Progress in Organic Coatings 63 (2008) 5–12

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Possibilities of monitoring the polymerization process of silicon-based water repellents and consolidants in stones through infrared and Raman spectroscopy

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ARTICLE INFO

Article history:
Received 27 July 2007
Received in revised form 29 February 2008
Accepted 7 March 2008

Keywords:
Building stones
Conservation
Polymerization
FTIR
Raman

ABSTRACT

The increasing use of Raman and infrared (IR) portable instruments for *in situ* diagnosis and characterization of materials and their conservation state in artworks, has led us to investigate in the laboratory the real possibilities that both vibrational spectroscopies could have for monitoring *in situ* and in real time the polymerization process of silicon-based water repellents and consolidants in stones, after application of the corresponding treatments. Initially, we took IR and Raman spectra of the selected conservation products deposited on inert surfaces along several weeks, in order to determine the spectral regions more sensitive to changes as polymerization proceeded. Afterwards, we tried to apply the same protocol to model stone specimens (Bateig stone widely used in the Spanish Architectural Heritage) impregnated with the conservation products. The stone was characterized, and weight recording, colour variation and SEM observations were carried out once a week during 6 weeks in order to complement the protocol. As far as silicon-based conservation treatments applied to calcite containing stones refer (as the Bateig one here employed), we do not foresee possibilities for *in situ* infrared reflectance spectroscopic monitoring of the corresponding polymerization processes. In the case of the Raman technique, stone fluorescence represented an additional problem. If it can be overcome, Raman data could provide some clues for assessing the polymerization state, especially for the consolidant case.

1. Introduction, background and research aims

For a variety of reasons, stone materials used in the construction of buildings and monuments that form part of historical and architectural heritage undergo processes of deterioration which require the application of remedial and conservation techniques. Of these, two of the most commonly used are the consolidation and protection of the stone. The purpose of consolidants is to strengthen weakened stone and slow down the rate of surface loss by binding loosened grains and crystals. The use of water repellents is aimed at preventing or reducing the penetration of water into the stonework, thereby minimizing the rate of decay. Over the past 20 years, a variety of materials has been used with varying degrees of success but no single method has been found to be effective on all stone types. The composition of these products may be inorganic or organic; the latter can also be divided into natural and synthetic. In recent decades, the most frequently used materials for stone conservation have been synthetic organic products. The major problem with polymeric materials is related to their macromolecular nature [1], which leads to difficulties in penetrating the stone. This mainly affects consolidants which require deep penetration. For this reason, most of the time, the monomer, not the preformed polymer, is carried inside the stone, polymerization being a subsequent process.

The present study was conceived in the context of the lack of a full understanding about the performance and effects of products applied to building stones to strengthen or protect them. Knowledge of the medium and long-term performance of consolidants and water repellents is minimal and there is a lack of agreement between experts in this field as to which materials are most appropriate for use. This casts doubt on the advisability of using these materials on important structures without extensive research and testing [2].

International recommendations and guidelines for scientists, architects and restorers suggest that before a conservation product is applied to any building material in a monument or historical

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doi:10.1016/j.porgcoat.2008.03.002

building, it should have been previously tested in the laboratory, which entails performing a series of tests on treated and untreated samples or specimens to assess the suitability, efficiency and durability of the applied treatments [3]. Laboratory testing is therefore strongly recommended in order to (1) select the most adequate product in each case, and (2) avoid restoration processes that might even speed up deterioration of the materials. Not knowing the time needed for curing and polymerization can invalidate results obtained in the laboratory for selecting the most suitable product to be applied to each stone material.

Following application of the product or products to the stone specimens, the first step prior to laboratory testing is to wait for the drying and curing process to be completed. The question is: How long is it necessary to wait? The usual advice is to wait either until constant weight of the treated specimens is reached (this is probably related to the solvent evaporation added to the product to help it penetrate the stone), or for the period of time recommended by the product manufacturer or supplier (Table 1); many product data sheets use expressions such as drying time, optimal efficiency time, time for full performance, time for re-treatment or reapplication, or application of any other product, time to reach the water repellent or consolidant character, initial cure time, complete cure time or full cure, dry to touch, dry to retreat, etc. The period of time in question may range from a few hours to 4 weeks. Testing treated specimens when the products applied have not completed their curing inside the stone will give rise to invalid or erroneous results.

The aim of this paper is to assess the evolution of some silicon-based treatments once they are applied to building stones, using several techniques. The first step was to determine curing times and relate them from a scientific perspective to what is actually happening, as the effects of drying and ageing of these type of products within the stone are still unknown [4]. Some attempts have already been made, mainly for the purposes of characterization [5–11]. The focus here is largely on molecular spectroscopic diagnosis (Raman and IR spectroscopies), due to the increasing use of portable instruments of this type for the conservation of stone and other objects forming part of cultural heritage [12,13]. In addition to their portability, the non-invasive and non-destructive character of these molecular techniques have made them a preferred method for *in situ* studies and characterization. This study sought to determine whether such spectroscopies can be useful for real-time monitoring of the polymerization process in silicon-based water repellents and consolidants after they are applied to stone.

2. Methods and materials

2.1. Stone substrates

The substrate selected for the purpose of this study was the *Bateig Llano* variety of stone (formerly known as *Novelda* stone, [14,15]). This stone has been used as a building material in Spanish architecture since the 12th century, particularly in the central and eastern areas of the country. It is extracted from the Bateig Hill quarries (Miocene age) in the Alicante region on Spain's Mediterranean coast.

Its texture (it is a biocalcarenite) and petrophysical properties favour its characteristic severe decay which may require application of these types of conservation treatments.

Samples were obtained and specimens cut according to the shape and dimensions required for each test and analysis. Three main types of specimen were used: (a) plates of approximately 3 cm × 1 cm × 0.5 cm for spectroscopic analyses, (b) small samples for SEM observation, and (c) specimens cut into 5 cm cubes for weight recording and petrophysical characterization (three were left blank, untreated, three were impregnated with consolidant and three were impregnated with water-repellent).

Table 1
Curing/drying time of stone conservation products recommended by manufacturers

Product	Effect	Composition	Manufacturer	Curing time
HIDRÓFUGO SH	Water repellent	Polysiloxane	Weber & Broutin	Drying time = 24 h, optimal efficiency time = 7 days
BIO ESTEL	Consolidant + biocide	Silicic acid esters + biocides	C.T.S. ESPAÑA	4 weeks
ESTEL 1000	Consolidant	Silicic acid esters	C.T.S. ESPAÑA	4 weeks[a]
ESTEL 1100	Water repellent	Oligomeric siloxanes	C.T.S. ESPAÑA	4 weeks[b]
TEGOSIVÍN HL 100	Water repellent	Oligomeric siloxane (no solvent)	Goldschmidt	7–10 days for the full water repellent performance to be built up.
Tegovakon V 100	Consolidant	Silicic acid esters	Goldschmidt	14 days to apply solvent-based systems and 4 weeks for water systems
KEIM LOTEXAN/N	Water repellent	Siloxanes	KEIM Mineral Paints	8–10 days to apply another product
PARROGUM INVISIBLE	Water repellent	Polyesters + polysiloxanes	PINTURAS PARROT	Water repellency is reached after 24 h
BPS 7700	Water repellent	Siloxanes	BPS Building Protection System	Wait 28 days for re-application
RADGUARD	Water repellent	Water-based alkyl silane	RADCRETE Development	Initial cure = 4 h, complete cure = 3 days
SIKAGUARD 70	Water repellent	Siloxanes	SIKA	Wait 5 h for re-application
WACKER BS OH 100	Consolidant	Ethylsilicate	WACKER SILICONE	Final hardness is reached after 2 weeks
	Water repelellent	Silicone + resins + mineral spirit	ROYAL Care Services	12 h complete curing time
Silicone water repellent ready to use	Water repellent	Silicone	Coronado Paint Company	Dry to touch = 2–4 h, dry to retreat = 12–14 h, full cure = 7 days
RAINSTOPPER RS200-400-500	Water repellent	Resin + solvent	Textured Coating of America Inc.	24 h for 2nd application, 72 h for application of any other product and 28 day for sealing concrete

[a] The manufacturer indicates that a study from the Trento University states that gelification starts 36 h after the product application.

[b] Same study gives a gelification time of 38 h.