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DIRECTION REGIONALE ILE-DE-FRANCE
Domaine de Saint-Paul
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78470 SAINT-REMY-LES-CHEVREUSE

TRIAL REPORT

TRIALS ACHIEVED:

CONTROL OF THE PROTECT-GUARD WATERPROOF EFFICIENCY TREATMENT

At the demand of and For the account of **A.W. Diffusion**

81 Sorins Street
93100 MONTREUIL

TRIAL LOCATION: St-Remy les Chevreuse Date: 1st trimester 1996

SAMPLES OR BODY PROOFS: **1 l of waterproof product**

Source: **A.W. Diffusion Society**

Taken by on:

Recieved at C.E.B.T.P. under n° 27323 on: January 15 1996

NATURE OF TRIALS:

According to estimation n° 3180-834 of October 1995

OBSERVATIONS:

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1/ OBJECT OF SURVEY

The A.W. Diffusion Society has entrusted the "Masonries - Historical Monuments" department of the C.E.B.T.P. to control the efficiency of the PROTECT-GUARD waterproof product, applied on two kinds of limestones:

*SAINT VAAST lès MELO Stone
*TUFFEAU de TOURAINE Stone

The test-tubes have been provided by the C.E.B.T.P. The treatments have been applied by Mr. HARTZ.

The data sheet of the PROTECT-GUARD treating product is given in annex.

2/ DESCRIPTION OF THE TEST-TUBES

2.1/ SAINT VAAST lès MELO Stone

It is a limestone deriving from the quarries located to the North of Oise.
It is a carbonated stone of weak compactness, having the following essential characteristics:

- Porosity : 45% $^{+}$/- 3%
- Capillarity : 38
- Apparent volumic mass : 1580 kg/m^3 $^{+}$/- 50 kg/m^3
- Sound diffusion speed : 2130 ms^{-1} $^{+}$/- 200 ms^{-1}

2.2/TUFFEAU Stone

It is a limestone extracted from Maine and Loire (SAINT CYR EN BOURG).
It is a very tender stone used in Touraine, and in a more general way, in the valley of the Loire, upto NANTES.

Its essential characteristics are the following:

- Porosity : 45% $^{+}$/- 3%
- Capillarity : 23
- Apparent volumic mass : 1430 kg/m^3 $^{+}$/- 50 kg/m^3
- Sound diffusion speed : 1530 ms^{-1} $^{+}$/- 150 ms^{-1}

The two stones chosen for this survey are therefore two stones of high porosity.
The stone from SAINT VAAST lès MELO is one of large pores.
The stone from TUFFEAU is one of fine pores.

3/EXECUTION OF TREATMENTS

In order to judge the effeciency of the treatments, the test-tubes were controlled beforehand from the viewpoint of their capillarity and of their permeability. The results will be compared to the ones obtained on the same test-tubes having received the waterproof treatment.

Waterproofing of the test-tubes

A first trial of treatment was achieved on December 13 1995. The following product consumption had been measured:

- SAINT VAAST lès MELO Stone : 1550 g/m^2
- TUFFEAU Stone : 470 g/m^2

Some capillarity tests carried out on the test-tubes treated on December 13, 1995, have shown that the quantities applied were inadequate, and that some water return was quickly observed

The capillarity coefficients had nevertheless decreased in an important way, but the effeciency of the treatments defined with the formula:

$$E\% = \frac{\text{Initial capillarity - After treatment capillarity}}{\text{Initial capillarity}} \times 100$$

were included between 82% and 99%.

The A.W. Diffusion Society has therefore decided on a second campaign of treatment by applying quantities clearly more important of the waterproof product to the surface of the studied test-tubes.

This second treatment was achieved by Mr. HARTZ on January 15, 1996 on new test-tubes.

The quantities applied on the test-tubes are reported in the following table:

Table 1: Quantities applied

Type of stone	Type of test-tube	Dimension in cm	Surface cm^2	Consumption in l/m^2
SAINT VAAST lès MELO	Disk 1 Disk 2 Disk 3	⊖ 11 ep : 1	95	2420 2440 2420 **Avg : 2425**
	Cube n° 1 Cube n° 2 Cube n° 3 Cube n° 4 Cube n° 5 Cube n° 6	7 x7 x 7	49	2420 2440 2450 2460 2520 2490 **Avg : 2465**
TUFFEAU	Disk 1 Disk 2 Disk 3	⊖ 11 ep : 1	95	890 920 920 **Avg : 910**
	Cube n° 1 Cube n° 2 Cube n° 3 Cube n° 4 Cube n° 5 Cube n° 6	7 x7 x 7	49	1630 1660 880 960 1220 1020 **Avg : 1230**

Comment:
We have encountered no difficulties to make the 2465 g/m^2 of product penetrate in the SAINT VAAST lès MELO stone, which would have accepted more product if one had continued the treatment.

On the other hand, the TUFFEAU stone was treated to some refusal, and the excess product had to be dabbed from the surface of the stone, which could no longer absorb.

The reported results in this report concern exclusively this second treatment achieved on January 15, 1996.

After executing the waterproof treatment, the test-tubes were maintained for a period of two weeks in the laboratory atmosphere, at a temperature of 20°C.
Chromaticity measures were carried out before treatment, after treatment, after 50 and 100 ageing cycles - paint type in industrial environment (Norm NF T 30-049).

4/EVOLUTION OF THE PHYSICAL CHARACTERISTICS OF THE TWO TYPES OF STONES HAVING RECEIVED THE WATERPROOF TREATMENT

4.1/Effects of the treatment on the respiration of the supports

4.1.1/Conduct of the behavior test on the vapors of water

This trial is carried out on three airtight disks, sealed according to their periphery, on cristalized glass of 110 mm of diametre. The trial carried out here is derived from norm NF P 84-402 of June 1989.
The permeability is first determined on the three non-treated samples, and then they receive the treatment defined in chaptêr 3.1/. The after-treatment measures are achieved two weeks after the application of the waterproof product.

Laboratory atmosphere

21°C $^{+}$/- 2°C and 50% relative humidity at $^{+}$/- 5%

The trial consists in noticing the quantity of water vapor escaping through the treated surface for a period of seven days. The flux of desorption is operated from the inside of the crystallizing dish (atmosphere 21°C, 100% R.H.) towards the atmosphere of the laboratory (21°C, 50% R.H.).

4.1.2/Expression of results

The permeability Pe of a material is given by the following formula:

$$Pe = \frac{A}{S\ P} \text{ in } \frac{g}{m^2.h.mm.Hg}$$

with:

S : section of stone disk ($9{,}5.10^{-3}$ m^2)
P : 10,5 mmHg (steam pressure gradient)
A : proportianal coefficient between the weight loss and the time expressed in g/hour

Table 2 : Trial Results

Type of stone	Before treatment			After treatment		
	N° test-tube	A	Pe	N° test-tube	A	Pe
SAINT VAAST lès MELO	1	$6{,}6.10^{-2}$	$6{,}6.10^{-1}$	1	$5{,}8.10^{-2}$	$5{,}8.10^{-1}$
	2	$6{,}35.10^{-2}$	$6{,}35.10^{-1}$	2	$5{,}3.10^{-2}$	$5{,}3.10^{-1}$
	3	$6{,}4.10^{-2}$	$6{,}4.10^{-1}$	3	$5{,}4.10^{-2}$	$5{,}4.10^{-1}$
	Moy	$\mathbf{6{,}45.10^{-2}}$	$\mathbf{6{,}45.10^{-1}}$	**Moy**	$\mathbf{5{,}5.10^{-2}}$	$\mathbf{5{,}5.10^{-1}}$
TUFFEAU	1	$8{,}8.10^{-2}$	$8{,}8.10^{-1}$	1	$6{,}4.10^{-2}$	$6{,}4.10^{-1}$
	2	$8{,}5.10^{-2}$	$8{,}5.10^{-1}$	2	$6{,}5.10^{-2}$	$6{,}5.10^{-1}$
	3	$8{,}6.10^{-2}$	$8{,}6.10^{-1}$	3	$6{,}7.10^{-2}$	$6{,}7.10^{-1}$
	Moy	$\mathbf{6{,}65.10^{-2}}$	$\mathbf{8{,}65.10^{-1}}$	**Moy**	$\mathbf{6{,}55.10^{-2}}$	$\mathbf{6{,}55.10^{-1}}$

Examination of results

For the SAINT VAAST lès MELLO stone, we observed a diminishing permeability to the vapor equal to 14% in average after treatment.

For the TUFFEAU stone, treated to some refusal, the diminishing permeability to the vapor attains 24% in average after treatment.

The product applied on the surface of these two types of stones allows the preservation of a good breathing to the water vapours of the treated supports.

4.2/Evolution of the capillarity of the supports

The capillarity measure were carried out on a 7 cm edge cube on which we have achieved a peripheral tightness of 1 cm in reversion of the treated face, so as to caution parasitic water penetrations.

Only the treated face is in direct contact with the water of the trial tank.

These trial are carried out conformly to norm NF B 10-502.

Table 3 : Value before treatment

SAINT VAAST lès MELO Stone		TUFFEAU Stone	
N° of test-tube	Capillarity coefficient	N° of test-tube	Capillarity coefficient
1	42.4	1	28.1
2	38.3	2	27.4
3	41.1	3	20.0
4	38.8	4	30.1
5	38.5	5	24.5
6	37.2	6	27.0
7	31.7	7	21.7
8	37.5	8	27.2
Moy	**38.2**	**Moy**	**22.7**

Table 4 : Value after treatment

Test-tubes n° 7 and n° 8 are not treated and are conserved as witnesses.

SAINT VAAST lès MELO Stone			TUFFEAU Stone		
N° of test-tube	Capillarity coefficient		N° of test-tube	Capillarity coefficient	
	T 1	T 2		T 1	T 2
1	0.10	0.10	1	0.60	1.15
2	0.50	1.6	2	0.55	1.15
3	0.15	0.15	3	0.60	1.35
4	0.20	0.20	4	0.75	1.15
5	0.15	0.15	5	0.50	1.15
6	0.10	0.10	6	1.2	1.7
Moy	**0.20**	**0.40**	**Moy**	**0.70**	**1.25**

T 1 : Capillarity coefficient measured between 0 and 100 min
T 2 : Capillarity coefficient measured between 100 min and 24 hrs.

Efficiency of treatment

It is defined by the formula:

$$E\,\% = \frac{\text{Initial capillarity - After treatment capillarity}}{\text{Initial capillarity}} \times 100$$

Table 5 : Efficiency of treatment

Nature of stone	Measured efficiency between 0 and 100 mins	Measured efficiency between 100 mins and 24 hrs.
SAINT VAAST lès MELO	99.5 %	99 %
TUFFEAU	97 %	94.5 %

4.3/Color variation caused by the treatment

Fluctuations of color and chromaticity are measured with the help of a colormetre MINOLTA CR 310 in the color space L*, a*, b*, according to the recommendations defined by the C.I.E. in 1976 and conformly to norms NF X 08-014 and NF X 08-015.

4.3.1/SAINT VAAST lès MELO Stone

Table 6

	L *	a *	b *
Before treatment	80.80	+ 1.95	+ 15.80
After treatment	79.70	+ 2.15	+ 18.40
After 50 aging cycles	79.45	+ 1.95	+ 15.0
After 100 aging cycles	80.07	+ 1.60	+ 14.51
After 50 aging cycles - witness test-tube	68.95	+ 4.40	+ 23.70
After 100 aging cycles - witness test-tube	69.34	+ 4.34	+ 24.09

Comments
In this table, we give the average values of the test-tubes affected to this type of control, namely:

- before treatment : 8 test-tubes
- after treatment: 6 test-tubes
- after 50 cycles: 3 treated test-tubes and 1 witness test-tube
- after 100 cycles : 3 treated test-tubes and 1 witness test-tube

The ageing process is described in chapter 4.5/.

4.3.2/TUFFEAU Stone

Table 7

	L *	a *	b *
Before treatment	80.25	- 0.18	+ 10.55
After treatment	78.90	- 0.16	+ 12.25
After 50 ageing cycles	78.70	- 0.38	+ 11.50
After 100 ageing cycles	78.17	- 0.42	+ 11.50
After 50 ageing cycles - witness test-tube	74.70	- 0.40	+ 14.15
After 100 ageing cycles - witness test-tube	74.75	- 0.26	+ 14.85

Comments

In this table, we give the average values of the test-tubes affected to this type of control, namely:

- before treatment : 8 test-tubes
- after treatment: 6 test-tubes
- after 50 cycles : 3 treated test-tubes and 1 witness test-tube
- after 100 cycles : 3 treated test-tubes and 1 witness test-tube

The ageing process is described in chapter 4.5/.

Examination of colormetre measures

In order to better understand the measuring procedures of the color in the space (L*, a*, b*) we will follow the chromaticity diagram on the next page.

a) SAINT VAAST lès MELO Stone

The treatment carried out on this kind of stone brings only a slight reduction of the clearness of the stone (- 1.1 clearness point).

From the viewpoint of the tint, one can solely measure a very light fluctuation, (+ 2.6 points) in the direction of a yellowish tint.

After 50 cycles, we notice no visible alterations, if only a return to the original color of the stone.

After 100 cycles, the measuring process detected only 0.5 points of evolution in comparison to the one recorded after 50 cycles of ageing.

b) Non- treated SAINT VAAST lès MELO Stone

Some very important fluctuations of clearness and tints are observed after only 50 cycles of accelerated ageing. We lost approximately 12 points of clearness. The highest fluctuations in tints are observed in the chromaticity of coordinates b*.
In effect, we measured an increase of almost 8 points being transmitted visually by a profound yellowness of the stone because of the reduction of clearness.

Between 50 and 100 cycles, we observe no significant evolution.

c) Treated TUFFEAU Stone

As for the SAINT VAAST lès MELO stone, the fluctuation of clearness stays minuscule (- 1.35 points).
We measure only a slight yellowness on the surface of the test-tubes (+ 1.7 points in b*)
After 50 ageing cycles for the SAINT VAAST lès MELO stone, the clearness and tint fluctuations remain minuscule, and we also note a tendancy of return to the original tints (in space b*).

After 100 cycles, we almost find the same values as those measured after 50 cycles of ageing.

d) Non-treated TUFFEAU Stone

After 50 cycles, as for the SAINT VAAST lès MELO stone, we measure a loss of clearness (-5.5 points).
A very slight yellowing is also measured (+ 3.6 points in the space b*).

Between 50 and 100 cycles, we observe no significant evolution.

4.4/Penetration depth of treatment

The penetration depth of the treatments is determined by the capillarity test after successive passages to the lapidary.
Each consecutive passage eliminates 1mm of thickness.
After each passage, the test-tubes are dried in a 40°C incubator and measured in capillarity.

Table 8 : Test results
Efficiency E% in regards to the depth

a) SAINT VAAST lès MELO Stone

N° of test-tube	Capillarity coefficient							
	- 1 mm	E %	- 2 mm	E %	- 4 mm	E %	- 6 mm	E %
4	0.2	99.5	0.25	99.35	0.40	99.0	6.6	83
5	0.15	99.5	0.20	99.5	0.55	98.6	5.4	86
6	0.15	99.5	0.50	98.6	0.40	98.9	9.3	75

Table 8 : Test results
Efficiency E% in regards to the depth

a) TUFFEAU Stone

N° of test-tube	Capillarity coefficient	
	- 1 mm	E %
4	27.0	10.3
5	23.2	5.3
6	23.7	12.2

Comments

For the SAINT VAAST lès MELO stone, we note an excellent efficiency upto 4 mm in depth. It remains superior to 98.6 %.

On the other hand, for the TUFFEAU stone, as early as to the first passage in the lapidary, the treatment almost lost its efficiency. The treatment is therefore efficient in the space O at - 1 mm.

4.5/Accelerated ageing trial

For each kind of treated stone, three cubic test-tubes are placed in an accelerated ageing enclosure and paint-like industrial environment, according to norm NF 30-049 of April 1985.

Ageing cycle phases

Water current between 10°C and 20°C	:	$^1/_2$ hour
Cold at -15°C	:	1 hour
Water vapours at 70°C	:	$^1/_2$ hour
Ultra-violet rays at 60°C - 65°C	:	1 hour

The supplementary stage is constituded by a 16 hour exposure to an environment containing 0.07 % of SO_2.

So as to control the efficiency of the product after the ageing process, capillary ascent tests are undertaken after 50 and 100 cycles.

Table 10 : Capillarity coefficiency after 50 cycles

SAINT VAAST lès MELO Stone			**TUFFEAU Stone**		
N° of test-tube	Capillarity coefficiency		N° of test-tube	Capillarity coefficiency	
	0 to 100m	100m to 24 h		0 to 100m	100m to 24 h
1	0.05	0.05	1	0.7	0.9
2	0.15	0.15	2	0.6	0.6
3	0.05	0.05	3	0.4	0.8

Table 11 : Capillarity coefficiency after 100 cycles

SAINT VAAST lès MELO Stone			**TUFFEAU Stone**		
N° of test-tube	Capillarity coefficiency		N° of test-tube	Capillarity coefficiency	
	0 to 100m	100m to 24 h		0 to 100m	100m to 24 h
1	0.06	0.06	1	3.7	9.8
2	0.37	0.37	2	0.60	0.60
3	0.06	0.06	3	0.60	0.60

Examination results after 50 ageing cycles

The results of table 10 are to be compared to the ones from tables n° 3 and n° 4.

a) SAINT VAAST lès MELO Stone

These results show the good holding capacity of the treatment after 50 cycles of ageing. A slight improvement appears in the efficiency of test-tube n° 2 in comparison to its measured value after treatment.

b) TUFFEAU Stone

The formulated comments for the SAINT VAAST lès MELO stone are also confirmed here, and in this particular case, we also note, for the three test-tubes, a slight improvement in the efficiency of the treatment after this series of measures carried out after 50 cycles of accelerated ageing.

Examination results after 100 ageing cycles

The results of table 11 are to be compared to the ones from tables n° 3 and n° 4.

a) SAINT VAAST lès MELO Stone

We notice the excellent behaviour of the test-tubes treated with the PROTECT GUARD product after 100 accelerated ageing cycles. The average capillarity of the three obsolescent test-tubes is 0.16, which represents an efficiency of 99.6 %.

b) TUFFEAU Stone

Two of the three obsolescent test-tubes still possess a very weak capillarity coefficiency (0.6 in a lapse of time between 0 and 24 hours). We observe a light decrease of the efficiency on test-tube n° 1 which sees its capillarity coefficiency rise to 3.7 during the first 100 minutes of the test, and to 9.8 between 100 minutes and 24 hours.

For test-tubes n° 2 and n° 3, the residual efficiency after 100 cycles remains at 97.4 %, while test-tube n° 1 is of only 83.7 % between 0 and 100 minutes and of 57 % between 100 minutes and 24 hours (particularly severe tests).

According to the observations carried out by the laboratory that has tended the ageing test, a slight swelling of the treated surface was observed on the test-tube after a formation of micro-fissures in the epoxidique guard paste cord, and this after 90 cycles.
An analysis of the concerned zone shows the presence to this area, of a small pyrite in the test-tubes' mass.

The behavior of the treatment for this test-tube has therefore slightly degraded between 90 and 100 cycles of ageing.

Without justification for this loss of punctual efficiency on one of the three test-tubes, the outgoing point for this alteration coincides with a homogeneity failure in the mass of the test-tube at the level of the surface treated.

5/GENERAL CONCLUSIONS

This study achieved on two kinds of carbonated stones, the SAINT VAAST lès MELO stone and the TUFFEAU de Touraine stone, allows us to conclude on the following strong points:

- In order to obtain its entire efficiency, the PROTECT GUARD waterproof treatment requires a search of optimal quantity.

- In the process of the study, the optimal quantities to be applied were the following:

SAINT VAAST lès MELO stone	: approximately 2.4 l/m^2 minimum
TUFFEAU stone	: with refusal and approximately 1.2 l/m^2 minimum

For the TUFFEAU stone treated to some refusal, the product surplus must be recovered by dabbing.

- The two kinds of treated limestones see their capillarity coefficient,

  lean towards 0.2 for the SAINT VAAST lès MELO stone
  and towards 0.70 for the TUFFEAU stone

in instant measures.

- The efficient penetration depth of the treatment is of 4 mm for the SAINT VAAST lès MELO stone, and of less than 1 mm for the TUFFEAU stone.

- The PROTECT GUARD treatment reduces by a 14 % average the permeability of the SAINT VAAST lès MELO stone, and a 24 % average for the TUFFEAU stone, which is acceptable, and still leaves the two kinds of stones, the possibility to let water evaporate in case of humidification of the treated surfaces.

- The PROTECT GUARD waterproof treatment applied on these two kinds of limestones brings only a slight variation to their clearness and to their chromaticity coordinates.
After 100 cycles of accelerated ageing, norm NF T 30-049, the test-tubes of SAINT PIERRE lès MELO stone and of TUFFEAU stone have preserved almost entirely their measured values before treatment.
On the other hand, for the non-treated test-tubes, we measured important clearness gaps (-11.5 clearness points for the SAINT VAAST lès MELO stone, and -5.5 points for the TUFFEAU stone), and a yellowing, almost browning (+ 8.3 yellowing points for the SAINT VAAST lès MELO stone and + 4.3 points for the TUFFEAU stone).

The PROTECT GUARD treatment therefore brings an adequate protection against the yellowing of the exposed stones in an industrial environment.

- After 100 cycles of aging, the treatment still shows a great efficiency on the SAINT VAAST lès MELO stone (E = 99.6 %).

For the TUFFEAU stone, on two of the three test-tubes, the residual efficiency is still equal to 97.4 %, but one test-tube sees its efficiency decrease significantly, but still stays equal to 83.7 % from 0 to 100 minutes. This loss of efficiency might be due to the presence of a slight alteration of the test-tube surface with the presence of small pyrites.

The slightest penetration of the PROTECT GUARD treatment on this fine pore TUFFEAU stone could bring an efficient protection on this test-tube for only 90 of the 100 cycles of aging carried out.

Our testing ground of SAINT REMY lès CHEVREUSE on the natural surface of the waterproof ageing products, allows us to achieve a good correlation between the results measured on the test-tubes, with an actual behaviour of these protectant products applied on small experimental walls.

One hundred accelerated ageing cycles in an industrial environment can be assimilated to ten years of ageing in an urban environment.

For the SAINT VAAST lès MELO stone, which showed no reduction in the efficiency of the treatment, we can expect a duration largely superior of approximately ten years.

For the TUFFEAU stone, where only two of the three test-tubes showed an efficiency superior to 97.4 %, we expect a duration of optimal efficiency equal to ten years.

Done in SAINT REMY on May 13, 1996

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