SWBSS 2011
19 - 22 October
Limassol, Cyprus

Salt Weathering on Buildings and Stone Sculptures

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ISBN 978-9963-7355-1-8

Nanoparticles for stabilization of salts in St. Nicholas Church, Pittsburgh, Pennsylvania

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ABSTRACT

The St. Nicholas First Croatian Catholic Church, located in Millvale, an adjacent neighborhood of Pittsburgh, Pennsylvania, contains expansive murals painted by the Croatian immigrant artist Maximilian Vanka. Pictorial content, which covers 11,000 square feet of interior space, includes scenes of industry, religion, social injustice, and the horrors of war. In the 75 years since their completion, the murals have been subjected to a wide variety of pollutants from industry, auto emissions and candles in the church. As a result, these pollutants accumulated, colors have darkened and water damage has affected some areas. Past hurricanes structurally damaged the building in 2004 resulting in local areas of efflorescence on the murals. Earlier interventions to the murals included the use of synthetic resins to treat efflorescence and the application of modern paint over interior walls. Elemental analysis identified salts and an inorganic conservation method was tested on the murals to determine feasible treatments using calcium and barium hydroxide nanoparticles to stabilize efflorescence.

Keywords: salts, efflorescence, analysis, treatment, nanoparticles

1 INTRODUCTION

The treatment of St. Nicholas Croatian Catholic Church (St. Nicholas) aimed to install preventive conservation measures, introduce no further elements of deterioration into the work, and achieve good and long-lasting results. Previous treatment on one of the murals was carried out in the 1990s using synthetic resins to stabilize areas of efflorescence. Few treatments would have been able to fend off damage from hurricane force winds and record-breaking water levels. The span of time since previous treatment and the new damage was less than one decade, and the necessity to re-treat was an opportunity to assess the success of previous measures. At the time these materials were selected for their inert properties and reversibility. Development of this new conservation program took into consideration shortcomings of previous materials used and the effects of previous interventions in the church as well as measures that offer a more positive outlook on long-term stability of the murals.

St. Nicholas is situated in Millvale, Pennsylvania, a former industrial suburb north easterly adjacent to the city of Pittsburgh along the Allegheny River. Many Croatian immigrants found jobs in steel mills and coalmines in the Pittsburgh area and settled in communities within the industrial neighborhoods along the Allegheny River. Escape from economic hardships, political oppression, and infringement of personal freedoms lead many Croatians to flee their homeland in the late 19th and early 20th centuries. It was estimated that 10 per cent of Croatians in

American lived in Pittsburgh in 1937. (*Bulletin Index*, 1937) St. Nicholas was established in 1894 to preserve language, customs and community unique to the Croatians.

Frederick C. Sauer, a German-born architect, and contractors, the Murphy Brothers, were hired to build the Romanesque style building. The Croatians insisted on using materials of the highest quality for their church design, which included electric lights and central heating. The first mass was held 25 November 1900. A fire destroyed the church on 26 March 1921 and church members again contracted Sauer to draw new plans for the church. This new building was dedicated 30 May 1922.

Father Albert Zagar of St. Nicholas commissioned Maximilian (Maxo) Vanka in 1937 to paint a series of murals on the church's white walls. The Croatian artist ended up calling the work his "contribution to America," and painted half of the 22 murals in the course of eight weeks in 1937. (Leopold, 2001) He painted another 11 over five months in 1941, and finished details in 1950. Vanka admired Zagar for breaking with tradition and allowing the artist to decorate walls of the church with images of "modern social significance." (Nayler, 1941) The murals' expansive imagery covers 11,000 sq. ft. (1,022 m^2) and reflects values of the Croatian immigrants in their new country combined with their Roman Catholic faith. Traditional religious images are mixed with messages of a central mother figure, industry, social injustice, horrors of war, and experiences of the immigrants. Vanka's murals are recognized for portraying imagery timeless in their social and religious meaning. St. Nicholas was added to the National Register of Historic Places in 1980.

Figure 1. *Pietà* before treatment with efflorescence along right edge.

1.1 Murals

Maxo Vanka worked on sketches in his New York studio while contractors prepared walls of the church according to his specific instructions. (Adamic, 1938) Unfortunately, Vanka's guidelines for these preparations were not documented. The murals were not executed in *buon fresco* and significant controversy exists regarding identification of the medium used by the artist. The medium has been previously identified as "dry fresco", (*TIME*, 1937) casein made from cheese, (*Bulletin Index*, 1937 and Nayler, 1941) dry powdered casein, (Demarest, 1981) distemper, (McDevitt, 1999) and egg tempera on plaster. (Leopold, 2001) In numerous early accounts the artist stated that he ground his pigments and mixed enough to work for a day, working in wet plaster, a technique consistent with *buon fresco.* It is evident that the mural consists of a paint layer applied over dry plaster. Photographs confirm that the artist carried out an underdrawing over the plaster in a wet medium and followed his preparatory drawings in paint. Vanka worked quickly and, in the heat of summer months his brushes became so sticky with the medium he had difficulty working. (Breig, 1941)

A sample of the artist's original medium from an area of brown paint, from the mural *Mati 1941* was analyzed. Results from Fourier transform infrared spectroscopy (FTIR) revealed a spectrum with N-H stretching and amide bands in the range of 3400 cm^{-1}, consistent with a protein binder. A broad hydroxyl group stretching demonstrates a general comparison to a reference spectrum for plant gum and the lack of any detectable carbon-hydrogen or carbonyl stretching indicates that no oil, resin, wax or synthetic is present in the original medium. (Martin, 2009)

1.2 Wall treatment

Square-shaped folk-patterned stencils were once painted on the wall adjacent to *Mati 1941*. Early photographs of the interior church walls depict decorative borders. Chevron patterns, some of which are still present around the murals, covered additional square footage.

2 CAUSES OF DETERIORATION

Observers in 1972 confirmed that the murals were in excellent condition. (Miller, 1972) However, subjected to a wide variety of pollutants from industry and auto emission, they eventually began to exhibit a heavy accumulation of these pollutants, which made them increasingly difficult to see. Pollutants from industry also contributed to degradation of the materials. Subject to water infiltration in the past from roof damage, "water spots" and "evidence of deterioration" was noted as early as 1981 (Demarest, 1981) and in the next decade a conservator documented that some of the murals exhibited efflorescence. (McDevitt, 1999) Significant damage resulted after remnants of Hurricanes Frances and Ivan came through Pittsburgh in 2004. The damage induced by hurricanes was not noticed, however, until a considerable amount of efflorescence appeared on interior walls around 2006. A building inspection revealed that the strong winds blew off part of the metal roof covering the sanctuary and fractured brick and mortar in the two bell towers with significant damage to the north bell tower. Windows constructed with wood frames on the second and third floors were also discovered to be failing. Record-breaking rainfalls of 2004 were granted easy migration through damages to the interior of the church.

Another contribution to alterations in the condition of the murals is the undocumented measure to paint over the decorative folk motifs covering non-mural walls with white oil-based commercial paint. The congregation concurred, however, that after these decorations were no longer visible, the bright white contrasted with the dark murals making them difficult to see.

The parish hired a contractor in the 1990s to paint the walls in medium grey and pale green, using synthetic interior paints and glazes, resulting in a very glossy impermeable surface.

2.1 Water damage

Water, entering through cracks, migrated through the walls and efflorescence is found primarily in areas of the murals *Pietà* and *Mati 1941*. *Pietà* is located in the corner of the interior of the building to the right of the high altar. Efflorescence is concentrated along the right edge of the mural. *Mati 1941* is located to the right of the large stained glass window, in the adjacent corner. Damage to *Mati 1941* from efflorescence is concentrated along the right edge and is characterized by a dry, fluffy white powder on the surface. Crystallization of infiltrates occurred at the interface of the plaster wall and paint layer. Increased volume of this new formation forced areas of original paint from the surface. Numerous losses resulted from small pockets filled with salts, and, having lost all inherent binding, fell from the wall. The ceiling in the choir loft and the stairwell leading to the north bell tower also exhibit extensive water damage and efflorescence, but these walls do not contain Vanka's paintings.

2.2 Previous interventions

Contributing to a further weakened condition is the previous conservation treatment carried out in the late 1990s on the *Pietà,* which was to address efflorescence and removal of surface dirt. Water damage from the 2004 hurricanes has appeared in areas of the *Pietà* previously treated. Efflorescence was handled by brushing away the salts and fragile areas were re-adhered with synthetic polymers in the earlier treatment. Fills were made with modern materials and retouching was executed in acrylic. The undamaged, original surface of the *Pietà* was matte while areas with synthetic adhesives appeared dark and saturated, particularly where these polymers had been heavily applied. These materials were chosen, no doubt, in the belief that they were easily reversed. Areas of modern fill were as saturated with salts as original plaster. Passages with modern retouch responded to new water damage by trapping salts beneath the relatively elastic layer and billowing from the surface due to volume of its contents. Earlier attempts to re-adhere weakened areas with polymers failed and delamination of paint from the wall re-occurred.

Further inspection of the glossy walls painted in grey revealed that salts were widely present beneath this synthetic layer. The modern coatings retained water and, as water migrated through the building, it was trapped beneath the paint. Moisture then either followed the path of least resistance by migrating to a surface more porous than itself (the mural), or remained behind the impermeable coating, slowly converting plaster into sulfates. Light hand pressure confirmed that pockets of delamination existed throughout the walls treated with the modern coating.

3 ANALYSIS

3.1 Salts analysis

The efflorescence was analyzed and indicated that compounds of calcium and sulfur constituted 50 per cent of the efflorescence. Magnesium, silicon, and carbon account for the bulk of the remainder. Additional trace elements are found in smaller percentages.

Table 1. Report of salts analysis from efflorescence of St. Nicholas Croatian Catholic Church

Material: *Salts from church walls* *SCL#: 10002766-01*
ID/Description: *Sample 1*

Test	Result	Units	Method	Instrument	Analysis Date
			AS RECEIVED		
Al2O3	0.25	Weight %	SCL-145	XRF	9/28/2010
CaO	24.83	Weight %	SCL-145	XRF	9/28/2010
Cl	0.32	Weight %	SCL-304	SISE	9/28/2010
Cr2O3	0.006	Weight %	SCL-145	XRF	9/28/2010
CuO	0.052	Weight %	SCL-145	XRF	9/28/2010
F	0.17	Weight %	SCL-311	SISE	9/28/2010
Fe2O3	0.15	Weight %	SCL-145	XRF	9/28/2010
K2O	0.062	Weight %	SCL-145	XRF	9/28/2010
Li2O	0.001	Weight %	SCL-402	ICP Ceramic	9/23/2010
MgO	19.72	Weight %	SCL-145	XRF	9/28/2010
MnO	<0.001	Weight %	SCL-145	XRF	9/28/2010
Na2O	0.11	Weight %	SCL-402	ICP Ceramic	9/23/2010
P2O5	0.005	Weight %	SCL-145	XRF	9/28/2010
SiO2	9.95	Weight %	SCL-145	XRF	9/28/2010
SO3	24.89	Weight %	SCL-XRF	XRF	9/28/2010
SrO	0.26	Weight %	SCL-145	XRF	9/28/2010
TiO2	0.007	Weight %	SCL-145	XRF	9/28/2010
ZrO2	0.025	Weight %	SCL-145	XRF	9/28/2010
			DRY BASIS		
CO2	19.17	Weight %	SCL-354	LECO C/S	9/28/2010

3.2 SEM/EDS Analysis

A sample of the efflorescence was examined with an AMRAY 1830 scanning electron microscope. Energy dispersive spectroscopy (EDS) performed on the sample exhibits a strong presence of sulfur, 66 per cent weight, and calcium in nearly 20 per cent of weight, followed by magnesium and trace elements. Identification of sulfates supports the degradation of the healthy calcium hydroxide $Ca(OH)_2$ into calcium sulfate $CaSO_4$ by environmental conditions.

4 TREATMENT

4.1 Preventive conservation measures

Removal of elements that contribute to deterioration, mainly pollutants and water, is paramount to a successful conservation treatment. Pittsburgh, having once earned the status as steel-making capital, underwent a dramatic transformation in the 1980s to clean up the city. The previously sooty black skies are blue again. The departure of industry and this "green" renaissance removed many sources of pollutants. Structural repairs made to the church in 2008 included repairs to the roof, replacement of fractured mortar and brick, and replacing weakened wood window frames with metal ones. Inspections carried out on completion concluded that structures were sound and more recent inspections confirmed that structural repairs were successful. Since repairs were made, no additional efflorescence or worsening of the condition has been noticed. Maintaining dry conditions in the building prevents the formation of new efflorescence on the walls.

A planned future removal of the modern coating on walls adjacent to murals would reduce the risk of the formation of future efflorescence on the walls of historic significance. While it may not be feasible to selectively remove the top layers of paint and reveal original folk decorations, it may be possible to selectively remove the layers in an area adjacent to walls with murals. These passages would allow any moisture in the future to be released through these "sacrificial" bands, mitigating damage to the murals. New fills in these areas should consist of a material more porous than the mural, such as lime and sand.

4.2 Ferroni-Dini method

Prior to consolidating damaged murals, sulfates which threatened physical stability had to be removed. The previous attempts to consolidate the mural with synthetic polymers were unsatisfactory. Prior adhesives darkened the original surface and were not sympathetic to the porosity of the wall, while contributing to further degradation processes. *Buon fresco* is not a common medium in the United States and routine treatments for fresco are not in common practice. Although the murals were not carried out in true *fresco*, the traditional training of the artist and his preparation of the wall inspired the exploration for alternative options for stabilizing efflorescence. Minute tests were carried out on the murals using the inorganic Ferroni-Dini (barium) method to remove salts and consolidate murals with flaking caused by efflorescence. The technique, developed in the late 1960s by Enzo Ferroni and improved upon by Dino Dini, is in wide use in Europe, but has not been incorporated into common American practice. The process involves multiples steps of applying poultices to remove sulfates and consolidate flaking wall material with inorganic materials. Earlier publications on this method should be consulted for a complete description of the chemical process. (Matteini, 1999; Giorgi, 2006; Baglioni, 2010)

The first step of the Ferroni-Dini method uses poultices of ammonium carbonate $(NH_4)_2CO_3$ to de-sulfate calcium sulfate by turning it into ammonium sulfate. The formed product is a soluble salt and is absorbed by the cellulose fibers of the poultice. Removal of sulfates reduces the volume of material. Once stable, the dry poultice material was exchanged for a new poultice of cellulose wet with distilled water. This step rinses the treated surface to help remove most of the soluble ammonium sulfate salts $(NH_4)_2SO_4$, which, if left on the surface, may lead to the formation of additional efflorescence.

The second step of the Ferroni-Dini method, barium hydroxide $Ba(OH)_2$ is applied in a super saturated solution in water to a fresh cellulose poultice. This step removes soluble ammonium sulfate $(NH_4)_2SO_4$ and provides inorganic consolidation of damaged mural by forming the insoluble salt of barium sulfate $BaSO_4$. Products of water and ammonia have a cleaning effect on the wall then evaporate while barium sulfate partly fills small losses in the plaster. The materials continue a gradual consolidation process by conversion of barium sulfate $BaSO_4$ into barium carbonate $BaCO_3$ and reformation of calcium hydroxide $Ca(OH)_2$. These two steps are the primary action of consolidation in the Ferroni-Dini method. By this method efflorescence on wall murals were de-sulfated and consolidation took place without the use of synthetic polymers.

Samples of a treated area of the wall were collected and examined again with SEM/EDS. Elemental analysis performed on a sample after treatment with the Ferroni-Dini method shows dominance of the presence of calcium at 43 per cent of the composition. Barium is present in nearly 52 per cent of composition. Sulfur, which constituted 66 per cent of the material prior to treatment, was reduced to almost 2 per cent. Reduction of sulfur and the reaction of the barium support the effectiveness of de-sulfating process and consolidation of the wall through the inorganic treatment method.

4.3 Nanoparticles

Experimenting with the Ferroni-Dini method was a preliminary measure to determine the feasibility of the use of nanoparticles for treatment on the painted murals. This treatment may not be effective on all types of efflorescence; it is most applicable on walls contaminated by sulfates. This was a very successful means of removing salts and strengthening mechanical attachment of original preparation and paint layers to the wall, but delivery of a nanoparticle consolidation material offers several advantages. Instead of delivery of material in an aqueous system, nanoparticles of barium hydroxide measuring micrometers in size were dispersed in isopropanol. Delivery in alcohol reduces surface tension, increases capillary action, and allows more thorough penetration of the barium hydroxide into interstices. These properties of the nanoparticles are considerably advantageous when the plaster has been painted. Nanoparticles are more effective in penetrating the paint layer to reach the layer in need of consolidation, but they are less easily absorbed in areas treated previously with polymers and acrylic. Nanoparticles were preferred because consolidation could take place in a non-aqueous delivery method, avoiding high pH levels, which are harmful to *secco*, and reduced the risk of migration of the water-sensitive binding medium.

A combination of methods was used in practical treatment of efflorescence on the painted murals. All areas of previous retouching in acrylic were removed. Due to salt build-up beneath the acrylic, this non-original layer was easily lifted. In areas of heavy loss of original paint and in areas previously covered with acrylic retouch, the Ferroni-Dini method was used to treat salts. Because original paint was no longer present, the aqueous component did not present a risk of additional damage. Areas of original paint affected by salts were treated with nanoparticles. Treatment in isopropanol assured less damage to the original medium and better penetration of the inorganic consolidation materials.

Unless a wall painting exhibits flaking without any salts present, any treatment begins with the poultices of ammonium carbonate in an aqueous solution to remove harmful efflorescence. Treated areas must be allowed to dry completely before introducing the nanoparticle dispersion of barium hydroxide alcohol. Like the aqueous application of barium hydroxide, complete consolidation is a gradual process. Areas too far damaged by efflorescence may lack the necessary calcium binder for barium hydroxide nanoparticles to convert for consolidation. In these instances treatment should be preceded by introduction of nanoparticles of calcium hydroxide in alcohol to wall or paint flakes. Direct application of calcium hydroxide is hindered by its low solubility in water. Dispersions of nanoparticles in isopropanol, however, have low surface tension and increase penetrability of the inorganic binding medium in the wall where needed.

4 CONCLUSIONS

It is difficult to predict the effects of natural disasters and safeguard a work of art against unforeseeable misfortunes. Some contributions to deterioration of the St. Nicholas murals were the effects of modern interventions. Local pollutants were reduced and controlled by means larger than the scope of the conservation campaign of the church. Their successful removal fortunately contributes to the long-term preservation of Maxo Vanka's murals. Previous measures to update the church interior with modern paints and the prior conservation treatment were made with the most earnest of intentions, but the passing of time revealed shortcomings in these decisions. It remains the goal to rectify these deficiencies, introduce treatment materials designed for durability, and achieve long-lasting results to ensure appropriate stewardship of the murals. The decades-long track record of the inorganic Ferroni-Dini treatment method in

Europe assures long-lasting results and does not introduce materials that could contribute to further degradation of the walls in St. Nicholas. Adjustment of the Ferroni-Dini method with nanoparticles was an appropriate selection to adjust for the painted layer in the traditional medium and improves efficacy in the inorganic treatment system.

I would like to express my gratitude to Dr. Piero Baglioni and Rodorico Giorgi, Department of Chemistry and CSGI of the University of Florence; Diane Novosel and the board from the Society to Preserve the Millvale Murals of Maxo Vanka; David Campbell and Todd Ault of West Penn Testing Group; as well as Patricia Buss, Cynthia Fiorini, and Rhonda Wozniak.

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