



A Research and Development Report from the Workshop

Removal of Damaging Conservation Treatments on Mural Paintings

November 2 & 3, 2007, Österbybruk, Uppland, Sweden

Author: Hélène Svahn Garreau

Research and Development Report
Author H el ene Svahn Garreau, 2007
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Box 5405, SE-114 84 Stockholm
www.raa.se
riksant@raa.se
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Preface

With funding from Research and Development at the Swedish National Heritage Board we had the opportunity to organize an international seminar and workshop in 2007.

The seminar focused on the techniques and methods for restoration and preservation of mural paintings. The seminar succeeded in the aim to make the knowledge accessible and to strengthening the scientific foundation, both methodological and theoretical. It was a meeting with a sharing of experiences and this is the final report from the seminar. The author takes full responsibility for the views and information presented in this report.

Inger Liliequist
Director General

Research and Development (R&D) grants support research projects and seminars concerned with the interface between cultural policy, knowledge relating to historic environments and different scientific disciplines.

Introduction

The Swedish National Heritage Board held a two-day workshop named “*Removal of Damaging Conservation Treatments on Mural Paintings*” on November 2 and 3, 2007 at Österbybruk and Vendel. The workshop was sponsored by “FoU-medel” (R&D funds), distributed by the Swedish National Heritage Board and from “Syskonen Bothéns stiftelse” distributed by ”Nordiska konservatorförbundet Svenska sektionen” (NKF-S). This is the final report, which includes a summary of the presentations and discussions during the workshop.

The main objective of the workshop was to discuss possible treatments of earlier destructive conservation treatments on mural paintings with special attention to the problems in Vendel Church in Uppland. Lecturers from Denmark, Germany and Italy were invited to share their experiences and to illustrate different solutions to similar problems.

Another motivation for the workshop was that the Swedish National Heritage Board was working on the conservation of the medieval mural paintings in Vendel Church between 2005 and 2008. In 1930 the mural paintings were uncovered and treated with casein. The casein has become brittle and the paint layer is flaking severely. Thus, there are two problems to address: 1) *the reattachment of the paint layer* and 2) *the reduction of the casein*. The problem is quite difficult and one of the purposes of the workshop was to discuss the problem and share our experiences with the preinvestigation of the paintings.



Figures 1 and 2. Tests in Vendel Church 2006. Photographs H el ene Svahn Garreau.

Summary of Presentations

“Introduction”, Architectural Conservator H el ene Svahn Garreau

H el ene Svahn Garreau welcomed the participants to the workshop. She hoped that the workshop would be successful and provide a good opportunity to discuss difficult conservation problems, especially in mural painting. Moreover, she invited the audience to bring forward conservation problems that they had found in their daily work. Such a conservation problem could become a future research topic for the Swedish National Heritage Board.

The presentation briefly portrayed the Swedish conservation and restoration practices in mural church painting over the centuries. After a short general introduction about mural church painting, the history of treatment in Sweden was summarized:

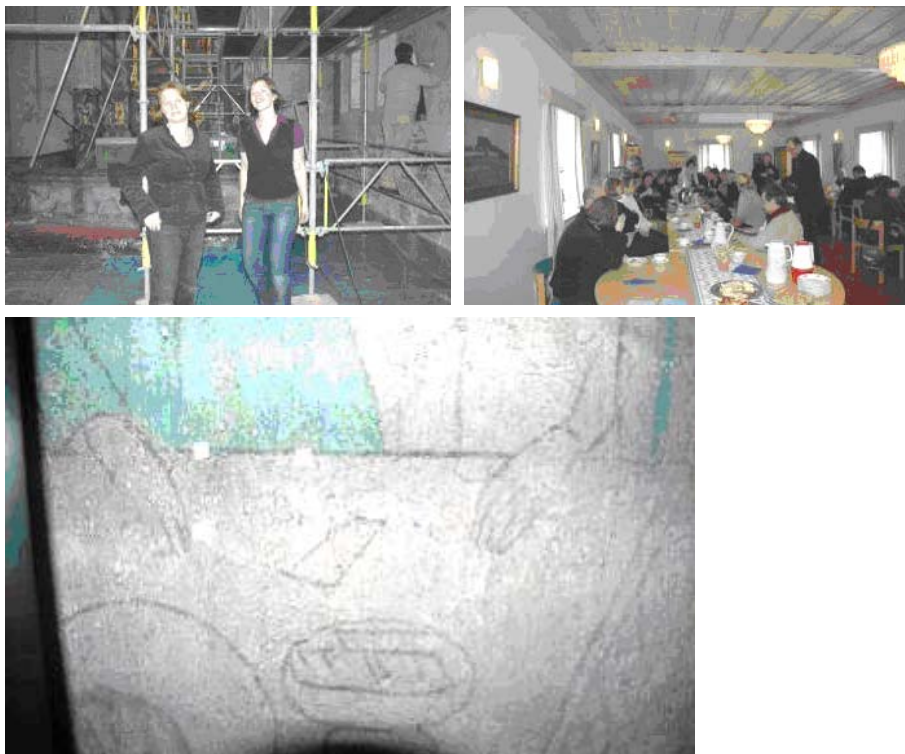


Figure 3. Lena  stlund and Ragnhild Claesson in Vendel Church.

Figure 4. Coffee break in the parish house during the workshop.

Figure 5. Test of microemulsion during the workshop.

Photograph Lena  stlund.

- Mural paintings were lime-washed from the 17th until the beginning of 19th century. A few paintings in vaults were never lime-washed, for example at Täby and Floda, painted by the medieval painter Albertus Pictor.
- The uncovering of paintings was made from the middle of the 19th century until the 1960s. The majority at the end of the 19th and beginning of the 20th century.
- Only a few examples of transfers are known (such as in Lund cathedral).
- Consolidation of the paint layer was made with casein, acrylics and lime water.
- Retouching was made with pigments in lime water, casein or acrylics. In the beginning of the 20th century until the 1930s the “Curman method” with scratching on the surfaces was used. From the 1930s neutrals and enhancement of “weak colours” were employed.
- For grouting gypsum, lime-mixtures, “adhesive nails” and PLM were used.
- For cleaning “gomma pane”, wishab and water were used.
- For attachment of flaking paintlayers acrylics were used.

After this some problems in mural paintings in Sweden were discussed. These were:

- Salt damage, such as in Vå, “Skåne”.
- Microbial problems, such as in Odensvi, “Småland”.
- Casein problems, such as in Vendel, “Uppland” and in Köpinge, “Skåne”.
- Climate problems, where an increase of microbial infestations has been noted in recent years.
- Aesthetic problems, such as removal of superficial dirt and retouching lacunae.

The aesthetic question was discussed in Sweden in the beginning of the 20th century, when Sigurd Curman introduced a new methodology. This methodology was very modern for its time and was inspired from his experiences in Italy and Germany. It was, however, abandoned at the end of the 1920s. After this stagnation in the theory occurred. Today, the old retouches are usually preserved and when retouching is required neutrals and reinforcements of the weak colour are used.

8 Summary of Presentations



Figure 6



Figure 7



Figure 8



Figure 9



Figure 10

Figure 6. Vendel cemetery. Photograph Lena Österlund.

Figure 7. Vendel Church, drawing made by A. Nilson. ATA Stockholm.

Figure 8. Mural paintings in Vä, Skåne.

Figure 9. Medieval mural paintings in Tensta Church retouched by the Conservator-Restorer Petterson in the 1920s.

Figure 10. Mural paintings in Strängnäs cathedral. Retouching made in 1907 by Curman's handpicked workers.

Photograph Hélène Svahn Garreau.

Hence, Svahn Garreau ended her presentation wishing to create a project about aesthetics in mural paintings for Swedish conservator-restorers, architects and curators. The reason for this is that the Italian theories such as Cesare Brandi's theory about retouching are almost unknown among curators and conservator-restorers in Sweden. Thus, Mora & Mora's "tratteggio" and the Florentine "selezione and astrazione cromatica" have not been introduced in mural painting conservation in Sweden. These Italian methods are used in many countries such as Italy, Spain and Germany and nowadays also in Denmark. There are a few exceptions, such as the mural paintings in the castle of Lemshaga outside Stockholm made by the Conservator-Restorer Svahn Garreau (with Ullenius Conservation Company) in the 1990s and the Romanesque paintings in the attic at Fornåsa Church in Småland made by the Conservator-Restorer Henningsson in 2003. Because of this Svahn Garreau believes that here is a need to discuss the theory behind the Italian methods and demonstrate their possibilities.

"Biotechnological Approach for the Removal of Damaging Casein-Layer on Medieval Wall Paintings", Dr. Sascha Beutel

Dr. Beutel presented his PhD-project *"Innovative Verfahren zur enzymatischen Abnahme von schädigenden Caseinüberzügen auf Wandmalereien"* (2000) that proposed an innovative controllable methodology for the removal of casein using enzymes from mural paintings. The project was carried out in cooperation with conservator-restorers, curators, microbiologists and biotechnologists.

The background of the project is that casein often has been used during the 20th century in wall painting conservation in Germany. Over time, problems provoked by the casein have occurred; for example darkening of paint layer, flaking and microbial infestation.

Dr. Beutel was invited to Sweden by the Swedish National Heritage Board in 2003 to demonstrate the enzyme method in Vendel Church. The method did not work since there were problems with the 2D fluorescence spectrophotometer device (see below). The sensor of the machine could not detect the casein on the wall. Thus, it was not possible to know if the casein was reduced.



Figure 11 and 12. Dr. Beutel demonstrates the enzyme method in Vendel in 2003.
Photograph H el ene Svahn Garreau.

Laboratory tests

The scope of the laboratory tests was to find a suitable enzyme, create a controllable methodology to remove the casein that makes it possible to measure the amount of casein that has been removed. Selected enzymes were tested on test panels coated with lime plaster and painted with different kinds of pigments. The plates were treated with casein and aged in a climate chamber for several months. After this different types of enzymes were tested. The enzyme Alcalase 2,5 DX L gave the best results. The protein digestion was confirmed with gel electrophoresis and enzyme screening. The chosen enzyme digested the casein within ten minutes.

Field tests

A controllable methodology using the chosen Alcalase was designed to be used in the field. It was important that no protein fragments were left on the substrate, that the removal of the casein was detected with a noninvasive technique and that the methodology did not wet the plaster (because of the risk of salt damage).

The chosen Alcalase was immobilized to a cellulose membrane stabilized with epoxy. The membrane was held together with a cushion (with the total area 9,2 cm²). A device was created that could hold the membrane and cushion in contact with the wall. A buffer stream of Na-HCO₃/Na₂CO₃ with pH 9.0 was pumped through the cushion/membrane to create a slightly moisturized surface. The purpose of the stream was to rinse the casein fragments from the wall. Another device with a 2-D Fluorescence spectrophotometer was created that made it possible to monitor the reduction of the casein (it measures the amount of tryptophan – a typical amino acid for casein).

There were some identified problems with the enzymatic method:

1. Problems to detect casein inside the plaster.
2. The Cu-pigments can be affected by too high pH.
3. Salt blossoms as well as some Cu-pigments and microorganisms can disturb the measuring of removed casein.

The amount of casein is possible to measure through the amino acids at a certain wavelength using 2D fluorescence. The result of the measurement depends on:

1. Which pigments there are on the surface.
2. The porosity of the plaster.
3. Which kind of casein that has been used.
4. Salt blossoms on the surface.
5. Microorganisms on the surface.

Discussion

- The portable 2D Fluorescence spectrophotometer did not work in Vendel. The question was why? Dr. Beutel believes that distribution in the measurement was caused by the fact that the amino acid was broken down (by UV light) in Vendel. Hence, the broken down tryptofan cannot be detected at the chosen wavelength that is measured with the sensor in the 2D fluorescence spectrophotometer.
- A question was asked about the possible temperature and buffers working with enzymes. Dr. Beutel said that working temperature can range from cold churches during wintertime to room temperature and up to around 30–40° C. Different buffers with different pH can also be used. The digestion time and efficiency varies with changes in pH and temperature.

- A discussion about the use of the method on large areas, such as Vendel, took place. Dr. Beutel said that the small cushion was for scientific studies, not made for large scale application.
- The membranes used in Vendel were really expensive and too stiff and expensive. Svahn Garreau mentioned that the Swedish National Heritage Board have had discussions with Robert Corkery at the Institute for Surface Chemistry in Stockholm about the possibility of using other membranes to immobilize the enzymes. Membranes such as Japanese paper are cheaper, could be easier to use as well as cut into sizes that the conservator requires. This however, requires research.

“German Experiments with Enzyme Reduction of Casein on Mural Paintings”, Conservator-Restorer Kerstin Klein

Klein is currently working on a PhD about casein use and problems in mural painting conservation. Her presentation described her work including tests in the laboratory and the field with Dr. Beutel’s enzymatic cleaning.

Casein in Conservation

To begin with there are many types of casein with different ingredients and additives, such as: oil, soda, salts and ammonium carbonate. The diversity of casein is as infinite as different kinds of cheese. Despite this only a few kinds of casein were used in Germany for conservation purposes during the 20th century. The caseins that were used were curd, milk acid casein, salt acid casein and Hammersten casein. The materials that were used for deflocculation were lime, ammoniac, Hartshorn salt and ammonium carbonate. To prevent microbial infestation lavender oil, clove oil, rosemary oil, tributylzinnoxid, boric acid, salicylic acid, cresol, and nipagin were used. For heat treatment and denaturizing formaldehyde and alum were used. This is important to know since the different kinds of casein that were used correspond to different properties and thus provoke different damage.

Laboratory tests

Tests in the laboratory were made on test panels. Several test panels were coated with plaster, lime wash and different types of pigments. These combinations were used: 1) *lime wash*, 2) *lime wash and paratacamite*, 3) *lime wash and red lead*, 4) *lime wash wet in wet with red ochre*, 5) *lime wash wet in*

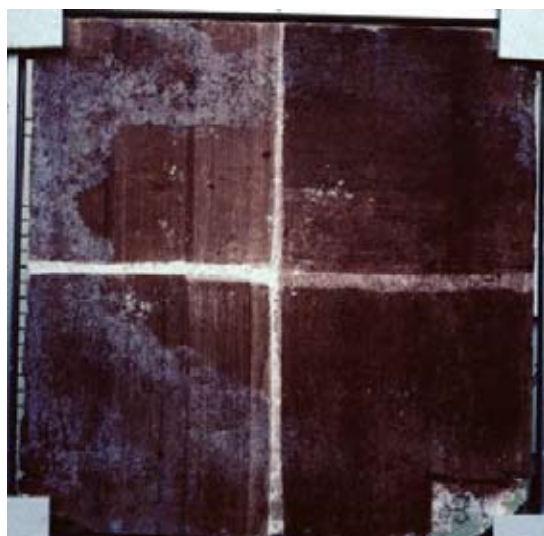
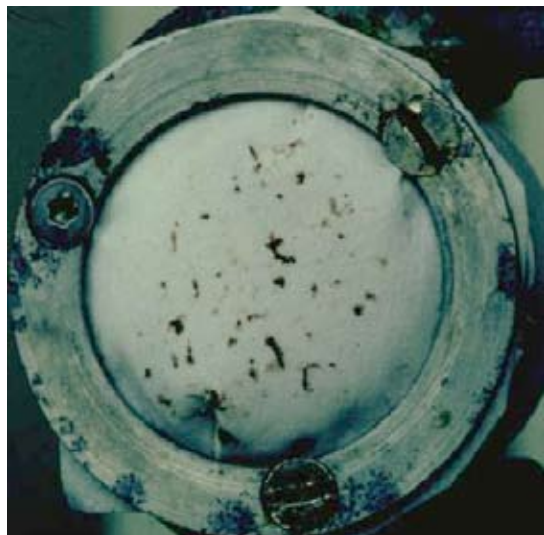


Figure 13. Test panels.

Figure 14. Test panel after ageing.

Figure 15. Test panels after salt damage has occurred.

Figure 16. Cushion with enzymes after cleaning.

Photograph Kerstin Klein



Figure 17. The Cloister of Allhallow in Wienhausen. Photograph Kerstin Klein.

wet with red ochre and 6) *lime wash with casein bounded red ochre*. After this a layer of ammonium casein and lime casein was applied (on the left side once, on the right side twice) and the panels were impregnated on the back with $Mg(NO_3)_2$ and NaCl.

The test panels were aged to provoke degrading and flaking of the casein. The disintegrated pigments were consolidated and casein flakes reattached with Klucel E® (a cellulose derivate) and Plextol B 52® (an acrylic). Afterwards the test panels were treated with enzymes according to the Beutel method to remove the casein. The result was positive and no enzyme residues were left on the surface of the painting.

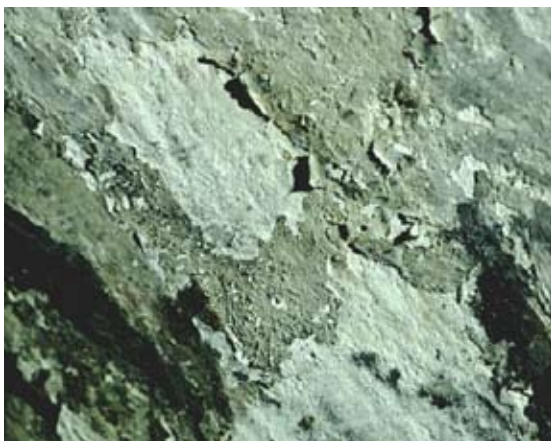
Field tests

Field tests were made in the Chapel of Allhallow in Wienhausen and in the sacristy in the Church of St. Alexandri in Wildeshausen in Niedersachsen in Germany. The wall paintings in the Chapel of Allhallow were decorated the first time around 1300. The paintings were partially repainted at the end of the 15th century, and restored for the first time in 1952.

The Beutel method was possible to use, however, not necessarily as other methods were available.

The wall paintings in the sacristy in the St. Alexandri Church were decorated with paintings about 1270. The second decorative painting was made around 1430. The paintings were lime washed later on and rediscovered in 1892. Since then they have been restored in 1953.

The result with the Beutel method was good.



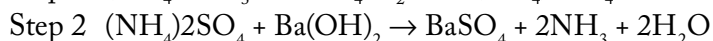
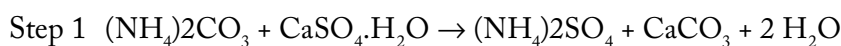
Figures 18 and 19. The paintings in the Chapel of Allhallow in Wienhausen.

Figure 20. Paintings in the Chapel of Allhallow in Wienhausen.

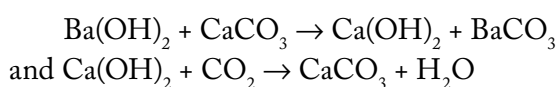
Figure 21. Flaking caused by casein.
Photographs Kerstin Klein.

“Nanoscience for the Conservation of Cultural Heritage”, Professor Piero Baglioni

Many of the conservation techniques in Italy are developed from the experiences and methods developed in 1966 after the floods in Florence and Venice. The need for a scientific approach to conservation problems became obvious and the actions of preservation contributed to a fast development of conservation science in Italy. Enzo Ferroni (1921–2007), a chemist at the Florence University at the time, developed together with the Conservator-Restorer Dino Dini a method for consolidation of mural paintings and reduction of gypsum, named the “Ferroni-Dini method” (or the “Florentin”, “Ferroni” or “Barium method”). It is a two step method: Step 1) *application of ammonium carbonate which reacts with the gypsum and creates calcium carbonate and water-soluble ammonium sulfate*, Step 2) *application of barium hydroxide which makes the sulfur insoluble (barium sulfate)*. The barium hydroxide starts a reaction which converts the calcium carbonate (lime) into calcium hydroxide (slaked lime) which means a new carbonation process will take place and create adhesion to the wall. The ammonium and water evaporates. The crystals of barium sulfate act as filler in the pores of the mural and can also be washed away:



Consolidation reaction:



The consolidation method with nanolime is a development from the Ferroni-Dini method. Lime is a compatible material in mural painting. Lime with a high concentration of calcium hydroxide particles in nano size is about thirty times more reactive than lime slaked in water. The increased surface area makes the material more reactive. The particles are dispersed in alcohol to prevent carbonation before the application. Because of the small particle size and the use of alcohol, the particles can penetrate in to the plaster and create bonds with the original lime and pigments. This does not occur with limewater. The application of nanolime is made with a brush through Japanese paper. A water compress to enhance the carbonation process is applied afterwards. Lime excess on the surface can easily be removed with carbonated water.

Professor Baglioni furthermore presented how microemulsions (ME) have been developed by his team to reduce and remove not wanted organic coatings on mural paintings. The method has been used to remove proteins or acrylic polymers, such as Paraloid. The degradation of Paraloid and other acrylic polymers can cause shrinkage, loss of material and yellowing. A problem with other cleaning methods, such as pure organic solvents, is that the dissolved polymer can get absorbed further into the porous system of the mural painting. This is prevented by the microemulsions. Microemulsions are micellar solutions, oil-in-water or water-in-oil solutions, with a dispersed face of microdroplets of a component insoluble in the continuous face, as oil in an oil-in-water emulsion. A cosolvent can act together with polar/non polar solvents (e.g. oil droplets) in the cleaning process. The active solvents are kept within the solution as a hydrophilic or hydrophobic “barrier” which is created between the surface and the emulsion. The active solvents and the polymer residues are thus prevented from being absorbed by the substrate. The excess of surfactant and the remains of the dissolved organic material are afterwards washed away with one or two water compresses.

Baglioni showed successful examples of nanolime consolidation of Maya paintings in the pyramids in Campeche, Mexico. Examples of successful removal of Paraloid from paintings in the Uffizi gallery in Florence with the use of microemulsions were also presented. He also demonstrated cleaning possibilities with nano magnetic sponges.



Figure 22. St. Alexandri Church.
Figure 23. St. Alexandri Church paintings.
Photographs Kerstin Klein.

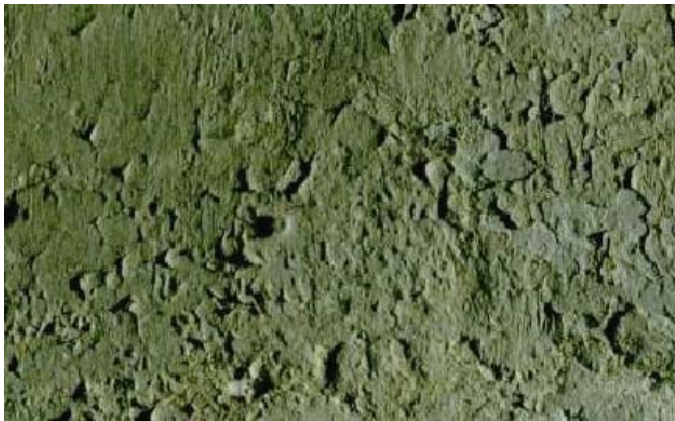


Figure 24. St. Alexandri Church paintings.
Figures 25 and 26. The flaking of colour, St. Alexandri Church paintings.
Figure 27. Before cleaning with enzymes.
Figure 28. After cleaning with enzymes.
Photographs Kerstin Klein.

“The Conservation of the Mural Paintings in Vendel”, Conservator-Restorer Ragnhild Claesson and Architectural Conservator H el ene Svahn Garreau

Background

The problems of conservation regarding the mural paintings in Vendel have a long history. Problems with flaking paint were already discovered in the chancel in 1979 by the arthistorian  ke Nisbeth at the Swedish National Heritage Board. At this time the conservation department at the Swedish National Heritage Board had no solution to the problem. The surface treatment was anyhow analyzed with a microchemical test but the problem was left unresolved. Svahn Garreau and Mellander R nn “rediscovered” the problem in 2000 and when Svahn Garreau started her PhD in 2001 about mural painting conservation in Sweden between 1880 and 1960 she chose the mural paintings in Vendel as a case study. At the same time she discovered a new German method that uses enzymes to remove casein from mural paintings (the Beutel method, see above). Because of this the conservator-restorer Asp at the Swedish National Heritage Board invited Dr. Beutel to Vendel to try the method in 2003. Unfortunately the results were not satisfying (see Beutel above). The challenge was to create a method that reduces the casein and reattaches the flaking paint in the same moment. To find the method the Swedish National Heritage Board had to wait for more funding and finally Svahn Garreau could not start the investigation until the autumn of 2006.

Vendel Church

The Church Vendel in northern Uppland is an extraordinarily well-preserved medieval church. The paintings are one of the most interesting painting schemes in the area and the artist Johannes Iwan is one of the few medieval painters that are known by name in Sweden. His names, as well as the year of completion, are memorized through inscriptions in the church. The church’s appearance today is the result of the restoration in 1930 led by the architect Erik Fant. The restoration followed a typical pattern of the time; for example, all white-painted surfaces were uncovered and restored, the lighting was modified to give an “authentic medieval atmosphere”, a new portal was designed and the heating system was changed. Furthermore; all old items were conserved and restored. The aim was to reveal the history of the church, hidden underneath the “unworthy” 18th century paint.



Figure 29. Vendel Church before the restoration in 1930. Photograph ATA.

Figure 30. Vendel Church after the restoration in 1930. Photograph ATA.

Figure 31. Vendel Church. Photograph Fredrika Mellander Rönn.

The church is constructed in brick. The vault in the chancel dates from the end of the 13th century. The vault in the chancel and in the sacristy and some parts of the walls were decorated in the beginning of 14th century. The vault in the nave (that is seen today) was raised in 1451. Before that there was probably a wooden vault in the nave. After the new vaults had been raised Iwan decorated the church with new paintings. There are thus two periods of mural paintings in the church today; some remnants from the paintings from the first period in the niches and in the vault in the chancel and sacristy and Iwan's dominant paintings.

Vendel Church was refurbished at the end of the 18th century. A new church wing and larger windows were added to the medieval construction. At the same time the medieval paintings were painted over until 1930.

The conservation of the mural paintings in 1930

The medieval paintings were uncovered in 1930 by the conservator-restorer Alfred Nilson. Nilson ran the largest conservation company in Sweden in the first half of the 20th century. He was chosen to uncover and restore the paintings in Vendel, even though his conservation proposal was more expensive than John Österlund's proposal. According to some people in the parish the Conservator-Restorer Österlund had left the paintings in Gamla Uppsala too fragmented. It is obvious that they believed that Nilson would provide a less fragmented appearance. Perhaps this is the reason why the paintings were so rigorously restored.

By this time the Curman retouching methods, such as using clear sgraffito marks on the reconstructed areas and only allowing retouching on the repetitive decorations, had almost been abandoned. It still was used, however in a random way. Because of this the retouching in Vendel is difficult to analyse. The problem is that the murals give a feeling of being authentic, when they actually have been rigorously retouched. In fact, some parts there consist of only 20% of the original and 80% is retouching. This can be seen in the few photographs that were taken before and after restoration. For example some faces were left unretouched and others were completely retouched (without marking the new parts). There are some examples of trials to mark the retouching; however the major part of the retouching is difficult to discriminate from the original.

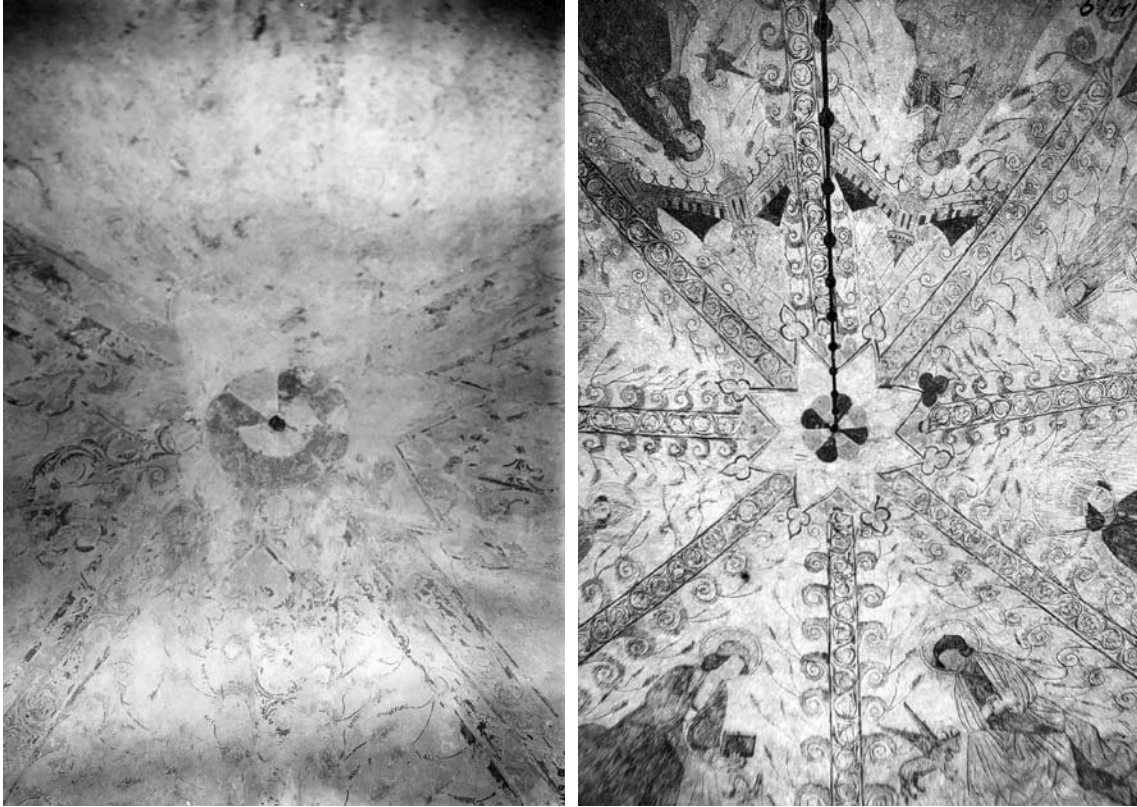


Figure 32. The Paintings in the chancel before treatment.

Figure 33. After treatment.

Photograph ATA.

Painting technique

The medieval painting was painted on a brick construction. It consists of a thin lime-based plaster, between 0.2–0.5 cm, covered by a limewash (maybe the walls were left white for a while before the paintings were made). Afterwards the painting scheme was sketched with red ochre and on top of that a new lime wash (the ground of the painting)). Finally the painting was painted on the wet limewash.

The painting was consecrated to Saint Mary; her life is depicted on the northern wall in the nave and the chancel. The original technique can be studied in the areas where there are more originals left (see above). Ivan used a delicate painting technique with fine brushes for details and larger brushes for large areas. The contours were made with red and black pigments.

The pigments were: red and yellow ochre, for intense red colours cinnabar and red lead (that darkened into HgS and PbO), sometimes a mixture of both red pigments were used for example for Saint Barbara's dress, white lead for pupils (also darkened), charcoal for blacks, malachite for green and azurite for blue.

The state of conservation – determination of the conservation problem

The painting's main damage phenomenon was the severe flaking of the surface layer in the choir. Some areas were more and others less affected. Another problem was the climate that was too warm and dry in wintertime (probably causing more harm). In addition, a whitish powder and some dark areas were noted on the surface. These problems had to be addressed to establish the threats and causes of damage before conservation and restoration could start and the questions that needed to be answered were:

- Was the surface treatment really casein?
- Were there any damaging salts present and do they cause harm (the whitish powder)?
- Was there any microbiology present (the dark areas)?
- How was the climate situation?

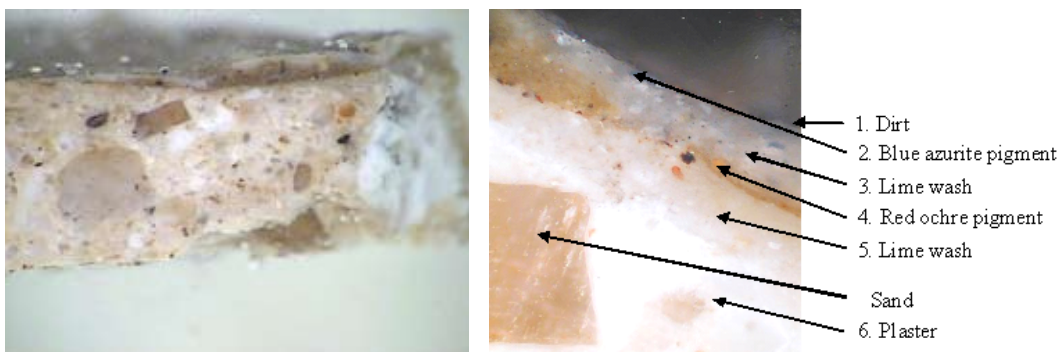


Figure 34. Cross section of the painting.

Figure 35. Cross section of the painting. Original scale 1:100.

Photographs H el ene Svahn Garreau.



Figures 36 and 37. Figures from the northern wall in the chancel that demonstrate the medieval painting technique. The brush-marks and the brushes used by Ivan were varied according to purpose. Thin brushes for the contours and details and larger brushes for hair, and so forth. Photographs H el ene Svahn Garreau.

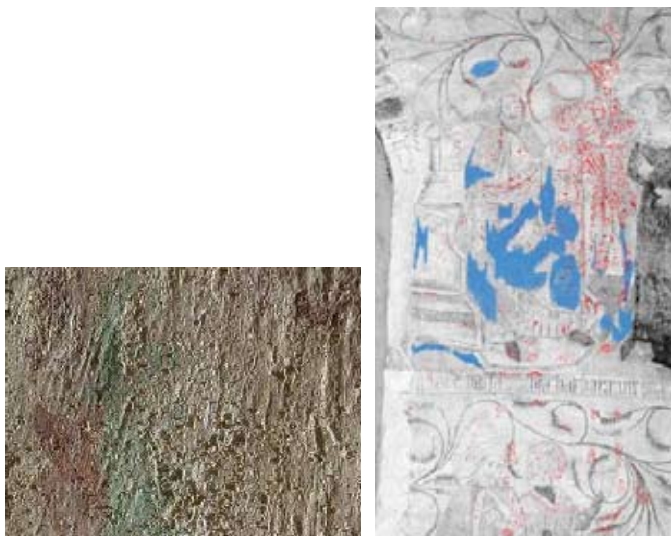


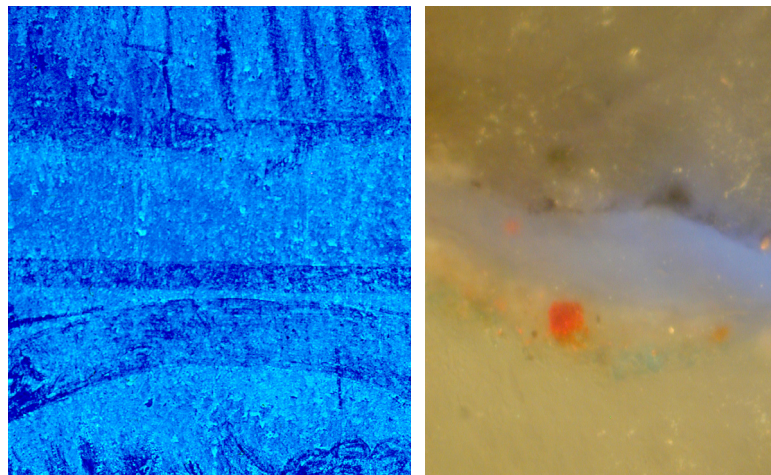
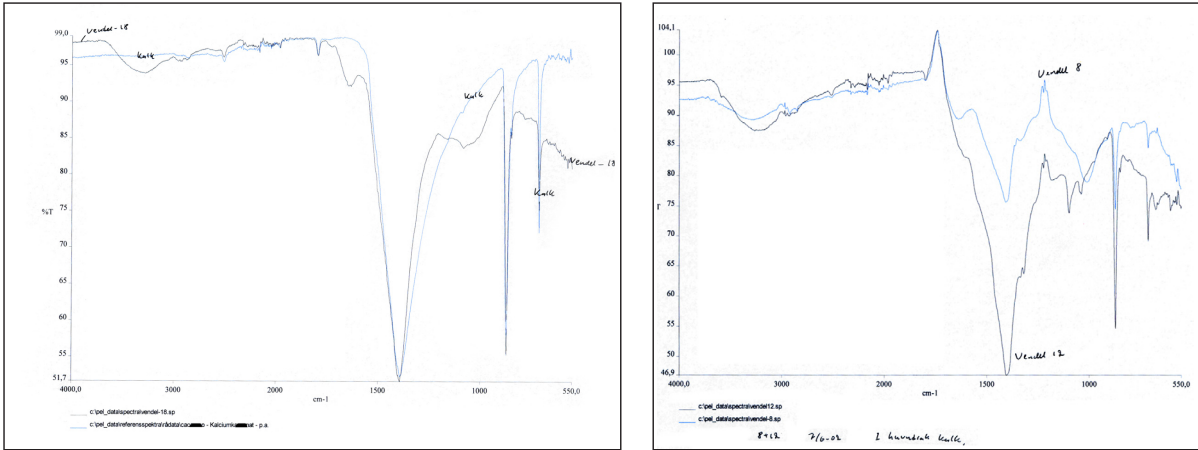
Figure 38. Flaking in the chancel.

Figure 39. Mapping of the flaking and glazed surface (blue).

Photographs H el ene Svahn Garreau

Was the surface treatment really casein?

Nilson used an unknown conservation treatment to “fix the weak paint layer” after uncovering the painting with hammers and knives. The treatment had, with time, become yellowish and the surface had a glazed appearance. The problem with the surface treatment was already discovered in 1979 and was investigated by the Swedish National Heritage Board with a microchemical Millon test (any protein containing tyrosine will give a positive answer). The result was positive and the protein was assumed to be casein. When reopening the problem in 2003 Svahn Garreau took samples of the treatment and sent them to the Analytical Department at the Swedish National Heritage Board. No proteins were found in FTIR – only calcium carbonate and a small amount of gypsum. Nevertheless, there was a yellowish coating on the surface. In UV-light it provoked a yellowish-whitish light phenomenon and underneath UV-light it was possible to see that the treatment had been spread rapidly and unevenly, which had caused it to flow down the wall leaving large droplets on the surface. It was reasonable to believe that it was casein (casein can give such a light phenomenon in UV-light). For some reason it was not detected by the FTIR. However, to be sure, further analysis was necessary, although it was not included in Svahn Garreau’s PhD work.

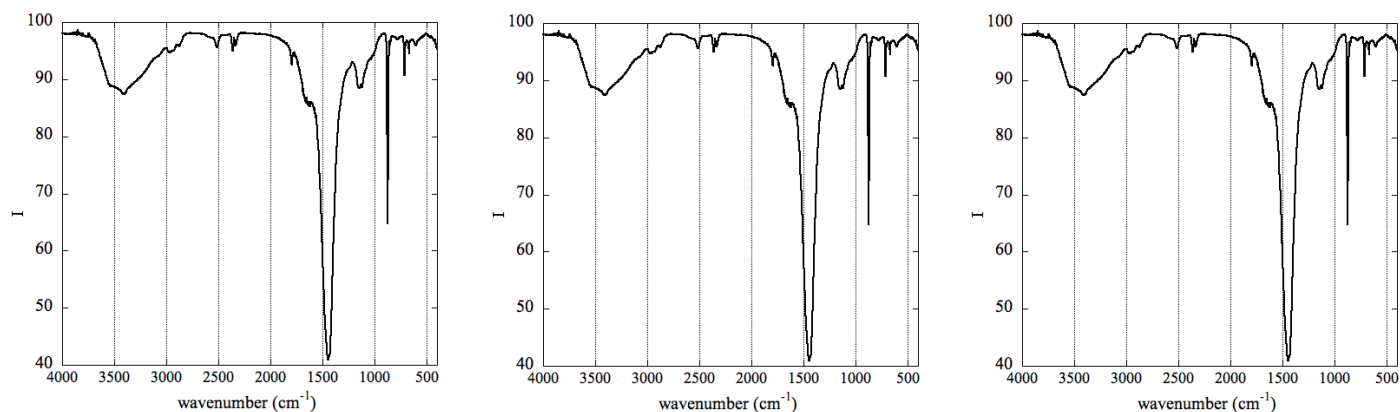


Figures 40 and 41. Results from FTIR from the Analytical Department at the Swedish National Heritage Board.

Figure 42. UV-light. Note the droplets. Photograph Gabriel Hildebrand.

Figure 43. Cross section in UV-light. Original scale:400. Photograph H el ene Svahn Garreau.

In 2003 Conservator-Restorer Misa Asp at the Swedish National Heritage Board invited Dr. Sasha Beutel to test the enzyme method developed in Germany (see above). The portable 2D fluorescence Spectrophotometer was not able to detect the casein on the wall. More samples were sent to the microbiologist Dr. Karin Petersen at Hildesheim's Conservation School. With an ELIZA test she could establish that the surface treatment really was casein. In 2006 more samples were analyzed by Dr. Robert Corkery at the Institute for Surface Chemistry in Stockholm in FTIR and Professor Piero Baglioni at Florence University in FTIR. Both found protein that was assumed to be casein.



Figures 44 and 45. FTIR of the surface treatment sample from the Chemical Department at Florence University.

Figure 46. FTIR of surface treatment. Sample analyzed at the Chemical Department at Florence University.

Were there any damaging salts present?

White powder samples were taken from the surface in 2006 and they were analyzed with X-ray analysis by Dr. Corkery in Stockholm. Only calcium carbonate and very small amounts of other salts were found – possibly pigments (that could not be analyzed with the normal X-ray instrument). Hence, the white powder on the surface was supposed to be leftovers from the whitewash.

The salt problem wasn't completely solved; in 2006 some samples from the painting were analyzed in FTIR by Professor Baglioni in Florence. He found some gypsum. Sulfates probably from gypsum had also been found in a few SEM-EDS analyses (where the purpose was to look for pigments) made by the Swedish National Heritage Board in 2003. The presence of gypsum gave rise to a few questions: Was there any ongoing sulfating process transforming calcium carbonate in the painting into gypsum? And if the answer was yes: Where did the sulfur come from? Was the process ongoing? It was hard to believe that there was an ongoing pollution attack (with sulfur) in the rural areas of northern Uppland. Hence, there must be another explanation. The sulfur could have come from the old stoves (heated with charcoal). However, the stoves were removed before the uncovering of the paintings and thus this explanation was not likely. It was decided that the most likely answer was that the gypsum came from the gypsum-based grout from 1930. Consequently, it was not believed to be

any ongoing sulfating process (the gypsum was not considered to be a serious threat). Albeit these results; three salts tests (according to a Löfvendhal method) were carried out in 2006 on three different levels of the south wall in the chancel. The motive was to ensure that no damaging water-soluble salts were in the plaster. The Löfvendhal method has been designed to determine the presence of water-soluble salts in porous materials. It is based on a conductivity measurement from a salt/water solution extracted from the wall. The salts are extracted with the help of a compress with water that is removed after one hour, soaked in water, sieved and finally the conductivity is measured. In Vendel only low conductivity (low amounts of water-soluble salts) was found and no further analysis was required.

The conclusions of the salt tests were that there were low amounts of gypsum present on the surface of the painting, but these were not the cause of the flaking and are of little danger to the painting. Furthermore; the low amounts of water-soluble salts are of no risk to the painting. The white powder on the surface is remains of the whitewash (calcium carbonate) and of no danger to the painting.

Was there any microbiology present?

Some black areas in the chancel and in the nave were suspected to contain microbiology. Five samples were sent to a laboratory to look for microbiology. Nothing was found. The black spots were assumed to be deposits of soot and other microparticles.

The climate situation

The heating system was based on 68 watercarried radiators underneath the benches and 2 radiators on the walls in the nave. The system was based on temperature, e.g. the temperature cannot reach lower than 13°C during winter. Before each Sunday sermon in winter the church was heated to 20°C.

The climate was measured with a data log (HOBO H80) twice in the chancel and once in the nave; between June 2003 and February 2004 and once between October 2006 and April 2007 (only in the chancel).

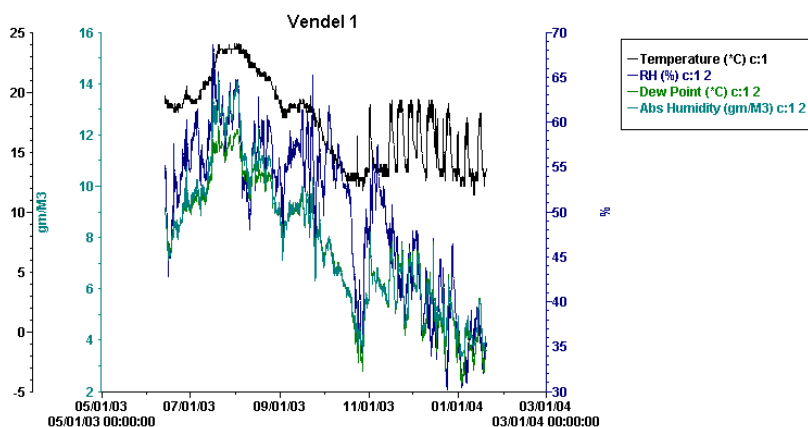


Figure 47. Climate measurement in the chancel with a data log (HOBO H80) between June 2003 and February 2004.

There were variations in humidity between 70% and 30% throughout the year and temperature, between a maximum of 24 °C (summer) and a minimum of 12 °C (winter). The RH changed from 50% in September to 30–35% in January. The result was evaluated by Tor Broström at Gotland University, who is an expert on climate in historic buildings. According to Dr. Broström the variation in RH was too big and the temperature too high in winter. The reason for the great variations in RH during wintertime was that the church was rapidly heated for mass on Sundays (the temperature changed from 13 °C on Friday to 19 °C on Sunday). Hence, Dr. Broström recommended changing the climate in order to achieve less variation in RH and a lower temperature in winter (18 °C maximum). For this purpose he suggested introducing a hygrostat that controls the RH instead of the temperature (between 40–60%).

Solving the Conservation Problem – Tested Products and Systems

After the initial study of the painting technique, the determination of the conservation problem and the actual solving of the problem could start. The challenge was to create a system that enabled the reduction of the casein and reattachment of the flakes at the same time (without losing the paint layer). One additional problem that had to be evaluated was the presence of green and blue copper pigments (that can be harmed in the presence of high pH).

To begin with, test plates simulating the Vendel painting were made in the laboratory. Methods for solving the problem were searched for among scientific articles and by contacting conservator-restorers and scientists in Denmark, Germany, Italy and Sweden.

A list was made with aspects that had to be taken into consideration when choosing the system. The methods had to be:

- Effective.
- Harmless to the object.
- Harmless to the environment, animals and humans.
- Workable on a scaffolding and on large areas.
- Durable.
- Compatible with the painting materials.
- Scientifically tested with references (good results).
- Inexpensive.
- Have a controllable process.
- Stable and not provoke change in colour, gloss or appearance of the object.

Considering these factors different chemicals/methods for reducing the casein were chosen to be tested in 2005.

- Purified water.
- Ethanol.
- Ammonium carbonate.
- Enzymes attached to a epoxy-membrane – a simplified Beutel method (see below).
- Free enzymes in a TRIS buffer.

After evaluation of the results some more chemicals/methods were tested in 2006:

- Gomma Pane.
- Microemulsions (ME of different formulae made by professor Baglioni, see below).

For reattaching the flakes these materials/methods were tested in 2005:

- Nanolime.
- Silester®/Kluce!®.
- Silester®, Remmers 300 HV® and Remmers 300 E®.
- Primal SF 016®.

After evaluation of the results some more materials/methods were tested in 2006:

- Paraloid B72®.
- Barium method.
- Lime slurry according to a Danish recipe with Rollovit®.

The tested methods in detail (the reports from the Swedish National Heritage Board contains more detailed information)

Enzymes

A modified Beutel method was utilized. Alcalase enzymes were fixed to an epoxy-membrane (SARTOBIND®) by Dr. Corkery and the membrane was held against the wall with the help of a carbonate buffer compress (pH 9). The compress was covered by a Melinex® film while the surface was heated until between 27–40°C for 15 minutes. Afterwards a compress with purified water was attached to the wall for one hour (to wash away the buffer) and finally the casein was removed with cotton swabs.

The free enzyme method was taken from Heike Pfund's Diplomarbeit from Fachhochschule in Cologne. Alcalase enzymes were mixed (40mg/l) with a Trisbuffer (pH 7.9). A compress with alcalase/Trisbuffer was attached to the wall. A Japanese paper was placed between the wall and the compress to protect the surface. The compress was covered by Melinex® film and heated until between 27–40 °C for 15 minutes. Another compress with purified water was afterwards attached to the wall for one hour to wash away the buffer and the enzymes and after that, finally, the casein was removed with cotton swabs.

Ammonium carbonate

After pre-wetting the chosen area with purified water a methyl cellulose compress with 4% ammonium carbonate in purified water (Ph 9.1) was attached to the wall (for between 15 minutes and three hours). Afterwards the casein was removed with cotton swabs and subsequently two compresses with purified water were left on the wall for one hour each (to remove salts).

Microemulsions (ME)

The ME solutions had been designed by Baglioni to remove different kinds of organic materials from mural paintings in Italy and Mexico (see Baglioni above). Several methods were tested; only one is described here; e.g. the oil-in-water emulsion system named Sistema 3. It consisted of purified water (92.6%), a surfactant Triton X-100 (4.9%), p-xylene (0.40%) and ammonium carbonate (2.1%).

Silester®/Remmers®/Klucel®

The Silester®/Klucel® mixture is a German method that combines an alkoxy silane (Silester®) with Klucel® to “adhesive” flakes and consolidate material of mineral origin. Klucel® is methyl cellulose that can be mixed with alcohol and alkoxy silane (in this case Silester®). The system works two ways; the Klucel® holds the flakes down (temporarily?) and the alkoxy silane consolidates the material in the long term.

Pure alcoxy silanes were also tested, for example a modified alcoxy silane from Remmers[®], especially made for limestone. The alcoxy silanes are not compatible with lime material and they are designed to consolidate materials rather than to reattach flakes. Another problem is that a long waiting period is required before any waterbased cleaning method can be used.

Nanolime

The nanolime has been developed by Professor Baglioni. It is used to reattach and consolidate mural paintings and limestone (see Baglioni above).

Gomma Pane

Gomma pane is a kind of cleaning dough, especially made for mural paintings. It is often used in Sweden and Denmark. It is made by baking water, Copper Sulfate, Sodium Carbonate and wheat flour together. The dough is rubbed against the wall to remove surface dirt (it cannot reduce the casein).

Paraloid B 72[®] and Primal SF 016[®]

The Paraloid B 72[®] and Primal SF 016[®] are synthetic acrylic polymers often used in conservation to attach flaking paint.

Lime slurry

Lime slurry made with Rollovit[®], a kind of very fine lime stone powder made in Denmark by Faxe kalk. Lime slurry is often used in Denmark to attach flaking paint layers on mural paintings.

Follow-up

To control that the casein had been properly reduced a UV-lamp was used. A dark chamber (made of a box and a black garbage bag!) was constructed in order to be able to use the UV-lamp in daylight.



Figure 48. The “dark chamber” constructed for testing if the casein has been reduced in UV-light. Photograph Lena Östlund.

Tested systems

The methods were combined into systems (attachment of the flakes/reduction of casein). One difficulty was that the methods had to be compatible with one and another. For example the alkoxy silanes cannot be followed by a water-based cleaning method if there is not a long waiting period. A few systems were tested on chosen areas of the painting, especially on blue and green pigments (and on the testing plates in the laboratory – not described here). In the first phase, in 2005, tests were made in the following order:

- 1) reattaching the flakes with: Klucel®/Silane®, Primal®, alcoxysilanes (Remmers® and Silane®), and nanolime.
- 2) reducing the casein with Alacalse enzymes, ammonium carbonate, purified water, pure carbonate buffer and alcohol.

More tests were made in 2006 with the Italian Barium method (see Baglioni above) and gamma pane. After some discussions with Professor Baglioni the methodology was reversed into wet-in-wet systems that: 1) *reduce the casein with ME (recipes from Baglioni)* and 2) *reattach the flakes with nanolime.*

In total eleven systems were tested:

System 1. Nanolime and ammonium carbonate (4%, pH 9.1).

System 2. Nanolime and enzymes (attached to membranes in a carbonate buffer (pH 9) or free enzymes in a buffer (pH 7.9).

System 3. ME and nanolime system (wet-in-wet-system). It consists of eight steps:

- 1) pre-wet the surface (to soften the brittle flakes).
- 2) attach a Japanese paper to the wet surface.
- 3) apply the ME in a compress and leave for 1–5 hours (keeping the compress wet with the help of a plastic film).
- 4) take away the paper pulp compresses with ME, leaving the Japanese paper on the surface (still wet).
- 5) rinse the surface with a compress with purified water for 1–5 hours (keeping it wet with a plastic film).
- 6) take away the compresses and the Japanese paper (the surface is still wet). The pigments and lime remain on the surface because of the natural adhesion when the pigments and the wall are still wet.
- 7) apply the nanolime until the painting is saturated.
- 8) wet the surface once or twice with water during a few hours and leave to dry slowly.

System 4. Silester®/Klucel® and Alacalse enzymes (it is necessary to wait for several weeks with the reduction).

System 5. Silester®/Klucel® and ammonium carbonate (it is necessary to wait for several weeks with the reduction).

System 6. Silester® and ammonium carbonate (it is necessary to wait for several weeks with the reduction).

System 7. Silester® and Alcalase enzyme (it is necessary to wait for several weeks with the reduction).

System 8. Primal SF 016® and ammonium carbonate.

System 9. Paraloid B 72® and gomma pane. Paraloid B 72® was used only on the decorated areas. The gomma pane thus removed the dirt on the surface and the flakes on the white background. It is therefore a partly destructive method.

System 10. Paraloid B 72® and ammonium carbonate.

System 11. The Italian Barium method (see Baglioni above)

Tests were made with methods that only reattach the flakes leaving the casein in the painting. These were: the Danish lime slurry method (with Rollovit®), Primal SF 016® and Paraloid B 72®. Moreover, a few methods were tested to see if they effectively reduced the casein (not reattaching the flakes). These were: purified water, carbonate buffer, and ethanol.



Figure 49



Figure 50



Figure 51



Figure 52

Figures 49, 50 and 51. Enzymatic cleaning.
Photographs H el ene Svahn Garreau and Ragnhild Cleasson.

Figure 52. Tests with enzymes, ammonium carbonate and nanolime.
Photographs H el ene Svahn Garreau.



Figure 53



Figure 54

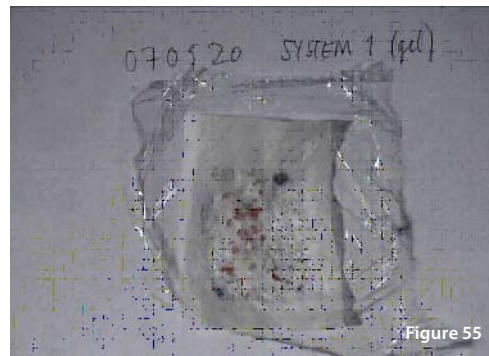


Figure 55



Figure 56



Figure 57

Figure 53. Tests with enzymes, ammonium carbonate and nanolime.
Photographs H el ene Svahn Garreau.

Figures 54 and 55. Tests with microemulsions and nanolime.
Photographs Lena  stlund.

Figures 56 and 57. Tests with microemulsions and nanolime.
Photographs Lena  stlund.

Discussion

Svahn Garreau and Claesson described the results from the tests in 2005 which unfortunately were not satisfying.

Reattaching the flakes. The nanolime was the best material (it was relatively harmless to the environment or humans, compatible and so on), but it was not effective enough. Regardless of this the nanolime had potential but needed to be customized for the problem in Vendel. The alcoxy silane methods were not effective at all. The reason for this was that the problem in Vendel was the flaking of the paint layers and the alcoxy silanes are not designed for this purpose (they are designed for consolidation). On the other hand the Silester®/Klucel® method effectively attached the flakes, but left the painting considerably darker. Moreover; Klucel® is not a durable material and thus it was impossible to afterwards reduce the casein without removing the Klucel® as well as a great part of the painting. Primal SF 012® and Paraloid B 72 ® effectively attached the flakes, but they are acrylics and consequently not compatible with the inorganic material in the painting. The acrylic polymers can become insoluble, brittle and yellow with time and if the coating is made too thick there is a risk of new flaking in the future.

Reducing the casein. It was clear that the enzymatic method was too expensive (the membrane costs about 6000 SEK each and can only be used three times), too complicated and too timeconsuming. Moreover; the membranes were too stiff to be held in contact with the wall. Even worse; a lot of original paint was lost, maybe because of the problems in controlling the operation. The carbonate buffer had a fairly high pH in itself and tests were made to use only the buffer. It was effective enough. In summary; the enzymatic method had to become more effective and controllable, less expensive and easier to use. A new enzymatic reduction method was proposed by Dr. Corkery. His idea was to attach the enzymes to a Japanese paper (it is flexible and less expensive) instead of the epoxy membrane. Since no funding was available, the method had to be abandoned. The ammonium carbonate was effective; however there was the risk of leaving water-soluble salts behind. Hence, tests were made with the Löfvendahl method (looking for water-soluble salts in the wall, see above). A slightly higher conductivity was detected, however it was not alarming. The purified water and ethanol were not effective at all; the methods only took away the dirt (not the casein). One positive result was that none of the methods harmed the blue or the green copper pigments.

New tests. Since none of the methods proved to be good enough, it was decided that more tests were required. Hence, new tests were made in 2006 with the Barium method, cleaning with gomma pane and attaching the flakes with Paraloid B 72®. The results with these methods were not satisfying. With the assistance of Professor Baglioni more tests were made with nanolime to attach the flakes and ME to reduce the casein. He proposed to reverse the methodology into a wet-in-wet system that first applies the ME and afterwards the nanolime. Finally, the results were good. The best results were achieved with nanolime and the oil-in-water ME (named Sistema 3 – see above). This system was effective, did not darken the painting, change the blue or green copper pigments, leave any salts, was easy to use, not too timeconsuming, available (professor Baglioni could provide the nanolime) and had a relatively low environmental and human risk. Moreover; the nanolime is completely compatible with the painting (it is same material). The only risk was if traces of the surfactant (Triton X 100) would remain in the painting. However, these traces would be removed with the washing compress.

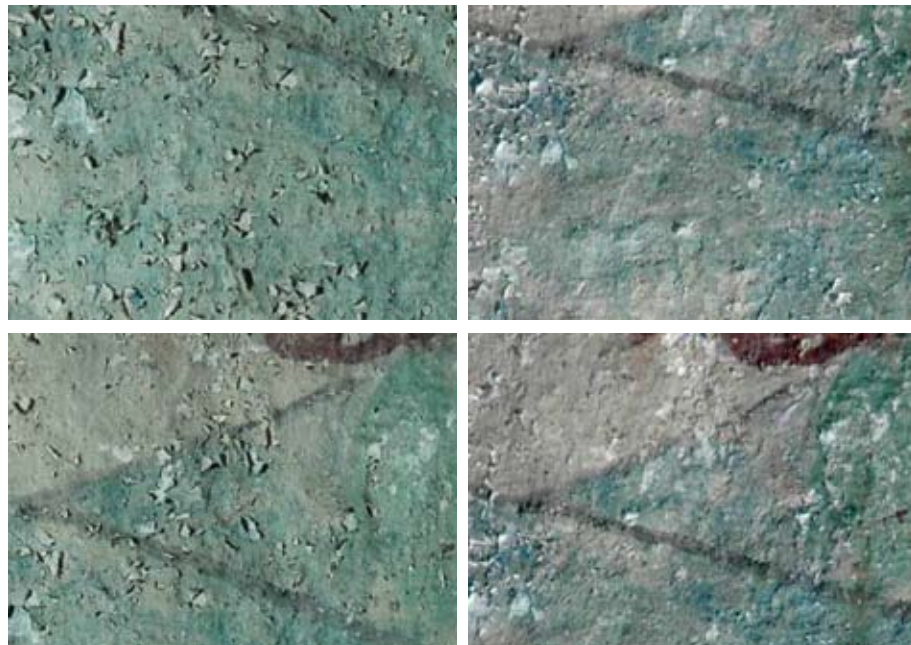


Figure 58. Before the nanolime/ME treatment (Sistema 3).

Figure 59. After the casein reduction with Sistema 3 and nanolime treatment.

Figure 60. Before the nanolime/ME treatment (Sistema 3).

Figure 61. After the casein reduction with Sistema 3 and nanolime treatment.

Photograph Lena Östlund.

Table 1. Results of the reduction of the casein

0 = none 1 = to some degree 2 = yes ? = not known - not effective

Factors that needs to be addressed/ Material	Effective	Harmless to the material	Harmless to the environment animals and humans	Controllable application process	Practicible	Inexpensive	No change of colour, gloss and appearance	Scientifically tested	Result
Enzymes	2	1	1	0	0	0	2	1	7
Micro emul-sions	2	2	1	2	2	2	2	2	15
Gomma pane	0	0	2	2	2	2	2	2	-
Ammonium carbonate	2	1	1	1	1	2	1	2	12

Table 2. Results re-attachment of the flakes

0 = none 1 = to some degree 2 = yes ? = not known - not effective

Factors that needs to be addressed/ Material	Effective	Harmless to the material	Harmless to the environment, animals or humans	Controllable application process	Practicible	Inexpensive	Durable	Compatible	No change of colour, gloss and appearance	Scientific tested with references	Result
KSE	0	?	1	0	2	2	2	1	0	0	-
Cellulose	2	?	2	2	2	2	1	0	0	1	12
Nanolime	2	2	1	0	2	2	2	2	2	1	16
Rollovit	0	2	1	0	2	2	2	2	2	2	-
Paraloid	2	1	1	1	2	2	1	0	1	0	11
Primal	2	1	1	1	2	2	1	0	1	0	11
Silester/ Klucel	1	?	1	0	2	2	1	0	0	?	6

Final results and recommendations

The final recommendations to the Conservation of the Medieval Paintings in Vendel was:

- 1) To reduce the casein:
 - Microemulsions customized by Professor Baglioni (Sistema 3)
- 2) To reattach the flakes:
 - Nanolime
- 3) To control that the casein has been removed:
 - UV light

A table with the aspects to consider when choosing the best method was constructed. The nanolime / ME method (Sistema 3) gave the best result!

Acknowledgements

The efforts to solve the conservation problem in Vendel has been a collaborative work between the conservator-restorers: H el ene Svahn Garreau, Ragnhild Claesson, Katarina Heiling, Misa Asp and Lena  stlund and the assistant Linda Karlsson at the Swedish National Heritage Board, with help from scientists; Dr. Robert Corkery at the Institute for Surface Chemistry in Stockholm, Dr. Sasha Beutel, the University of Hannover, chemists Anders Nord and Kate Tronner at the Swedish National Heritage Board, professor Piero Baglioni, Florence University, and professor Karin Petersen at the Conservation School in Hildesheim.

Answers and comments from questions and discussion

- Isabelle Brajer asked how time-consuming the recommended methods are. Svahn Garreau answered that one of the reason why the Swedish National Heritage Board chose the method was that it was the least time-consuming method with as few steps as possible. In fact it was the most effective and fastest method.
- Isabelle Brajer mentioned that microlime for consolidation has been used a lot in Denmark.
- Conservator-Restorer Anna Henningsson asked if this was the first time this method had been used for secco paintings. And if there are differences in painting technique between Sweden and Italy. Does this affect the methods? According to Baglioni have the methods been used successfully on both frescoes and secco with similar properties in Italy.
- Moreover Anna Henningsson asked if there are any other not known side effects. Svahn Garreau replied that one problem is that it is a new method (hence it has not been tested for a long time). According to Baglioni there are no other negative sides of the method more than that there is a risk that some small fractions of the surfactant are left on the surface that will be removed with the washing anyway.

“Problems with Casein Glue on Wall Paintings Transferred to Canvas”, Senior Research Conservator-Restorer Isabelle Brajer

Brajer lectured about the history of detachment of mural paintings in Denmark - in particular the problems of removing casein-based backing on detached murals made by the artist Risebye and his students. The strappo methodology (the process by which only the paint layer is removed from the wall) was imported to Denmark by Italian conservators that were hired in 1913 to detach Joakim Skovgaard’s salt-damaged frescoes.

Skovgaard asked the famous Italian Steffanoni family from Bergamo to do a strappo on the damaged part of the painting. The Steffanonis were specialized in the strappo technique and worked all over Europe during the beginning of the 20th century. One interesting example was the numerous transfers of mural church paintings in Spain between 1919 and 1923 that can be seen in the Museum of Catalonian Art in Barcelona.



Figure 62. Joakim Skovgaard working in Viborg cathedral.,
Photograph Nationalmuseum Denmark.



Figure 63. Elof Risebye, Nationalmuseum Denmark.

The Steffanoni family were secretive about their working methods. Consequently, Steffanoni and his assistant locked the door when they were working inside Viborg cathedral. However, the Church Verger Christian B. Møller sneaked around, trying to find out about the working process. He took notes, which he passed on to Skovgaard. Skovgaard gave the notes in turn to his assistant Elof Rise-by.

The problem was that the Church Verger had only seen when the Italians made the facing and not the backing of the strappo. Hence, he missed one important fact: that the facing and the backing have to be made with different kinds of adhesives. A transfer is made in a system that has to consider solubility, where the surface adhesive has to be water-soluble but the backing adhesive has to be water insoluble. The adhesive that was used by Steffanoni for the facing was animal glue and for the backing casein glue dissolved in slaked lime. However, Risebye was not aware of this and experimented with different kinds of casein glues. The problem was that casein can make both water-soluble and water insoluble adhesive. Here are some recipes:

Water absorption of various casein adhesives

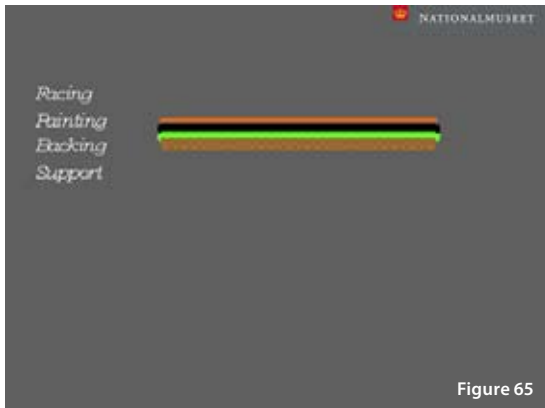
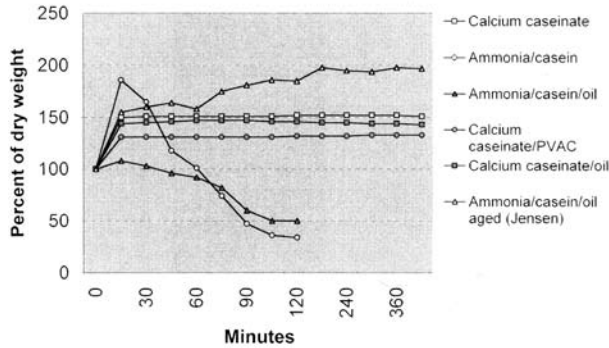


Figure 65

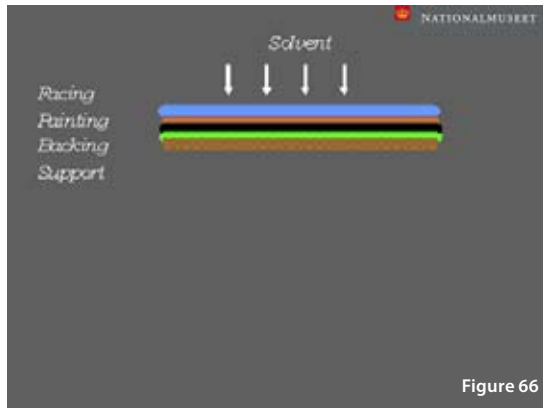


Figure 66



Figure 67



Figure 68

Figure 64. A diagram demonstrating the water absorption of different kinds of casein adhesives. Nationalmuseum Denmark.

Figure 65. A strappo after it has been removed from its original support consists of a temporary facing (with a carrier protecting the surface), the paint layer, the backing and a support. Isabelle Brajer, Nationalmuseum Denmark.

Figure 66. The solvent (in this case water) has to solve the facing and not the backing. Isabelle Brajer, Nationalmuseum Denmark.

Figure 67. With the right technique, the painting is intact after the facing has been removed. Isabelle Brajer, Nationalmuseum Denmark.

Figure 68. With the wrong technique, parts of the paint layer are lost when the facing is removed. Isabelle Brajer, Nationalmuseum, Denmark.



Figure 69. The strappo made by Steffanoni in Klaksvik Cathedral.
Photograph Isabelle Brajer, Nationalmuseum Denmark.

Casein + $\text{Ca}(\text{OH})_2$ [slaked lime] *waterproof adhesive*

Casein + NH_4OH [aqueous solution of ammonia] *water-soluble adhesive*

Casein + $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ [borax] *water-soluble adhesive*

Risebye chose the wrong casein. He used a mixture of casein dissolved in ammonia and linseed oil for the backing (which is water-soluble). This choice caused problems when he removed the facing of the strappo with water and the water sensitive backing would also have been affected (see figures below). Furthermore, if the climate where the transfers were stored was inappropriate (for example with too large changes in RH) the problems would accelerate, provoking cracking, bulking, attacks by microorganisms and finally loss of the paint layer (see figure 63 that demonstrates the water absorption of different kinds of casein).

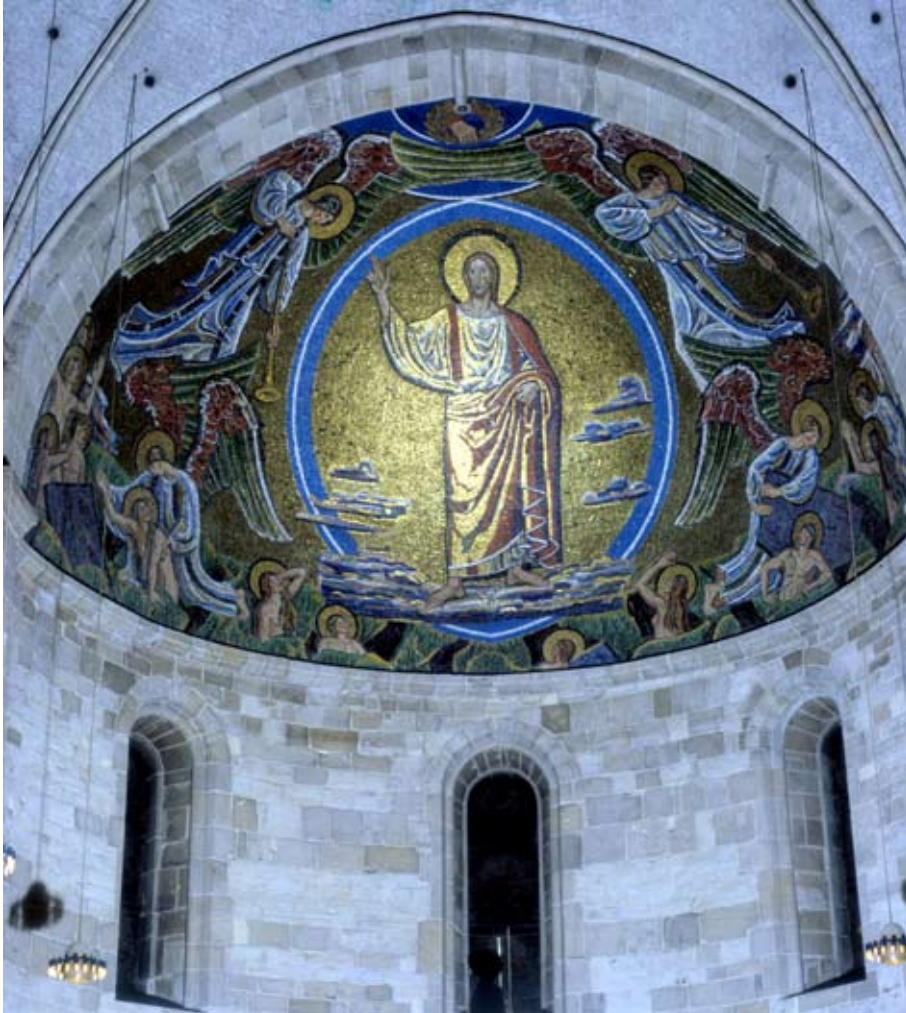


Figure 70. Skovgaard's mosaics in Lund cathedral.
Photograph Nationalmuseum Denmark.

The fresco from Viborg cathedral that was detached by Steffanoni was later on sent and placed in Klaksvik cathedral on the Faeroe Islands.

Risebye used the faulty technique when he was commissioned to do a strappo of Skoovgard's mural (oil and mosaic) in Lund cathedral (Sweden) in 1922.

The strappo in Lund cathedral suffered from the treatment and a great part (60%) was lost. Despite this, Risebye continued to use the misapprehended technique and performed many strappos into the 1960s in the same manner. For example, he was commissioned to do more strappos of the mural in Viborg in the 1940s. He was also the leader of the Mosaic



Figure 71



Figure 72



Figure 73



Figure 75



Figure 74

Figures 71 and 72. Viborg cathedral.
Figures 73, 74 and 75. Pictures of the preparation of the strappo in Viborg cathedral 1994.
Photographs Isabelle Brajer, Nationalmuseum Denmark.



Figure 76



Figure 77



Figure 78

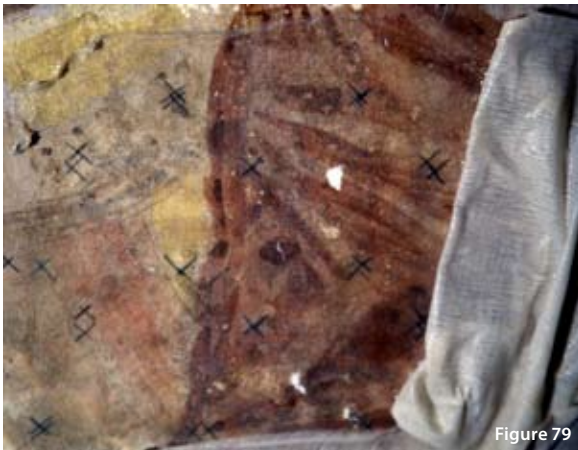


Figure 79



Figure 80

Figures 76, 77 and 78. The strappo made in Viborg cathedral in 1994. It is transported into the conservation laboratory at Nationalmuseum. **Figures 79 and 80.** The facing is removed from the detached murals in Viborg cathedral in 1994. Photographs Isabelle Brajer, Nationalmuseum Denmark.

and Fresco school in Copenhagen where he taught students the method. Today, these transfers are suffering from many problems such as yellowing, detachment and flaking.

Brajer presented some examples of how the strappos made with the faulty technique have been treated by the Conservation Department at the Nationalmuseum in Denmark. Nowadays, detachments of mural paintings are rare. It is common knowledge that detached paintings often suffer from deformation, loss of original painting technique, connection with architecture and authenticity. In 1994 Brajer conserved Risebye's (and his assistants) strappos of Skovgaard's paintings in Viborg cathedral. The mural in question was detached by Risebye's assistants in 1963. The strappo was glued on canvas with the oil caseinate and afterwards glued directly onto the plaster again. This treatment had harmed the painting which suffered from severe flaking, detachment and loss of the paint layer. Brajer decided to detach the paint layer (strappo), fix it to a honeycomb plate, which afterwards was mounted back in the original position. The plaster on the wall was removed so that the plate could fit into position and not be on a different level than the surrounding scenes that were not treated.

Brajer also presented some other conservation work of strappos made by Risebye and his students, for example a transfer made by Leo Neuschwang and a mural moved by Sophie B Jensen in 1953, now found in Duborg Skole in Flensburg. The paintings suffered from deformation and flaking. Brajer developed a successful conservation methodology using a low pressure vacuum table. She removed as much as possible of the oil caseinate and the old canvas, used PVA in ethanol for the new facing and BEVA 371[®] to attach margins on the low pressure vacuum table. Afterwards the strappo was remounted using BEVA 371[®] onto rigid Honeycomb plates.



Figure 81. The strappo. Photograph Isabelle Brajer, Nationalmuseum Denmark.

Figure 82. Back of the painting made by Sophie B. Jensen.
Photograph Roberto Fortuna, Nationalmuseum Denmark.

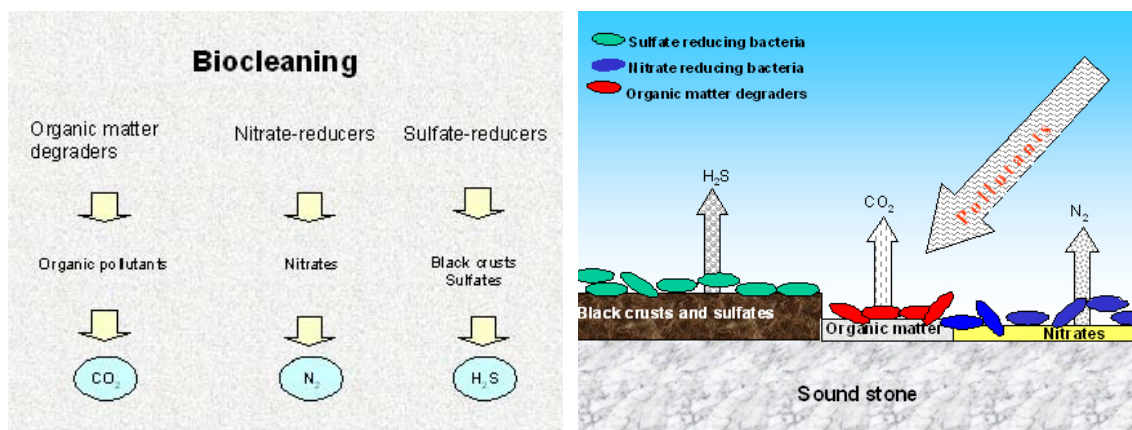
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Figures 89 and 90. The biocleaning reduces organic matter, nitrate and sulfate products into volatile gases.
 Dr. Francesca Cappitelli, DISTAM, University of Milan

“Removal of Undesirable Compounds from Stone and Frescoes using Bacteria”, Dr. Francesca Cappitelli

Dr. Cappitelli lectured about biocleaning methods developed by Prof. Sorlini of the University of Milan and her group in Italy. The methods have been developed during the last ten years in Italy and employ viable bacteria for the removal of undesirable compounds such as *sulfates* (including *black crusts*), *nitrates* and *organic matter* (from oil combustion and previous conservation treatments). The biocleaning procedure consists of: 1) *selection of the appropriate bacteria* (which are safe for the work of art, humans and the environment), 2) *selection of the delivery system to immobilise the bacteria and adapt it for easy application*, 3) *removal of the bacteria* and 5) *long-term monitoring of the effect of the treatment*.

The bacteria that have been used so far are: *Desulfovibrio desulfuricans* and *Desulfovibrio vulgaris* to remove sulfates, *Pseudomonas denitrificans* to remove nitrates and *Pseudomonas stutzeri* on frescoes to remove organic compounds. *Sepiolite powder* was first used as the delivery system (an inorganic material) but it was substituted by *Carbogel* (an organic support matrix).

The temperature and humidity was monitored during application, (they influence the performance of the bacteria). How long the bacteria were left on the surface depended on the kind of material that was being removed. For example, the curing time for the bacteria that removed organic material from frescoes about twelve hours and for removing sulfates from stones between 15 to 36 hours. Sometimes several applications were needed. The

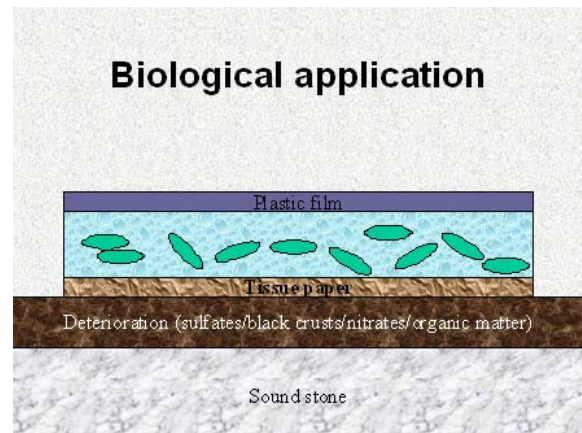


Figure 91. The biocleaning "package". Francesca Cappitelli
DISTAM, University of Milan

treated surfaces had to be gently cleaned with water afterwards to remove the bacteria as well as the unwanted material. A check was carried out after one or several months to make sure that the bacteria were properly removed and to monitor the cultural heritage surfaces.

Removal of black crusts

Sulfates

A biocleaning method with bacteria was tested to remove black crusts (mainly sulfates and carbon particles) on Candoglia marble at the cathedral of Milan in comparison with a traditional method that employs compresses with ammonium carbonate and EDTA. To be able to compare the methods the criteria for successful cleaning according to Vergés-Belmin was used. She proposed the following criteria for assessment of a cleaning method. It has to:

- 1) preserve as much as possible of the patina noble (that gives an aged character to the surface and has a preservative function)
- 2) cause no physical and chemical harm
- 3) achieve homogeneity of the treatment
- 4) achieve persistence
- 5) achieve high efficiency
- 6) not cause change in colour
- 7) not harm the aesthetics

The outcome was that the bacterial cleaning gave the best result and that both methods took the same amount of time.

Result of the chemical cleaning (according to V Vergés-Belmin):

- High efficiency
- The aesthetics and colour were slightly changed because of the patchy result
- Removes patina nobile
- Some physical harm: a degradation of the material (calcite) between grains was visible which leads with time to decohesion and cracks
- Higher pH (8)

The result of the biocleaning (according to Vergés-Belmin):

- High efficiency
- The result was homogenic and hence the aesthetics and colour were not changed
- Preserved the patina nobile
- Neutral pH (7)

Nitrates

Another example was the bioremoval of nitrates in Matera Cathedral in Italy (an European project named BIOBRUSH). The cathedral had a very porous stone (tufa) with nitrates and small quantities of sulfates.

The evaluation was made with ion chromatography measurement, Colour measurement and microbial counts. The bacteria left the stone 80% clean. Hence; the result was good.

Biocleaning has also been used on Michelangelo's Pietà Rondanini with good results. The problem in this case was the rests of products used for casting replicas (gypsum and calcite). These were removed with biocleaning.

Organic Matter Removal

The fresco "Le Conversione di San Efsio" in Pisa made by Spinello Arcino has also been treated with biocleaning. The fresco had been detached with a strappo technique but it was never finished. The facing had been left on the surface for several years and with time it had become insoluble. With the help of biocleaning it was possible to remove the adhesive as well as the facing. The removal was made with the bacteria *Pseudomonas stutzeri* and the residues further removed with enzymes.

The result with the bacteria was the best. The fresco was treated successfully with a biocleaning methodology with cotton strips soaked in bacteria.

Advantages and drawbacks of biocleaning and consolidation compared to chemical and enzymatic cleaning

The sulphate-reducing bacteria used for bioremoval of sulfates can also provoke carbonate precipitation (as well as other materials). Hence, these bacteria can be used both to remove unwanted material and to consolidate and protect carbonate stone. The consolidation is however still in the experimental stadium. The advantages of the bio-formed carbonates are for example that they are more resistant to mechanical stress and less soluble than other kinds of carbonates. In the past, one drawback of the use of bacteria was the potential growth of microorganisms, due to the introduction of organic nutrients for the bacterial growth and the longlasting experiments (more than 15 days). Hence, Dr. Cappitelli suspended the bacteria in a phosphate buffer with a low quantity of lactate that don't provide enough organic material for microbial colonization. The application lasted two days. In comparison, the chemical cleaning has other serious drawbacks such as the potential of leaving undesirable salts in the stone (sodium sulfate).

Dr. Cappitelli, moreover, discussed the enzyme cleaning in comparison with the biocleaning. In fact biocleaning is a kind of enzymatic cleaning since the bacteria use enzymes to degrade the undesirable compound. In summary, the advantages of the bacteria in comparison to the enzymes:

- bacteria produce enzymes that are not available on the market,
- bacteria produce a pool of enzymes depending on the binds to break down, whereas the enzyme only has a particular use that is highly specific for one purpose,
- bacteria are more adaptable and less influenced by the surrounding environmental factors (enzymes are more dependent on temperature and pH).

Answers and comments from questions and discussion

- Brajer asked if there is no risk that bacteria are left on the surface afterwards. Dr. Cappitelli answered that the bacteria dies after the removal of the delivery system and when there are no more nutrients. In fact most of them die because of the conditions on the surface that are not adapted to the bacteria. They need the delivery system for example Carbogel otherwise they die within minutes or hours.
- Svahn Garreau asked if the bacteria could be harmful to humans. Dr. Cappitelli answered that the bacteria do not cause allergic reactions. The chosen bacteria are common bacteria, which we are used to being exposed to in high concentrations during normal circumstances. However, as a good practice one should use gloves.

- Someone asked if there is any risk that they stay too long. Dr. Cappitelli replied that there are no such risks. She had left them for one day on the surface without problems. The method is very controllable.
- Several people asked where to buy the bacteria. Dr. Cappitelli answered that there are no commercial products on the market yet. She hoped that commercial products will become spin-off effects from the research. As the situation is today she can deliver the bacteria. In the future she hopes that it will be possible to send the bacteria dry, since it is much easier to send them in a dried condition.
- How much is needed? The amount of liquid bacteria is roughly 25 litres for a large fresco like the one in Pisa. The concentration of the bacteria is about 10^8 cells/ml.
- Svahn Garreau thought that it would be wonderful to be able to use biocleaning for both the removal and the consolidation at the same time. Dr. Cappitelli commented that there are no biocleaning and bioconsolidation systems available yet.
- Baglioni commented that it is possible to first consolidate with nanolime and afterwards use biocleaning to remove the undesirable compounds.

“Problems with Past Conservation Treatments on the Wall Paintings in Undløse Church”, Senior Research Conservator-Restorer Isabelle Brajer

Brajer presented a difficult conservation problem regarding the 15th century murals painted by the “Union Master” in Undløse Church in Denmark (who also painted murals in Strängnäs Cathedral in Sweden). The paintings had been treated with the famous “Carlsberg preparation” – a mysterious Danish conservation treatment frequently used during the first three decades of the 20th century. The project that was presented was the result of the investigation of the condition of the painting, and the influence past treatments have had on it. Having this knowledge, the next goal was to design diverse cleaning methods to remove ingrained soot and surface soiling without harming the painting.

The murals

The mural paintings in Undløse are of great importance to Danish art history, in fact the church has been placed on the list of Denmark’s most important artworks!



Figure 92. Undløse Church Denmark.

Figure 93. Undløse Church Denmark. Note the dark figures in the painting.
Photograph Roberto Fortuna, Nationalmuseum, Denmark.

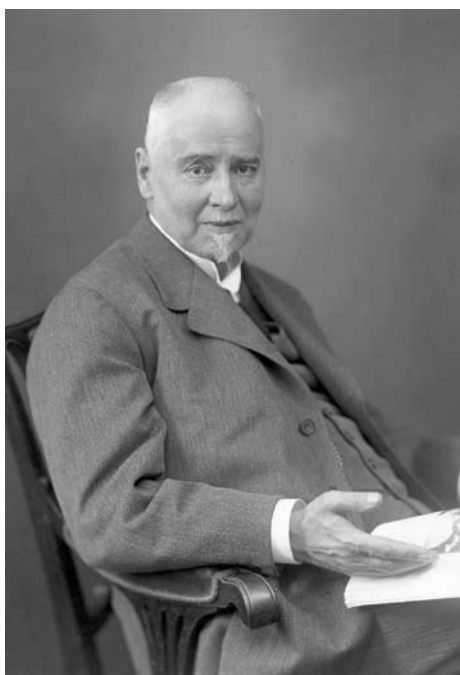


Figure 94. Eigil Rothe (1868–929). Conservator at Nationalmuseum 1897–1929. Photograph Nationalmuseum, Denmark.

Figure 95. Undløse Church, the murals in 1918.

Photograph Roberto Fortuna, Nationalmuseum Denmark.

Figure 96. Undløse Church, the murals 1918.

Photograph Roberto Fortuna, Nationalmuseum Denmark.

Figure 97. Hans Jessen-Hansen (seated on left) and Prof. S. P. Sørensen (in dark coat) Photograph Carlsberg Archive.

The conservation history

The medieval paintings were uncovered and conserved in 1918 by the “Father of Danish wall painting conservation” Eigel Rothe (1868–1929). Rothe developed a product for the protection of paint layers, which is popularly known as the “Carlsberg Preparation”. Rothe’s goal was a conservation product that:

1. made the paint layer water-insoluble so that the painting could be cleaned with water in the future
2. formed a protective barrier against salt precipitation

When Brajer started the investigation no one knew what the preparation was actually made of. Through archival investigations she found out that Rothe cooperated with different laboratories in order to make the preparation. These were:

- 1916–1919 “Teknisk Institut” chemist J. Rosenkjær
- 1919–1924 “Dons Laboratoriet” chemist Rudolf Dons
- 1924–1930 “Carlsberg Laboratoriet” (belonging to the Carlsberg Brewery), chemist Hans Jessen-Hansen

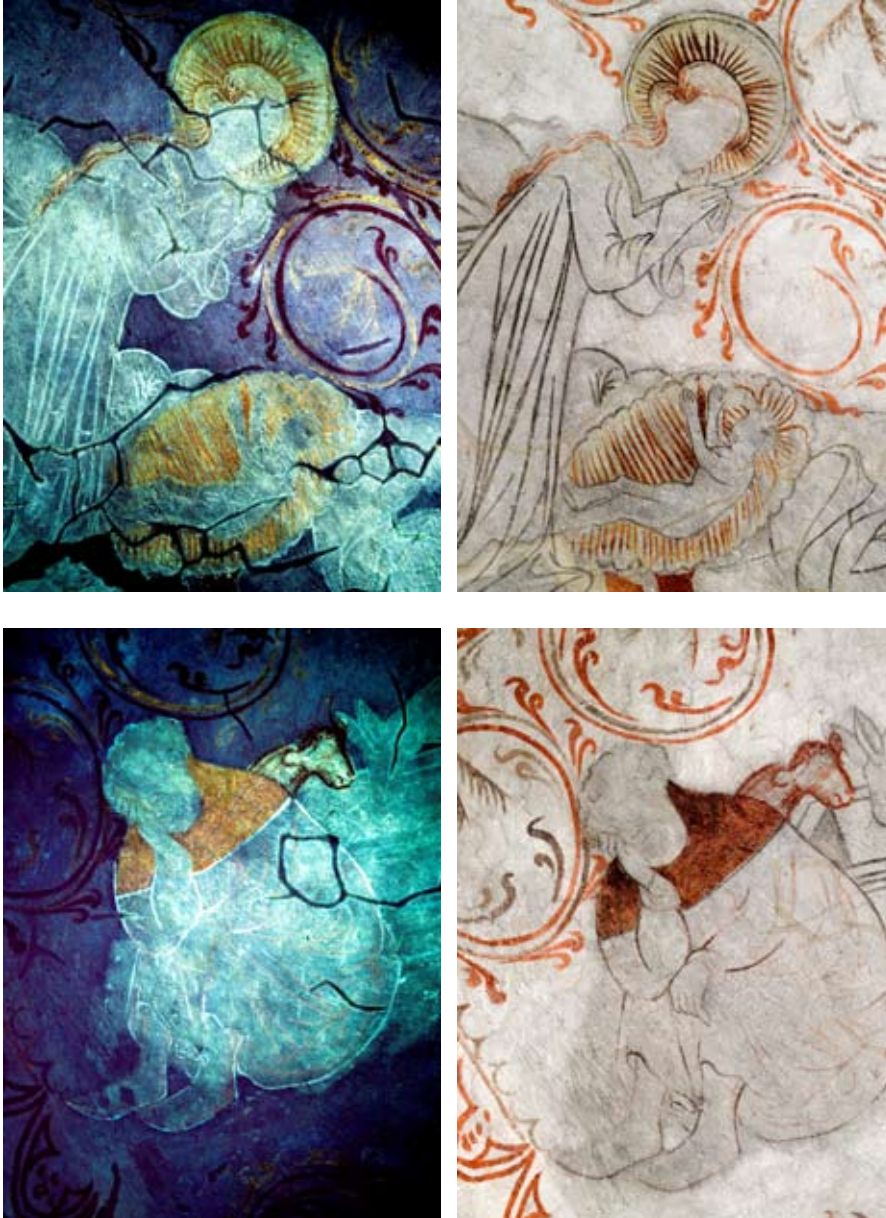
In the archives at Carlsberg Laboratoriet Brajer found a recipe that was made by the assistant to the famous chemist S.P. Sørensen (who is known for inventing the pH scale) – Hans Jessen-Hansen. The actual design of the preparation had evolved over many years through the collaboration between Rothe and the chemists.

The ingredients of the Carlsberg Preparation were:

- Aluminum soap (in aqueous solution)
- Varnish (oil + resin)
- Casein/borax (aqueous solution)

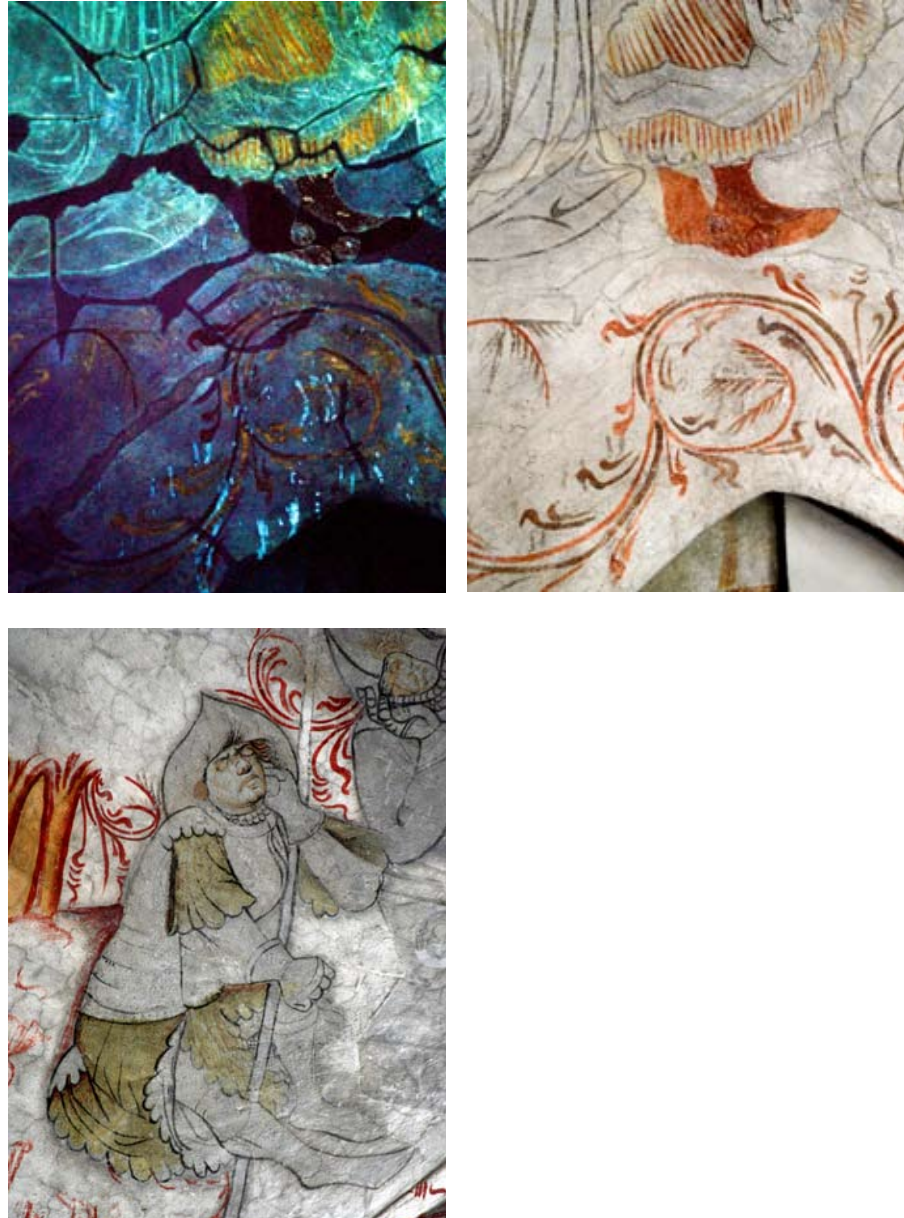
These ingredients were mixed together and afterwards turpentine, wax, camphor and siccative were added. The amount of each ingredient actually varied and Brajer found up to 80 different recipe variations!

The production of the Carlsberg Preparation required laboratory equipment and was expensive, and therefore it was used sparingly. In Undløse Church Rothe used it only on the most important areas (the contours of the figures). The figures were treated with a simpler mixture of colophony and poppy seed oil, which the conservator probably mixed himself. The organic substances on the surface of the paintings have caused problems with time: the treated surfaces attract dirt. Consequently, the treated areas are darker than the surrounding areas, which disturb the enjoyment of



Figures 98 and 99. The murals in Undløse Church in UV-light and normal light. On the UV photograph, the yellowish-whitish areas are where the resin/oil has been used, and the luminous contours are where the Carlsberg Preparation (casein, poppy seed oil/colophony) has been used. Note that these areas are darker than the untreated areas in the normal light photograph. Photographs Roberto Fortuna, Nationalmuseum Denmark.

Figures 100 and 101. The murals in Undløse church in UV-light and normal light. In the UV-photo the area that fluoresces corresponds to the area that is dirty in the photograph taken in normal light. Photographs Roberto Fortuna, Nationalmuseum Denmark.



Figures 102 and 103. The murals in Undløse Church in UV-light and normal light. In the UV-photo small drips and splashes visible as strong white fluorescence have been identified as milk, which was used in the restoration of the wall paintings in 1956 in connection with the plaster repairs (black forms on the UV-light photograph). Photographs Roberto Fortuna, Nationalmuseum Denmark.

Figure 104. Mural painting in Undløse Church. The figures that have been treated with the Carlsberg preparation and oil/resin are darker than the surrounding areas because they attract dust. Photograph Roberto Fortuna, Nationalmuseum Denmark.

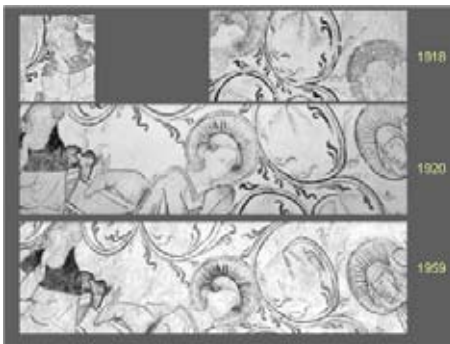


Figure 105. Mural painting in Undløse church 2006. Note the dark sooty areas. Photograph Roberto Fortuna, Nationalmuseum Denmark.

Figure 106. A part of the mural painting in Undløse Church in 1959. The photograph disproves the theory that the previous cleaning was limited to the background, leaving the figure dirtier than the rest of the painting. Photograph Nationalmuseum Denmark.

Figures 107 and 108. Mural painting in Undløse Church. The same areas have been photographed 1918, 1920, 1959 and 2006. It is possible to study how the painting has changed during these years. It has lost parts of the details due to weathering. Photograph Roberto Fortuna, Nationalmuseum Denmark.

the delicate paintings. If salt and moisture would have been present in the church, the preparation would have caused even more problems (contrary to Rothe's intention). Luckily, there are no salt problems in Undløse and the preparation has actually protected the paintings instead. Studying old photographs it is possible to see that the non-treated details are more weathered than the treated areas (however dirty).

The Conservation problem in Undløse

Towards the end of the lecture Brajer described and discussed the conservation problem in Undløse. The problem that needed to be solved was the removal of dirt (most of all soot) and previous conservation treatments without harming the painting.

The different compounds that had to be removed were:

- 1) The Carlsberg preparation on the contours.
- 2) Soot (found in pores of the limewash).
- 3) The oil/resin on the surface areas of the figures.

Brajer suggested a combination of enzymes or bacteria to remove the Carlsberg preparation and the casein, for the removal of the soot laser (YAG) and for the removal of oil/resin with triammonium gels with citrate, enzymes or microemulsion ((in combination with cyclododecan on sensitive areas).

Answers and comments from questions and discussion

- Brajer asked if someone in the audience had any other suggestions on how to solve the problem. Baglioni thought it was possible to use microemulsions or enzymes. However, he had to investigate the problem first to be able to customize the microemulsion.
- A discussion followed; that discussed if it really was necessary to remove the preparation. Maybe the dark areas could be hidden by retouching. Brajer replied that the great importance of the painting made it necessary to strive for a complete cleaning programme.

Acknowledgements

The summaries are based on notes made by Ragnhild Claesson and Lena Östlund during the workshop.

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102. The murals in Undløse church in UV-light. Photograph Roberto Fortuna, Nationalmuseum Denmark.
103. The murals in Undløse church in normal light. Photograph Roberto Fortuna, Nationalmuseum Denmark.
104. Mural painting in Undløse church. Photograph Roberto Fortuna, Nationalmuseum Denmark.
105. Mural painting in Undløse church 2006. Photograph Roberto Fortuna, Nationalmuseum Denmark.
106. A part of the mural painting in Undløse church in 1959, Photograph Nationalmuseum Denmark.
107. Mural painting in Undløse church. The same areas have been photographed 1918, 1920, 1959 and 2006. It is possible to study how the painting has changed during these years. Photographs Nationalmuseum Denmark.
108. Mural painting in Undløse church 2006. Photograph Roberto Fortuna, Nationalmuseum Denmark.

Workshop programme

Friday November 2

8.00 Departure from Stockholm by bus from Diplomat Hotel, Strandvägen 7

9.45 Arrival at Gammel Tammen, Österbybruk

10.00–10.30 Coffee

10.30–11.15 "Introduction". Architectural Conservator-Restorer Hélène Svahn Garreau, Conservation Department, National Heritage Board, Stockholm, Sweden

11.15–12.00 "Biotechnological Approach for the Removal of Damaging Casein-Layers on Medieval Wall Paintings." Dr. Sascha Beutel, Institute for Technical Chemistry, Leibniz University of Hannover, Germany

12.00–13.15 Lunch

13.15–14.00 "German Experiments with Enzyme Reduction of Casein on Mural Paintings". Conservator-restorer Kerstin Klein, Niedersächsisches Landesamt für Denkmalpflege, Hannover, Germany

14.00–14.45 "Nanoscience for the Conservation of Cultural Heritage". Cleaning with microemulsions/gels and nanoparticles for consolidation on fresco paintings. Professor Piero Baglioni, Department of Chemistry and CSGI, University of Florence, Florence, Italy

14.45–15.15 Coffee

15.15–16.00 "The Conservation of the Medieval Mural Paintings in Vendel." Architectural Conservator Hélène Svahn Garreau and Conservator-Restorer Ragnhild Claesson, Conservation Department, National Heritage Board, Stockholm, Sweden

16.00–16.30 "Problems with Casein Glue on Wall Paintings Transferred to Canvas". Senior Research Conservator-restorer Isabelle Brajer, National Museum, Denmark

16.30–17.00 Questions and Discussion. Moderator Architectural Conservator Hélène Svahn Garreau

17.30–18.30 Guided tour of Österbybruk and the Old Forge

19.00 Dinner at Gammel Tammen

Saturday November 3

7.00–8.00 Breakfast

8.00 Departure to Vendel Church from Gammel Tammen with bus

8.30–9.30 Vendel Church; see the paintings and discuss the problem on-site

9.30–10.00 Coffee is served in the parish house

10.00–12.20 Bus Tour to visit Tensta Church and Dannemora Church

12.20 Departure from Dannemora to Gammel Tammen

12.30–13.30 Lunch at Gammel Tammen, Österbybruk

13.30–14.15 "Removal of Undesirable Compounds from Stone and Frescoes using Bacteria." Dr. Francesca Cappitelli, DISTAM, University of Milan, Italy

14.15–15.00 "Problems with Past Conservation Treatments on the Wall Church Paintings in Undløse". Senior Research Conservator-Restorer Isabelle Brajer, National Museum, Denmark

15.00–15.45 Coffee and Concluding Discussion. Moderator Architectural Conservator Hélène Svahn Garreau

16.00 Departure to Stockholm

18.00 Arrival at Stockholm Central Station

18.15 (ca) Arrival at Diplomat Hotel, Stockholm City

Participants in the workshop

Andersson, Herman
 Conservator-Restorer
 herman.andersson@telia.com
 Herman Andersson AB, Tollarp

Asp, Misa
 Conservator-Restorer
 misa.asp@bredband.net
 Konservator Misa Asp
 Stockholm

Baglioni, Piero
 Professor
 baglioni@csgi.unifi.it
 Dep. of Chemistry and CSGI,
 Florence University
 Florence, Italy

Bergström, Karin
 Conservator-Restorer
 karin@enfantsterrible.se
 Stockholms målerikonserverer
 Stockholm

Berntsen, Hilde Viker
 Conservator-Restorer
 hilde.berntsen@niku.no
 NIKU
 Oslo, Norway

Beutel, Sasha, PhD
 beutel@iftc.uni-hannover.de
 Institut für Technische Chemie
 der Universität Hannover
 Hannover, Germany

Brajer, Isabelle
 Senior Research Conservator-Restorer
 isabelle.brajer@natmus.dk
 National Museum
 Copenhagen, Denmark

Brandi, Anna
 Conservator-Restorer
 anna.brandi@raa.se
 National Heritage Board
 Stockholm

Böllingtoft, Peder
 Conservator-Restorer/Teacher
 pbo@kons.dk
 School of Conservation
 Copenhagen, Denmark

Cappitelli, Francesca PhD
 francesca.cappitelli@unimi.it
 Dip. Scienze e Tecnologie Alimentari
 E Microbiologiche, DiSTAM,
 University of Milan, Italy

Claesson, Ragnhild
 Conservator-Restorer
 ragnhild.claesson@raa.se
 National Heritage Board
 Stockholm

Corkery, Robert,
 Dr, Area manager
 robert.corkery@surfchem.kth.se
 Nanostructured Materials,
 Institute of Surface chemistry, YKI
 Stockholm

Ernfridsson, Eva
 Conservator-Restorer
 eva.ernfridsson@vgregion.se
 Studio Västsvensk Konservering,
 SVK, Göteborg

Flarup, Anna
 Conservator-Restorer
 anna_flarup@yahoo.se
 Herman Andersson AB
 Tollarp

Fyrand, Kristin
 Conservator-Restorer
 kristin@konservering.se
 Stockholms målerikonserverer
 Stockholm

Garreau, Hélène Svahn
 Architectural Conservator
 hsv@raa.se
 National Heritage Board
 Stockholm

Heberlein, Christina
 Conservator-Restorer
 christina_heberlein@hotmail.com
 Conservator J.T.F. Petéus AB
 Göteborg

Heiling, Katarina
 Conservator-Restorer
 KatarinaHeiling@web.de
 Esperke
 Germany

Hench, Joanna
 Conservation student
 joannahench@hotmail.com
 Norway

Henningsson, Anna
 Conservator-Restorer
 info@kah.se
 Konservator Anna Henningsson,
 KAH, Stockholm

Johansson, Sölve
 Architectural Conservator, PhD
 solve@bksjab.se
 Byggkonsult Sölve Johansson AB
 Trollhättan

70 Participants in the workshop

Järnerot, Eva
Conservator-Restorer
eva.jarnerotkonservering@telia.com
Uppsala Konservering
Uppsala

Jørgensen, Anne-Marie
Conservator-Restorer
hotamnj@hotmail.com
National Museum
Copenhagen, Denmark

Kettunen, Rebeca
Conservator-Restorer
rebeca.kettunen@glocalnet.net
Byggnadshyttan på Gotland
Visby

Klein, Kerstin
Conservator-Restorer
kerstin.klein@NLD.Niedersachsen.de
Niedersächsische Landesamt für
Denkmalpflege, Hannover, Germany

Leijon, Ulf
Conservator-Restorer
petal.roberts-leijon@comhem.se
Konservator Ulf Leijon
Uppsala

Mild, Anne-Marie
Conservator-Restorer
ann-marie.mild@vgregion.se
Studio Västsvensk Konservering,
SVK, Göteborg

Nilsson, Jessica
Conservator-Restorer
jessica.nilsson@statenskonstrad.se
Statens konstråd
Stockholm

Perea, Sergio
Conservator-Restorer
sergio.perea@spray.se
Konservator Sergio Perea
Uppsala

Petéus, Thomas
Conservator-Restorer
info@conservatorab.se
J.T.F. Petéus AB
Göteborg

Söderdahl, Katarina
Conservator-Restorer
katti.gotland@hotmail.com
Romakloster

Ullenius, Henrik
Conservator-Restorer
henrik.ullenius@ullenius-ateljeer.se
Ullenius ateljéer AB
Sunne

Ullenius, Urban
Conservator-Restorer
urban.ullenius@ullenius-ateljeer.se
Ullenius ateljéer AB
Sunne

Wetterström, Kerstin
Conservator-Restorer
kerstin.wetterstrom@ylm.se
Länsmuseet Västernorrland
Härnösand

Östlund, Lena
Conservator-Restorer
lena_karin@hotmail.com
National Museum
Copenhagen, Denmark

