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Modification of Protective Lime Coating Systems for the Porous Limestone Using Lime Nanomaterials: Assessment of Mechanical Properties and Ageing Resistance

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Abstract: Within the area of care for sculptural and architectonic monuments of limestone in Austria there has been a historic continuity of use of protective lime coatings. In the regions of Upper and Lower Austria, Vienna and Burgenland mainly Leitha limestone (named after the Leitha Mountains) are dealt with. In Czech lands such approach was disrupted from 19th century by application of the “purist” idea of bare surface of stone. Nevertheless, this treatment of stone surface has been coming back into use for many various reasons in the past few decades. Requirements for preservation of pieces of art and handcraft made of limestone using lime coatings are most often applied in the regions of Vysočina, South Moravia and South Bohemia, which directly border on the Northern States of Austria. Owing to the resource locations of Leitha limestone in these regions, there is a higher representation of cultural heritage monuments made of this type of stone in the Czech Republic.

Based on existing findings and practical experience, besides other favourable characteristics lime coatings and even nanolime products fulfil also the theoretical requirement for so called material compatibility with limestone – stones consisting of mainly calcium carbonate. Having followed the instructions for their application conditions they should not cause any undesirable physical or chemical changes in the treated material. Nowadays their use corresponds to the current requirements of cultural heritage preservation for retreatibility and reconservation. Their characteristics and relatively easy removability does not prevent prospective conservation and restoration treatments in the future and at the same time they provide long-term and repeatable preventive care. Their limited adhesion to the types of limestone with compact surfaces of low porosity and soakability might be considered as a certain drawback of the use of lime coatings for surface preservation. In addition, their decreased resistance to the impacts of environment and corrosion could be viewed as a problem; currently these would include above all air pollution by acid atmospheric pollutants and the effects of water soluble salts.

Within the Nanolith project (cross-boundary Austrian-Czech collaboration), there has been a series of tests carried out focused on possible modifications of protective lime coating systems by means of alcohol nanosuspensions of calcium hydroxide. The purpose of the modification was to increase the lifespan of lime coating systems in exterior conditions with the use of various types of nanolime products. Within the described experiment, nanolime products were tested in various combinations as primers as well as final fixatives of lime coating systems. The purpose of the testing was to find out if the proposed combination of lime coatings with nanolime products positively influenced adhesion of the coatings to the stone surface, their cohesion and resistance to aging in exterior conditions. Part of the testing was to determine suitable application conditions and the way of application of nanolime products.

Choosing suitable methods to assess the characteristics and resistance of individual modified coating systems proved to be quite difficult. The inconveniences were caused by the absence of available published papers dealing with the given issues as well as norms and standards designated for lime of inorganic coatings testing generally. Because of such limitations, partially modified methods based on existing norms in the field of organic coatings testing and the methodology proposed by the ITAM AS CZ / CET Telč in collaboration with FR UPCE were used.

Choosing and finding a suitable substrate – a support for the application of the tested lime coating systems was not easy either. For the given type of sedimentary stone a notable variation might have been expected in the physical characteristics of the prepared test specimens, which makes the testing result assessment more difficult. Adhesion of coating treatment is closely related to the differences of these characteristics, mainly to soakability, porosity or compactness of stone, thus also their lifespan to a great extent. For that reason, individual test specimens, which differed in the above mentioned characteristics, were set with these parameters and subsequently taken into account when the resistance of the applied system of lime coatings was assessed.

As support for the testing of modified lime coating systems test specimens of Leitha limestone from the quarry near the municipality of Loretto (Burgenland) in Austria were used. For the preparation of the lime coating slaked lime from Dullinger Kalk in Austria was employed. Nanolime products were chosen from the product line of the firm IBZ Freiberg from Germany. For the primary adhesive layer – primer – nanoproducts CaLoSiL® E50 (concentration of 50 g Ca(OH)2 / a litre of the product) and CaLoXiL® Lime Glaze (concentration of 120 g Ca(OH)2 /a litre of the product) were chosen. For the final fixative layer – fixative – nanosuspension CaLoSiL® E25 (concentration of 25 g Ca(OH)2 / a litre of the product) was used.

For the testing itself and the assessment of characteristics of the lime coating systems the following testing and assessment methods were used: cross cut adhesion test for the assessment of adhesion of the coating system to the surface of stone; climatic accelerated aging testing – cyclic changes of temperature and relative humidity, exposure to mixed air pollution by the gases of SO_2 a NO_x and resistance to salt crystallization using sodium chloride; water resistance test; water drop test of paint wettability; resistance test by dropping with hydrochloric acid – assessment of coating system resistance to acidic pollutants; peeling test – assessment of adhesion and cohesion of the coatings; drying test; test of application of a fixative to pigmented lime coatings – assessment of optical changes of tinted lime coatings after the final fixative application; tests of suitable application method of a fixative – assessment of the distribution of the fixative during application; visual assessment in dispersed day light and sharp raking light; study of the microstructure of surface layers – microphotography by means of a special camera; optical and scanning electron microscopy; setting the basic physical characteristics of the support with the coating system – bulk density; open porosity accessible by water; water absorption and pore size distribution.

The results of laboratory testing have suggested that in the tests of modified lime coating systems similar trends can be observed. Treatment of the support (limestone) under the lime coating itself by means of a primer based on lime nanosuspension increased adhesion, resistance and durability of the lime coating on all the types of lime test specimens. A positive effect has been noted both in the case of limestone of high porosity, soakability and structured on the surface as well as in the problematic ones with compact surfaces, lower porosity and soakability. The best results have been achieved with the use of CaLoXiL® Lime Glaze – a highly concentrated nanosuspension. Application of a fixative – less concentrated lime nanosuspension CaLoSiL® E25 – a final fixing layer of lime coating seems to have been positive only if the by homogenous distribution using low concentration of lime nanosuspension.

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