. The tests have been focused on the raw material as well as on their performance efficiency after application by testing them under natural and artificial weathering.

The need to characterize raw materials comes from the professionals in the field asking for simple methods to perform an initial quality control on the chemical product. Considering this as one of the main objectives, quick and simple tests were chosen having in mind they should be able to be carried out in the working site and also by users that are not scientists.

The basic tests proposed in this paper are based on the characterization of colour, turbidity [6] and viscosity by direct analysis and comparative techniques [7].

Colour is often reported – generically – in the technical data sheet, (as shown in Table 2), that means without referring to specific standards. In limited cases, the iodine colour number is reported in the technical data sheet according to the DIN 53995 (as in Tegosivin HL 100 and Tegosivin HL 40).

Table 2: Comparative table of the Gardner colour scale values and the colour reported on the technical or material safety data sheets

Products	Gardner colour value	Colour as reported in the technical or material safety* data sheet	Reported Standard
Tegosivin WF (Tego)	< 1	clear / yellow, clear*	none
Hydrofugeant H224 (Rhodia)	< 1	colourless to light yellow	none
Hydrofugeant H240 (Rhodia)	< 1	colourless to light yellow	none
Dynasylan BSM 40% (Degussa)	< 1	colourless liquid	none
Wacker SMK 1311 (Wacker)	> 5	yellowish to reddish / yellowish*	none
Wacker SMK 550 (Wacker)	4 - 5	yellowish to red-brown / yellowish*	none

The Gardner Colour Scale [8] (with values ranging from 1 to 18 from lightest to darkest, respectively) was chosen as a preliminary test.

Similarly, the Bubble Method [10] viscosimeters was chosen as the instrument/method for users to determine the approximate viscosity so as to cross-check the information provided in the technical data sheets or to record the changes between supplies or batches. In this way the user can eliminate doubts to whether the product is partially hydrolysed as a result of unsuitable stocking conditions (and thus its turbidity).

The information related to the viscosity reported in the technical data sheets was confirmed with tests performed with the rotational viscosimeters Haake RS600 with plate/cone C60/1 and Haake DC50 K10 at 25 ºC. With rotational viscosimeter it is possible to obtain an elevated number of data on the rheological behaviour as a function of temperature changes. These results were compared with the reported data in the data sheets, and although most of the viscosities obtained coincided with the reported value, some of these had to be converted from mm^2/s or Stokes to Pa/s, to have a uniform comparison. In addition to this, there is a lack of consistency because related standard methods are omitted. In the Bubble Method Viscosimeters the product is placed within a coded range of pre-defined viscosities. This quick

Table 3: List of products selected weathering tests with the used solvents and proportions

Protectives	Solvent	Product:Solvent Ratio
Hydrofugeant H224 (Rhodia)	White Spirit	1:9
Idrorepellente BSO 166 (Degussa)	White Spirit	1:9
Wacker BS 290 (Wacker)	White Spirit	1:15
Wacker 1311 (Wacker)	Distilled Water	1:14
Tegosivin HE 328 (Tego)	Distilled Water	1:9
Tegosivin HL 100 (Tego)	Distilled Water	1:4
Hydrophase (Phase)	Distilled Water	1:9

and simple system is easily applied and satisfies one of the quality control requirements at the time of purchase and of its stability during the stocking period in the site.

Besides studying the rheological properties, the functional groups and the presence of solvents were determined in the products using the Fourier Transform Infrared (FTIR) spectrometer.

From the 22 tested products (16 protectives and 6 consolidants) seven products were chosen for weathering tests.

These products were applied on white Carrara marble, which facilitates determining chromatic changes, and were exposed to artificial weathering by exposing them to solar radiation induced stress (Xenon lamp chamber) [11] according to the standard method UNI 10925 [12]; the applied energy was 1,000,000 KJ/m^2 at 700 W and 40 °C. Another set of samples was separately exposed to humidity stress in the climatic chamber [13]. Alongside the same products applied on the same type of marble were exposed in the Colosseum [14] in the third order and outdoors. Environmental monitoring sensors [15] for SO_2, NO_x and O_3 were placed near the samples so as to measure particles in the surrounding environment [16].

All samples – naturally and artificially weathered – were periodically measured for their chromatic changes using reflectance spectrophotometry [17] using the Yellow Index as parameters, according to the ASTM E313 and evaluations on the ability to hydrophobize within certain periods of time, as the beading effect (Figure 1) can demonstrate according to the standard method DIN 52103 [18].

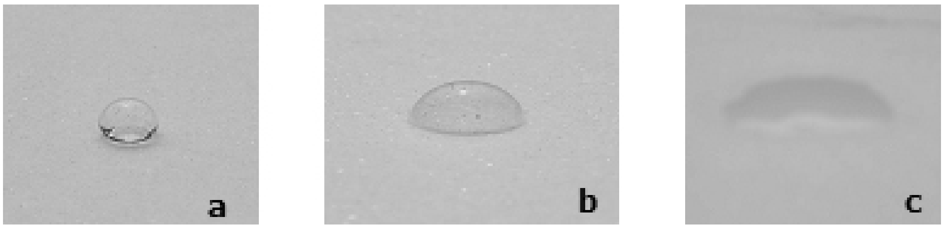

Figure 1: Three examples of the beading effect after one month of outdoor exposure. Note the different shape of the droplet from the treated and the untreated sample. a. Tegosivin HE 328 b. Wacker SMK 1311 c. Untreated sample

The aim of the outdoor experiment was to evaluate the behaviour of some of the most readily available products when exposed to the external atmospheric stress, while with the laboratory experiments aims at evaluating possible performance variations that the product can undergo and to determine if the chosen methods were ideal for determining differences in their behaviour.

3 Methodology

The study reveals the need for defining a methodological approach for the characterization of products and their performance. We propose two main directions so as to further develop this research:

First, and most easily attainable: refers to the possibility of unifying a series of tests within UNI-NORMAL Beni Culturali [19] applicable on raw materials and standard supports for treatments (to be defined).

Second and most challenging: to settle a relationship between the porosity of the substrate and the viscosity of the product and the necessary intervention.

The first proposal (definition of specific standards) would permit the restorator a more technical instrument other than evaluating the performance of the product by direct application on the artifact.

Often it is observed that many studies report the direct comparison between commercial products that are not chemically comparable. In these cases, defining the best or worst products leads not to useful results for conservation and R&D. When in effect it would be more significant to undertake studies that focus on products within the same type of chemical composition so as to determine the most ideal products given a determined application procedure and their properties.

The second proposal (classification of interventions) foresees the need of a close collaboration between manufacturers, conservation scientists, and restorators. In fact, the typology of the requested intervention, the application method, and the nature of the support (porosity, deterioration, etc.) define the need to identify ad hoc products addressing specific requirements.

4 Conclusion

This study seeks to define certain parameters that permit the operator within the field of cultural heritage to move with more security within the products for the protection and consolidation of stone materials. The principal objective is to begin to define a methodology (as most simple and accessible as possible) that considers past and recent information [20] in relation to the application of silicon-based products on historic artifacts.

It seeks to coordinate the most possible information on the nature of the products (through technical and safety data sheets), application methods, and weathering, through a compiled bibliography that can function as a data bank on a CD or accessible through the Internet by all professionals in these fields, translated and frequently updated.

In this sense, the minimum requirement for a practical information sheet for each product should list: class of chemical product (for instance acrylic or Si-organic), manufacturer contact, name and quantity of the active component(s), the type and quantity of solvent (and if present), presence of catalyst (if applicable), colour, viscosity, pH (if applicable), specific use and application procedures without omitting to state the standard methods.

This requires the collaboration between chemical manufacturers, conservation scientists and restorators: by converging each specialists' knowledge and maintaining the constant rapport assuring a constant update as well on each other's needs.

The methodology should become an instrument to improve the relationship between demand and offer: It would provide an instrument to have a better notion on the nature, structure and behaviour of the products for restorators. At the same time it would promote R&D to respond to the operators' needs with higher precision.

5 Reference

[1] Silicates in Conservative Treatments: Tests, Improvements and Evaluations of Consolidating Performance. Held in Turin, Italy, February 13-15th 2002

[2] E. Borrelli, M.L. Santarelli, Silicates in Conservation, (CD-Rom distributed on request), ICCROM June 2002, Rome.

[3] Also with the financial support of Chemspec S.r.l., Milan, Italy.

[4] For example, the product known in the United States of America Aqua-Trete BSM 20 (Degussa) is known in the European Union as Dynasylan BSM 20% (Degussa).

[5] Material Safety Data Sheets are more detailed having to respond to precise legislation (at least within the European Union).

[6] There are turbidimeters in the market that conform to ES ISO 7027:2001.

[7] In addition to the foregoing parameters we consider the possibility of determining other additional simple tests, as density or refractive index, so as to verify if these can improve the control procedure.

[8] ASTM D 1544-98 / DIN ISO 4630 Standard Test Method for Color of Transparent Liquids (Gardner Color Scale)

[9] The following safety data sheets were consulted:
Dynasylan BSM 40 %, revision date 08/08/2003 version 4.1, Degussa;
Tegosivin WF, revision date 15/08/2003 version 2.1, Tego Chemie;
Hydrogugeant H224, revision date 19/08/1997 version 3, Rhodia;
Hydrogugeant H240, revision date 08/02/2001 version 1.04, Rhodia;
Wacker SMK 1311, revision date 16/05/2003 version 1.6, Wacker Chemie;
Wacker SMK 550, revision date 28/07/2002 version 1.3, Wacker Chemie

[10] ASTM D 1545 – 98 Standard Test Method for Viscosity of Transparent Liquids by Bubble Time Method

[11] Suntest CPS Plus ATLAS

[12] UNI-NORMAL standard method UNI 10925 Method for Artificial Solar Light Test (Feb 2001)

[13] Angelantoni climatic chamber

[14] Anticipating a future restoration work.

[15] The sensors used are those manufactured by Aquaria S.r.l. featuring the radiello technology

[16] Aerosol Spectrometer (Environmental Dust Monitors) Model 1.108, Grimm Aerosol Technik GmbH & Co., Germany. www.grimm-aerosol.com

[17] Minolta CM 2002 Spectrophotometer

[18] This is also in line with the concept of applying extremely simple methods where possible.

[19] ASTM E 2767 – 01 Standard Guide for Selection and Use of Stone Consolidants

[20] UNI-Normal Standard method UNI 1921 Water Repellents – Application on samples and determination of their properties in laboratory, February 2001.