Evaluation of the Artificial Aging Rate Through UV Radiation Exposure of Indigenous Carbonate Rocks, Treated with Water - solvated Nano-dispersions, with the Interest of Consolidation and the Formation of a Waterproof Character

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*The present paper presents experimental data on the evolution of polychromy and the aesthetics of a number of indigenous carbonate rocks originating from the Paun–Repedea area in Iasi, which were treated with the aim of hydrophobization and consolidation with water-solvated emulsions, Nanopro-C and Nano-Seal, all commercially available products. The chromatic movement, initiated as a direct result of exposure to UV radiation, was established through CIE L*a*b* colorimetry, while the compositional and surface-level modifications were determined through optical microscopy (OM), as well as electronic scanning microscopy, coupled with X-ray dispersion spectrometry (SEM-EDX).*

*Keywords: Oolithic limestone, nano-molecular water-solvated emulsions, hidrophobyzation, consolidation, accelerated aging, UV radiation, CIE L*a*b* colorimetry, MO, SEM-EDX.*

As already acknowledged and accepted by the global scientific community, the main factor of aggression for geomaterials used in the construction of heritage goods is *water* and/or *excessive humidity* [1-3], especially in the case of the use of porous calcareous rocks, such as those found in the Repedea Hill – Iasi area [4]. Therefore, in order to ensure the better maintenance of a calcareous lithic material of this nature, the use of a hydrophobic preventive treatment is required. Another alteration factor in the case of lithic materials is *natural light*, which can also bring about undesirable results, in the case of hydrophobic treatment, through chromatic modifications of the surfaces subjected to treatment, which are influenced by UV radiation [5].

In this sense, the present study presents a series of data regarding the chromatic deviation and accelerated aging of lithic materials exposed to a source of UV radiation, after the carrying out of hydrophobisation treatments and consolidation with water-solvated emulsions, Nanopro-C and Nano-Seal, both produced by Isomat Greece. The chromatic deviation has been determined through the utilization of CIE *L*a*b* colorimetry* [6-15], while the evaluation of structural and compositional modifications has been carried out through optical microscopy (OM), as well as electronic scanning microscopy, coupled with X-ray spectrometry (SEM-EDX).

Experimental part

Materials

The investigations were carried out on two samples of calcareous rock (fig. 1a and b), the chemical products used experimentally for treatments being of commercial provenance (namely Nanopro-C and Nano-Seal, both produced by Isomat Greece). The areas subjected to treatment were given the notations P1 (in the case of Nanopro-C) and P2 (in the case of Nano-Seal, respectively), while the notation for the control area was set to P0.

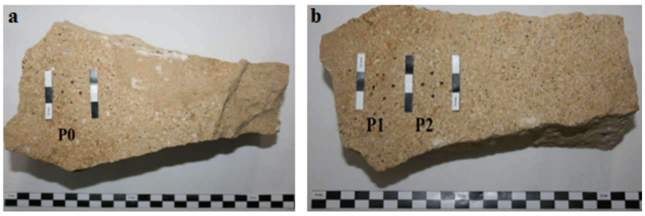

Fig. 1. Calcareous rock samples from the Repedea – Paun Hill area. The delimitation of areas subject to investigation is as follows: a – the control area (P0); b – the areas subjected to hydrophobization treatment (P1, P2)

The main characteristics and effects for the two solutions are listed in table 1. Other utilized materials include: distilled water, marked 1 ml dropper, paintbrushes and cleaning brush.

Techniques involved in the analysis

Colorimetry

The evaluation of chromatic modifications was made with the help of a LOVIBOND RT 300 (Reflectance Tintometer) spectrophotometer. This instrument allowed for the gradual recording of chromatic deviation directly on the sample, both before and after treatment, with aid from the CIE *L*a*b** system. Subsequently, the data was digitally transferred and processed, which allowed for the setting the foundations of the discussions and conclusion pertaining to the results of the investigations [8-13].

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Table 1
DESCRIPTION OF CHEMICAL PRODUCTS UTILIZED IN EXPERIMENTS

Solution	Nanopro-C	Nano-Seal
Characteristics and effects	Watery dispersion, in the form of an emulsion, with a nano-molecular structure. Impregnant with antifungal role for absorbent surfaces. .	Watery resin-based dispersion, with high penetrability, owing to its nanomolecular structure. It is applied on porous surfaces, which it protects from humidity and salt formation, thus also eliminating fungi and mould
Physical and chemical properties	White emulsion with specific smell, with a pH of 7.5 and specific weight of 0.99 g/cm^3.	Blue-coloured emulsion, with a pH of 8,5 and a specific weight of 1.00 g/cm^3.

Optical microscopy (OM)

The morphological characteristics of lithic surfaces were studied with the aid of a Zeiss Imager A1m optical microscope, which also possesses an AXIOCAM camera attached to it, as well as a specialised software.

Electronic scanning microscopy (ESM), coupled with X-ray dispersion spectrometry (XDE)

In order to visualise the porous lithic structures and film resulting from the hydrophobic treatment, an electronic scanning microscope was used, specifically a SEM model VEGA II LSH, produced by TESCAN – Czech Republic, which possesses an X-ray dispersing spectrometer, of a QUANTAX QX2 variety, produced by BRUKER / ROENTEC – Germany, with which the elemental composition of samples, both before and after treatment, was determined. The resulting images are made up of secondary electrons (SE) or, alternatively, backscattered electrons (BSE), at a magnification rate of 200X.

Exposure to UV radiation

The samples subjected to hydrophobic treatment, alongside those left untreated, were both exposed to UV-A radiation, with a predominant wavelength of 365 nm, so as to be capable of carrying out a differentiated analysis regarding their reaction towards artificial aging. Thus, the UV radiations were emitted by a 250 W mercury vapour lamp, and through magnification the radiation surface obtained was of 0.785 cm^2, in the form of a circle with a diameter of 1 cm.

Spectrophotometry

The wavelengths emitted by UV lamp radiations, coupled with part of those pertaining to the solar spectrum both in and around the laboratory area have been measured with the aid of an AVANTES – Ava Spec 2048 optic-fibre spectrophotometer.

Luminous intensity

Luminous intensity has been determined with the aid of a TYP-MDLx analogic lux metre, as well as an LX 1010 B digital model.

Experimental part

Delimitation of surfaces subject to analysis

After the cleaning of the residual dust (through soft brushing), a control area of approximately 9 cm^2, noted P0 (fig. 1a) and two treatment zones, with approximately equal dimensions as the control area, marked with P1 and P2, respectively (fig. 1b) were established.

Treatment of surfaces with commercially available products and determination of the absorption rate of distilled water.

After the delimitation of necessary areas, an approximate quantity of 0.2 mL of each chemical product was applied by *brushing* on the P1 and P2 surfaces. Twenty-four hours after the aforementioned treatment, 0.1 mL quantities of distilled water were gently sprinkled over all areas, including the control area of the experiment, so as to be able to successfully analyse the degree of absorption of the surfaces subjected to experimentation (fig. 2).

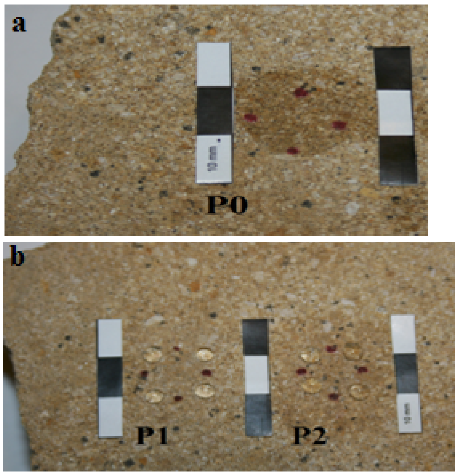


Fig. 2.Dropping distilled water over: a – the control area P0; b – the treated areas, P1 and P2

Determination of chromatic deviation

The colorimetric deviation was measured starting from the initial state of surfaces subject to experimentation, without coating treatment, and after the chemical hydrophobisation and anti-fungal treatment, successive measurements were carried out in the investigated areas, at regular 24 h intervals [14, 15].

Colorimetric measurements simultaneous to UV radiation exposure

After the application of hydrophobic and anti-fungal treatments on the areas of P1 and P2, regular 24 h measurements (over a 96 h timespan) were carried out in order to establish if the chromatic deviation reached a certain level of constancy. Moreover, all samples (both treated and otherwise) were exposed, in laboratory conditions, to UV radiation, for a total interval of 24 h, after which all measurements were carried out on an hourly basis.

As far as the colorimetric evolution is concerned, the change in colour was calculated in the case of every coordinate (L^*, a^* and b^*), as compared with its initial value, on the same sample and in the same point. The chromatic deviation (ΔE^*) was determined with the aid of equation [6-22]:

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

in which:

- ΔL^* represents the change in light intensity in the respective point, at different time intervals, as compared to the initial value: $\Delta L^* = L^*_1 - L^*_{initial}$;
- Δa^* represents the chromatic modification of the coordinates of axis a^* (colours blue and green), from the same point, at different time intervals, as compared to its initial value:

$$\Delta a^* = a^*_1 - a^*_{initial};$$

- Δb^* represents the chromatic modification of the coordinates of axis b^* (colours blue and yellow), while respecting the same method of calculation:

$\Delta b^* = b^*_1 - b^*_{initial}$.

Results and discussions

Fifteen minutes after the two solutions were treated, the first signs of differentiation between the colours of the surfaces subjected to treatment began to manifest (fig. 3). This aspect is influenced by the manner in which the products involved within the study interacted with the porous surface [22], in which case a certain tendency for colour accentuation on surface P2, treated with the product Nanopro-Seal, manifests itself more strongly than in the case of surface P1, which was treated with the product Nanopro-C.

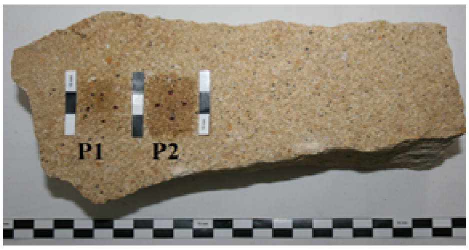


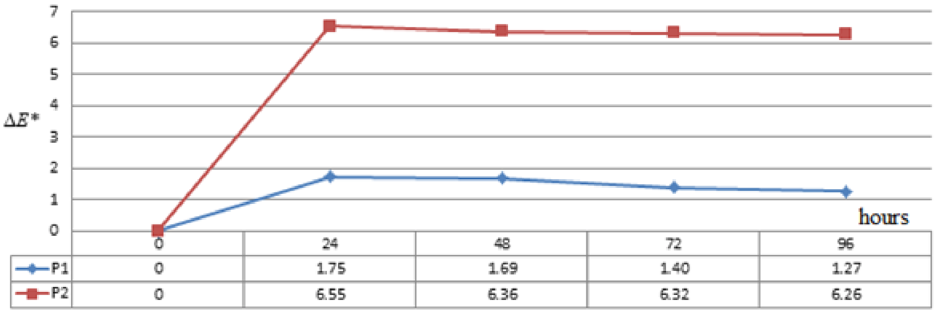
Fig. 3. Image taken 15 min after the hydrophobic treatment

This fact is also visible in the graphical representation of the evolution of the ΔE^* index, over a 96 h timeframe (fig.4). Thus, it may be observed that treatment with the product Nano-Seal led to notable changes in the chromatic deviation, in the case of surface P2, as specialised works may also ascertain [7, 8, 11-22]. In this respect, the value of ΔE^*_{96h} is 6.26.

In the case of surface P1, ΔE^*_{96h} has a value of 1.27, a fact which indicates an insignificant change in terms of chromatics. In both cases, the variation of ΔE^* is largely influenced by the luminosity index (ΔL^*), as may also be induced from the data found in table 2.

These aspects have all necessitated discussions, as pertaining to the subject matter of geomaterials, through prolonged exposure to UV radiation, in laboratory conditions.

Thus, it may be noted that, after a short period (24 h) of exposure to UV radiation, the Nano-Seal product tends to apparently modify the chromatic aspect of surface P2, as compared to the control area P0 and surface P1. In this case, both the strengths and weaknesses of the two hydrophobic and anti-fungal products can be discussed,



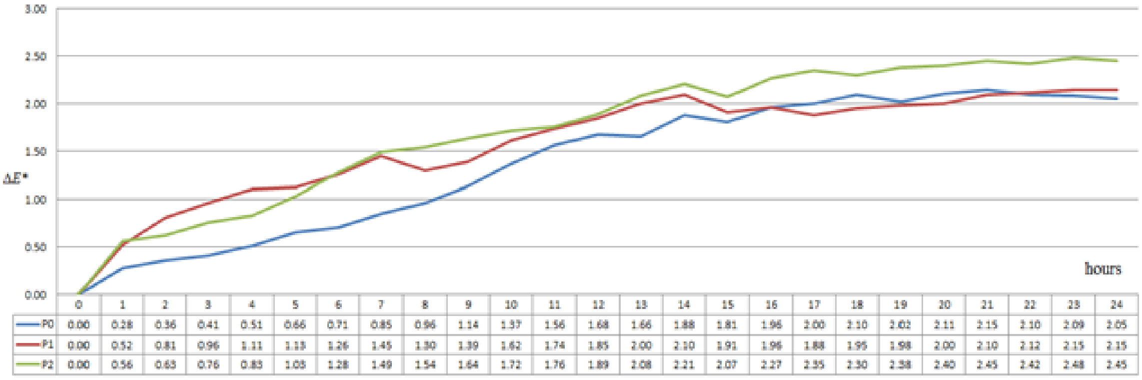
	0	24	48	72	96
P1	0	1.75	1.69	1.40	1.27
P2	0	6.55	6.36	6.32	6.26

Fig. 4. Evolution graph of the ΔE^* index, on surfaces subject to hydrophobic treatment.

Table 2

COLORIMETRIC DATA OBTAINED THROUGH SUCCESIVE MEASUREMENTS, AFTER THE PERFORMANCE OF CHEMICAL TREATMENT

Hours	P1			ΔE* – P1	P2			ΔE* – P2
	*L**	*a**	*b**		*L**	*a**	*b**	
0	65	8.65	26.78		66.28	7.76	24.44	
24	63.62	9.12	27.74	1.75	60.81	9.91	27.32	6.55
48	63.55	9.05	27.56	1.69	61.00	9.91	27.26	6.36
72	63.90	9.01	27.57	1.40	60.97	9.82	27.19	6.32
96	63.94	8.94	27.41	1.27	60.99	9.90	27.01	6.26



	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
P0	0.00	0.28	0.36	0.41	0.51	0.66	0.71	0.85	0.96	1.14	1.37	1.56	1.68	1.66	1.88	1.81	1.96	2.00	2.10	2.02	2.11	2.15	2.10	2.09	2.05
P1	0.00	0.52	0.81	0.96	1.11	1.13	1.26	1.45	1.30	1.39	1.62	1.74	1.85	2.00	2.10	1.91	1.96	1.88	1.95	1.98	2.00	2.10	2.12	2.15	2.15
P2	0.00	0.56	0.63	0.76	0.83	1.03	1.28	1.49	1.54	1.64	1.72	1.76	1.89	2.08	2.21	2.07	2.27	2.35	2.30	2.38	2.40	2.45	2.42	2.48	2.45

Fig. 5. Evolution graph of the ΔE^* index on calcareous-rock surfaces exposed to UV radiation

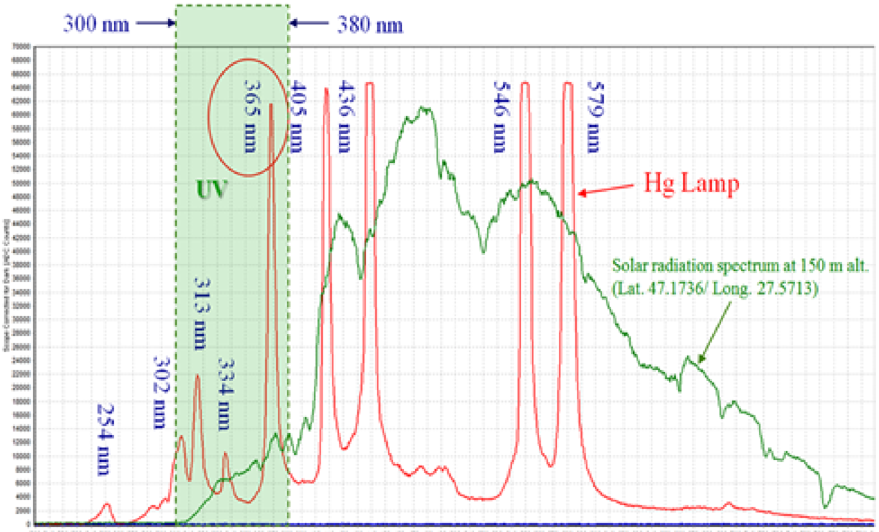


Fig. 6. Spectra of radiations emmitted by the UV lamp, as compared to the solar spectrum existent within the Iasi city area [14, 15]

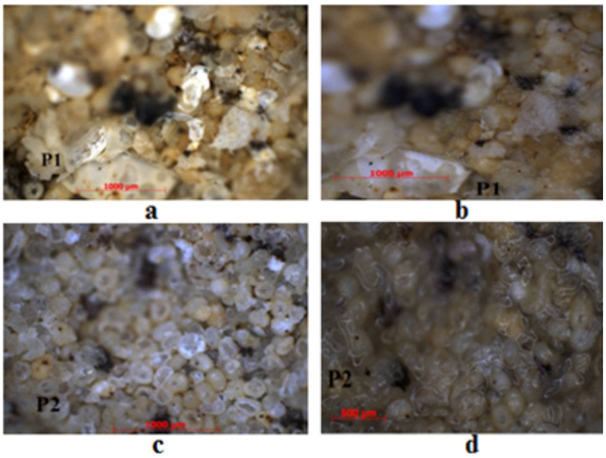


Fig. 7. MO images for areas P1 and P2:
a and c - before treatment; b and d - after treatment;

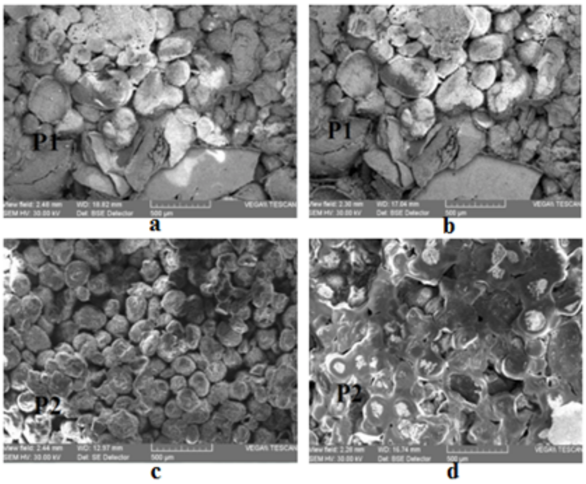


Fig. 8. SEM images for areas P1 and P2:
a and c - before treatment; b and d - after treatment

Table 3

ELEMENTAL COMPOSITION OF AREAS SUBJECT TO INVESTIGATION, BEFORE AND AFTER CHEMICAL TREATMENT

Investigated areas	Elemental composition in percentages (%)											
	Ca	Si	Fe	Al	Mg	Na	P	Mn	K	S	C	O
P0 - control	44.50	9.34	1.97	1.11	1.25	-	-	-	-	-	0.59	41.25
P1 -untreated	55.79	4.91	2.10	1.21	0.82	0.87	0.51	0.82	3.31	-	0.09	29.57
P1 - treated	48.01	11.65	2.67	0.85	1.08	-	0.57	0.93	-	-	0.33	33.91
P2 -untreated	48.90	14.05	1.81	1.09	0.81	-	0.57	-	5.59	-	0.05	27.11
P2 -treated	7.40	2.16	-	0.84	1.38	2.90	-	-	-	1.17	23.16	60.99

by correlating these observations with the effect confirmed by the droplet test (fig. 3), where it is possible to note that areas subject to treatment (P1 and P2, respectively) develop a hydrophobic character. These characteristics have also been highlighted by the MO (fig. 7) and SEM (fig. 8) analyses.

From the EDX analysis (table 3), one may observe the way in which these two products bring about changes in the elemental composition from the surface of the lithic material subjected to analysis, as according to the following:

-in the case of surfaces P1 and P2, after impregnation, the mass of calcium decreases, Ca variation for surface P2 being the most significant in this respect: from 48.9% to just 7.40%;

-the mass of silicon varies in different ways; in the case of surface P1, a growth from 4.91 to 11.65% can be registered, whereas in the case of surface P2, a sharp decrease is apparent, from 14.05 to 2.16%;

-chemical elements such as Fe, Al and Mg vary insignificantly in both cases;

-carbon and oxygen masses are subject to change in the case of both treatments, notably in the case of sample P2 with a growth from 0.05 to 23.16% for carbon and from 27.11% to 60.99% for oxygen.

By associating the elemental compositions with the descriptions of chemical products found in table 1, the two hydro-repellent products can be clearly differentiated into two distinct hydrophobic groups, as follows:

-Nanopro-C – silicon compounds group (confirmed by the growth in mass of both silicon and oxygen in the case of the P1 treated surface);

-Nano-Seal – organic polymer group (confirmed by the substantial growth of both carbon and oxygen masses, in the case of treated surface P2, coupled with the filmy aesthetic aspect, which may be observed by employing the use of SEM imagery (fig. 8d). Thus, it is possible to explain the specific cause which determines an increase in terms of the total colour change index (ΔE^*_{96h}= 6.26)

Conclusions

The following conclusions can be drawn from the study:

-the two chemical processes can ensure the hydrophobisation of porous calcareous rocks, such as those found in the Repedea Hill – Iasi area;

-as far as consolidation and decrease in frailty are concerned, the product Nanopro-C presents certain silicon compound-specific deficiencies, such as the capacity of the OH found in water to form covalent bonds with substrates, a fact which, over time, can lead to a decrease in the efficiency of this repellent;

-although the superior mechanical properties of the resin found within the Nano-Seal product are already well-known, as a result of impregnation, a significant chromatic deviation of the film which is formed upon the surface subject to treatment tends to be caused. Furthermore, this type of product (watery, resin-based dispersion) is also susceptible to photochemical degradation caused by UV radiation exposure more easily than siliconic resin-based products, an aspect which shall lead to a differentiated aging of the lithic materials subject to treatment with the two distinct products.

In order to be able to utilize these products within the context of heritage goods restoration, further tests are needed in order to evaluate conservation properties, especially with regard to the chromatic modifications registered in local environmental conditions.

Acknowledgement This paper has been financially supported as part of the POSDRU/187/1.5/S/155397 project entitled Through PhD grants towards a new generation of elite researchers, cofinanced through the Social European Fund, on behalf of the 2007-2013, Sectorial Operational Human Resource Development Programme 2007–2013.

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Manuscript received: 26.02.2016