Hydrophobe III -
3rd International Conference on Surface Technology with Water Repellent Agents,
Aedificatio Publishers, 233 – 244 (2001)

Comparative Study of the Efficiency of Protective Treatments Applied to Stone

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Abstract

The paper descibes the evaluation procedure followed to determine the efficiency of protective treatments applied to seven different calcareous stones. The efficienty assessment is performed according to a set of tests, such as colour evolution, water vapour permeability, capillarity and evaporation, micro-drop measurements, etc. For this study four protective treatments were tested. They represent the main families of water-repellents used in stone conservation: an acrylic dispersion, an oligomeric alkylpolysiloxane, a silicone resin in solution and an alkylalkoxysiloxane in aqueous micro-emulsion. Results show that, because of stone diversity in terms of petrophysical nature and properties, there can be no universal protective treatment. The different efficiency characterization tests show the distinctive impact that each treatment has on each stone type. A treatment can be very efficient for one type of stone—providing adequate protection against capillary imbibition whilst assuring a perfect innocuousness towards other physical properties—but can be completely useless or even dangerous for the good behaviour of another stone. Tests to evaluate the efficiency of protective agents exposed to natural environmental conditions are in progress.

1 Introduction

The stone monuments in the Champagne-Ardenne region, whether listed as historical monuments or not, were built with a large variety of materials with different origins, properties and aspects. For some decades significant alterations of these materials have been observed and resulted frequently in the replacement of the deteriorated stones. An increasing emphasis on the conservation of the original material as opposed to its replacement, associated to financial preoccupations, lead those responsible for the monuments to be interested in stone protection products. Their durability has been tested through accelerated ageing, but because their behaviour in real on-site conditions isn't well known as yet, they have been used with caution until now.

This paper presents the results from the evaluation of four protective treatments tested on a set of seven different calcareous stones. Their durability is also being examined in natural ageing situations on 3 French historical monuments: Reims, Charleville-Mézières and Langres cathedrals; but the results are not as yet not available.

The final objective is to bring concrete help to architects in the choice of water repellents as a function of the type of stone and exposure climate.

2 Experimental protocol

2.1 Materials

2.1.1 Treatments

Four water repellents were chosen according to such criteria as adequate efficiency after artificial ageing tests (freeze/thaw, Xenon light irradiation-rain) [1]. They also represent the main families of water repellents used for the protection of historical buildings.

2.1.2 Stones

Many different types of stone can be found in the Champagne-Ardenne region [2]. Besides, the history of a building is very often punctuated by restorations during which stone blocks are replaced. When possible, replacement elements are extracted from the same layer of the same quarry, but in many cases this isn't always possible. In this case, the replacement is made with another type of stone, chosen for its similarity to the original stone. When the decision to protect a façade is taken, the whole façade is treated, including both the original materials and the previously replaced elements. But the behaviour of a protective product is not the same from one type of stone to another. For this reason the study tested stones which were used during the original construction of the monuments as well as for their subsequent substitution (table 2).

	Composition and solvent	Product (manufacturer supplier)	total solids
T1	alkylalkoxysiloxane in aqueous micro emulsion	VP1311 (Wacker)	68%
T2	oligomeric alkylpolysiloxane	Rhoximat HD224 (Rhodia)	69%
T3	acrylic dispersion	IMLAR CPC 1175 (Dörken)	31-34%
T4	silicone resin in solution	DF104 (General Electric)	70%

Table 1: nature of the tested water repellents

	Stone	Description
A	Courville limestone	Thin limestone with micritic matrix, white cream, with few shellfish
B	Savonnières limestone	Oolitic limestone, cream with some whitish to sallow veiny, with coarse grain
C	Champagne chalk	Very tender thin limestone, white, without macro fossils
D	Charentenay limestone	Oolitic limestone, harmonious cream, with thin grains, including some average size holes
E	Jaumont limestone	Oolitic limestone, yellow, with homogeneous grains and shells remnant
F	Langres limestone	Entrochal limestone, greatly dolomitic, brownish colour and with average size grain
G	“Gaize d’Argonne” sandstone	Siliceous stone, fine and slightly clayey and chalky, including remnants of sponges, greenish colour and rich in glauconite grain [3,4]

Table 2: stone description

Figure 1 gives a graphic representation of the main physical properties: porosity and capillarity and absorption/drying kinetics of the selected stones. In terms of porosity the range is very wide: from low porosity with few interconnections (stones F and G), to average porosity with low capillarity (stones A and E) and to high capillarity (stone D) and high porosity with large and unconnected pores (stone B) or large interconnections (stone C).

Similarly, in terms of capillarity-drying velocity, we can also observe the representative distribution of the set of stones. Both absorption and drying kinetics are governed by stone porosimetry. Very microporous stones (stone A) with a bimodal porous system have very slow absorption/drying kinetics. Stones with a high pore content (stone E) possess a fast drying velocity because the exchanges between water contained in the material and the outside air are not limited by pore geometry to the same extent.

2.2 Sample preparation

Water repellent treatments were applied in accordance with supplier prescriptions, with a brush (T1, T2 and T4 treatments) or with a roller (T3 treatment) and up to the recommended consumption or stone saturation. The following figure presents the consumption of the different stones.

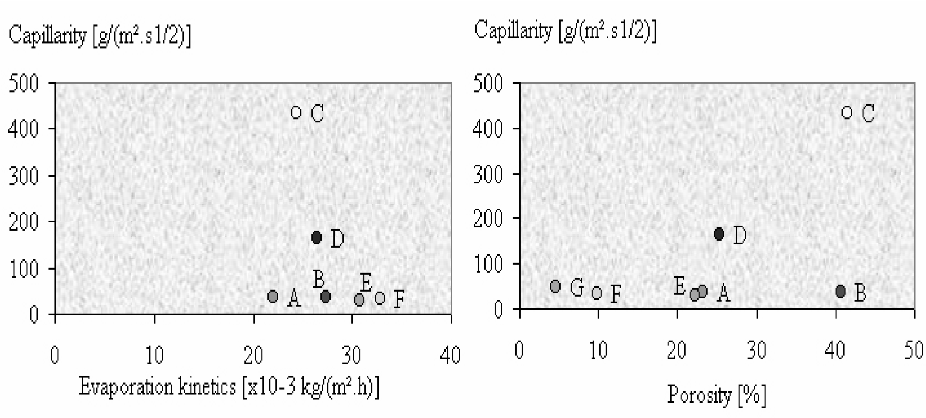

Figure 1: porosity and capillarity & absorption / evaporation kinetics of selected stones.

Stone	Pore family [µm]	pore volume/stone volume [%]
A	0.1 0.25	2.25 3.3
B	0.1 1.0	1.1 4.0
C	0.6	20
D	0.7	6.5
E	0.4 1.0 3.0	1.3 1.1 1.6
F	?	?
G	?	?

Table 3: Pore-size distribution (Rilem I.5)

3 Results of water repellent efficiency

3.1 Impact on stone colour

In order to quantify the impact of a water repellent on the initial colour of a stone, colorimetric measurements were carried out before and after treatment, in controlled relative humidity (58%) and temperature (22°C) conditions. A Minolta CR110 colorimeter using a trichromatic method (L*a*b* measurement colour sys-

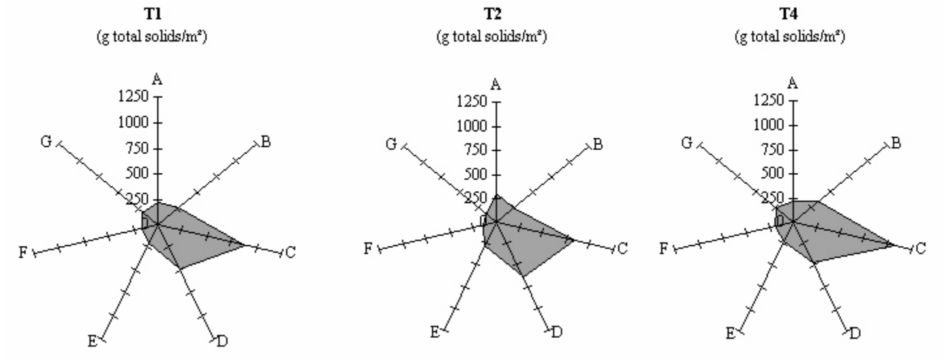

Figure 2: Water repellent consumption

Stones	Water repellent treatments			
	T1	T2	T3	T4
A	☺	☺	☺	☺
B	☹	☹	☹	☹
C	☺	☺	☹	😐
D	☹	☹	☺	☹
E	☺	☺	☺	☺
F	☹	😐	😐	😐
G	☺	☺	☺	☺

Key : ☺ no influence ; 😐 minor visible influence ; ☹ major visible influence

Table 4: Impact of treatments on colour

tem) was employed. The global colour difference ΔE (eq. 1) measured between the studied material (*f*) and its initial reference (*i*) is :

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (1)$$

with

$\Delta L^* = L_f^* - L_i^*$ = difference of clarity
$\Delta a^* = a_f^* - a_i^*$ = difference of chromaticity (id. with Δb^*)

The human eye only detects colour variations ΔE above 3.

Table 4 shows the different cases where the treatment has provoked visible colour variations.

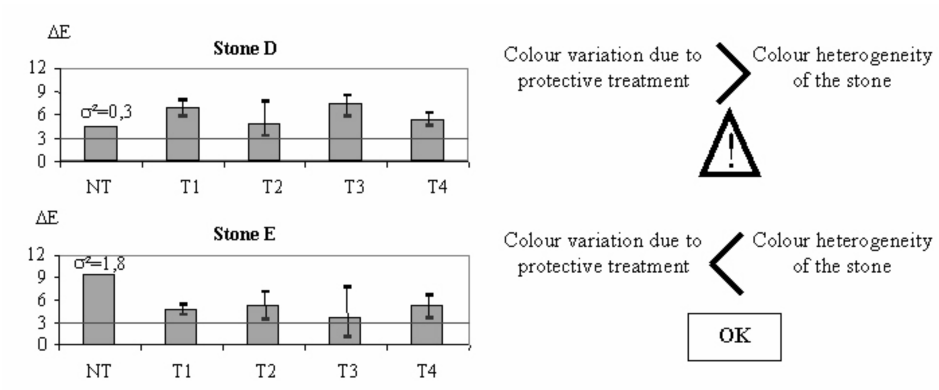

Figure 3: Two different cases of colour impact of water repellent

The colour variations resulting from treatments are often lower than the natural colour heterogeneity of the stone (E and G cases) and thus blend into its natural aspect. On the other hand, some stones are more sensitive to water repellent treatment (mainly stones B and D) and the resulting colour variations are greater than the natural heterogeneity of the stone. Theses two cases are illustrated in figure 3.

3.2 Impact on stone transfer properties

3.2.1 Air permeability

In order to ensure that the application of a water repellent does not modify the gaseous fluid transfer properties of the stone, e.g., by plugging up the pore system, air permeability measures were carried out on both treated and untreated stones. The results were inconclusive because of the heterogeneity of the stone that did not allow to determine any changes in air permeability induced by the treatment.

3.2.2 Water vapour permeability (WVP)

WVP measurements serve to determine significant changes of water vapour conductivity induced by an applied treatment. It is generally admitted that a 30% WVP decrease can pose problems for a treated stone.

Results of WVP measurement show that hydrophobic treatment is difficult for Champagne chalk stone. Results show that only the T4 treatment does not provoke an excessive water vapour permeability reduction. This major reduction of WVP as well as the excessive water repellent consumption (cf. figure 2) is probably a result of the high porosity of stone C.

3.2.3 Capillarity coefficient and drying velocity

The efficiency of a water repellent treatment is mainly assessed through water capillary absorption measurements while the drying velocity measurements show

	stone A	stone B	stone C	stone D	
Treatment with no effect on WVP (<30% reduction)	T1 T2 T3	T4 T3 T2	T4	T1 T4 T2	↑ adequate
Treatment with effect on WVP (≈30% reduction)		T1			
Treatment with major effect on WVP (>>30% reduction)			T2 T3 T1	T3	inadequate

Table 5: Treatment impact on water vapour permeability

whether the treatment modifies the drying kinetics of the material. To be efficient, a water repellent treatment must limit capillary water imbibition while not preventing its evaporation from the stone. This avoids negative effects, as in the case of an accidental water rise from the foundation of a building.

The efficiency of a water repellent (eq. 2) can be estimated from the capillarity reduction coefficient (pr EN 1925). The nearer the %cap.red is to 100%, the more efficient the water repellent.

Similarly, it is possible to calculate the reduction coefficient of the drying flux density, %drying red., (eq.3). The closer it is to 100%, the greater the modification of the drying flux.

$$\%\text{cap. red.} = \frac{\text{Capillarity.coeff(treated stone)} - \text{Capillarity.coeff(untreated stone)}}{\text{Capillarity.coeff(untreated stone)}} \qquad (2)$$

$$\%\text{drying. red.} = \frac{\text{flux density (treated stone)} - \text{flux density (untreated stone)}}{\text{flux density (untreated stone)}} \qquad (3)$$

Polysiloxanes (T1 and T2) noticeably show adequate efficiency on most of the stones (%cap.red between 88 and 100%). However, they also reduce drying velocity significantly.

Silicon resin (T4) is efficient on both high (C and D) or low porosity (E and F) stones. Most of the tested products clearly reduce the drying velocity.

3.2.4 Water micro drop absorption

Water repellent efficiency is also assessed using two parameters relative to water micro drop absorption: contact angle and drop absorption speed. Five categories of

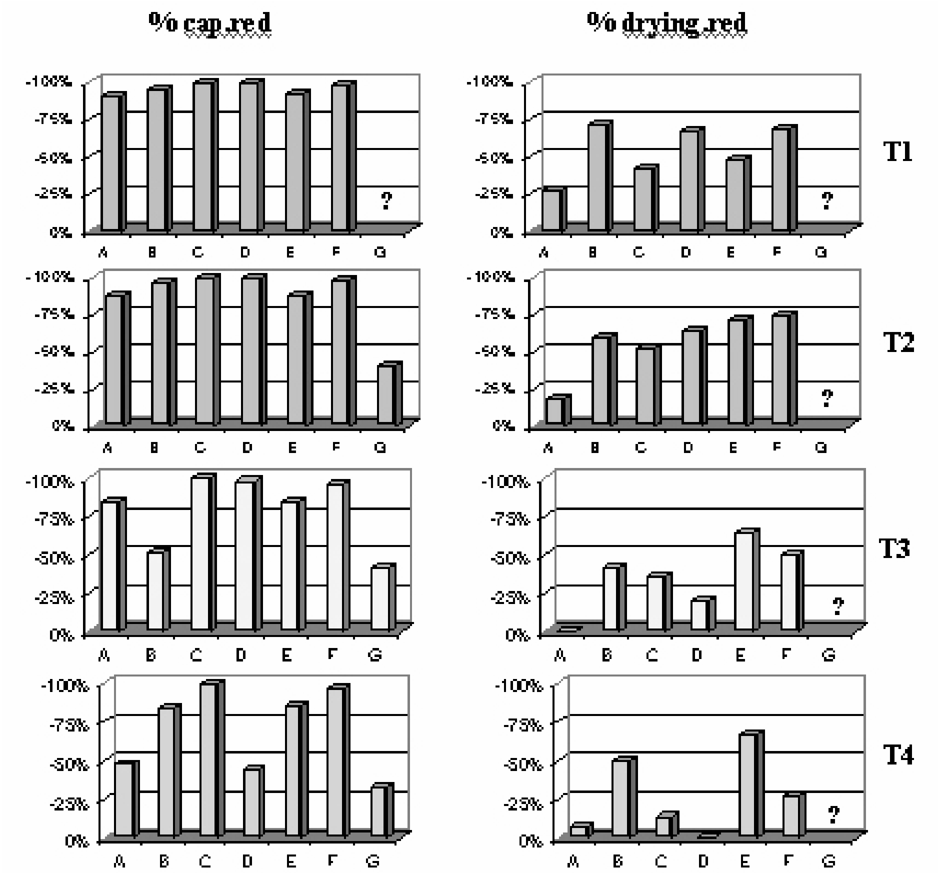

Figure 4: reduction coefficient of capillary and drying speed

contact angle are considered. If the contact angle between the drop and the treated stone surface is above 90° the water repellent is usually regarded as efficient

The water drop absorption (WA) is also measured (eq. 4 and 5). The nearer the WR=100-WA is to 100%, the more efficient the hydrophobization. For all the stones, the WR nearly reaches 100%.

$$\mathrm{WA}(\%) = \left(1 - \frac{tx - tn}{tx}\right)100 \qquad (4)$$

$$WA(\%) = \left(1 - \left(\frac{tx - tn}{tx} \cdot \frac{te}{tx}\right)\right) 100 \qquad (5)$$

if tx>0.05 te
with

tx	time for total absorption of the water drop by treated sample
tn	time for total absorption of the water drop by untreated sample
te	drying time for the water drop on a glass lame

It can be observed on Table 6 that water repellents with an aromatic solvent (T2 and T4) induce a better contact angle (>90°C) than aqueous phase products (T1 and T3). Two stones (F and G) are barely hydrophobized with any of the tested water repellents. Stone G contains clays (montmorillonite) which possibly interfere with the applied treatment.

4 Evaluation of the water repellent effect on stone

The various laboratory measurements and analyses carried out on the stones before and after treatment allow for an evaluation of the efficiency of the treatments depending on the type of stone. Table 6 summarizes the results obtained for each type of stone. The efficiency criteria of a protective product are ranked by order of importance. The main parameter is a significant reduction of water imbibition. Thus, for the seven tested stones, the effect of the various water repellents is illustrated with the following symbols:

☺ : hydrophobization is efficient and meets the objectives

😐 : hydrophobization is efficient to some extent

☹ : hydrophobization is not efficient and does not meet the objectives

☠ : hydrophobization is not efficient and its application can involve some risk

? : test has not been carried out or results are inconclusive

5 Conclusion

Because of the diversity in petrophysical nature and properties of stone, in particular for those of the Champagne-Ardenne region which are considered in this study, no single protective treatment can be applied to all stones.

Four main water repellent families were tested on a set of seven stone types frequently used in the construction and/or restoration of historical monuments.

Stones	Treatments T1	T2	T3	T4
A	60 et 90°	> 90°	60 et 90°	> 90°
B	≈ 90°	≈ 90°	30 et 60°	≈ 90°
C	≈ 90°	≈ 90°	30 et 60°	≈ 90°
D	30 et 60°	> 90°	≈ 90°	> 90°
E	≈ 90°	≈ 90°	30 et 60°	≈ 90°
F	< 30°	≈ 90°	30 et 60°	30 et 60°
G	< 30°	?	30 et 60°	≈ 90°

Table 6: contact angle micro-drop classes (20µl droplet of distilled water)

The different evaluation tests for the treatments applied to each of these stones have revealed their distinctive effect on each lithotype. A treatment can be very efficient on one type of stone, provide adequate protection against capillary water imbibition without inducing negative effects on other physical properties of the stone. However, in the case of another stone, this same treatment can be completely useless, and even dangerous to the material.

Some stones are noticeably easier to hydrophobize. For example, the four water repellents give good results and do not show negative effects when applied to the Courville stone (A). On the other hand, other stones are more difficult to hydrophobize. Although the tested water repellents provide adequate protection against water infiltration they significantly modify drying or water transfer kinetics when applied to the Jaumont limestone (E) or the Charentenay limestone (D). Therefore, water repellent treatment of these types of stone could lead to a possible acceleration of the deterioration processes.

Stones		A				B				C				D				E				F				G			
Efficacity levels		☺	😐	☹	☠	☺	😐	☹	☠	☺	😐	☹	☠	☺	😐	☹	☠	☺	😐	☹	☠	☺	😐	☹	☠	☺	😐	☹	☠
Capillary reduction	T1	x				x				x				x				x				x					?		
	T2	x				x				x				x				x				x					x		
	T3	x						x		x				x				x				x					x		
	T4			x		x				x						x		x				x						x	
Micro drop absorption	T1		x			x				x				x				x				x				x			
	T2	x				x				x				x				x				x					?		
	T3	x				x								x				x				x				x			
	T4	x				x				x				x				x				x				x			
Drying innocuity	T1	x							x		x						x		x					x			?		
	T2	x						x				x					x			x				x			?		
	T3	x					x				x			x						x			x				?		
	T4	x					x			x				x						x		x					?		
Vapour transfert innocuity	T1	x							x				x	x					?				?				?		
	T2	x				x							x	x					?				?				?		
	T3	x				x							x				x		?				?				?		
	T4	x				x				x				x					?				?				?		
Colour impact	T1	x						x		x						x		x					x			x			
	T2	x				x				x						x		x					x			x			
	T3	x						x				x		x				x					x			x			
	T4	x					x				x					x		x					x			x			

Table 7: evaluation of the impact of water repellent application

When a water repellent is chosen, it is also essential to consider its efficiency in time. This point is not addressed in this paper since the weathering exposure tests are currently underway. Stone samples, both treated and untreated, have already been installated on the roofs of three cathedrals which are sujected to different climate and pollution conditions but the data is not avaialable as yet. The resulting information will provide additional information for improving the choice of an appropriate product.

6 Acknowledgements

We thank « Météofrance » , « Atmo Champagne-Ardenne » for their participation. This project is backed up by the "Cercle des Partenaires du Patrimoine" (association of sponsor companies : "Caisse des Dépôts et Consignations", "Calcia-Ciments Français", "Delphi automotive Systems", "Lafarge", "Usinor"), the French Ministère de la Culture, the DRAC and the Conseil Régional de Champagne-Ardenne.

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