

**Deutsche Bundesstiftung Umwelt**

An der Bornau 2

49090 Osnabrück

**Funding subject 12:** Preservation and safeguarding of nationally valuable cultural assets from harmful environmental influences

**AZ. 38807/01**

## **Project Report**

UNDERSTANDING THE IMPACT IN RELATIVE HUMIDITY FLUCTUATIONS ON THE  
STABILITY OF POROUS UNDERBOUND PAINT LAYERS

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**Allocated funds: 85,052 €**

**Project start: 01.05.2023**

**Project duration: 18 months (extended)**



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## **Abstract:**

When the German Museums Association published its recommendation for an expanded climate corridor in museums, it recognized the need to investigate its effects on sensitive materials. In response, the CICS conducted a pilot project entitled “Understanding the Impact of Relative Humidity Fluctuations on the Stability of Porous Underbound Paint Layers” (2023–2025), funded by the German Federal Environmental Foundation (DBU). The morphology and distribution of the hygroscopic binder in porous paint layers were characterized, and methods for assessing cohesion loss were developed. The preliminary results focus on the paint layer excluding the influence of the substrate, show trends but no statistically significant effects of the expanded climate corridor over a seven-year period. The combination of abrasive and adhesive cohesion tests suggests an alteration of the distribution of the binder towards the paint surface. A detailed analysis of the binder distribution is required to confirm this hypothesis. All results will be available in open access peer reviewed publications.

The project identified several open questions that need to be addressed in order to develop tailored recommendations for the preventive conservation of this group of materials.

## **Zusammenfassung**

Der Deutsche Museumsbund hat bei der Veröffentlichung der Empfehlung für einen erweiterten Klimakorridor in Museen den Bedarf erkannt, dessen Auswirkungen auf empfindliche Materialien zu erforschen. Als Antwort führte das CICS ein Pilotprojekt mit dem Titel „Understanding the Impact of Relative Humidity Fluctuations on the Stability of Porous Underbound Paint Layers“ (2023–2025) durch, das von der Deutschen Bundesstiftung Umwelt (DBU) gefördert wird. Die Morphologie und Verteilung des hygroskopischen Bindemittels in porösen Malschichten wurde charakterisiert und Methoden zur Bewertung des Kohäsionsverlusts entwickelt. Die vorläufigen Ergebnisse zur Veränderung der Kohäsion nach kurzer künstlicher Alterung, die sich nur auf die Malschicht konzentrieren und den Einfluss des Trägers ausschließen, zeigen Tendenzen, jedoch keine statistisch signifikanten Auswirkungen des erweiterten Klimakorridors über einen Zeitraum von sieben Jahren. Die Kombination von Abrasions- und Adhäsionstests deutet auf eine veränderte Verteilung des Bindemittels zur Oberfläche hin. Die X-ray tomography Datenauswertung ist noch nicht abgeschlossen. Das Projekt identifizierte eine Reihe offener Fragen, die beantwortet werden müssen, um maßgeschneiderte Empfehlungen für die präventive Konservierung dieser Materialgruppe zu entwickeln.

## 1. Introduction

In September 2022, the German Museums Association (Deutscher Museumsbund) published a '*Recommendation on energy savings through the introduction of an extended climate corridor for museum air conditioning*'.<sup>1</sup>

This recommendation advocates for a widened climate corridor for museum air conditioning and thus for extending the previously narrowly defined target values for temperature and relative humidity. The recommended climate corridor has a relative humidity range of 40-60% (max. +/- 5 percentage points within 24 hours) and a temperature range of 18°C-26°C (max. +/-2 °C within 24 hours). In 2023 the Bizot's Green protocol, recognized and supported by the National Museums Directors Council (NMDC), ICOM-CC (The international Council of Museums Conservation Committee) and the International Committee for Museums and Collections of Modern Art (CINAM) published a revised climate corridor recommendation:

-relative humidity range of 40-60% (max. +/- 10 percentage points within 24 hours) and a temperature range of 16°C-25°C.<sup>2</sup>

This new recommendation aims the reducing the energy use and carbon footprint of museums as public institutions.

Although the extended climate corridor is presumably unproblematic for many materials in museum collections, the risk assessment for particularly climate-sensitive materials requires additional investigations. The German Museums Association calls for this risk assessment by conservators, natural scientists and material experts in paragraph 5 of the recommendation, where it says:

*“As the collection items in various museums are highly diverse, the requirements for the environmental conditions can vary greatly. An assessment must therefore be carried out by experts such as conservators. In addition, care must be taken to ensure that all changes to existing climate parameters in the environment of collection items are accompanied and analysed by adequate monitoring and evaluations.”*

Porous paint layers that contain a small amount of hygroscopic binder form one of these particularly climate-sensitive material categories.

With our project we aim to contribute to this risk assessment through investigating the impact of cyclically repeating fluctuation of the relative humidity in the range of 40-60% on the cohesion of porous paint layers with hygroscopic binders and on the contact area

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<sup>1</sup> <https://www.museumsbund.de/wp-content/uploads/2022/11/klimakorridor-fuer-sammlungsgut.pdf>

<sup>2</sup> <https://www.cimam.org/sustainability-and-ecology-museum-practice/bizot-green-protocol/>

between the pigment surface and the binder. The small scale project aims equally to assess the methodology here developed to evaluate loss of cohesion and morphology of binding medium in porous paint layers.

The German Federal Environmental Foundation (Deutsche Bundes Stiftung Umwelt - DBU) is funding the research project with 85,000 euros. The project is being carried out at the Cologne Institute of Conservation Sciences (CICS)/TH Köln, under the direction of Prof. Dr Ester S.B Ferreira.

## **2. Objectives of the project**

The ultimate objective of this project is the investigation of the extent by which fluctuations in relative humidity impact the cohesion and integrity of porous underbound paint layers. Furthermore the project aims to understand the mechanisms involved in loss of cohesion.

The methodology developed it would be suitable to assess consolidation treatments of fragile porous paint layers.

For testing the cohesion, a mechanized and standardized cohesion test will be developed as currently there are no available standardized and established methods to assess the cohesion of paint layers. The evaluation/validation of the cohesion testing method(s) is equally an objective of the project.

For that, mock-ups whose materials are representative of a large number of painted art and cultural heritage objects will be prepared and artificially aged.

Additionally, in order to help the assessment of changes in cohesion, if observed, laboratory and synchrotron-based methods for 3D characterization of the morphology and distribution of the porosity and binder bridges are evaluated and applied to provide a comparative accurate nanoscale model of the porous underbound paint layers before and after exposure to environmental stress through artificial ageing.

In this multidimensional approach, not only the influence of artificial ageing on the cohesion of paint layers is investigated, but potentially also the relationship between cohesion and possible changes in binder morphology thus providing a link between microstructure and macro properties.

The question we want to answer with the proposed study is:

- What is the impact of relative humidity fluctuations (widened climate corridor: 40-60%, previous climate recommendation: 45-55%, uncontrolled environment: 30-80%) on the effective cohesion of the paint layer prepared with a selection of pigments and hygroscopic binders?

- What is the impact of relative humidity fluctuations (widened climate corridor: 40-60%, previous climate recommendation: 45-55%, uncontrolled environment: 30-80%) on the distribution of the binder?

The knowledge gained through our study provides the method development first step towards founded risk assessment of the relaxation of climate control regulations as recommended by the German Museums Association for art objects with porous paint layers containing hygroscopic binding media.

Additionally, in an informal collaboration with Prof. Eggert partner at the DBU project 38338/01 "Schutz national wertvoller Kulturgüter durch Einsatz gesättigter Salzlösungen in Vitrinen zur Absorption anthropogener Luftschadstoffe" we evaluate the use of saturated magnesium nitrate salt solutions as relative humidity fluctuation buffer and stabilizer.

The ultimate aim of this project is to contribute the generated knowledge into concrete preventive conservation recommendations for practical working conservators and decision makers in museums, housing cultural assets with fragile porous, underbound paint layers containing a hygroscopic binder. These are of relevance for a large number of museums in Germany and abroad. Further work expanding the current results and validated methodology onto more complex sample sets with hygroscopic substrates is required for a full assessment of the new widened climatic corridor in particularly sensitive objects.

### **3. Project partners**

Project employees are Charlotte N. Stahmann (M.A.) and the student assistants Emma Helfrich and Thanh Vu. Emma Helfrich is bachelor student at the Cologne Institute of Conservation Sciences/TH Köln and Thanh Vu bachelor student at the Institute of Product Development and Engineering Design/TH Köln. It was a wish to offer students, at an early stage of their education, the possibility to contribute to a research project and through this involvement gain valuable insight into the processes and working methods such a project entails. So far, this experience has been very valuable on both sides.

Internal partners in the project are Prof. Dr Jörg Lüderich and Andreas Käckel from the Institute of Product Development and Engineering Design/TH Köln. As the name of the institute already reveals it is committed to the development and engineering of products and automated machines. In order to generate coherent, statistically valid, and comparable results, it is essential that the method and the parameters are the same for every test carried out. In our case of testing the cohesion, this means that the pressure and friction applied to the paint layer must always be the same. This cannot be achieved manually and

as no tool is available yet to perform such tests, we relied on the development of on a custom-made automated process, which only became possible through this cooperation.

External partners are Martin Muckelbauer (Powerlyze GmbH, Nuremberg) for the sample preparation using Focus-Ion-Beam, Dr Nicholas Phillips (Paul-Scheerer-Institute, Villigen, Switzerland) for the 3D imaging of samples using ptychography nano tomography, and Dr Adrian Mikitisin for combined Focus-Ion Beam sample preparation and laboratory based nanotomography.

#### **4. Work packages and Methods**

The project is divided into the four work packages:

- Mock-up preparation
- Artificial Ageing
- Cohesion Test
- Laboratory based Nano x-ray computed tomography and Synchrotron based Ptychographic x-ray computed tomography

The work packages give a chronological structure to the project. Some of them can be worked on in parallel, others need to be processed successively. During each work package a different constellation of project members is working together. In this way responsibilities and tasks are clearly defined and regular project meetings provide a platform for exchange. In the following the methodologies and first results of the working packages will be described in detail.

##### **4.1. Mock up preparation**

The mock-ups are the foundation for all the following working steps of the project. Therefore, their well thought through design, and their standardized, and well documented preparation requires special attention.

###### **4.1.1. Choice of materials**

It started with the question which pigments in combination with which binding media to study. The research question already narrowed down the possible choice of binding media to hygroscopic ones such as proteins and polysaccharides. Therefore, as binders, representative for the chemical group of proteins, Casein (#7555) and Gelatine Bloom 180

(#4274), and as representative for the group of polysaccharides, Gum Arabic (#4159) were chosen. All polymers were purchased by Carl Roth and have laboratory quality.



Fig. 1: Selected binders and pigments for the preparation of the mock-ups

The choice of pigments fell on the calcium carbonate “Chalk from Champagne” ( $\text{CaCO}_3$ , #58000,), the iron oxide “Red Moroccan Ochre” ( $\text{Fe}_2\text{O}_3$ , #116430) and the carbon “Vine Black, German” (C, #47000), all purchased from Kremer Pigmente.

With this choice of pigments, representatives of different chemical compositions are present, each having a different surface energy. This allows to additionally investigate the interesting question of what influence the surface energy of the pigment surface has on the pigment’s wettability by the binding medium. The wettability of the pigment by the binding medium might impact the rheology of the wet paint and possibly the adhesion between the binder and pigment surface in the dried paint film.

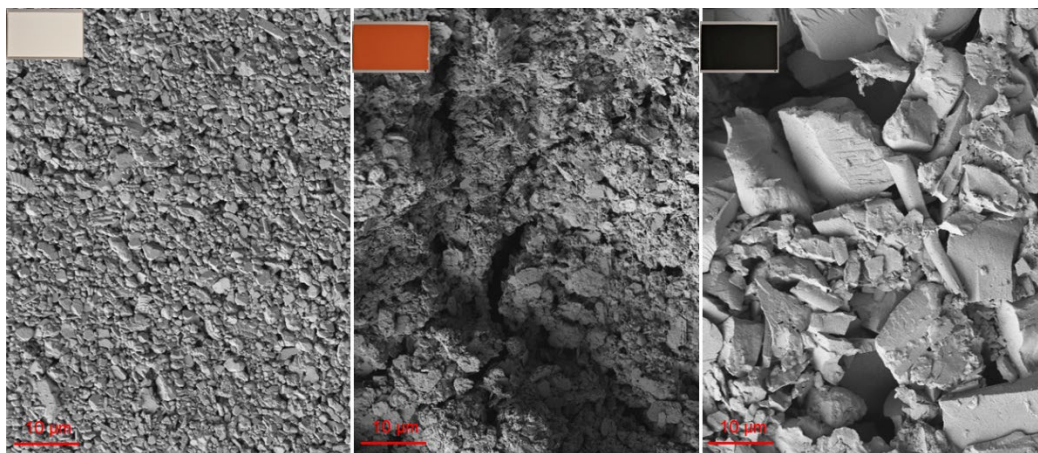


Fig. 2: Scanning electron microscope images of the selected pigments (3000 x magnification)

The choice of materials is also representative for cultural assets that have repeatedly been mentioned in literature as having underbound and cohesively weak paint structure. Interestingly these cultural assets are from various geographical origins. They include ceremonial masks from Papua New Guinea; Australian indigenous bark paintings; decorative distemper paintings in Norwegian stave churches; ground layers as for example in European paintings and sculptures; and decorative paint on Egyptian coffins.

As a support medium for the paint layers, cast, satinised Polymethyl methacrylate/PMMA, namely Plexiglas® Satinice Clear (Crystal) 0F00DC by Röhm, was used. The Plexiglas® was purchased in pre-cut pieces of 80x120 mm. The chosen Plexiglas® is produced by casting liquid PMMA in between two glass plates with a finely structured surface. In this way the resulting cast acrylic glass receives a finely structured surface. This structured surface has a larger surface than a smooth acrylic glass would have, allowing also water-based paint media to adhere on to the inherently hydrophobic surface.

The choice deliberately fell on a hard, homogeneous, and non-hygroscopic material as a support for the paint layers. The reason for this is that in this first step of the research, we solely want to investigate the influence of fluctuating relative humidity on the paint layer itself. The impact of a hygroscopic support on the stress induced on a paint layer during fluctuating relative humidity is expected to be significant and will therefore be studied in a in future research.

It was observed that the surface roughness on one and the same Plexiglas® piece is different on each side and it varies from batch to batch. So, in case that a uniform surface roughness is important, pieces from one acrylic glass plate (which are usually produced in 2x3 m large plates) and from the same side should be used.

#### **4.1.2. Choice of material ratios**

The chosen three pigments and three binders result in a total of 9 pigment-binder combinations. These nine combinations were produced in a well-bound paint set and an underbound paint set. Resulting in 18 mock-up types of each ten samples were prepared. Wehlte (1992) and Doerner (2001) recommend a binder concentration of 4-6% for gelatine and 4% for casein. These values served for orientation, when choosing the concentrations for the well-bound paint films. For the preparation of underbound paint the recommended binder concentration was halved. The systems were prepared so that after drying the pigment/binder ratio either 4% (w/w) for well bound paint systems or 2% (w/w) for underbound samples. Pre-tests determined that in order to make a paint systems that could

be applied with a film applicator, additional water had to be added. We observed that if the the order of addition of the paint and binder components played a role of the homogeneity of the binder distribution. That is if the 2% binder was mixed with the given weight of pigment and the resulting paint was too viscous for a film applicator, the thinning of the paint with water products a paint system with a very heterogenous distribution of binder. (figure 11) For that reason the determined required water volume was added to the binder and homogenised before the addition of pigment.

#### 4.1.3. Preparation of the paint

To make the paint, first the binding media were prepared in the desired concentrations using demineralised water. The binder solutions and the previously determined quantity of additional water were pre-mixed on a magnetic stirrer, before the pigment was gradually sieved in. Both chalk from champagne and red ochre were wetted by the binding media through capillary action. In contrast, the vine black pigment was not wetted on its own and additional force had to be applied, through manually mixing the pigment for ~2.5 minutes with a spatula into the binder solution. After the pigment was completely wetted by the liquid phase, the mixture was transferred to a glass plate and manually mixed for three minutes using a glass muller. Building up a working station, helped keeping the workflow systematic and tidy. On the front table, seen on Figure 2, the paints were prepared. On the table in the back the paint was applied on the acrylic glass supports.



Fig. 3: Setup for mock-up paint preparation.

The rheological behaviour of paint systems is significantly impacted by the used pigment. Paints prepared with carbon black show a distinct shear-thickening behaviour – meaning that the viscosity increases when the paint is sheared and reduces when it is left to rest. This is not the case for paints prepared with red ochre and chalk.

#### 4.1.4. Application of the paint

The Plexiglas® pieces came with a protective foil on both sides. Before applying the paint the protective foil was removed on the back side, to label the mock-up. On the front side the foil was cut in, offset inwards by 5mm, along the longer sides of the Plexiglas® using a scalpel. Immediately before the paint application only the middle part of the foil was removed using tweezers. The foil raids along the long sides served as an even and smooth surface on which, the film applicator could run (Fig. 2). Multiple measurements of the foil showed that it has an average thickness of 60µm.

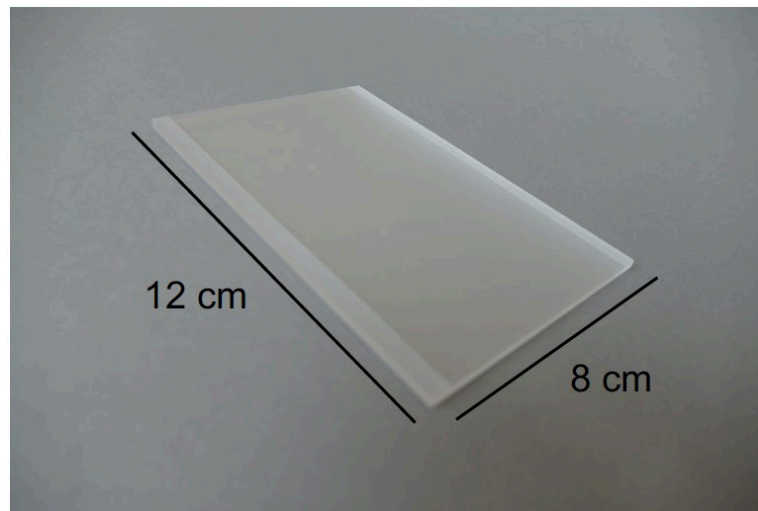


Fig. 4: Substrate for mock-ups.

For the application 8-10 gram of the liquid paint was filled into a four-frame film applicator (fig 4) which was automatically pushed at a defined speed (10mm/s) over the acrylic glass, using a film applicator by BYK. The wet film thickness for all paints was 210 µm (150µm gap width of the film applicator plus 60µm foil thickness).

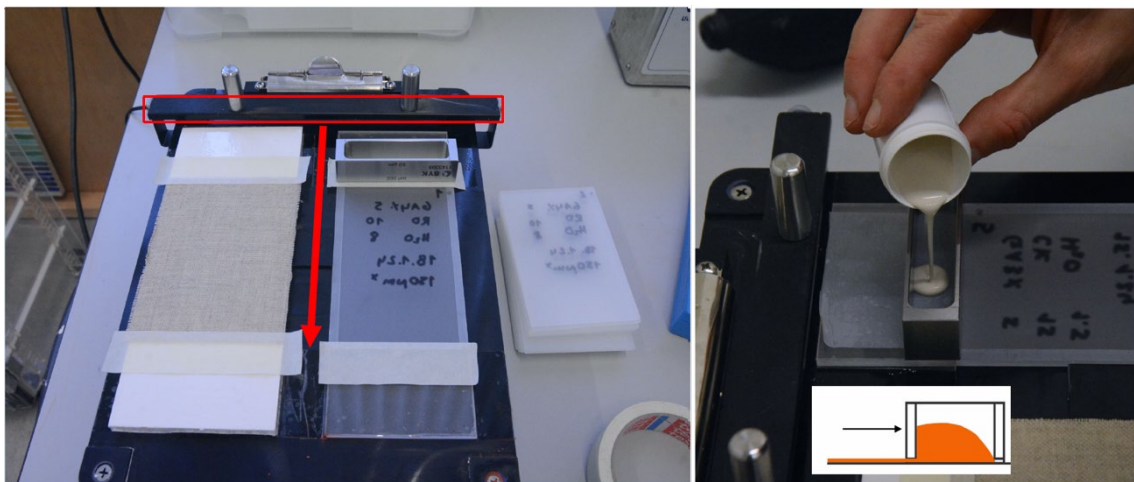


Fig. 5: Application of paint.

Result of the mock-up preparation were 180 mock-ups (Fig 5).

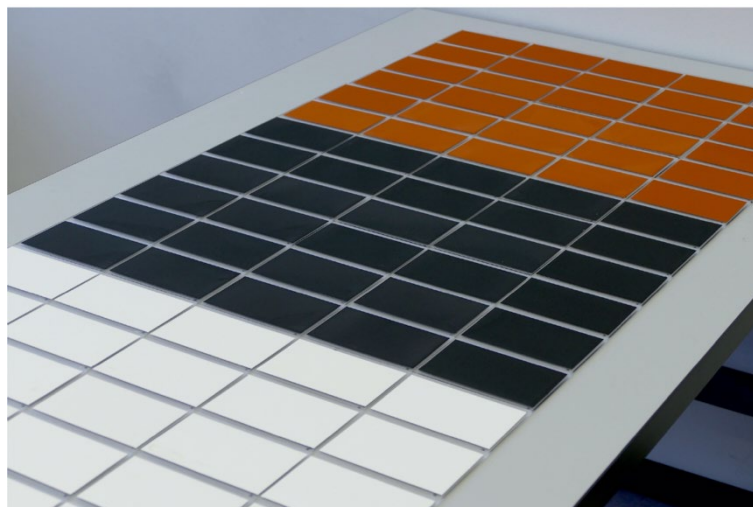


Fig. 6: Prepared mock-ups

#### **4.1.5. Drying of mock-ups**

The mock-ups were allowed to dry for 24 hours in the room where they were prepared. The relative humidity was kept between 50-55% using a humidifier with a temperature ranging from 18-23°C.

#### **4.1.6. Storage of mock-ups**

After drying for 24 hours in the above-described way, the mock-ups were stored in a climate stable environment at 54% RH and 22°C. To provide this environment a hermetically closed desiccator cabinet (Siccio Tower-Star-Exsikkator 310x735x735mm, PMMA/Alu) was prepared with a saturated salt solution. Using a saturated solution of Magnesium nitrate hexahydrate (>98%, p.a., ACS, #233-826-7, Carl Roth) we could provide a very stable relative humidity of 54% at 22°C in a temperature regulated room. The mock-ups will be permanently stored in this environment, except for the periods in which they will undergo artificial ageing.

Concerning the relative humidity adjustment via saturated salt solutions an exchange with Prof. Dr. Eggert has been established, who is with his team, currently working on a DBU-funded project (AZ38338/01) dealing with the potential to reduce air pollutants in show cases through the use of saturated salt solutions.



Fig. 7: Mock-up storage system Sicco tower. A tray with magnesium nitrate saturated solution guaranteed a stable environment (54% RH) in a climatized room (Temperature 22 °C)

#### 4.1.7. General recommendations for mock-up preparation

In the following some general recommendations and aspects to consider when preparing paint mock-ups were collected.

- Ensure constant and controlled ambient conditions: temperature, relative humidity, air flow
- Care for a dust-free environment (regular cleaning) and use of lint-free materials (lint-free cloths, wearing gowns to avoid fibres)
- Use an accurate and calibrated scales with at least two decimal places
- Use materials from the same product batch. Ordering enough material so that everything can be made from one batch (support, pigment, binder). When ordering, inform the manufacturer that the materials should be from one batch.
- Every step should follow a standardised procedure, amongst other this concerns the preconditioning of used materials, the quantities and sequencing when mixing together materials and the paint application
- Thorough cleaning of all tools and containers that come into contact with the materials used for mock-up production first with water and then with ethanol
- Strict documentation of everything that is weighed. Documentation in words and photos of the process and all observed peculiarities

## 5. Artificial ageing

Three artificial ageing sessions have been completed on full sets of mockups.

In addition to the humidity fluctuations between **40-60%** - which aim to represent the new recommendations for a widened climate corridor by the German Museums Association, for comparison, full sets of mock-ups were exposed to artificial ageing program of:

- **45-55%** representative for the previously widely used climate recommendation proposed by the American Society of Heating, Refrigerating and Air-Conditioning Engineers.
- as well as **30-80%**, representative for an uncontrolled environment

A reference set of mock-ups will be kept at stable relative humidity of 54%, adjusted in a desiccator using a saturated solution of Magnesium nitrate hexahydrate.

During the artificial ageing the relative humidity will change in two-hour cycles from the lower to the higher relative humidity limit at a constant temperature of 22°C for 8 weeks. For the ageing a climatic chamber by Weiss Technik is used.

## 6. Cohesion tests

Currently there are no available standardized and established methods to test the cohesion of paint layers – neither on mock-ups nor on actual cultural assets. This poses a problem as objectively study the effect of ageing on paint layer cohesion and objectively evaluating the success of consolidation treatments of cohesively weak paint layers is presently not possible. The endeavour to develop a suitable method for cohesion testing of paint layers has been addressed in student projects [Stahmann, 2022 Ben Yossef, 2021] in the field of conservation sciences, but no work has been fully dedicated to this important and urgently needed subject yet.

### 6.1. Adhesive cohesion tests

For the cohesion testing on mock-ups this project aims to develop a mechanized and highly standardized cohesion test in collaboration with our cooperation partners from the Institute of Product Development and Engineering Design/TH Köln. In this test cohesion was assessed by quantifying the unbound loose particles at the paint surface.

The test machine combines three different components

- a self-adhering elastomer roller
- an automated multiaxial table
- and a pneumatic cylinder set-up

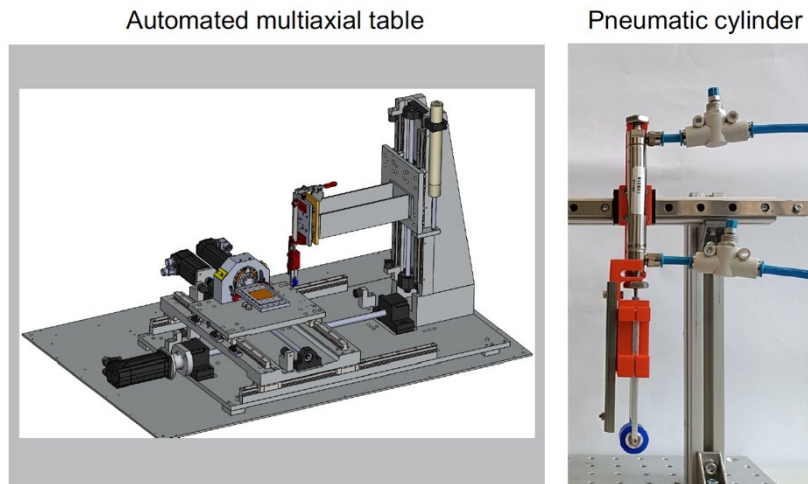


Fig. 8: Elements of the adhesive cohesion test.

The self-adhering elastomer roller with handle (*Asmetec*, METOCLEAN hand roller HRM-10, 10 mm), is produced for the cleanroom industry to remove loose particles such as dust from sensitive surfaces, without affecting them or leaving any residues. The material characterization (FTIR) identified silicone based elastomer.

Cleaning rollers of this type have already been tested for the surface cleaning of sensitive paint layers in a master's thesis by Svenja Voßkamp at CICS in 2014.

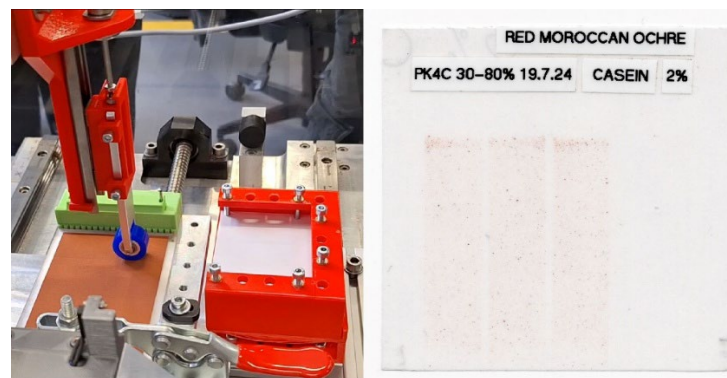


Fig. 9: Adhesive cohesion test set up and transferred collected particles fixed and scanned.

The automated multiaxial table holds both the mock-up and the elastomer roller. It will move the mock-up in one axis at a defined speed using a programmed server motor. During this movement the elastomer roller is in contact with the paint surface and will roll over the surface with one rotation, while collecting loose pigment particles (figure 9). The pressure (force/area) of the elastomer roller during the rotation is controlled (set at 1N) and corrected by a precision pressure regulator and a pneumatic cylinder system, which are together directly connected to the elastomer roller.



### 6.3. Cohesion test results overview

The cohesion is evaluated by quantifying the amount of material collected measured from the scanned abrasive and adhesive tests as illustrated above. The results for the red ochre paints are illustrated in the graph below. The higher the value measured, the more material is collected during the test, interpreted as a lower cohesion of the paint.

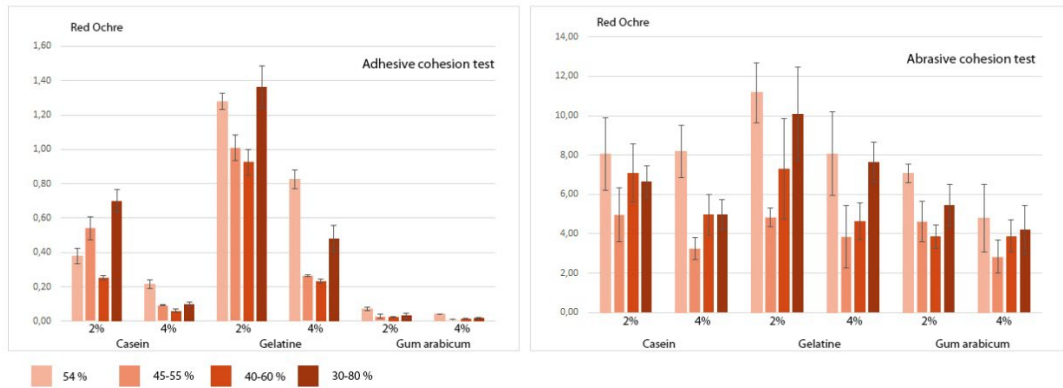


Fig. 11: Quantitative evaluation of abrasive and adhesive cohesion tests of the red ochre paint system with different binders and binder concentration and aged under RH programs.

The results show that:

#### Test reproducibility

- Adhesive cohesion method using the clean room elastomer roll generated more reproducible results with standard deviations values up 9%.
- the data scattering (difference between the values measured in repeated measurements in the same sample) in abrasive cohesion tests was higher (standard deviation up 35%).

#### Impact of binder to pigment ratio

- The reduction of the amount of binding medium from 4% to 2% reduces the cohesion as measured both by the abrasive and adhesive tests.

#### Impact of binder type

- The sensitivity of the paint systems to the fluctuating relative humidity in different environments varies with the binding medium type (casein, gelatine or gum arabicum). Casein bound paint systems showed less change in cohesion upon ageing that gelatine bound paints.

#### Impact of fluctuating relative humidity

- The length (equivalent to 7 years) of the test was insufficient for a clear conclusions. A period equivalent to 21 years (overall 6 months in climatic chamber) is advisable.

- Interestingly reference samples kept at RH 54% T 22 °C (in the presence of magnesium nitrate saturated solution) for the duration of the project showed lower cohesion than the aged samples, in future projects the saturated salt solution of magnesium nitrate will be replaced by potassium carbonate (RH 43%).
- The uncontrolled environment 30-80 % RH induces the highest loss of cohesion when comparing the three ageing regimes, detected both in adhesive and abrasive cohesion tests supporting the hypothesis that fluctuating relative humidity induces a loss of cohesion.
- The impact of the extended climatic corridor 40-60% relative to 45-55% is within the measurement error range. On the one hand: the abrasive cohesion tests suggest a reduction in the cohesion of paint systems when expanding the RH corridor from 45-55% to 46-60% however the data scattering within each sample set is too high compared to the cohesion differences between sets and therefore the results are not statistically representative. On the other hand: the adhesive cohesion test (loose particles on the paint surface) show a slight improvement in the surface cohesion for the samples exposed to the 40-60 % RH in comparison to those exposed to 45-55% RH fluctuations. The combination of these two results (less loose particles on the surface but slightly lower film cohesion) seem to indicate a change in the distribution of the binding medium towards the paint surface.
- The testing of this hypothesis requires the comparative visualisation of the distribution of the binder.
- The results of the current test series enables the development of a better protocol to be tested in subsequent research steps.

## 7. Ptychographic X-ray tomography and Segmentation

Ptychographic X-ray tomography (PXCT) is performed at the Paul-Scherrer-Institute (PSI) in far-field at the cSAXS-X12SA, PXTC, OMNY instrument. To prevent radiation damage of the organic binder with a cryo-stage at 90 K will be used. Differential laser interferometry will provide accurate sample positioning during measurements.

Access to the ptychographic tomography beamline at PSI for 88 hours had been granted for the end of June 2023. Data processing, segmentation and analysis is performed on the acquired workstation, using Avizo 9.0 software at CICS. This means that the different materials in the sample, differentiable due to their material specific electron density, will be segmented into different phases and quantified. The samples prepared in 2023 were test samples prepared in smaller volume which meant that the paint rapidly changed rheology due to water evaporation. As a consequence, water had to be added when applying the paint and the paint homogenised before preparing the films with the film applicator. From the PXCT data it can be seen that the proteinaceous binder does not redissolve and an heterogenous distribution of the binder with a poor build-up of nanobridges network as had been achieved in 2021. For this reason, sample preparation protocol was adapted.

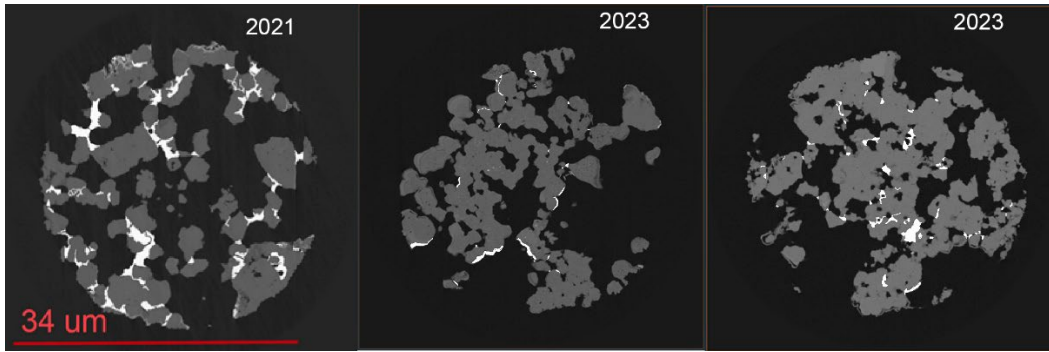


Fig 12. PXCT of samples prepared in 2021 and 2023.

Due to an accelerator ring upgrade, PSI SLS in general and cSAXS beamline in particular, were offline from October 2023 to October 2025. Although first light a cSAXS beamline is now available the beamline will only be available for external users in October 2026. Alternative solutions for the imaging of the binder have been sought including an application in March 2025 to DESY Hamburg Petra IV beamline P06 Ptychographic Nano-Analytical Microscope (PtyNAMI). The nanoscope of the beamline P06 operated at room temperature and pressure whereas cSAXS OMNY operates at cryo temperatures. Our application was rejected as it was argued that the it had not been demonstrated that the lack of cooling would not cause damage to the binder in the sample. To address this we resorted to laboratory based nano tomography (64 nm and 128 nm resolution) in absorption and phase contrast mode at the RWTH Aachen (Dr. Adrian Mikitisin, Röntgen- und Elektronenmikroskopie, CARL – Center for Ageing, Reliability and Lifetime Prediction of Electrochemical and Power Electronic Systems) for stability assessment. First comparative tests were done on existing samples studied in cSAXS. The results of this comparative evaluation were presented in a conference and will be published. As a final stage of the project 5 samples of red ochre with gelatine as binder under different ageing protocols and binder concentrations were analysed and the evaluated data will be published in combination with the cohesion tests.

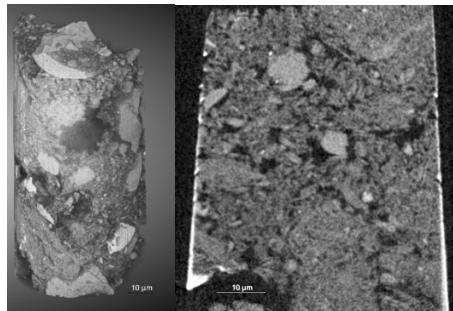


Fig 13. Volume reconstruction and single slice. Nano tomography images of red ochre samples.

An additional goal was to evaluate the proposed methods for the assessment of consolidation treatments. For that a small area of casein bound paint was consolidated

with methylcellulose solution. A sample was collected, mounted on OMNY pin, cut into a 40 µm cylinder by the project partners at Powerlyze and imaged by Ptychography at cSAXS beamline in July 2023. This experiment could show that the electron density of methylcellulose and casein is distinct and these two phases can be distinguished. This shows that Ptychography is a suitable method for evaluating the distribution of consolidant following consolidation treatments, and combined with the cohesion measuring tests a powerful set of tools for systematic assessment of new consolidation materials and methods.

## **8. Discussion**

The goal of developing a methodology for assessing cohesion was achieved. The adhesive method showed good reproducibility, less so for the abrasive method but this method will most likely be useful for the evaluation of samples exposed to longer ageing cycles. Abrasive testing was suitable for all three pigments, the adhesive method was best suited for red ochre pigment. In contrast vine black particle size was too large to be picked up homogeneously by the elastomer role through electrostatic forces. Finally the loose chalk particles could be easily picked up by the elastomer by challenging to document the amount of picked up particles. Illumination under UV was required to image the chalk particles on the adhesive pad. In future tests pigments with large particle sizes and with poor contrast with the adhesive transfer pad will be avoided.

In future tests some protocol alterations will be incorporated:

- a) Cohesion will be tested before and after ageing in the same sample.
- b) Sets of samples with hygroscopic substrates will be incorporated.
- c) The artificial ageing protocol will be adjusted/changed/prolonged for more relevant long-term cohesion stability prognostics. This is translated to 2hr cycles for 45-55% but 4hr cycles for 40-60%.

The collaboration with the various partners was very productive, in particular internal in the TH Köln. Unfortunately, some delays in the start of the project led to only have one opportunity to access cSAXS beamline (Paul Scheerer Institute, CH) in July 2023 and required to search for alternative partners and tests laboratory based nano x-ray computer tomography providing a lower material contrast and less straightforward data processing mostly still ongoing. Having said that the samples used in nano x-ray computer tomography can be re-analysed by Ptychography x-ray tomography once the beamline is again available to users for comparison with current results.

## 9. Dissemination

The results of this research project will feed into Bachelor and PhD projects, and the teaching at the CICS. The findings were and will further be shared and made accessible in form of conference presentations and publications in high impact, open access journals and used as base for the preparation of future research projects.

The first presentation on the project with the title “Understanding the impact of RH fluctuations on the stability of porous underbound paint layers” was given at a public lecture at CICS on the 29th of April 2024 as part of the Institute’s Ringvorlesung series.

Full list of dissemination initiatives include:

- CICS website [https://www.th-koeln.de/kulturwissenschaften/cics---dbu---understanding-the-impact---forschungsprojekt\\_128407.php](https://www.th-koeln.de/kulturwissenschaften/cics---dbu---understanding-the-impact---forschungsprojekt_128407.php)
- April 2024 CICS Ringvorlesung series Project presentation
- April 2025 CICS Ringvorlesung series Project progress
- 3<sup>rd</sup>-4<sup>th</sup> April 2025 JAAP Journey into the Ageing and Alterations of Paintings Amsterdam, NL. *Addressing the Challenges of Visualising Organic Binding Media Networks in Porous Painting Layers*. Presenter Ester S.B. Ferreira
- 6<sup>th</sup> -9<sup>th</sup> May 2025 Technart Perugia, IT. *Visualising Organic Binding Medium Networks in Porous Paint Layers and Paint Reconstructions*. Presenter: Charlotte Nora Stahmann.

Planned

- C.N. Stahmann, D. Müller, N.W. Phillips, M. Holler, M. Muckelbauer, E. Storevik-Tveit, E.S.B. Ferreira *Imaging the organic binder network in porous paint used by Edvard Munch*, submitted.
- Emma Helfrich, Thanh Vu, Charlotte N. Stahmann, Andreas Käckel, Jörg Luderich, Ester S.B. Ferreira *Two Methods for Quantification of Cohesion in Porous Paints*, in preparation.
- Further publications including those addressing the evaluation of the recently collected nano computed tomography analysis of mock ups after different ageing programs.

In addition to dissemination formats with a high outreach, we value one to one exchange with professionals working on related subject or conservators working in institutions that have cultural assets with cohesively weak paint layers in their collection, such as:

- Prof. Dr. Gerhard Eggert (Akademie der Künste Stuttgart)
- Prof. Dr. Karolina Soppa (Hochschule der Künste Bern)
- Stephanie Luerßen (Rautenstraße Joest Museum, Köln)
- Karen Mengshoel (Norwegian Institute for Cultural Heritage Research, Oslo)

- Beata Tworek-Matuszkiewicz (National Gallery of Australia)

## 10. Conclusions

During this pilot project, significant steps have been made in developing methods for assessing cohesion and the impact of relative humidity fluctuation on cohesion. The validated methods in this proof of principle phase will be used as base for further steps in the research, significantly reducing the risk of future research funding, as many of unknown factors have here been clarified. As detailed in the discussion, the results and experience gathered has shown that modifications to the ageing protocol, the material choice for mockups (including the addition of relative humidity sensitive substrates such as canvas and wooden) and the protocol for cohesion measurement (i.e. include self-referencing samples) are required in order to resolve several problems encountered. Furthermore, the results show with consistency that the relative humidity has an impact in cohesion and validates the requirement for this line of research to be carried out with precision and validated methodology.

**Note:** All dissemination and publication which include the results of this project, even is published after the conclusion of the financed period, will make direct reference to the project number and funding source that enabled it.

## 11. Literature

Wehlte K. Werkstoffe und Techniken der Malerei, p.424, 1992

Doerner M. Malmaterial und seine Verwendung im Bilde. 18. Aufl. Berlin: Urania 2001. P. 178, p. 180.

Stahmann C, Soppa K, Glösen B, et al. Low molecular weight cellulose ethers as aerosols for the consolidation of cohesively weak paint layers. *International Journal of Conservation Sciences* 2022; (13): 1583–602.

Ben Yossef, Alma: Comparison of Consolidation Methods for Underbound Chalk Layers on a Wooden Substrate. *Studienarbeit TH Köln (CICS, HOM)* 2018, S. 8-10.

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