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DIPLOMOVÁ PRÁCE

TMELY PRO VÝPLŇ DEFEKTŮ VE STRUKTUŘE PODKLADOVÉ A BAREVNÉ VRSTVY MALBY NA PLÁTĚNÉ PODLOŽCE

FILLING MATERIALS USED IN STRUCTURAL CONSERVATION OF EASEL PAINTINGS ON CANVAS

Vypracoval*a: Alžběta Mirjam Procházková

Vedoucí diplomové práce: doc. MgA. Adam POKORNÝ , Ph.D.

Oponent*ka diplomové práce: Kate Seymour MA FIIC

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Diplomová práce je koncipována jako restaurátorská příručka pojednávající o různých, nejen materiálových, možnostech pro vytvoření vhodného tmelu pro defekty v barevné a podkladové vrstvě obrazů na textilní podložce. Cílem práce bylo vytvořit souhrnné dílo, které na několika stránkách nabízí různé alternativy a varianty. Každé dílo je unikátní a je třeba k němu přistupovat individuálně, citlivě a s pokorou k dílu samotnému. Proto tato práce otevírá těžké dveře do spektakulárního restaurátorského světa naplněného materiály, prostředky a možnostmi. Čtenáři-restaurátorovi nabízí ucelený vhled do problematiky tmelů, včetně kritérií pro výběr, alternativ aplikace, reintegrace a imitace povrchu s okolní malbou. Záměrem bylo nabídnout praktickou příručku, kde se na jednom místě nachází několik druhů tmelů s návodem na jejich přípravu i s různými materiálovými alternativami dostupnými ve střední Evropě. Jedná se o základní vhled do tohoto tématu, který má velký potenciál výraznějšího prohloubení. Postupné zaplňování mezery, chybějícího místa, v restaurátorských skriptech.

Problematika tmelení defektů je komplexní téma, které bylo v různých historických etapách diskutováno a řešeno na základě v té době přístupných materiálů. Již ve středověkých receptářích se nachází poznámky ke způsobům, jak poškození maskovat. Obvykle tuto úlohu plnili sami autoři a používali materiály pro ně běžně dostupné. Proto se můžeme setkat s tmely složenými nejen z olovnaté běloby, křídy, vosku, pryskyřice, ale i mouky a medu. S postupným rozšiřováním oboru restaurování a systematickým budováním citlivějšího přístupu ke konzervování a vystavování uměleckých děl, začaly od 19. století vznikat restaurátorské příručky, které doporučují čím dál tím širší paletu materiálů, které je vhodné použít pro namíchání tmelu. Jedná se o materiály přírodního původu, které byly s přelomem do 20. století, a především v období během a po 2. světové válce, rozšířeny i o materiály syntetické. V dnešní době je na trhu obrovské množství nejrůznějších produktů různé kvality a záměrů k použití. Produkce těchto materiálů je zaměřena i na obor restaurování a konzervování uměleckých děl. S rozšířením základní myšlenky restaurátorského zásahu jakožto co nejméně invazivní práce, minimalizování rozsahu na pouze strukturálně a esteticky nutné zákroky, reversibility a snadného odstranění použitých materiálu a individualizovaném přístupu, předpoklady a nároky na složení tmelu se proměnily. Základní principy tmelů jsou kompatibilita s materiály použitými v originálním díle, reversibilita (nebo spíše snadné odstranění), chemická inertnost materiálů v tmelu a jejich schopnost přizpůsobení se klimatickým změnám (především teplota a relativní vlhkost). Z tohoto důvodu se chemický a fyzikální výzkum rozšířil i do pole stárnutí a degradace přírodních a syntetických materiálů používaných v restaurátorském odvětví a existuje velké množství publikací na toto téma. Nicméně je důležité mít na paměti, že jakýkoliv materiál přirozeně degraduje a stárne ze své podstavy, otázkou je ovšem jakým způsobem a jakou rychlostí.

Teoretická diplomová práce je rozdělena do několika kapitol. První část se věnuje především definici pojmu tmel, jeho kritériím a základním předpokladům vzhledem k současnému přístupu k restaurování. Z těchto kritérií poté vyvstává několik konkrétních tmelů doplněných o informace k jednotlivým materiálům použitým v jejich kompozici. Vedle celé řady tmelů, které mohou být použity pro výplň defektů v malbách na textilní podložce, existují i tmely komerční. Tyto ready-to-use tmely jsou v práci zmíněny pouze krátce, vzhledem k tomu, že nejsou nijak výrazně rozšířeny v České republice, i když jsou velmi často preferované v jiných nejen evropských zemích pro jejich jednoduché a efektivní použití. Nicméně producenti těchto tmelů velmi často neudávají veškeré informace o jejich složení, a proto může být jejich volba vnímána mírně problematicky. Z tohoto důvodu a také jejich horší dostupnosti v České republice, do praktické části práce zařazeny nebyly.

V praktické části diplomové práce se tedy věnuji pouze tmelům, které je možné namíchat v ateliéru a použít jako výplňový materiál podkladové a barevné vrstvy obrazu na textilní podložce. Pro práci bylo vybráno devět kategorií, respektive devět různých pojiv (adhesiv), které byly míchány s několika druhy plniv. Materiály byly vybrány vzhledem ke středoevropské tradici i s přesahem do materiálů používaných v jižní a západní Evropě. V práci jsou tyto materiály popsány i včetně základních chemických i fyzikálních vlastností, historické i geografické tradici v použití materiálu nejen na tmely a krátkým shrnutím výzkumů zabývajících se jejich degradaci a stárnutím. Následuje konkrétní recept na přípravu tmelu z konkrétního pojiva včetně alternativ a variant, které je možno využít. Součástí receptu je i fotografická dokumentace pro snadnější představu přípravy. V návaznosti na jednotlivé recepty jsou popsány aplikace jednotlivých tmelů do defektů, v převážné většině případů i doplněny o konkrétní příkladové studie, kde byl konkrétní tmel použit doplněným o vysvětlení, z jakého důvodu byl tento tmel v tomto konkrétním případě preferován a jakým způsobem byl povrchově zpracován a upraven i s volbou materiálu pro závěrečnou retuš.

Tato praktická část je doplněna o výsledky z testování namíchaných vzorků tmelu. Cílem testování bylo prozkoumat mechanické vlastnosti konkrétních formulací a jejich změny během procesu stárnutí. Z tohoto důvodu byly připraveny čtyři vzorkovnice, plátna napnutá na napínací rám, na které byly stejným způsobem naneseny všechny vzorky tmelů. Tři vzorkovnice byly připraveny z nového přepraného plátna izolovaného 5% želatinovým roztokem, jedna byla připravena ze starého dublovacího plátna s výrazným obsahem reziduí rentoalážní vosko-pryskyřičné směsi. Tato vzorkovnice měla imitovat originální obraz, který již prošel dřívějším restaurátorským zásahem s použitím hluboce penetrujících materiálu prostupujících do všech vrstev obrazu s prakticky nemožností odstranění. Naopak zbývající tři vzorkovnice byly připraveny stejným způsobem jako intarzie, záplaty a rekonstrukce, tedy nové upravené plátno vložené do strukturálního defektu v originální podložce. Na všechny vzorkovnice byl pokaždé nanesen jeden vzorek od každého tmelu. První vzorkovnice byla uzavřena do černého boxu bez přístupu světla a uložena do stabilizovaných klimatických podmínek. druhá byla vystavena dennímu světlu s přirozeným UV osvitem. Zbylé dvě byly vloženy do stárnoucí komory, kde byl nastaven program imitujících velmi radikální změny teploty a vlhkosti, kterým může být dílo vystaveno v nemuzeálních podmínkách. Výsledkem testování byla komparace změn základních vlastností tmelů (dimenzionální změny, ztráta koheze materiálů a adheze k podložce, změna barevnosti a tvrdosti, reversibilita). Naprostá většina tmelů ve stárnoucím procesu obstála. Ačkoliv k menším změnám došlo u velké části vzorku, nicméně tyto změny nebyly vyhodnoceny jako závažné a znemožňující použití tmelů. Za zmínku ovšem stojí výrazný fenomén změny barevnosti a lesku u tmelů nanesených na staré dublovací plátno. U velké části tmelů byla po umělém stárnutí zaznamenána výrazná změna způsobena výraznými výkyvy klimatických podmínek, které zapříčinily penetraci vosko-pryskyřičné směsi do materiálů tmelů. Výjimkou byly polyvinyl alkoholových tmelů, které barevné degradaci zcela obstály.

Nemalá závěrečná část diplomové práce je také věnována způsobům a tipům pro aplikaci tmelů a jejich povrchové úpravě. Jedná se o velmi výraznou, i když mírně zdlouhavou, část fáze tmelení, jejíž dobré provedení přináší blahodárnou odměnu. Platí zde totiž pravidlo, že i sebelepší imitativní retuš provedená na nevhodně upraveném tmelu, nikdy nebude dostatečně adekvátně začleněna do originální malby, naopak bude přitahovat divákovu pozornost. Tato kapitola se proto věnuje různým metodám strukturování povrchu tmelu, imitování krakelury, expresivních nánosů pastózní malby, tahů štětce i propsání charakteru textilní podložky.

Teoretická diplomová práce svou formou více či méně obsáhle vhlíží do problematiky tmelů pro defekty v barevné a podkladové vrstvě obrazů na textilní podložce. Její rozsáhlost je dána komplexitou tohoto tématu a možnostmi jeho řešení. Záměrem bylo představit širokou paletu materiálů včetně velmi detailně popsaných přípravných receptů a možností aplikace. Variant a alternativ, které do práce zařazeny nebyly, je nadále ještě velké množství, avšak nebylo již v mých kapacitách jim vytvořit dostatečný prostor. Jedná se tedy o základní vhled do tohoto tématu, který má velký potenciál výraznějšího prohloubení.

THEORETICAL DIPLOMA THESIS

THE INFILLING MATERIALS FOR LOSSES IN PAINT AND GROUND LAYER OF PAINTINGS ON A TEXTILE SUPPORT

Alžběta Mirjam Procházková



The Academy of Fine Arts in Prague
The Studio of Restoration of Painted Artworks and Polychrome Sculpture
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ABSTRACT

The aim of the diploma thesis is to provide a comprehensive overview of the materials used in current conservation practices as infillings for losses in paint and ground layers of paintings on textile support. The purpose of the work is to describe and compare different materials that could be used as components of a particular filler. One of the impulses for choosing this topic was the lack of complex information or compendious publications regarding these various possibilities from which a conservator-restorer could select the proper formulation of the putty suitable for the particular work of art. The approach of the work is to offer a complex handbook, describing the requirements of infilling materials, key and advanced properties to consider when selecting a particular filler.

Based on the introduction to the problematic of fillers and their characteristics, the basic composition of the filler is defined, including the specification of binding medium and bulking agents. The main part of the thesis is dedicated to nine different binding medias for fillers and their variations, with recipes and application methods exhibited. Each filler formula was mixed in the studio and tested. An important section is the evaluation of mechanical and visual properties, based on the preparation of four mock-ups with filler samples exposed to light efflorescence and accelerated environmental changes achieved in environmental chamber (non-museal conditions). The results of the accelerated aging process are documented, and their comparison with the unaged samples is evaluated.

At the second part of the thesis, chapters dedicated to the adjustment of the filler surfaces are introduced. It is highly advisable to pay attention to the reintegration of the filler properly into the structure and surface of the particular painting. When the filler is accurately applied in terms of being well-inserted into the loss and its surface is adjusted to imitate the surrounding painting‘s surface, the pictorial reintegration after inpainting is significantly enhanced. Different methods and techniques are described in this chapter.

Comprehensively, the thesis is composed in a manner that fills the gap, I missed, in the inconsitant and therefore spectacular art of the restoration universe. However, it is only an introduction to this problematic and further investigation is neccessary, therefore this topic obtains a huge potential for any future deeper examination and research.

ANOTACE

Diplomová práce je koncipována jako komplexní restaurátorská příručka pojednávající o různých, nejen materiálových, možnostech pro vytvoření vhodného tmelu pro defekty v barevné a podkladové vrstvě obrazů na textilní podložce. Cílem práce bylo vytvořit souhrnné dílo, které na několika stránkách nabízí různé alternativy a varianty. Každé umělecké dílo je unikátní a je třeba k němu přistupovat individuálně, citlivě a s pokorou k předmětu samotnému. Proto tato práce nabízí čtenáři-restaurátorovi ucelený vhled do problematiky tmelů, včetně kritérií pro výběr, alternativ aplikace, reintegrace a imitace povrchu s okolní malbou. Záměrem bylo nabídnout praktickou příručku, kde se na jednom místě nachází několik druhů tmelů s návodem na jejich přípravu i s různými materiálovými alternativami dostupnými ve střední Evropě. Jedná se o základní vhled do tohoto tématu, který má velký potenciál výraznějšího prohloubení. Postupné zaplňování mezery, chybějícího místa, v restaurátorských skriptech.

Teoretická diplomová práce je rozdělena do několika kapitol. První část se věnuje především definici pojmu tmel, jeho kritériím a základním předpokladům vzhledem k současnému přístupu k restaurování. Z těchto kritérií poté vyvstává několik konkrétních tmelů, které jsou hlavním předmětem práce. Vedle celé řady tmelů, které mohou být použity pro výplň defektů v malbách na textilní podložce, existují i tmely komerční. Tyto ready-to-use tmely jsou v práci zmíněny pouze krátce, vzhledem k tomu, že nejsou nijak výrazně rozšířeny v České republice. V praktické části diplomové práce se tedy věnuji pouze tmelům, které je možné namíchat v ateliéru. Pro práci bylo vybráno devět kategorií, respektive devět různých pojiv (adhesiv), které byly míchány s několika druhy plniv. Materiály byly vybrány vzhledem ke středoevropské tradici i s přesahem do materiálů používaných v jižní a západní Evropě. V práci jsou tyto materiály popsány i včetně základních chemických i fyzikálních vlastností, historické i geografické tradici v použití materiálu nejen na tmely a krátkým shrnutím výzkumů zabývajících se jejich degradací a stárnutím. Následuje konkrétní recept na přípravu tmelu z konkrétního pojiva včetně alternativ a variant, které je možno využít. Tato praktická část je doplněna o výsledky z testování namíchaných vzorků tmelu. Cílem testování bylo prozkoumat mechanické vlastnosti konkrétních formulací a jejich změny během procesu stárnutí, který byl urychlen pomocí klimatické stárnoucí komory.

Nemalá závěrečná část diplomové práce je také věnována způsobům a tipům pro aplikaci tmelů a jejich povrchové úpravě. Tato kapitola se věnuje různým metodám strukturování povrchu tmelu, imitování krakelury, expresivních nánosů pastózní malby, tahů štětce i propsání charakteru textilní podložky.

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1. DEFINITION OF FILLERS AND THE MANNER OF USE

Filling the painting is one of the most beneficial phases of the restoration treatment. It is a key operation crucial for the resulting appearance of the artwork. Pictorial reintegration may not be sufficient if fillings are not executed perfectly. Furthermore, the materials used should meet several criteria based on the current approach to the work of conservator-restorator (which has developed historically and, of course, as with many other materials and methods used in conservation treatments, could be transformed again). Additionally, the necessities of the painting itself, such as the type of support, technique, and materials used for the artwork, are criteria that lead to a proper selection of the filler content, method of application, surface adjustment, and reintegration. It is deeply beneficial to dedicate significant attention to this phase of work, as properly considered and thoughtfully executed work will yield results far beyond what could have been expected.

A painting on canvas is basically a 3D object. It is composed of a textile support, mostly canvas, although synthetic textiles are used especially in modern and contemporary art[1]. Multiple layers are applied onto the support, which is illustrated on the Figure 1. The stratigraphy usually consists of preparation ground layer, paint and varnish layers. However, it‘s important to note that each artwork is unique, and paintings without ground layers or varnishes also exist. Whether the painting obtain or not the preparation layer, it could therefore significantly change the mechanical properties of the artwork. A painting is a complex heterogeneous laminate structure, in which each material can respond differently to external forces, stresses, and loads applied. Consequently, every artwork exhibits unique physical-mechanical behavior. Furthermore, all materials are inherently subjected to deterioration, each following its own pathway of deterioration. This complex interaction within and between each layer of the painting may accelerate damage, especially inter-laminar damage, under certain conditions. These damages could result in the loss of cohesion of each layer, flaking paint, loss of cohesion between forces within the material, leading to powdering or cracking of the ground and paint layers, and often resulting in cupping and flaking of the layers or even leading to creation of losses and consequential textural alteration. These damages could have either a natural origin caused by the degradation of the materials, as described, or they could be caused by accidental or intentional harm, such as during transport, vandalism, or improper handling and storage.[2]

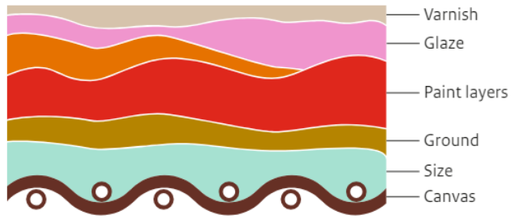


Figure 1: Stratigraphy of painting
source: Van den Burg, J. M., Seymour, K. (2024): 5

These defects could have a further structural character. The damage may cause a loss of material throughout all the layers, including the support/substrate of the painting. In this case, we refer to the structural damage. This category includes defects in the textile support such as tears, holes, punctures, etc.[3] These damages are treated in a phase of restoration treatment called structural work and include operations such as tear mending and inserting a new canvas by patches or intarsias. However, this thesis only covers fillers that are suitable for losses in the paint and ground layers. Defects in the canvas require more robust material capable of resisting tensile and shear forces. The fillers that are the subject of this study are (mainly) applied after the structural work is completed. However, some of the fillers could be applied on a new canvas which was inserted to the sturctural demage and therefore fillers could also play a role of the alteration of a missing ground layer on which an inpainting is later applied. This type of treatment is purposed as a reconstruction of the stratigraphy of a painting.

The losses in the paint and ground layer, also referred to as lacunae in literature, can have different origins, characters, sizes, and depths. These losses in a pictorial image typically distract the viewer‘s attention and draw the observer‘s eye to the defective area rather than the remaining parts of the artwork. It is caused due to the fact that the loss typicaly do not respect the depicting picture and transcends it bounderies, within its form, sillhouette, shape, colour, etc. Furthermore, the character, size, and pattern of the loss could be so dominant that they completely capture the viewer‘s attention, making them more memorable than the intact surface of the painting. This phenomenon is for example described by Cesare Brandi, who indroduced a concept called Gestalt psychology[4] in the transition to conservation field, based on the perception and summurization of theories within the italian conservators. This term reffears to the aesthetic reintegration which cessates the distraction of the observer‘s eye. The main principle of Gestalt is as follows: ‚The whole is more than the sum of its parts,‘ meaning that reality is not perceived as a mere collection of individual sensations, but as a unified entity. Once the lacuna is registered in our minds as a foreign element, it ceases to be part of the preparation and becomes a figure on the painting. In fact, what is registered is the figure and not the background. The new figure becomes the protagonist and distracts us from the painting, leading to devaluation, relegating it to a background role.[5]

1 CHIANTORE, O., RAVA, A. (2005). „New materials in contemporary art“ in *Conserving Contemporary Art: Issues, Methods, Materials and Research*, The Getty Conservation Institute, Getty Publications, Los Angelies, USA, pp. 20-33

2 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 6

3 NICOLAUS, Knut. (2005).“Types of demage and how they are caused“ in *Restoration of Painting*, Könemann, ISBN 3895089222, pp. 80-90

4 BRANDI, Cesare. (1963). *Theory of Restoration.* Nardini editore, Instituto centrale per il restauro

5 AGULLI, G., SILVA, L. (2005). *Treatment of lacunae, Gestalt psychology and Cesare Brandi. From theory to practice*, III. International Meeting of Retouching of Cultural Heritage, Postprints RECH3, Bailao, pp 95-102

It‘s important to realize that in the case of modern (abstract) art, the intention of the artist could be completely lost by any disruption to the composition.

Losses may be present only in the top layers of the painting, such as glazes or varnish layers (including abrasion and erosion). In those cases, filling is not always required, especially if the original painting is still intact. Therefore, the conservation treatment could be limited to the retouching process only. However, for the most severe losses, when both the paint and ground layers are missing, compensation must involve the reconstruction of the preparatory layer with filling material, as well as subsequent retouching of the fill.[6]

The filling is a time-consuming phase of the treatment; however, it is highly advisable to give proper attention to this phase, as emphasized by Dr. Marco Ciatti, who was an art historian and director of the Painting Conservation Department and Superintendent of the Laboratories of the Opificio delle Pietre Dure in Florence:
„The filling is a critical step and reconciles the need for structural and aesthetic characteristics. Just think of a perfect reintegration performed on a filling that has not been well-accomplished, in the end gives an aesthetically unsatisfactory result.“[7]

The filler is basically a mixture of materials (an inert bulking agent and an adhesive binding medium) inserted into the losses in a painting aiming to arrive at a level just below the surface. Filling could be ferrair to a operation that is undertakent for sealing of demage to a picture layer by inserting a filler, that consists of a smoothed down or structured substance. Fillers fill in defected area and bridge uneven parts of a picture to create an even level, how it is illustrated on the Figure. 2.

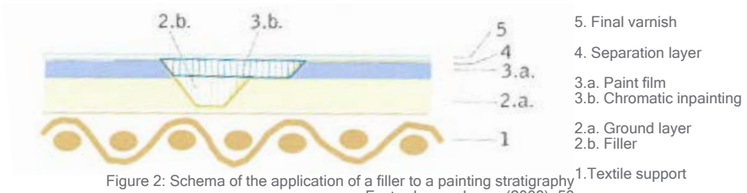


Figure 2: Schema of the application of a filler to a painting stratigraphy
source: Fuster-Lopez, Laura (2008): 53

Losses have been a concern in the treatment of painting throughtout history. A thousands of paintings have already undergone some restoration treatments, which also included the filling of defects. Losses have been filled for many centuries by artists or artist-restorers, and different types of materials were used.[8] Various recipes and formulations can be found in historical treatises (the earliet written by Cennino Cenini, Gorgio Vasari, or later by Robert Dossie, Pietro Edwards, Pacheco, etc.) However, sometimes it is necessary to remove the old fills as part of the restoration treatment. On the other hand, it is also possible to conserve the old fill if it is suitable for the painting. The decision whether the old filler is removed or preserved depends on its quality and state of preservation.

Good reasons for removal include:

- distortions or development of diverse crack patterns from the original
- a total lack of structures or inadequate structures
- and overfilling of the original painting

There could be several forms of distortion observed on the old fillers. For example, in cases when the filler is composed of a large amount of binding material, resultant strain can distort filled areas. In extreme cases, they cup and form their own network of cracks. Generally, old fillings are seldom well-structured. In a raking light, old fills could be identified either by their evidently too-smoothed surface or by too pronounced or false-looking structure. Another phenomenon could be observed up to the 20th century, whereas it was a normal practice to coat not only the defected areas but also the surrounding original painting with filler. These overfillings are usually detected during the painting‘s surface cleaning and removing the varnish (very often the old retouching on top of the filler degraded and changed the color, therefore, it has to be removed for pictorial reintegration, and after the removal, the overfillings become visible). Unfortunately, these overfillings are thicker and harder than the original paint and, moreover, resistant and almost insoluble. The removal is therefore quite problematic; mechanical action is required, and sometimes the old fills could be swollen by solvent gels or aqueous solutions, also in gelled form (selected and controllable application). Commonly, glue-based fills without drying oils and resin components are relatively easy to remove. However, the greater the proportion of drying oils in the filling putty, and the older the filling is, the harder it is to remove. Pure oil filler that has thoroughly oxidized and polymerized, especially linseed oil-white lead fillings, can be removed from the original picture layer or from the defected area only with significant difficulty. However, these fillers become stone-like material and with a high probability cause or may in the future cause a lot of damage, whetherr they do not react flexibly with the surrounding paint and tensile streas exposed by the textile support.[9]

The theoretical and ethical principles of the work of conservators rapidly changed during the 20th century. Furthermore, the development of new synthetic materials on the market rapidly increased. These advancements led conservators to investigate and utilize new formulas for almost every part of the treatment process. Therefore, alongside discussions about the purpose and attitudes towards restoration (which significantly vary worldwide based on technical, scientific, social, and economic considerations), these new materials have allowed conservation to adopt a strategy of long-term but easily removable care for artworks. The principle of retreability

6 FUSTER LOPEZ, Laura. (2012). ‘Filling‘: in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings,* USA and Canada: Rouledge, ISBN 978-0-7506-8199-5, p. 586

7 CIATTI, Marco. (2010). *Le fasi finali nel restauro tra teoria e pratica, alcune riflessioni*, proceeding of Conference CESMAR7, Trento 2009 2010, Italy

8 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, pp. 21-22

9 NICOLAUS, Knut. (2005).“Filling“ in *Restoration of Painting*, Könemann, ISBN 3895089222, p. 253

has become a cornerstone of restoration requirements.[10] This attitude can also be observed in terms of filling.

In the latter part of the 20th century the process of filling became a topic of discussion. The principal theories were enhanced and slightly adjusted. In 1981, J. Green and J. Seddon presented the requirements of fillings at the 6th Triennial ICOM-CC Meeting in Ottawa. They pronounced[11] that „the chief purpose of the filling material is to effect a convincing repair, fully integrated with the paint surface, and that good filling is a prerequisite for good retouching." The criteria for fillings are as follows[12]:

- The filling must have good adhesion.
- It should have good working properties. It should be simple to prepare; if complicated, it should remain usable for some time, particularly if losses to be filled are large or numerous. It should have a suitable drying rate, neither too slow nor too fast.
- It should have strength and flexibility. If the filling is much more brittle than the support, it will not accommodate itself to slight movements. Ideally, it should have some plasticity and the ability to take a surface texture.
- It should have high stability under varying conditions of temperature and humidity. It must not crack or develop mould.
- It should have minimum shrinkage. This is especially important when texturing fills, as dramatic shrinkage on drying will cause the loss of a cast texture.
- It should be reversible but not too readily soluble; the restorer may wish to remove the varnish and retouching layer without disturbing good fillings.
- The porosity of the filler should match that of the surrounding area; otherwise, it may absorb varnish and retouchings differently from the original, becoming too matte or shiny. (This may be adjusted by applying an isolating layer before varnishing.)

These requirements are still adhered to when deciding on selecting the proper filling material. An important value, which was not properly discussed yet is the adaptability of the filling material to the tensile stress of the textile support of the painting. They must be able to withstand the stresses generated within the painting. This means that they must maintain a proper distribution of forces (Fig. 3). The presence of filling materials in the painting structure alters the normal distribution of forces, since the filler force (F2) is usually greater than the support force (F3) (Fig. 4). For that reason, if tensile forces are acting within a painting, both filler and canvas will behave in a different way, and the filler will contract. A very weak or excessively flexible filler can also cause out-ofplane deformation. Therefore the filling material must be as stiff as old paint, to maintain proper in-plane continuity.[13]

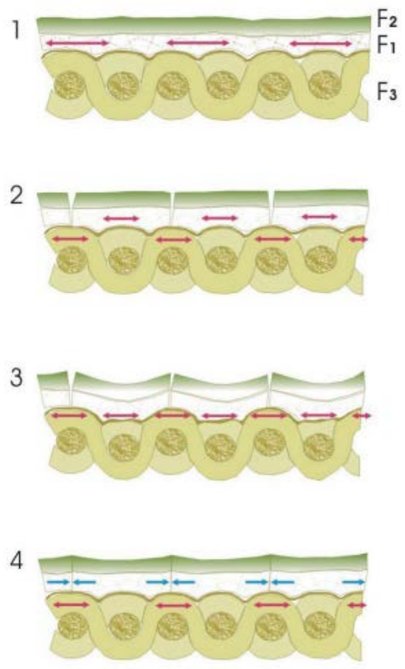


Figure 3: Location of the geometric centre of forces in a painting:
(1) prior to cracking of ground and paint film;
(2) force relocation immediately after cracking of ground and paint film
(3) force realignment displacing all layers out of picture plane, causing'cupping';
(4) forces in unrestrained painting in low RH: the glue is in tension whereas ground and paint layers are in compression
source: Fuster-Lopez, L., et. al, (2008):181

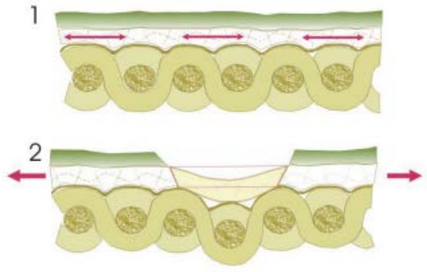


Figure 4: Location of fillers in the structure of a canvas painting:
(1) geometric centre of forces in a painting;
(2) different behaviour of filler and paint under tension
source: Fuster-Lopez, L., et. al, (2008):181

Therefore, according to the studies of tensile stress and its influence on the filling material, the required properties could be further referred as follows:

- A strong and resistant filler is required, ensuring strong cohesion and adhesion. Adequate internal strength is essential to prevent cracking and failure. It must effectively adhere to the textile support and other materials within the painting.
- Moreover, achieving dimensional stability is crucial, especially considering the limited response of old paints to fluctuations in temperature or relative humidity.
- During the drying process, it is essential that the material maintains its integrity without cracking, indicating sufficient cohesion. Additionally, preventing the formation of lumps or air bubbles in the mixture is equally important to avoid surface irregularities that could lead to fissures and eventual cracking.

Additionally, the successful infilling hinges on several factors[14]:

- Ensuring compatibility of the filling materials, including assessing their chemical, physical, and mechanical properties, with both the original materials of the artwork and those to be used in subsequent conservation treatments.
- Prioritizing the ease of removal of the filler without causing damage to the paint film.
- Pre-determining the methods and materials for final retouching and varnishing before selecting the fill materials. For instance, not all fillers may lend themselves to carving for achieving specific textures, or they may not be compatible with aqueous retouching techniques.

1.1 CRITERIA FOR SELECTION OF THE FILLER IN PRACTICE

Traditionally, filler is composed from an inert filling (or bulking) material and adhesive binding material, so-called medium. There is a huge number of these materials available on the market. The considerations and criteria for the choice between all the possibilities were already described in a previous chapter. But can be summarised as below.

REVERSIBILITY

It has been emphasized on numerous occasions that the filler must be reversible, or rather, removable without causing damage to the painting. This is currently a fundamental principle of the restoration treatment in any part. Ethically, any material applied to the artwork that could hinder or impede future actions or treatments should be avoided. Components of the filler may degrade over time, and unfortunately, every material will degrade to some extent at some point. It is also possible that the filler will no longer meet the requirements of the loss. Therefore, reversibility or removability is imperative for successful infilling work.

COMPATIBILITY WITH THE ORIGINAL MATERIAL

The filling materials must be compatible not only with the original materials of the artwork but also with the materials used for the restoration treatment. This applies to the mechanical, physical, and chemical properties of both the binder and inert material of the putty. The selection of the fill should be carefully considered in relation to the selection of inpainting and varnishing materials before application.

ABILITY TO ADJUST TO ENVIRONMENTAL CHANGES

The materials used to formulate and mix the filler should not be overly responsive to environmental changes or the strains and forces in the laminate structure of the artwork. Otherwise, it could cause premature damage to either the fill (such as cracking and crumbling) or the loss of adhesion to the surrounding area.

These criterias indicate in general the required properties of the filler which should be considered[15]:

- The viscosity and flow properties of the filling material, and the compatibility of the solvents required with the original materials to adjust these properties if needed;
- The drying or curing time;
- The flexibility, and whether this changes over time when exposed to environmental changes;
- The short- and long-term stability (its aging properties);
- The reversibility/ease of removal;
- The degree of shrinkage or expansion on drying/curing;
- The ease of surface manipulation (carving or imprinting);
- The ease of application;
- The colour (and ease of adjustment of the colour);
- The pH on application;
- The weight, and whether this can be adjusted;
- The compatibility of the fll with the original materials of the artwork, and with other conservation materials required;
- The surface gloss and texture (and ease of adjustment);
- The application temperature (if relevant);
- The Tg of the adhesive component;

Before delving into detailed information about the materials used for mixing fillers, a brief note on terminology is necessary. In the thesis as well in the conservation field a term filler, infilling, fill and putty is often used, as well as gesso. The term gesso traditionally refers to an animal-glue bound ground containing calcium sulfate or gypsum. In fact, gesso literally means gypsum. However, mainly in Italy and also for some art suppliers (commercially produced fillers such as BEVA-P Gesso) this term also refers to filler. The distinction between „filler" and „putty" varies across sources. Generally, based on definitions from non-conservation resources, „filler" is used for filling gaps and holes in walls and wood, often in decayed wood, while „putty" is used to smooth relatively small uneven surfaces caused by screw holes, scratches, or coarse materials[16]. Unfortunately, in the conservation field, exact terminology is lacking, and it

10 ALTHÖFER, Heinz. (1981). *Historical and ethical priciples of restoration*, ICOM Committee for Conservation 6th Triennial Meeting, Ottawa, Canada

11 However, their thesis based on much older theories for example pronounced already in 1780s by Pietro Edwards.

12 GREEN, J., SEDDON, J. (1981). *A study for materials for filling losses in easel paintings, and their receptiveness to casting the textures,* ICOM Committee for Conservation 6th Triennial Meeting, Ottawa, Canada

13 FUSTER LOPEZ, Laura, MECKLENBURG, Marion F., CASTELL, M., and GUEROLA, V. (2008). „Filling materials for easel paintings: when the ground reintegration becomes a structural concern." in Preparation for Painting: The Artist's Choice and its Consequences, edited by Townsend, J. H., Doherty, T., Heydenreich, G., and Ridge, J. London: Archetype Books, p. 181

14 FUSTER LOPEZ, Laura. (2012). 'Filling': in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings,* USA and Canada: Rouledge, ISBN 978-0-7506-8199-5, p. 587

15 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 24

16 https://www.ncbi.nlm.nih.gov/books/NBK563309/ [15/05/2024]

often depends on the particular author or art material producer or supplier. Moreover, the term „filler“ encompasses materials used as bulking agents added to polymers for various reasons, such as extending, increasing strength and hardness, adjusting viscosity, and enhancing resistance to flow. In this thesis, the terms „filler,“ „fill,“ „infilling,“ and „putty“ all refer to the same material composed of an inert bulking agent and a binding medium.

1.2 BULKING AGENTS

In general, the requirements of bulking agents are their inertness, particle size (which determines the amount of material that could be incorporated), weight, hardness, colour, availability and compatibility with the substrate. It usually tends to be an inexpensive mineral in powder form, which is also used by artists as part of the fabrication of artworks.
The most commonly used bulking agents for putty were chalk and gesso (hydrated calcium sulfate). It was possible to obtain chalk in a variaty of qualities, with or without a presence of impurities. A number of additives were included in the filler or putty, such as pigments (lead white, zinc white, earth pigments) or other materials which could (but not always) change the properties of the resulting filler (pumice, talcum, barium sulphate). Lately, during the second half of 20th century and till now, another types af material begun to be used, such as kaolin, aluminium hydroxide, silica and fumed silica, arbocel powder, glassfibers (crushed glass), glass of phenol micro-balloons, etc. Not all available bulking agents were chosen for the study described in this thesis. The selection was made considering European historical and present practices with the aim of showcasing the variety of products available on the European market and especially in the Czech Republic.

CHALK

Chalk (often in literature reffered as whiting) is a form of limestone, mosty komposed of of tiny fragments of the calcite shells or skeletons of plankton, such as foraminifera or coccolithophores. Chalk is typically almost pure calcite, $CaCO_3$, with just 2% to 4% of other minerals. These are usually quartz and clay minerals, though collophane (cryptocrystalline apatite, a phosphate mineral) is also sometimes present. In some chalk beds, the calcite has been converted to dolomite, $CaMg(CO_3)_2$, and in a few cases the chalk called Lime white has been dedolomitized back to calcite.[17]
Chalk is stable to light exposure and is not affected by atmospheric conditions. However, this mineral is affected by acidic environments an in such condition it will decompose, producing carbon dioxide CO_2. It is insoluble, but will swell in water.
It is a highly porous, fine-textured and soft material. Depending on the impurities, amount of clay components and mineral content as well on the place of origin, there are various types of chalk.

Lime white

This type of chalk is mainly used in Central Europe, especially in the Czech Republic, under the name *plavená křída*. Historical filler recipes mostly include this type of chalk, and it is still widely used today.
The name ‚Lime white‘ refers to the origin of the limestone from which it is produced. It is obtained by melting and slaking dolomitic minerals, which are a double carbonate of calcium and magnesium. In fact, the mineral composition falls approximately within this values[18], although it may vary slightly: $CaCO_3$ 51%
$MgCO_3$ 40%
Mg 12%


Figure 5: Lime white

Champagne chalk

The name of this type of chalk, sometimes referred to as chalk from Champagne, refers to its place of origin - Champagne in France.
It is prepared from almost pure, microcrystalline chalk, although it contains small amounts of other minerals: $CaCO_3$ 98%
$MgCO_2$ 0.5%
Fe_2O_3 ..... 0.2%
HCl, insoluble 1.2%
It is a very fine type of chalk with middle particle diameter (D50%) 2.4 µm and 42% content of practicle lower than 2 µm.[19]
This type of chalk is very often used as a filler in western Europe and USA.

Chalk from Ruegen

Like Chalk from Champagne is chalk from Ruegen a natural chalk consisting of particles of calcium carbonate of fossil origin. Chalk from Ruegen is slightly coarser and more grayish than Chalk from Champagne.
This chalk is obtained from cliffs in Ruegen, an island in north Germany. The sedimented fragments of the thin-shelled calcareous housings formed the solidified carbonated chalk, which is visible to everyone in the form of the Jasmund chalk coast.
The content of mineral is as follows: calcium carbonate $CaCo_3$ ..... 97 %
silicon dioxide SiO_2 ..... 1,0 %
iron-III-oxide Fe_2O_3 ..... 0,1 %
sulfur trioxide SO_3 ..... 0,2 %
HCl insoluble ..... 1,0 %
The crystallites from 0.3 - approx. 40 µm grain size are usually isometrically shaped and form microporous aggregates.[20]

17 JACKSON, Julia A., ed. (1997). „Chalk“. in *Glossary of geology,* 4th ed. Alexandria, Virginia: American Geological Institute. ISBN 0922152349

18 https://www.sciencemadness.org/talk/viewthread.php?tid=28796 [25/04/2024]

19 Values specification in detailed information of products by Kremer Pigmente GmbH & Co. KG up to date 05/2024: https://www.kremer-pigmente.com/elements/resources/products/files/58000e.pdf

20 Values specification in detailed information of products by Kremer Pigmente GmbH & Co. KG up to date 05/2024: https://www.kremer-pigmente.com/elements/resources/products/files/58010.pdf

Bolognese chalk

The type of chalk known also as Chalk of Bologna is a natural mixture of calcium sulfate (gypsum) and calcium carbonate. The composition of these products may vary in terms of gypsum content, which primarily comprises calcium sulfate. Gypsum is a naturally occurring sulfate mineral. It is formed in nature by precipitation during evaporation of seawater, which naturally contains 0.13% slurried gypsum. Extracted in its raw form as gypsum stone from open-pit mines, it is then transported to designated production facilities for industrial processing.
Bologna‘s urban history is deeply intertwined with gypsum, showcasing the close connection between the city and this mineral. Situated near gypsum outcrops, Bologna utilized this stone extensively in its architectural endeavors. Indeed, the city‘s initial fortifications were constructed using gypsum blocks. However, significant mining activities emerged towards the late 19th century and intensified post-World War II, posing environmental threats to the karst landscape. Consequently, in 1973, the gypsum quarries were closed for this reason.
The mineral content of this particular type of chalk is as follows:


Figure 6: Chalk of Bologna

calcium carbonate $CaCO_3$ ..... 48,37 %
calcium oxide CaO ..... 16.98 %
sulfur trioxide SO_3 ..... 23,45 %
silicon dioxide SiO_2 ..... 0,86 %
aluminum oxide Al_2O_3 ..... 0.34 %
iron-III-oxide Fe_2O_3 ..... 0,12 %
magnesium oxide MgO ..... 1.07 %
bentonite ..... 0.90 %
water ..... 7,91 %

The grain size of this chalk type is 30 - 40 µm. Additionally, Kremer Pigmente offers another product known as Chalk of Bologna, Light, with a grain size of 50 - 60 µm.[21]

Bolognese chalk was widely used historically especialy in Itally, even in medieval times, for gesso layers in gilding panels and polychrome sculptures. Its hardness and ability to be ground to a smooth surface were essential for applying giding.

Additionally, various types of chalk are available on the market that can be used as fillers, including stone chalk, Belgian chalk, or mountain chalk.

Gypsum

Gypsum has also been widely used in the past as a filler, and it remains a bulking component today. It is named calcium sulphate or calcium suphate dihydrate ($CaSO_4.2H_2O$) in chemical term. However, in conservation practice terms such as gesso, alabaster, gilder‘s whiting or Plaster of Paris are used. It may contain impurities such as quarz or selenite, which depends mainly on a place of origin. It is important to note that when mixed with gypsum, the mixture does not shrink upon setting; instead, it expands slightly, because the unhydraged gypsum swells in the water as it absorbs moisture. Therefore, its use should be avoided for closed or limited voids[22].

Particle size, the presence of additional minerals, and compatibility with water and solvents are important factors to consider when selecting a bulking agent. Furthermore, it is possible to blend different types of chalk together, depending on the desired qualities and properties of the filler the conservator aims to achieve. Conducting tests before the actual infilling of the original painting is recommended. Moreover, not all suppliers of artistic materials offer the same products. Last but not least, pure calcium carbonate is also a viable option.

Calcium carbonate

Calcium carbonate is a naturally occurring product derived from calcite, aragonite and vaterite, but could be also processed by chemical reaction called carbonation from calcium oxide or could be obtained by crystalization of calium chloride[23]. It is therefore nearly free from any impurities. The calcium carbonate content ranges from 98.5% to 100.5%. The particle size for 97% of the product is a maximum of 18.0 µm. Calcium carbonate is a white, odorless, and insoluble powder. The whiteness value falls within the range of 97.3% to 99.3%. However, the loss on drying is ≤ 2.0%[24], which could be increased or decreased depending on the specific medium of the filler. However, in the restoration field calcium carbonate is often used as a comprehensive term for any type of chalks. The pure calcium carbonate is often quite expensive when compared to the other types of bulking agent. Moreover, based on the trials I conducted, shrinkage occurred with the filler containing only calcium carbonate. Therefore, I would recommend mixing the powder with another type of chalk.


Figure 7: Calcium carbonate

KAOLIN

Kaolin, sometimes refrered as China clay, is hydrated aluminium silicate $Al_2H_4O_9Si_2$ with clearly definable crystal lattice of plate-like, hexagonal structure. It naturally contains admixtures such as traces of quartz, muscovite, magnetite, etc.

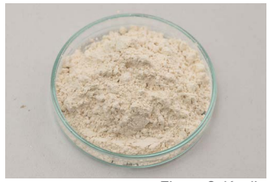
21 Values specification in detailed information of products by Kremer Pigmente GmbH & Co. KG up to date 05/2024: https://www.kremer-pigmente.com/elements/resources/products/files/58100-58150e.pdf

22 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*. Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 32

23 https://web.archive.org/web/20140111165543/http://www.lime.org/uses_of_lime/other_uses/precip_cc.asp [14/05/2024]

24 Values specification in detailed information of products by Kremer Pigmente GmbH & Co. KG up to date 05/2024: https://www.kremer-pigmente.com/elements/resources/products/files/58490e.pdf

It usually represents pure, iron-free clay, developing through the decomposition and transformation of silicate rocks. Kaolin derives its name from the Kaoling Pass in the Chinese province of Kiangsi, where it was first discovered. The earliest sites of its discovery, in the 18th century, were in Germany at Aue and Hafnerzell; in France at Limoges; in England in the province of Cornwall; in Italy at Vicenza; and in Denmark on Bornholm.
Its relatively low reflectivity results in off-white mixtures with most binders and a slight translucency. It is available on the market in both slightly yellowish-toned powder or whitened forms. The practical size distribution is > 45 µm at 0.03% and < 2 µm at 51%.[25]
Additionally, other types of clay could be used, such as pipe clay and bole (a very refined, fine clay).
Kaolin may be used as the sole bulking agent, but it can also be added to another one. It helps to smooth the filler after drying, due to its ability to compact the filler components and make them less porous and absorbent. In the Dutch brochure *Filling Losses in Paint*[26], it is suggested that only a small amount, up to 10-15%, of kaolin could be added to the bulking materials mixture. The reason is that kaolin expands up to 15% when it is in contact with water. However, depending on the specific application and the nature of the original painting, it is possible to use kaolin as the main bulking agent as well. These kaolin fillers should exhibit less ‚ghosting' (blanching) than other materials. This happens due to the very close refractive indices of kaolin and many retouching media or synthetic resins used for surface coatings and varnishes. The refractive indices of other inert minerals used as compounds of bulking agents differ considerably from the retouching media and, therefore, appear opaque.


Figure 8: Kaolin

ALUMINIUM HYDROXIDE
Alumina, also known as aluminium(III) oxide or aluminium hydroxide, refers to a white crystalline powder chemically described as Al_2O_3. It is solled by several art suppliers as aluminium hydroxide/oxide (such as Kremer Pigmente GmbH & Co. KG, C.T.S. Conservation, etc.) and is also available commercially under the name Portafil® A40 by Sibelco company. It is demanded to be a more stable version of aluminium hydroxide[27]. It is widely used in different field. For example in the paint industry as a whitener to latex paints, in combination with unsaturated polyester resin or methacrylic resin is used to produce artificial agate or artificial marble, or due to its inertness also a a filler for toothpastes[28]. Aluminium hydroxide became popular as a bulking agent for commercial fillers, such as Polyfilla Fine Surface[29], as well the one prepared in studio.


Figure 9: Aluminium hydroxide

SILICA
Silicon dioxide SiO_2 is a white powder often found as a natural impurity of calcium minerals. When bonded in a medium, it produces a semi-translucent color. [30]. It is frequently added to filling materials to increase flexibility of the filler[31]. Towards the end of the 20th century, fumed silica was also explored as a matting agent for coatings and a bulking agent for paints and fillers[32]. Based on the trials I conducted, fumed silica produced significant shrinkage in all tested binding media; therefore, its use is not recommended.

GLASS and PHENOLIC MICROBALLOOS
These lightweight fillers became widespreadly used towards the end of the 20th century. Glass microballoons are made of hollow spheres composed of glass, typically borosilicate glass. Phenolic microballoons are composed of hollow spheres made from phenolic resin, a type of synthetic polymer. Their average size ranges between 46 - 200 µm, depending on the specifications of the particular product. They may be added to ground layers or primers for surfaces, as well as to fillers. Different grades are available.[33] The advantages include their inertness, lightweight nature, and reduced shrinking on drying, among others. Nowadays, they are mostly used as bulking agents for fillers for panels and polychrome sculptures. Ococianally, they are also applied to fillers for canvas painting; however, they were not included in this study.

ARBOCEL®
Arbocel is a trademark for cellulose fibers. It is a fluffy powder made of cellulose, available in different grades. Primarily, it is used as an inert filler for putties in artworks made of wood (panels, polychrome sculptures) or paper. It produces a lightweight filler, often mixed with another bulking agent, such as calcium carbonate. It maintains its hydroscopicity and therefore acts also partialy as a binder.[34]
CELLULOSE ETHERS
Cellulose is a homopolymer composed of glucose and can be considered a polyhydric alcohol (each glucose unit contains a primary alcohol group and two secondary alcohol groups). The reaction leading to the formation of cellulose ethers takes place incompletely, therefore, only a limited number of alcohol groups are alkylated. Depending on the desired properties, each polymer is determined not only by its chain length or degree of polymerization but also by the degree of substitution. Cellulose ethers, also known as alkyl cellulose, can be divided into ionic (e.g. carboxymethyl cellulose) and non-ionic derivatives (described in Table 1), which include many products used in conservation as consolidants, adhesives, and thickening agents. Although they appeared on the market in Germany in the 1920s and later in the USA, they were introduced to the conservation field in the 1970s[35]. Due to the complexity and length of chemical names, abbreviations are usually used to identify the different classes. They are produced by various manufacturers under more or less the same names. The properties of these polymers can be summarized as follows: thermoplasticity, non-stickiness (even at high humidity), high (but adjustable) viscosity of solutions, neutral pH of aqueous solutions, surfactant properties of solutions, thickening capacity, and absolutely non-toxic nature.[36] In Table 1, the commercially trade products are dedived into cathegories in order to its chemical basis and the trade name.
In addition to their application as consolidants or (low) adhesives, these materials could also be used as bulking agents for fillers. They could be added to the filler's formula for several reasons. They help maintain water solubility and can improve the properties of each filler[37] since they obtain also a binding funcion, such as better handling properties and adjustment of the viscosity of originally more liquid fillers, allowing for superficial insertion.

chemical name	acronym	trade name	producer
carboxymethylcellulose - sodium salt	CMC	Tylose C Cellofas	Hoechst ICI
methyl hydroxyethyl cellulose	MHEC	Tylose MH	Hoechst
methylcellulose	MC	Glutofix Tylose MB Methocel A Cluminal MC Benecel A	Hoechst Dow Aqualon®Hercules
ethylcellulose	EC	Ethylcellulose Ethocel	Aqualon®Hercules Dow
hydroxypropyl cellulose	HPC	Klucel G Klucel H Klucel E	Aqualon®Hercules
methyl hydroxypropyl cellulose	MHPC	Culminal MHCP	Aqualon®Hercules

Table 1: Cellulose ethers available on the market used in the conservation field
source: Cremonesi, Paolo, (2019): 164

PIGMENTS
It is possible to add pigment to a filler's formula both as the sole bulking agent and as a combination to another material. This will provide the tint or color of a ground layer or underpainting of the painting, simplifying the subsequent retouching process. Alternatively, if a colored filler is required (for example, for modern paintings or infilling in the monochrome background of a painting), the filler could be colored to match the surrounding area, eliminating the need for retouching. It's important to note that different pigments will absorb the media differently, and some types of pigment are excessively hygroscopic (indigo, cobalt chloride).
Anyway, it's always good to keep in mind the extensive discussions surrounding colored fillers, particularly whether their use is required, as they could make it more difficult to distinguish them from the original painting. For that reason, it's another question that should be taken into account when decisions are made.

1.3 BINDING MEDIUM

There is a wide range of binding media that could be used for fillers. Some of them are still present in current practice in the same or similar way as they were utilized in history. Some are relatively new and appeared in production during the 20th century. It is possible to use them in different ways and combinations. The following chapters will be dedicated to each ‚family' of both natural and (semi-) synthetic adhesives, providing a description of their chemical properties along with insights into conservation application and accelerated aging of the products.
Not all available binding media were chosen for the study described in this thesis. The selection was made considering European historical and present practices with the aim of showcasing the variety of products available on the European market and especially in the Czech Republic.

1.4 COMMERCIAL READY-TO-USE PUTTIES

It must also be noted that, since the 1980s, various synthetic and commercially prepared materials were rapidly developed thanks to technological and scientific research. Numerous new materials have become available for industrial usage and rapidly modified also for conservation field. These commercial putties were specially designed for filling, modeling, and imitating impasto textures. Therefore, alongside studio-prepared fillings, commercial putties are available on the market too. However, the exact composition of these materials is usually unknown, although they have been tested several times in various studies[38].

Current commercial putties could be divided into two categories[39]: putties specially created for conservation purposes and those imported from other fields. There is a wide range of different companies producing these putties. Some of them are formulated similarly to traditional glue fillers, composed of hide glue and inert materials, but also contain preservatives that enhance their long-term use. First commercial fillers especially designed for conservaation field were from the CPC Conservation in 1997, based on BEVA 371 and vermiculite, sold in two variants BEVA Gesso-P and BEVA Gesso-V, therefore refered as vinyl resin fillers[40]. In the 1990s, DAP Vinyl Spackling, Polyfix and Polyfilla (based on microcrystalline waxes) became popular, these are the axaple of fillers imported from other fields - bulding supply and household technical equipment markets. However, as they are no longer in production, the commercial

25 Values specification in detailed information of products by Kremer Pigmente GmbH & Co. KG up to date 05/2024: https://www.kremer-pigmente.com/elements/resources/products/files/58250e.pdf; and https://www.kremer-pigmente.com/elements/resources/products/files/58200e.pdf

26 BURG, Julia M. Van den, SEYMOUR, Kate, 2024, *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 50

27 https://coatings.sibelcotools.com/wp-content/uploads/2017/03/Portafill-A_TDS_12-2015_EN.pdf [27/04/2024]

28 https://www.linkedin.com/pulse/use-aluminum-hydroxide-filler-jim-zhai [13/05/2024]

29 Safety data sheet of Polyfilla within the information about the content of aluminium hydroxied available on: https://plascon.co.za/wp-content/uploads/2022/04/polycell_polyfilla_interior_sds.pdf [13/05/2024].

30 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 33

31 FUSTER LOPEZ, Laura. (2008). *El estuco en la restauración de la pintira sobre lienzo: criterios, materiales y procesos,* Spain: Universitad Politecnica de Valenciax, ISBN 978-84-8363-221-5, p. 99

32 BAILAO, A. CARDEIRA, L. (2017). *Mixing ans matching. A survey of retouching materials*. RECH4 Postprint, 4th International Meeting on Retouching of Cultural Heritage, Croatia, pp. 248-255

33 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 33

34 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, pp. 33-34

35 The evaluation of stability and potential possible usage in conservation field was tested by several researches. One of the important study was conducted by R. L. Feller and M. Wilt published in 1990 by Gety Conservation Institute: *Evaluation of Cellulose Ethers for Conservation.*

36 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substences used in restoration: Cellulose ethers", in *The synthetic resins used in the treatment of the polychrome works of art,*De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 163-170

37 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 34

38 For example, one of the firSt study was conducted already by Seddon and Green in 1981 (*A study for materials for filling losses in easel paintings, and their receptiveness to casting the textures,* ICOM Committee for Conservation 6th Triennial Meeting, Ottawa, Canada) or one of the recent comparative studies conducted by Laura Fuster-Lopez et al (*Filling materials for easel paintings: when the ground reintegration becomes a structural concern)* in 2008.

39 FUSTER LOPEZ, Laura. (2012). 'Filling': in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings,* USA and Canada: Rouledge, ISBN 978-0-7506-8199-5, pp. 593-594

40 CRAFT, Meg, Loew, SOLZ, Julie, A.. (1998). *Commercial vinyl and acrylic fill materials*, Journal for American Institute for Conservation, JAIC, vol. 37, pp. 23-34

formula CSS Filler (Conservation Support System, USA) was designed to substitute them. It is based on polyvinyl acetate dispersion with calcium carbonate. Similar products include Moltofill (Molto, Germany), Becker Latexspackel (Beckers, Sweden), Flügger Acrylspalter (Flügger, Denmark), Do It Best Lightweight Spackling (Do It Best, USA), Blumestukko (Rayt, Spain), and Modostuc (Plasveroi, Italy), among others. A recent trend in industry and conservation is to partially or completely replace any bulking agent (natural ones could content impurities, which may influence the inertness, see above) with one-hundred-percent inert materials - hollow glass microballoons or other silicate particles.The advantages also include their lightweight nature, non-absorption of moisture, and therefore no shrinkage of the filler during drying, easily tooled, sanded, or burnished. Despite all the advantages of ready-to-use commercial putties and their worldwide use, the lack of information about the exact composition and additives may be problematic. Furthermore, recent studies have demonstrated structural deficiencies and RH-related dimensional instability in many of them. Taking into account all this information and disadvantages, commercial ready-to-use putties were not included in this study.

2. METHODOLOGY OF EVALUATION OF ACCELERATED AGING TESTS, CRITERIA AND THEIR COMPARISON

Based on the key properties and requirements of infilling materials for painting on textile supports described in previous chapter, a methodology for evaluating particular filler formulas was fabricated. Four mock-ups, each with a different filler composition, were prepared. Each filler was applied to every mock-up in the same manner and from the same batch. The selection of filler formulas was made after examining different materials used worldwide, especially in Europe. Each binding medium was mixed with severalbulking agents and their combinations, especially those commonly used in the Czech Republic and Western Europe. The mixtures were applied in the same manner to four mock-ups made of canvas supports. The canvases were stretched on stretchers, whether three of them were prepared from new canvas, pre-washed and isolated with a 5% gelatine solution in distilled water.
One mock-up consisted of an old canvas previously used as a lining canvas for war-resin lining, with residues of adhesives present. The choice of these canvas supports aimed to simulate both a new canvas that could be inserted in tears and losses in a painting support, as well as the imitation of an old painting canvas that underwent previous historical treatments, such as consolidation or lining with wax or resin adhesives.

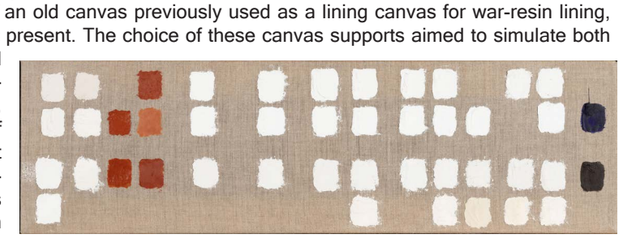
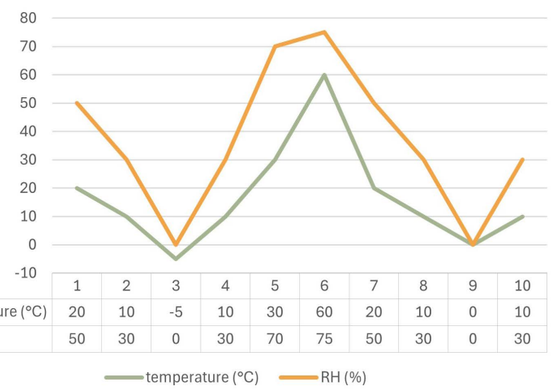




Figure 10: Mock-ups prepared for accelerated aging tests; new canvas (left) and old canvas with wax-resin linging adhesive residues (right)

The aim of applying fillers was to create both thin and thick layers, as the character of the particular losses could vary. All fillers were applied using spatulas and slightly smoothed. The thick layers were applied in one step, but this approach was later found to be unadequate. Some of the fillers may exhibit better properties when applied in several thin layers using spatulas or brushes. Unfortunately, there was no time left to make changes or prepare new mock-ups. However, for any future repetitions or revisions of the trials, it is recommended to consider using a drawdown bar for equally thin-layered fillers and a gradation bar for equally gradient layer films of filler. This would ensure equal starting conditions for each filler.

The first mock-up was enclosed inside a black box where no daylight could reach, and stored in a very stable environment without significant fluctuations (20°C and 50% RH). The second mock-up was placed on a table in a restoration studio next to a window for approximately three months. In the studio, the temperature and relative humidity slightly varied over time, with some fluctuations occurring (18-26°C and 40-60% RH). Daylight efflorescence naturally within the UV radiation was occasionally present, as indicated by the weather conditions. The third and fourth mock-ups, one made of new canvas and one from the old canvas with wax-resin lining adhesive residues, were placed in an environmental chamber. The program for changing humidity and temperature was designed to simulate possible changes experienced when paintings are exposed in households, churches, castles, or other environments where humidity and temperature conditions are not stable. Based on documentation of environmental conditions in churches, temperatures could drop below freezing point, while exposure to direct sunlight through window glass could raise temperatures up to 65-70°C. Relative humidity varies in response to temperature changes.[1]
Both mock-ups subjected to accelerated aging tests were exposed in an environmental humidity chamber for 52 days, equivalent to 1248 hours. Graph 01 illustrates the process of one cycle, which took approximately 20 hours. After the finish of one cycle step change to the first phase of program followed. Therefore, the mock-ups underwent 62 cycles.



	1	2	3	4	5	6	7	8	9	10
temperature (°C)	20	10	-5	10	30	60	20	10	0	10
RH (%)	50	30	0	30	70	75	50	30	0	30

Graph 01: One cycle in environmental chamber

1 Information based on the lecture by klimatolog ing. Jan Červeňák, took place in AVU for students of restoration 6. 3. 2024. An example of paper published by Červeňák refaring to the relative humidity in historical buildings „Údržba památkových objektů“ webinary by *Společnost pro údržbu památkových objektů*, pp. 57-62.

Afterwards, each sample was examined and compared within the ‚unaged‘ sample stored in a black box in a stable environment, a sample exposed to light efflorescence within UV radiation, and two samples (one on a new canvas and one on an old canvas) exposed in the environmental chamber. The properties examined within the testing method are described in the following paragraphs and reported in tables dedicated to each filler‘s composition at the end of the chapter referring to the particular binding medium (chapters 3.2-3.10). Furthermore, each sample was documanted before and after aging process by captures of macrophotopraphs in day and raking light. These pictures are also placed in the tables for particular visual copmarition.

DRYING DIMENSIONAL CHANGE

The filler samples were observed during and directly after the drying process. It was examined whether the filler lost any dimensions in terms of weight and height, whether the material cracked or shrank due to solvent evaporation, and whether the textile support it was applied on warped or deformed. The results were compared among samples applied on stretched or free textile or a Melinex sheet. The dimensional change was further compared between thin and thick layered fillers and among different types of bulking agents used for the particular binding medium.

COLOUR CHANGE

The surface of each sample was measured using a portable spectrocolorimeter RM200QC. This device measures and compares values by capturing 27 images of different colours and angles using eight different light sources and one UV LED. Each unaged filler sample was measured first as a standard (Fig.12a), which was then compared with the appropriate filler sample exhibiting light efflorescence within the UV radiation and samples that underwent the accelerated aging process (Fig.12b). The values recorded in the tables are based on a tolerance set to a ΔE limit of 2.0, where ΔE refers to colour deviation measured using all several methods: CIE Lab, CMC, CIE94, and 2000. The resulting values are indicated on axes L* (brightness), a* (green-red axis), b* (blue-yellow axis), and C* (glossiness).[2] For every sample, three measurements were captured, and the average value is indicated in the tables.



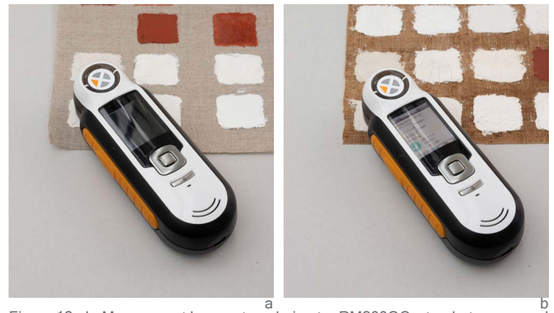
Functions L*a*b*C*H* provides precise values of the differences between sample and standardized color.

Verbal description of colours aids understanding to the type of colour variation.

Samples measurment which displays an alert, whether the paint has passed the test or failed.

Colour diagram shows the difference between the standard and sample.

Figure 11: Spectrocolorimeter measurments explanation source: https://elcometer.cz/fileadmin/user_upload/X-Rite_RM200QC_02.pdf [cit. 10/05/2024]



a b

Figure 12a,b: Measurment by spectrocolorimeter RM200QC; standart on unaged sample (a) and sample which underwent accelerated aging process (b)

CRAQUELURE

The macrophotographs of filler samples captured after application and drying were compared with the same samples which underwent the aging processes, including exposure to light efflorescence and accelerated aging in an environmental chamber. The extension, shape, and depth of the filler‘s crackle were examined and compared to determine if they occurred within a wider range, which raises questions about the amount and range of dimensional change during the aging process. The differences between thin and thick layered fillers were analyzed and described in tables.

SURFACE DUSTING

The surfaces of each sample were individually examined and compared between the unaged samples and samples that underwent exposure to light efflorescence and accelerated aging in an environmental chamber. More specific information was evaluated by the mechanical action. The surface of each filler was gently brushed with a black cotton swab (ten times rotation), which was then observed under the microscope. The amount of residues was examined and described in tables. The black cotton swab effectively simplified the observation, especially since most of the fillers are in white tones.



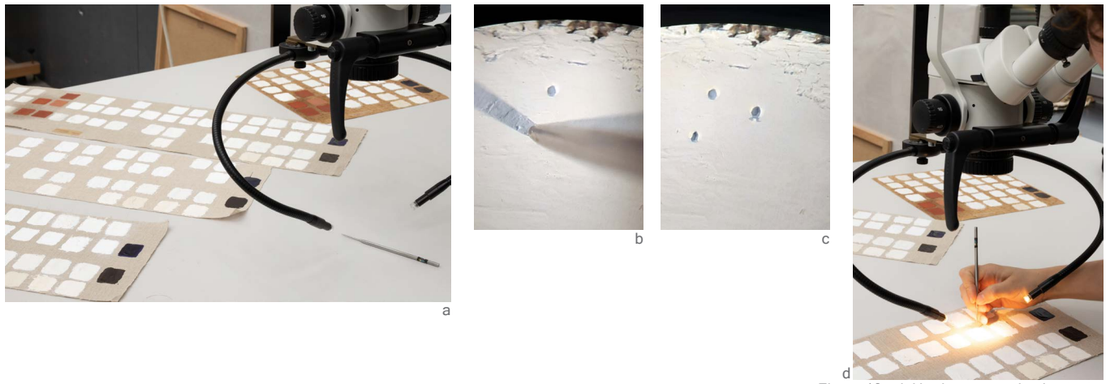
a b c d

Figure 13a-d: Examination of surface dusting of each sample by black cotton swab under the microscope; process (a), observation under microscope (c,d), comparison between unaged and aged samples (c)

2 Information indicated in a technical sheet of the device, available on: https://www.elcometer.cz/fileadmin/user_upload/X-Rite_RM200QC_02.pdf.[10/05/2024]

HARDNESS

The hardness of each filler sample was compared between the unaged samples and samples that underwent exposure to light efflorescence and accelerated aging in an environmental chamber. The change and diversity of hardness were evaluated using a test based on the system of The Rockwell hardness tester. Since many school studios and common practices do not dispose within this device, I personally conducted the test. A slightly blunted dental needle was used to make a dimple in the surface of each filler, and the pressure required for the action and the depth of each dimple were compared within thin and thick layered filler samples. Approximately ten measurements were conducted on each sample, and the results were evaluated by averaging the features of each action.

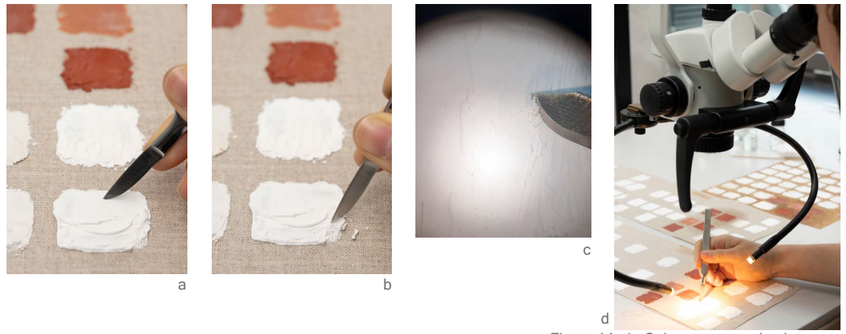


a b c d

Figure 13a-d: Hardness examination tests;
preparation (a), process (d), work and observation under the microscope (b,c)

COHERENCE

The samples were examined to assess whether the filler materials are losing cohesion and integrity, and to what extent. Each sample was observed under the microscope while mechanical action was conducted using a scalpel. The extent of powdering, crumbling, and segregation of the materials caused by the lack of cohesion and degradation of binding media was compared between the unaged samples and samples that underwent exposure to light efflorescence and accelerated aging in an environmental chamber. However, it is important to note that some degree of mechanical removal of the filler is necessary for future treatments and optional removment of the filler.

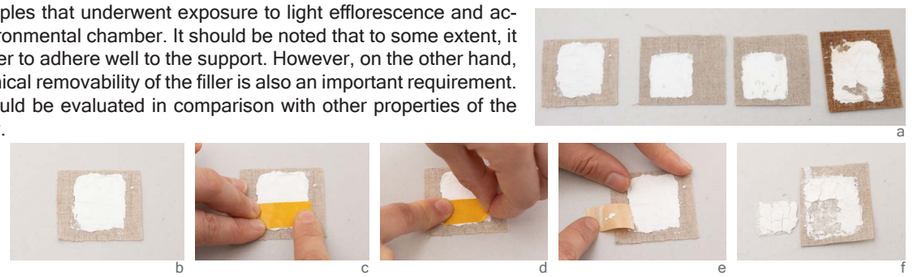


a b c d

Figure 14a-b: Coherence examination tests
copmarition of hardness between unaged (a) and aged sample (b), process of work under the microssope (c,d)

ADHESION TO THE GROUND

For evaluating the adhesion of the filling material to the textile support, a Scotch Tape Test was chosen. This test is considered as an extreme method for determining the degree of adherence of the filler to the textile support. A piece of tape is applied and adhered to a section of the filler, and then gently pulled off. The mechanical stability and delamination of the filler were compared between the unaged samples and samples that underwent exposure to light efflorescence and accelerated aging in an environmental chamber. It should be noted that to some extent, it is a requirement for the filler to adhere well to the support. However, on the other hand, easy and effective mechanical removability of the filler is also an important requirement. Therefore, the results should be evaluated in comparison with other properties of the filler, including reversibility.

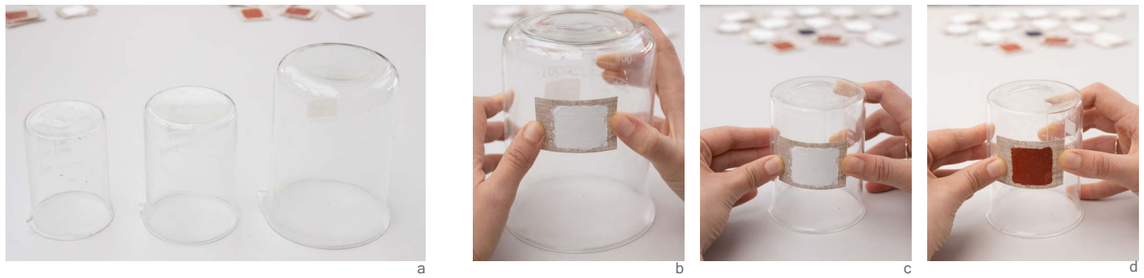


a b c d e f

Figure 15a-f: Adhesion to the ground tests;
coparison between all samples from one filler's formula(a), Scotch Tate Test: sample (b), adhesion of tape (c), tape removal (d,e), obsarvation of result (f)

FLEXIBILITY

The degree of flexibility exhibited by the specific filler sample was assessed through a bendability test. This test is based on Standard Test Methods for Bend Testing of Materials for Ductility[3], which offer a straightforward means of evaluating material quality by their capacity to withstand cracking or other surface irregularities during continuous bending. Since the studio lacked a proper device, the testing method was simplified to some extent. Various types of beakers with different diameters (ø8 cm, ø7 cm, ø5 cm, and ø4 cm) were utilized to create standardized bending surfaces. Each sample was initially bent around the thickest beaker, and if no cracking occurred, it was subsequently bent around each of the other beakers in descending order of size. If a sample did crack during the bending process, the size of the beaker was recorded in the appropriate table.



a b c d

Figure 16: Flexibility/bendability tests
beakers with different diameters (a), process of bendind the sample around the beaker (c,d,e)

CHANGE IN REVERSIBILITY

Changes in reversibility were compared between unaged samples and those exposed to light efflorescence and accelerated aging in an environmental chamber. The evaluation system was inspired by the Fife Solvent Star diagram[4] (Fig. 17), which is effective tool for testing solubility and comparing different solvents. This system was significantly simplified by testing solubility only by rolling a swab over the surface of a filler, and after each 5 rolls, the swab was examined whether any material was removed. Black cotton swabs were used for fillers in white tones for easier evaluation, while white cotton swabs were used for pigmented filler samples. Four different solvents were tested: distilled water, White Spirit, toluene, and ethanol. Each result was recorded in the appropriate table.

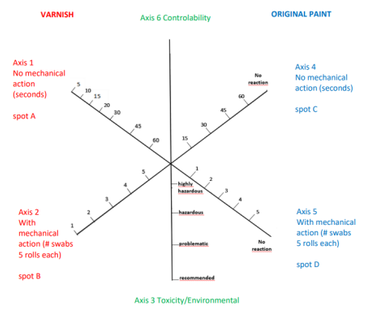
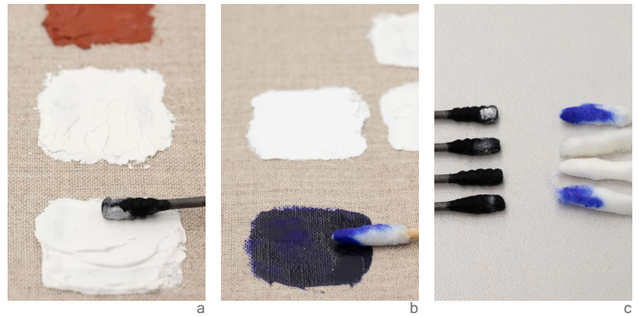


Figure 17: Fife Solvent Star diagram



a b c

Figure 18: Change in reversibility tests;
work with black swab on white filler (a) and with white of pigmented (b),
comparison of the amount of removed material (c)

3 American Society for Testing and Materials, 2014; https://www.astm.org/e0290-14.html

4 Developed at SRAL and published in: *Fife, G.R., 'The Solvent Star: assessing and documenting solvent selection.' The Picture Restorer (number 56, spring 2020), https://www.bapcr.org.uk/the-picture-restorer/* and *Fife G.R., 'Solvents and Paint Films: Practical Solutions, SRAL, 20-22 October 201.*

3. FILLING RECIPES

The fillers can be categorized into two groups based on the characteristic of their composition:
- Filler formulas that cure by loss of solvent.
- Filler formulas that are thermoplastic in nature.

The following chapter is dedicated to recipes for each filler selected for this study. The recipes are divided into ten categories depending on the binding media used for each „filler family." For every binding media, the material's development, characterization, properties, and stability tests are described, as well as the historical attitude toward the application of the material focused on its application as a binding media for fillers. Furthermore, the application and its possibilities are presented. And finally, the conclusion of accelerated aging tests performed within the tables promoting the tested criteria are declared.

3.1 TABLE OF RECIPES FOR SELECTED TESTED FILLERS

This table summarizes the filler recipes that were tested. Several different bulking agents were tested for each binding medium. Each „filler family" is on a particular row; for some of the binding media, two types or recipes were used, therefore there are two columns on one row. By colour, they are divided into two categories: the green one refers to the fillers which are water- or solvent-based and are applied by spatula in cold and fluid condition. The brownish one refers to the fillers which are thermoplastic in nature and are applied by reactivation with a heated spatula.

TRADITIONAL SKIN-GLUE „GESSO" FILLER • 10g rabbit skin glue • 180 ml distilled water • bulking agent I. lime white : bolognese chalk 1 : 1 II. calcium carbonate : bolognese chalk 1:1 III. calcium carbonate IV. aluminium hydroxide	
PARALOID B-72 FILLER • 90 ml 20% Paraloid B-72 in toluene • 96 g bulking agent I. calcium carbonate II. calcium carbonate : bolognese chalk 1:1 III. kaolin : bolognese chalk 2:1	
PLEXTOL B500 FILLER • Plextol B500 in distilled water in ratio 2:1 • bulking agent I. aluminium hydroxide II. calcium carbonate : bolognese chalk 1:1 III. calcium carbonate : kaolin 2:1	
POLYVINYL ALCOHOL FILLER • 6-9% polyvinyl alcohol (PVA) solution in distilled water • bulking agent I. aluminium hydroxide II. calcium carbonate III. calcium carbonate : bolognese chalk 2:1 IV. calcium carbonate : kaolin 3:1	POLYVINYL ALCOHOL + TYLOSE 300 FILLER • 25 g solution of Tylose C300 in distilled water • 5 g solution of 6-9% PVA solution in destilled water • 60 g bulking agent I. aluminium hydroxide II. calcium carbonate III. calcium carbonate : bolognese chalk 1:1

Table 2: Table of recipes for selected tested fillers_part 1

EVACON R FILLER • 25 g solution of Tylose C300 in distilled water • 5 g Evacon R • 60 g bulking agent I. aluminium hydroxide II. calcium carbonate III. calcium carbonate : bolognese chalk 1:1	LASCAUX 498 HV FILLER • 25 g solution of Tylose C300 in distilled water • 5 g Lascaux 498 HV • 60 g bulking agent I. aluminium hydroxide II. calcium carbonate III. calcium carbonate : bolognese chalk 1:1
AQUAZOL 200 FILLER • 10% Aquazol 200 in distilled water + few drops of Ethanol 96% • bulking agent I. aluminium hydroxide II. calcium carbonate III. calcium carbonate : bolognese chalk 1:1 IV. calcium carbonate : kaolin 2:1	BODIED AQUAZOL FILLER • 40% solution of Aquazol 50, 200 and 500 in proportion 1:1:1 in distilled water or Ethanol 99,9% • pigment I. ultramarin dark II. raw umber
EMULSION WAX-RESIN-OIL FILLER • 10 g gelatine • 100 ml distilled water • 1:4 solution of gelatin in distilled water : bulking agent by volume • 15 g mixture of resin dammar and whiten beeswax in proportion 1:1 • 15 g polymerized linseed oil bulking agent: I. Lime white : bolognese chalk 1:1 II. calcium carbonate III. aluminium hydroxide	
PIGMENTED WAX-RESIN FILLER_GAMBLIN FORMULA • 3 parts beeswax • 1 part microcrystalline wax (in the tested series Cosmoloid H80 was used) • 1 part syntetic resin Laropal A81 • 5 parts pigment *all parts measured by weight	PIGMENTED WAX-RESIN FILLER_NOVA-PWR • 1,5 part microcrystalline wax Cosmoloid H80 • 1 part Regalrez 1126 • 1-2 parts bulking agent I. bolognese chalk : pigment 1:1 *all parts measured by weight
BEVA FILLER • 3 parts BEVA 371b • 1 part microcrystalline wax Cosmoloid H80 • 2 parts aluminium hydroxide (Al_2O_3) or 7 parts Kaolin • 1 part pigment for colouring	BEVA FILLER_alternative recipe • 90 g BEVA 371b • 60 g microcrystalline wax Cosmoloid H80 • 60 g Kaolin • 4 g Titanium white (or another type of pigment) • 26 g Chalk, calcium carbonate ($CaCO_3$)

Table 2: Table of recipes for selected tested fillers_part 2

3.2 SKIN GLUE-CHALK FILLER

Glues have been used in art and art conservation praxis for centuries. They played a role of one of the strongest adhesives available before the development of synthetic materials. Till the current times they are keeping a significant position in the conservation field. It has 10 000 year record of use. It has been used in ancient Egypt, mediavel Europe, through the Industrial Revolution and into the present[1]

This type of filler was widely used in history. The process of preparation was (and still is, even nowadays) very similar to the preparation of a ground layer (gesso) for paintings on panel desks or polychromies on wooden sculptures. The word „gesso" comes from Latin „gypsum," and it is also called „glue gesso" or „Italian gesso." It is a mixture of binder (glue) and filler (chalk, gypsum, pigment, and combinations of these). Rabbit skin glue was usually preferred for its high quality, but it was not the only option. In ancient and medieval times, the gesso for wooden panels was prepared in specialized workshops along with the panels themselves. These workshops had their own preparation practices, tips, and know-hows, enabling them to prepare large dimensional painting supports. From historical recipe handbooks, we can read about a wide range of components that could be added to the gesso, such as oils, waxes, resins, egg yolk, ox gall, etc. Even at that time, there were scattered mentions of filler compositions in these handbooks. Alongside the changing attitudes towards art history and the development of the conservation field, comprehensive discussions of filling materials can be found in literature from the first half of the nineteenth century. Detailed guidelines for the proper selection of fillers and their integration can be found in Vicente Poleró y Toledo's treatise *Arte de la Restauración* (1853) or Ulisse Forni's *Manuale del pittore restauratore* (1866). Besides oil or wax fillers, the traditional gesso filler with „coletta" (a variation of glue preparation with additives to achieve better binding qualities, described below) is mentioned in these books. Based on studies of these treatises, fillers based on hide glues and containing a wide variety of additives have remained in continuous use over the last two centuries.[2]

Therefore, there are hundreds of recipes for the glue/chalk filler. Various types of chalk could be used for the filling material: stone, Bolognese, champagne, etc., either alone or in combination with different materials such as gypsum or kaolin. It is important to be aware of the amounts of the different components, the proportions of the binder and bulking agent, and the percentage of glue in the water solution. Primarily, if the solution contains too high or too low an amount of glue, the filler could crack and shrink. Furthermore, it could be problematic to adjust its surface by sharpening or thickening. The ratio of the skin glue to water varies from 0.5 to 1 part of glue to 10 parts of water. It is necessary to soak the glue in water for 24 hours to hydrate the skin glue particles. The chalk (or mixture of types of chalk) is then gradually added to the warm glue solution until the desired consistency is achieved. It is recommended to apply the filler in thin layers; otherwise, cracking could occur as well.

Bohuslav Slánský described a possible way of adjusting the filler after drying. He was a significant figure in the Czech conservation tradition, often hailed as a founder of the „Czech restoration school." He studied at the Prague Academy, and his first scholarship travel took him to Italy, where he delved into restoration techniques. This was followed by visits to Munich, Dresden, Vienna, and Haarlem, where he absorbed new technologies that he later integrated into Czech restoration practices. Slánský published a book titled *The Painting Technique*, in which he described not only the materials and techniques for painting but also those for the restoration of artworks. In a recipe for glue-chalk filler, several methods for refining and adjusting the surface of the filler are described. The dry or wet method involves using metal spatulas, a wet cloth, or wet cork. He also advises conservators to isolate the area of the defect with a gelatin solution in water and then apply the filler immediately afterwards[3]. This practice was widely used in Central Europe.

Colleta italiana

The recipe for the chalk/glue filler, also known as gesso filler, has not significantly changed. There are several modifications or improvements applied in conservation practices. They mainly consist of rabbit skin glue, although some are based on „coletta italiana." This adhesive, as its name indicates, has Italian origins and has been used for several centuries. It is a mixture of glue with several other components to serve as a highly effective adhesive with excellent gluing properties. Its primary function was to consolidate the pictorial film and serve as an adhesive for the relining pastes. In the past, this recipe was prepared with strong glues such as beef, horse, lamb, rabbit, or fish glue, along with water, cane molasses (cane sugar), ox gall extracted from the animal's liver, vinegar, and fungicide. The preparation took several days because the mixture was reheated multiple times and left to dry out. First, the glue was hydrated by soaking in water for 24 hours. After that time, any excess water was eliminated, and the mixture was heated in a bain-marie water bath. The rest of the components were added except for phenol, which was incorporated once the mixture was properly melted. The solution was poured into trays to a thickness of approximately two fingers. The water was allowed to evaporate properly, and then it was left to cool. When the plates reached a gel-like condition, they were cut into squares and turned over to allow proper evaporation of water from both sides. The process of heating in a water bath and drying in squares was repeated for several days.

In 2009, there was a workshop in Valencia led by a group of conservators focused on the traditional preparation of „coletta italiana". The process was documented and published on the online blog *Formando Restauradores*[4]. The components were slightly adjusted: fish and rabbit skin glue (prepared in two separate batches), which provide adhesion; water, acting as a diluent; ox gall, which acts as a surfactant, reducing surface tension and improving wetting and adhesion of the glue; phenol acts as a fungicide; vinegar, which, like the ox gall, promotes penetration due to the acetic acid it contains (4-5%), having a strong penetrating power and slow evaporation, thus delaying the gelation of the glue and facilitating penetration. It acts by breaking down the protein macromolecules into smaller particles, leading to hydrolysis. Additionally, it prevents the appearance of microorganisms.

COMPONENTS OF THE TRADITIONAL „GESSO" GLUE-CHALK FILLER

GLUE

Glue is the soluble protein made by heating, breaking down, and dissolving collagen from animal connective tissues, such as skin (including parchment) and bones. Connective tissue in skin, bone, and other tissues is made up of proteins (polyamides), primarily collagen, along with many other components. Collagen is the strong, white fibrous protein found in skin and bone. The methods used to remove the other components have a considerable influence on the resultant glue.
Collagen is a polyamide polymerized from amino acid monomers in the body, forming a long rod about 300 nm long and 1.5 nm in diameter. The collagen molecule is a helix of three subchains, each with a molecular weight of about 100,000, wound around each other and assembled into an increasingly complex structure. Collagen molecules are held together by a few covalent and many hydrogen bonds. As the animal ages, cross-links form both within and between the chains.
When collagen is heated, the helix uncoils, releasing the chains. The collagen network denatures and shrinks, allowing the glue to be dissolved out. The temperature at which this occurs is called the shrinkage temperature. Mammal collagens from cattle, pigs, rabbits, etc., are fairly similar and have fewer hydroxyproline amino acid units, resulting in shrinkage temperatures between 6 and 32°C. Upon cooling, the glue becomes a gel at a temperature depending on the source species, molecular weight, and concentration.
Acids, alkalis, and enzymes are used to clean the collagen network for extraction, though the various pretreatments have effects on the resulting glue. The initial extraction releases completely denatured chains that are lightly bound to their neighbors. These large molecules produce the strongest glue with the lightest color. As the extraction conditions become more severe, the cross-linked molecules are degraded and released from the network, resulting in weaker, more colored glues.
The solution is then evaporated to create the solid glue, which may contain fats and minerals. Collagen in young animals (e.g., rabbits) has fewer cross-links, and the extracted glue will be less degraded[5].



Figure 19: Different types of glues available and used in conservation practice

Solubility and gelling properties

On cooling, glue solutions set to gels when the molecules associate and reestablish the triple helix structure in small areas, acting as heat-sensitive cross-links. Mammal glue solutions form a gel at room temperature, and most fish glues need refrigeration to gel. Gels melt on heating when the helices unwind. The strength of solid glue films is difficult to measure, so in practice, the properties of glue solutions are used for specification. The strength of the gel in g Bloom[6] is a standard method; the higher the value, the stronger the gel and the glue.
If a glue solution is kept molten at a higher temperature, the glue degrades.
Solutions are easily spoiled by microorganisms, which also cause degradation. Keeping the glue solutions in the refrigerator could extend the storage time.Solutions are easily spoiled by microorganisms, which also cause degradation. Keeping the glue solutions at refrigerator could extend the storage time.
Glue is swelled in cold water to form a gel. The gel is then melted on heating (about 6°C for fish glues and 30-50°C for animal glues). Glue is soluble in a few unusual solvents at room temperature (2,2,2-trifluoroethanol) and formamide. Water, glacial acetic acid, and dimethyl sulfoxide require heating. It is degraded rapidly in acetic acid (pH <3) or alkaline (pH >9) conditions and by enzymes[7]. Glue contains DNA from its source animal (or even humans), and this can cause significant contamination when analyzing objects[8].

Rabbit skin glue

It is a type of animal glue that is essentially refined rabbit collagen. The glue has been used for centuries for stretching and priming canvases for oil painting. It has also been an ingredient in traditional gesso[9]. Rabbit skin glue can be bought in powder form, little pellets or in larger chunks or cubes. The colour is yellowish to brown and the pH value is between 5.5 - 6.5, the gelatinous strenght is approximately 340 - 360 Bloomgrams (17h 10°C), depending on the type and quality of the particular glue production[10]. The glue particles are melted when slowly heated in a double boiler between 50 and 60°C.



Figure 20: Rabbit skin glue

1 HORIE, C. V. (2010). 'Natural water-soluble polymers', *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britain, Routledge, ISBN 0 7506 6905 5, p.233

2 FUSTER LOPEZ, Laura. (2012). 'Filling': in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings,* USA and Canada: Rouledge, ISBN 978-0-7506-8199-5, pp. 587-590

3 SLÁNSKÝ, Bohuslav. (1955). 'Tmelení deefektů v malbě', in *Technika malby, část II: Průzkum a restaurování obrazů,* 2nd, Prague, Paseka, ISBN 80-7185-623-1, pp. 204-206

4 https://victoriavivancos.blogspot.com/2009/02/preparacion-de-coletta-italiana.html [16/04/2024]

5 HORIE, C. V. (2010). 'Natural water-soluble polymers', *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britan, Routledge, ISBN 0 7506 6905 5, pp.228-230

6 ISO 9665:2000. (2000). *Adhesives - animal glues, methods of sampling and testing.* International Standarts Organization

7 HORIE, C. V. (2010). 'Natural water-soluble polymers', *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britan, Routledge, ISBN 0 7506 6905 5, pp.231-233

8 NICHOLSON et al. (2002). *Detection of bone glue treatment as a major source of contamination in ancient DNA analyses,* American Journal of Physical Antropology, pp. 117-120

9 MAYER, Ralph. (1991). *The artist's handbook of materials and techniques,* 5th, New Yourk, ISBN 0-670-83701-6

10 Values from the rabbit skin glue produces by Kremer Pigmente GmbH & Co. KG up to date 04/2024, https://www.kremer-pigmente.com/elements/resources/products/files/63025e.pdf

RECIPE FOR TRADITIONAL „GESSO“ FILLER:

- 10g rabbit skin glue
- 180 ml distilled water
- bulking agent

The traditional „colletta“ filler is a very old recipe that is still widely used till these days. The base of this filler is similar to the preparation of traditional gesso, which is the ground layer for paintings on panels and polychromy on wooden sculptures. The main difference is the amount of filling materials added to the colletta.

First step in mixing this filler is to prepare the mixture of water and rabbit skin glue(a). For a high-quality putty, distilled water and rabbit skin glue are predominantly used. The measured amount of rabbit skin glue is placed into the measured amount of distilled water and left overnight(b). The rabbit skin glue particles swell during this time to enhance their adhesive properties(c). The next day, the mixture is dissolved into a slightly viscous solution using a water bath(e,f). It is important to note that the water in the water bath should not be boiling; ideally, the temperature should be around 60°C, since the skin glue loses its adhesive properties at higher temperatures. Once the solution is dissolved, the bulking agent is gradually added while still keeping the mixture in the water bath(g).

It is highly recommended to add the filling materials after sieving to avoid creating lumps and clumps(d). The solution should not be mixed too quickly to prevent the formation of air bubbles. The amount of filling materials added depends on the desired density and stiffness of the filler. If during work the conservator finds that the filler is not stiff enough or on the other hand stiff too much, more filling material or colletta mixture (with the same proportion of rabbit skin glue and water) can be added.

Regarding the choice of bulking agent:
After several tests and comparisons of different types of filling materials used for the preparation of the filler, I would recommend several combinations of chalk and calcium carbonate. The use of only calcium carbonate can lead to widespread shrinking and cracking of the filler. A mixture of calcium carbonate with various types of chalk (such as Bolognese, Champagne, Mountain chalk) has proven to be quite sufficient and acceptable for treatment purposes.

From my perspective, I would primarily recommend a mixture of calcium carbonate and Bolognese chalk in a 1:1 proportion.

Additionally, there is another bucking agent, aluminium hydroxide, which is also possible to use for this filler. The mixture of colletta with aluminum hydroxide results in a very smooth and creamy filler. This variant of the traditional gesso filler has less intermolecular tension and offers a wide range of possible uses.

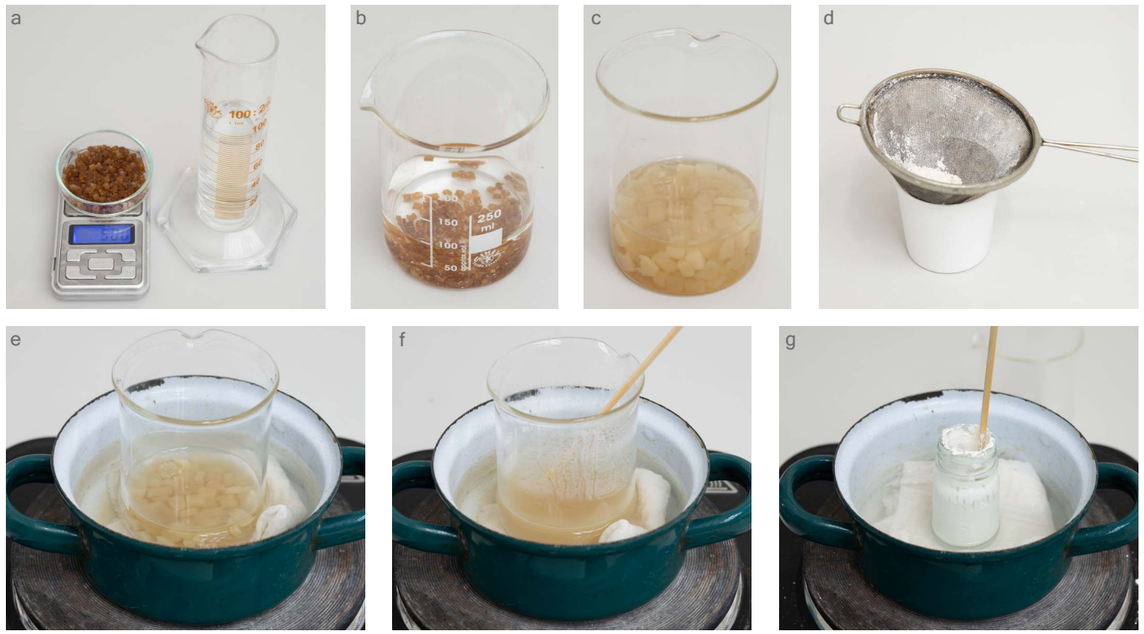


Figure 21a - g: Preparation of traditional „gesso“ filler

APPLICATION

The gesso glue chalk filler is one of the most traditional putty applied widely in history to defects both in panels and canvas supports. Basically it is the oldest form of filling material[1]. It could be used as a filling material for either small or large losses.

The filler is applied into the loss when it is slightly warmed up in a water bath. If the filler is applied cold, wide shrinkage could occur. The choice of instruments used for the application depends on the nature of the defects. The filler can be inserted into losses by a metal spatula, or in the case of more substantial losses, a fluid filler can be applied with a brush.

For deeper defects, it is recommended to apply the filler in several layers, allowing each layer to dry before applying the next one. Applying a thick amount of filler all at once may lead to cracking. Furthermore, the filler tends to shrink during drying. Therefore, it is required to apply a second layer after drying.

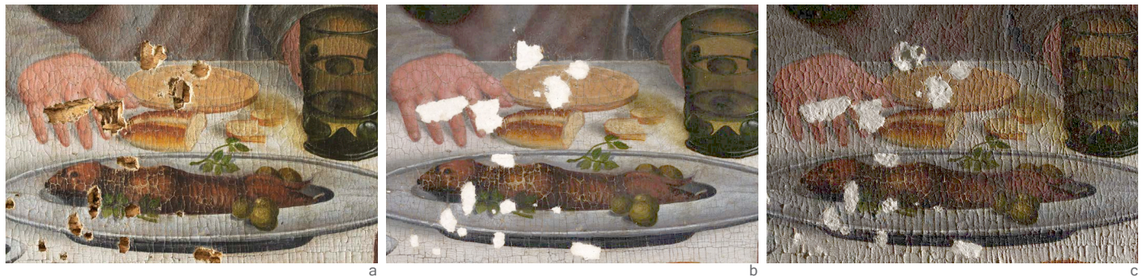
Any excess of filler is removed mechanically by scalpel or within a wet cotton swab or a piece of cloth.

Leveling and smoothing of the filler surface is sufficiently and effectively done with a piece of balsa wood or a cork slightly dipped in distilled water, rotating over the surface. Alternatively, a piece of suede or felt cloth could be adjusted around the cork, and the same operation is conducted.

The surface can be further modified by brushing the liquid filler (by adding more rabbit skin glue-water solution in the same proportion) to recreate the appearance of impastos or brushstrokes. Alternatively, scalpels and sharp-tipped spatulas can be helpful for creating the craquelure effect on the painting surface. Imprinting of a textile texture or mold obtained from the painting surface is also possible; easier work is when the filler is still slightly wet or it could be activated by a certain amount of distilled water on a cotton swab. The temperature for reactivation of the filler surface is also possible.

The surface of the filler is very hydrophilic; therefore, it is recommended to apply a separating layer before retouching. All kinds of retouching material could be used.

The filler should be stored only in a cold environment, such as the refrigerator. Before application, it should be checked whether any molds occur in the mixture. If the filler has thickened, a small amount of rabbit skin glue solution in distilled water (in the same ratio used for preparation) could be gradually added during reheating.



CASE STUDY vol.1_Augustus Cordus: Predella with the Last Supper from Loket (1579)
In this case, application of the filler is illustrated on the panel desk treatment, although the same system could be applied on the painting on canvas support. The filler was inserted into the losses by leveling each layer of warmed formula. It was applied either by brush and by spatula. (For the deeper losses, firstly a filler consisting of Arbocel and Klucel was applied and after drying the second type of a filler was inserted.) The surface reintegration was made by incision with the scalpel's tip. The fillings were separated by dammar resin varnish before retouching.

Figure 22: Augustus Cordus: Predella with the Last Supper from Loket; macro-photographs in raking light before infilling(a); and after filling in day (b) and raking light (c)
Work and photo credit: Sára Syslová and Alena Studlarová

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

Characteristic properties of rabbit skin glue fillers remain approximately unchanged after the accelerated aging process.
The filler is not very soft and flexible; however, the flexibility and hardness could be slightly enhanced when aluminum hydroxide is chosen as a bulking agent. On the other hand, the filler bulked with aluminum hydroxide exhibited extensive cracking compared to the other bulking materials.
Based on the tests, it is not recommended to use pure calcium carbonate as the only bulking agent because the filler tends to increase hardness and lose flexibility. Mixing calcium carbonate with different types of chalk seems to be a very suitable option.
The disadvantage of this type of filler is slight dimensional change; therefore, it has to be applied in several thin layers. Also, flexibility is not necessarily the most important property. However, the surface of the filler remains soft for easy adjustment, the coherence and adhesion are approximately the same, and there is no difference in solubility over time.
The only colour change occurred due to the migration of wax-resin adhesive residues from the old lining canvas, which was observed on the fourth mock-up.

1 NICOLAUS, Knut. (2005).“The Paint Layer: Filling“, in *Restoration of Painting*, Könemann, Germany, ISBN 3895089222, p. 237

GESSO FILLER - RABBIT SKIN GLUE
LIME WHITE : BOLOGNESE CHALK 1 : 1

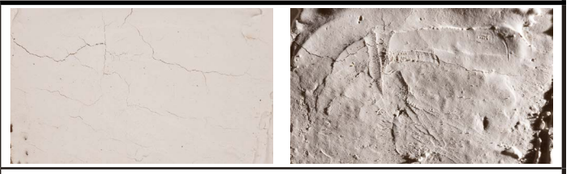
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	Only a slight less of volume, better to apply in several thinner layers.			
colour change	L* 90.9 a* 0.5 b* 5.3 C* 5.3 h* 85.0	ΔE = 0.8 slightly darker	ΔE = 1.2 slightly darker and yellower	ΔE = 3.8 darker, yellower and redder the sample failed the tolerance
craquelure		No cracking developed. 	No cracking developed. 	The drying cracks became significantly deeper and extended. 
surface dusting	The cotton swab is slightly white, microscopic particles of a bulking agent are catched.	Approximately the same amount of microscopic particles of a bulking agent are catched on the cotton swab.	The cotton swab is approximately twice as white as before aging, and the microscopic particles of the bulking material are forming larger configurations.	The cotton swab is approximately twice as white as before aging, and the microscopic particles of the bulking material are forming larger configurations.
hardness	The filler is not very soft, some pressure must be applied. However, it is not rigorous.	The hardness remains the same comapered to the unaged sample.	The filler is slightly softer compared to the unaged sample.	The filler is slightly softer compared to the unaged sample; moreover, it became slightly brittle, around the area where pressure was applied, the filler cracked and started to flake.
coherence	The cohesion of the filler is sufficient; when scratched, some pressure must be applied, and the material tends to flake rather than powder, making it removable in larger particles from the support.	The cohesion remains unchanged.	The cohesion remains unchanged; however, the material exhibits slightly more powdering when scratched compared to the unaged sample.	The cohesion remains unchanged; however, the material exhibits slightly more powdering when scratched compared to the unaged sample.
adhesion to the support	very good	remains very good	remains very good	remains very good
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene no ethanol no	distilled water 5 rolls White Spirit no toluene no ethanol no	distilled water 10 rolls White Spirit very very slightly after 30 rolls toluene no ethanol no	distilled water 10 rolls White Spirit very very slightly after 30 rolls toluene no ethanol no

Table 3: Rabbit skin glue filler bulked with dolomitic and bolognese chalk (1:1)_evaluation of the properties based on accelerated aging tests

GESSO FILLER - RABBIT SKIN GLUE
CALCIUM CARBONATE : BOLOGNESE CHALK 1:1

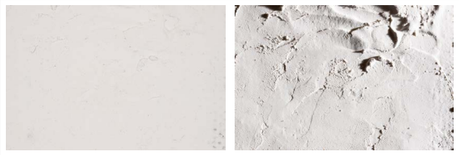
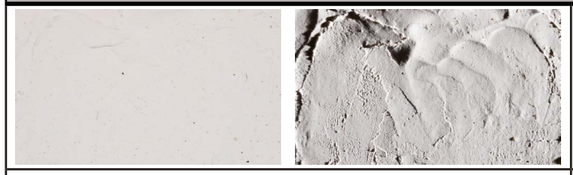
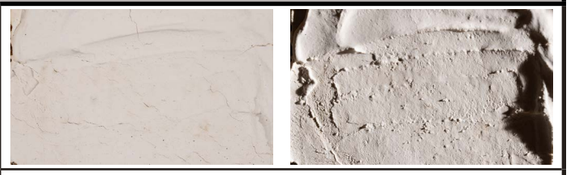
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The drying cracks in thick layered application were developed, very sufficient srinkage also whether a thin layer of filler is applied.			
colour change	L* 94.7 a* 0.0 b* 3.1 C* 3.1 h* 89.8	ΔE = 0.6 slightly duller	ΔE = 0.7 slightly darker	ΔE = 4.7 darker and yellower the sample failed the tolerance
craquelure		No cracking developed. 	No cracking developed. 	A very sufficinet cracks developed on the area with thiner layer of filler applied. 
surface dusting	The cotton swab is only very little white, only a microscopic dust of the material was captured.	The cotton swab is slightly more white, however still only a microscopic dust of the material was captured.	The cotton swab is whiter, approximately by 0.5 times, however, only a microscopic amount of dust from the material was caught.	The cotton swab is significanly more white, approximately twice times more compared to the sample before aging.
hardness	The filler is not very soft, some pressure must be applied. However, it is not rigorous.	The hardness remains the same compared to the unaged sample.	The filler is slightly softer compared to the unaged sample.	The filler is slightly softer compared to the unaged sample.
coherence	The cohesion of the filler is sufficient; when scratched, the material tends to powder, making it removable in larger particles from the support. Easier mechanical action and softer compared to the previous sample.	The cohesion remains unchanged.	The cohesion remains unchanged; however, the material exhibits slightly more powdering when scratched compared to the unaged sample.	The cohesion remains unchanged; however, the material exhibits slightly more powdering when scratched compared to the unaged sample.
adhesion to the support	A few material removed.	remains the same	remains the same	A litlle more of material removed.
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene no ethanol no	distilled water 5 rolls White Spirit no toluene no ethanol no	distilled water 10 rolls White Spirit no toluene no ethanol no	distilled water 10 rolls White Spirit no toluene no ethanol no

Table 4: Rabbit skin glue filler bulked with calcium carbonate and bolognese chalk (1:1)_evaluation of the properties based on accelerated aging tests

GESSO FILLER - RABBIT SKIN GLUE
CALCIUM CARBONATE

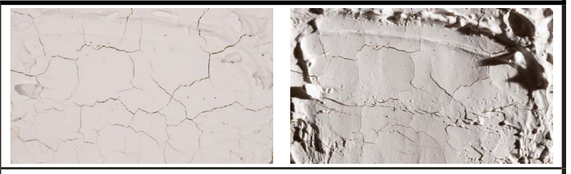
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The drying cracks in thick layered application were developed, very sufficient shrinkage also whether a thin layer of filler is applied.			
colour change	L* 98.4 a* -0.5 b* 1.5 C* 1.5 h* 107.6	ΔE = 1.0 slightly darker and redder	ΔE = 1.0 slightly darker and yellower	ΔE = 5.5 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	The drying cracks got sligthly deeper and extended. 	The drying cracks became significantly deeper and extended over the whole sample. 
surface dusting	The cotton swab is sligthly white; this time not only white dust made of bulking material was caught but also microscopic particles of the filling material are picked up.	The cotton swab is very sligthly white, less than the unaged sample; this time only white dust made of bulking material was captured.	The cotton swab picked up approximately same white residue and same amount of both dust and bucking agent particles compered to the unaged sample.	The cotton swab picked up approximately twice as much white residue and twice the amount of both dust and bucking agent particles compared to the unaged sample.
hardness	The filler is soft, only a little pressure must be applied to make a dimple.	The filler remains soft, only a little pressure must be applied to make a dimple.	The filler became tougher, a little more preassure must be applied to make a dimple; moreover within more pressure, the filler is losing intergity and starting to crumble.	The filler became tougher, a little more preassure must be applied to make a dimple; moreover within more pressure, the filler is losing intergity and starting to crumble.
coherence	The cohesion of the filler is sufficient; when scratched, the material tends to powder, making it removable in larger particles from the support. Even more easily disturbed and softer comparred to the previous samples with the same binder.	The cohesion remains unchanged.	The cohesion remains unchanged; however, the material exhibits slightly more powdering when scratched compared to the unaged sample.	The cohesion remains unchanged; however, the material tends to peel off in larger particles from the support compared to the unaged sample.
adhesion to the support	very good	good	material slightly removed slightly loss of the adhesion	material slightly removed slightly loss of the adhesion
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 10 rolls White Spirit no toluene no ethanol slightly after 30 rolls	distilled water 10 rolls White Spirit no toluene no ethanol slightly after 30 rolls	distilled water 15 rolls White Spirit no toluene no ethanol slightly after 20 rolls	distilled water 15 rolls White Spirit no toluene no ethanol slightly after 20 rolls

Table 5: Rabbit skin glue filler bulked with calcium carbonate_evaluation of the properties based accelerated aging tests

GESSO FILLER - RABBIT SKIN GLUE
ALUMINIUM HYDROXIDE

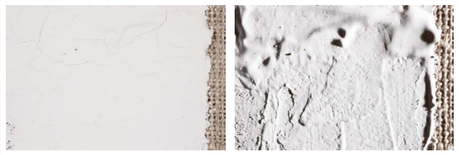
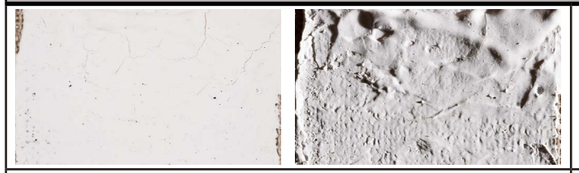
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The drying cracks in thick layered application were developed, no cracking whether a very thin layer of filler is applied.			
colour change	L* 98.9 a* 0.1 b* 1.1 C* 1.1 h* 84.5	ΔE = 0.4	ΔE = 0.4	ΔE = 1.4 slightly lighter and yellower
craquelure		No cracking caused by aging developed. 	The drying cracks got slightly extended. 	A large amount of cracks caused by accelerated aging developed. 
surface dusting	Almost no material was cought on the cotton swab. Only very little amount of white dust is present on the swab, observable under the microscope.	The cotton swab is sligthly white; however, only white dust made of bulking material was caught on the swab.	The cotton swab is approximately same as white as the one captured from the sample kept in stable studio environment; only white dust made of bulking material was caught on the swab.	The cotton swab is approximately same as white as the one captured from the sample kept in stable studio environment; only white dust made of bulking material was caught on the swab.
hardness	The filler is quite soft, it is the squashiest formula from this group of skin glue gesso fillers; only a very little pressure must be applied to make a dimple.	The filler remains quite soft; only a very little pressure must be applied to make a dimple.	The filler became even softer; only a little pressure must be applied to make a dimple. Moreover, the filler is losing integrity and starting to crumble.	The filler became even softer; only a little pressure must be applied to make a dimple. Moreover, the filler is losing integrity and starting to crumble and flake.
coherence	The cohesion of the filler is sufficient; since the material is very soft, when scrached it is powdering; It is the most easily disturbed and softer filler compared to the previous samples with the same binder.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged; however, the material tends to peel off in larger particles from the support compared to the unaged sample.
adhesion to the support	very good	good	material slightly removed	most of the material removed huge loss of adhesion compared to the unaged samle
flexibility	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene swelled after 20 rolls ethanol slightly after 15 rolls	distilled water 5 rolls White Spirit no toluene swelled after 20 rolls ethanol slightly after 15 rolls	distilled water 5 rolls White Spirit slightly after 20 rolls toluene swelled after 20 rolls ethanol slihtly after 10 rolls	distilled water 5 rolls White Spirit slightly after 20 rolls toluene swelled after 20 rolls ethanol slightly after 10 rolls

Table 6: Rabbit skin glue filler bulked with aluminium hydroxide_evaluation of the properties based accelerated aging tests

3.3 SYNTHETIC RESIN_PARALOID B 72

The majority of acrylic polymers used in conservation are made from two families of monomers: the acrylates, derived from acrylic acid, and the methacrylates, derived from methacrylic acid, which is used in acrylate and methacrylate polymers.[1] By using two acids, acrylic acid and methacrylic acid, acrylic esters (including methacrylic esters) can be obtained with different -R groups. For example, from methyl, ethyl, propyl and butyl alcohol by the reaction with acids, methyl-, ethyl-, propyl- and butyl- acrylate and methacrylate will be obtained. The so-called acrylic and methacrylic resins are poly-addition polymers. They are in general thermoplastic resins, however in particular condition they can be made thermosetting (by modifying their chemical structure). Both homo-polymers and copolymers are possible: in general the latter are „more plastic“, as the co-presence of other monomer is used to „internally plasticize“ the polymer.[2]

PARALOID™ B-72

Paraloid B-72 is certainly the most studied synthetic resin in the restoration field. Since the 1950s, this product has become a best-seller among others, used in a variety of applications such as an adhesive, consolidating agent, final varnish for paintings, binding medium for retouching paintings, or as a water-repellent protector for stone. There is a vast body of literature referring to the properties of this resin. Widely used since the mid-1960s, alongside accelerated aging tests in climatic and UV radiation chambers, the results from natural aging are also broadly evaluated.

It is a copolymer consisting of 30% methyl acrylate and 70% ethyl methacrylate (MA-EMA). The molecular weight is around 70,000 amu. It is soluble in ketones, esters, alcohol-ethers, chlorinated and aromatic hydrocarbons. It is insoluble in aliphatic hydrocarbons and slightly soluble in ethyl alcohol.[3] The glass transition temperature (Tg) is 40°C and as it is a resin with a high molar mass, thus, it does not have a defined melting point. It starts to melt at 70 - 75°C; the flowing point is at 145 - 150°C.[4]

In 1978, R. L. Feller composed a list of *Standards in the evaluation of thermoplastic resins*. He divided them into five categories which indicate the classification of each synthetic resin in terms of stability. Paraloid B-72 was placed in the A category, which refers to excellently stable materials lasting more than 100 years. However, Feller and his coworkers classified the higher quality products based on an overview of impurities and residues in the synthetic process.[5]

Nevertheless, according to Feller's studies, the material was assumed to be used in a UV-protected environment. In such instances, aging tests were conducted without the influence of UV radiation. Since the material yielded such good experiences and results, it began to be the first choice also as a protective and consolidating agent, even outdoors, without adequate tests of resistance in the combined presence of water and UV exposure. Under UV influence, Paraloid mainly undergoes chain splitting and the formation of light by-products such as methanol, CO, CO_2, and methane. This leads to a loss of the water repellency characteristics. Moreover, accelerated aging leads to the total disappearance of the product. However, it should be noted that this phenomenon is significant only in cases where a thin layer of the film is exposed to UV radiation.[6]

In 1996, there was a massive adhesive testing conducted at the Canadian Conservation Institute. The aim of the study was to evaluate the results of accelerated aging, which lasted for 13 years, on selected poly (vinyl acetate) and acrylic adhesives. In total, 52 resins were tested (27 vinyls and 25 acrylics). Two different series of materials were prepared: one for aging in the dark and the other for exposure to light (700-800 lux and 190 µW/lm-1, with UV). The samples were analyzed before aging, at various intervals during aging, and finally after aging. For comparison of the variety of adhesives, five parameters were considered: pH, emission of volatile substances, mechanical tensile strength, flexibility, and color. As a result, Paraloid B-72 emerged as the best-performing acrylic, surpassing the vinyls, with excellent stable properties. The only unexpected finding was the change in pH after three years of light aging to 4.7, whereas the natural pH of Paraloid B-72, depending on the solvent in which it is diluted, is more or less neutral or slightly acidic.[7]

However, negative results were also reported in terms of reversibility. A catastrophic flood struck Florence in 1966, causing massive damage, not only to the cultural heritage of Italy. Many artworks were stabilized using Paraloid B-72 solutions to prevent immediate collapse. After several years and subsequent conservation treatments, it was discovered that the resin applied back then is, after 30 years, reversible only in some solvents (such as toluene, xylene, etc.), which also led to the dissolution of the pictorial layer. This is due to an increase in cross-linking within the resin's structure, resulting in reduced long-term reversibility and increasing of the polarity necessary for re-solubilisation, particularly when the ambient temperatures are high and the resin approaches its glass transition temperature (Tg).[8]

Considering the qualities of the Paraloid B-72 resin described above, the use of Paraloid as a medium for gap-fillers increased significantly in the conservation field. Among its advantages is its solubility in solvents, allowing intervention on water-sensitive surfaces of artworks. In 1998, Down M. Wilson published a study on further use of Paraloid B-72 as an infilling system for gilded, painted, and lacquered wood. He highlighted the properties of the resin, which is soluble in aromatic hydrocarbons, making it suitable for surfaces sensitive to both water and polar solvents such as alcohols or ketones. The case studies in his research included gilded decorative artworks with varnish-coated water gilding; New Mexican Santos with varnished, water-sensitive paints; and lacquer objects with solvent-sensitive urushi coating damaged by UV light. Noteworthy is the character of the filler, allowing quick application and polishing or burnishing to match the subtle reflective surfaces, as well as the possibility to shape and texture the filler or cast from molds to imitate the surface textures of aged, painted wood.
His recipe is as follows:

- 90 ml Paraloid B-72 20% w/v in toluene or appropriate solvent
- 96 g calcium carbonate/kaolin mixture, 2:1 by weight

The whiting mixture is slowly sifted into the Paraloid B-72 solution without stirring until no additional whiting can be absorbed. The formula is gently stirred until the whiting is evenly incorporated into the resin solution. Before use, the filler is strained through a fine cloth or screen.
The „gesso“ filler is applied by brush to the sites of loss that have first been sealed with clear Paraloid B-72, 20% w/v in toluene. To level the infills, cloth-covered leveling tools made from wood are used with toluene to avoid the need for abrasive materials or sandpaper. The resulting „gesso“ approximates well the surface characteristics of rabbit skin glue gesso.[9]

An interesting usage of Paraloid B-72 filler is also found in archaeological conservation for fossils and bones. In a study conducted by a group of Egyptian researchers, three types of pastes used as gap-fillers were tested, with two of them based on Paraloid B-72. For both, a solution of 15% Paraloid B-72 in acetone was prepared. The first one was mixed with calcium carbonate, and the second one with glass microballoons (both in approximately a 1:1 ratio). The second paste was evaluated as the best, showing high quality after accelerated aging.[10] Another example is a comparative study of various commercial and studio-made fillers for archaeological bone conservation treatment by Marilyn Fox. Among the 126 samples, Paraloid B-72 in a 25% concentration in solvents or solvent mixtures (acetone; acetone/ethanol 50/50) with glass microballoons and microfibers were tested, yielding satisfactory results (additionally, as bulking agents, kaolin, marble dust, and fumed silica were also tested, however the results were not in this case reported).[11]

Paraloid B-72 fillers are commonly used in ceramic conservation[12], particularly for porous surfaces, and as effective gap-fillers for indoor exposed stone sculptures. The extensive variety of bulking agents and the moderate concentration of Paraloid B-72 solution are especially valuable for treating marble supports. This allows the creation of a filler without the necessity of inpainting.[13]

In painting conservation, Paraloid B-72 fillers are commonly used for artworks on copper and panel desks. Laura Fuster-Lopez recommends this type of filler for paintings on canvas support as well, especially for large losses thanks to the high flexibility of the putty. The filler she describes consists of a 20% Paraloid B-72 solution in toluene or xylene combined with calcium carbonate in approximately a 1:1 ratio. This achieves a viscous liquid consistency. Silica (SiO_2) may be added to prevent the filler film from cracking and shrinking during drying.[14]



Figure 23: Paraloid™ B 72
source: https://www.kremer-pigmente.com/en/shop/mediums-binders-glues/67400-paraloid-b-72.html [cit. 03/05/2024]

1 HORIE, C. V. (2010). 'Acrylic polymers', *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britain, Routledge, ISBN 0 7506 6905 5, p.15

2 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Acrylic esters“, in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 118-119

3 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Acrylic esters“, in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 127-128

4 https://www.kremer-pigmente.com/elements/resources/products/files/67400e.pdf [23/03/2024]

5 FELLER, R., L., (1978). *Standards in the evaluation of thermoplastic resins.* ICOM

6 MELO, M., J., BRACCI, S., CAMAITI, M., CHIANTORE, O., PIACENTI, F. (1999). „Photodegradation of acrylic resins used in the conservation of stone“, in *Polymer Degradation and Stability*, Torino, Italy. pp. 23-30

7 DOWN, J., L., MACDONALD, M., A., TÉTREAULT, J., WILLIAMS, R., S. (1996). A*dhesives Testing at the Canadian Conservation Institute: An Evaluation of Selected Poly (Vinyl Acetate) and Acrylic Adhesives*., Studies in Conservation, Volume 41 pp. 19-44

8 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Acrylic esters“, in *The synthetic resins used in the treatment of the polychrome works of ar*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131*t,* pp. 37*,* 127

9 WILSON, D., M. (1998). „Further uses for Paraloid B-72: Infilling systems for gilded, painted and lacquered wood“, in *Wooden Artifacts Conservator*, Watertown, MA, WAG Postprints, Alexandria, Virginia

10 ABDEL-MAKSOUD, G., SOBH, R., TAREK, A., SAMAHA, S., H. (2020). „Evaluation of Montmorillonite (MMT)/polymer Nanocomposite in Gap Filling of Archaeological Bones“, in *Egyptian Journal of Chemistry*, Vol. 63, pp. 1585-1603

11 FOX, Marilyn. (2001). *Searching for a filler of my dreams: An Odyssey in gabs and glues.* Yeale Peabody Museum of Natural History, Platform Presentation at the Society of Vertebrate Paleontology Annual Meeting, Bozeman, Montana

12 FELICIANO, Anes, at al. (2019). *The Conservation of a Late Renaissance Tiled Stove: A Non-Aqueous Approach*, Recent Advances in Glass and Ceramics Conservation, Interim Meeting of the ICOM-CC Working Group, London, England

13 WOLFE, Julie, O'CONNOR, Talitha. (2005). „Properties of fillers in putties based on Acryloid B-72“, in *Objects Specialty Group Postprints*, Vol. twelve, American Institute for Conservation of Historic & Artistic Works, Washington, DC, pp. 91-117

14 FUSTER LOPEZ, Laura. (2008). *El estuco en la restauración de la pintira sobre lienzo: criterios, materiales y procesos*, Spain: Universitad Politecnica de Valencia, ISBN 978-84-8363-221-5, pp. 106-108

RECIPE FOR PARALOID B 72 FILLER

- 90 ml 20% Paraloid B 72 in toluene
- 96 g bulking agent

First of all the solution of Paraloid B 72 is prepared. Weight the 20 grams of Paraloid B 72 and put them together with 100 ml of toluene into a glass jar(a). Shake the mixture inside the container and leave it to dissolve overnight(b). It is possible to dissolve Paraloid B 72 in different kinds of solvents in several compositions with aromatic hydrocarbons. The preferred solvent mixture depends on the time required for proper dissolving of the Paraloid particles. Mixing the solution inside the container on a magnetic stirrer may speed up the process.

Pour 90 ml of the 20% Paraloid B 72 solution into a beaker(c). Weight 96 grams of filling material(d) and add it gradually into the solution without mixing. Moderately strew little by little of the powder and leave it to be soaked by the solution(e). Delicately and carefully mix the mixture with wooden or glass stick(f,g,h,i). Do not speed up the process of preparation; it could cause creation of lumps and bubbles.

Basically the preparation of Paraloid B 72 filler is very similar to the preparation of traditional gesso filler (page 8) only without warming the solution.

It is possible to add pigments into the mixture as a last component if the filler is required to be coloured.

Keep the filler in a lidded glass container(j). However it cannot be stored for a longer time. The solvents inside the solution evaporates and the filler becomes stiff and stony. It is possible to moisture it with solvents later on but it would change the propositions of Paraloid B 72 inside the mixture so it is not recommended.

There is a wide range of bucking agents possible to be used as a filling material. Different kinds of fillers could be added to the Paraloid B 72 solution alone or in a combination with another one in several ratios. The ones chosen for the trials were calcium carbonate separately and in a combination with bolognese chalk and kaolin.



Figure 24 a - j: Preparation of Paraloid B 72 filler

APPLICATION

The consistency of the Paraloid B 72 filler is that of a high-viscosity liquid. Therefore, it is important to apply the formula in thin layers by brush (Fig. 25), one by one, after the previous layer has almost dried out (Fig. 26). Depending on the particular type of loss, the specific quantity of the layer is obtained. Manipulating the filler should be done fairly quickly; otherwise, the mixture may dry on the brush. The surface could be leveled after drying and smoothed by a cork, suede or felt cloth dipped in appropriate solvent (Fig. 27, 28).



Figure 25: Paraloid B 72 filler applied by brush

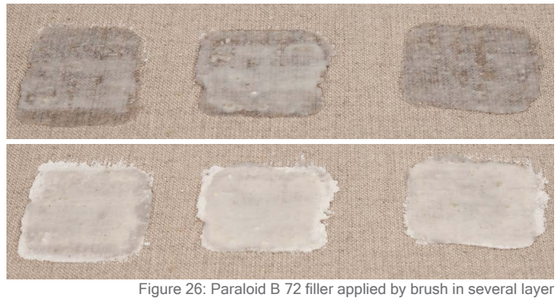


Figure 26: Paraloid B 72 filler applied by brush in several layer

The filler could be used for both small or large losses, thanks to its flexibility and adaptability to the movement of the canvas weave.

The imitation of the brushstrokes on the painting is easily achievable during the application of each filler layer with a brush. More brushstrokes or impastos are possible and adjustable after drying, using different types of brushes with a small amount of filler. However, for better working conditions, it is more effective to soften the dried filler's surface with a solvent and then scratch or create imitation craquelure with scalpels or needles.

It is possible to hydrophobize the surface of the loss with a layer of isolation consisting of 20% Paraloid B 72 diluted in toluene or a different type of aromatic organic solvent in which the resin is soluble.

Any excess filler over the original painting can be removed using aromatic organic hydrosolvents or acetone. Moreover, if the overlaps are thicker, scalpels can be used, and any remaining residues can be removed with toluene.

Since the properties of Paraloid B72 indicate solubility in a wide range of organic aromatic solvents, the filler can also be used on specifically sensitive surfaces. However, a disadvantage is that dissolution in some types of solvents could take several days.

The properties of the filler depend on the solvent in which the resin is dissolved as well as a bulking agent which is selected to fill the formula. By Wilson[1], the combination of calcium carbonate with kaolin is recommended in ratio 2:1. The filler obtains good flexibility and hardness and is easily further adjustable.

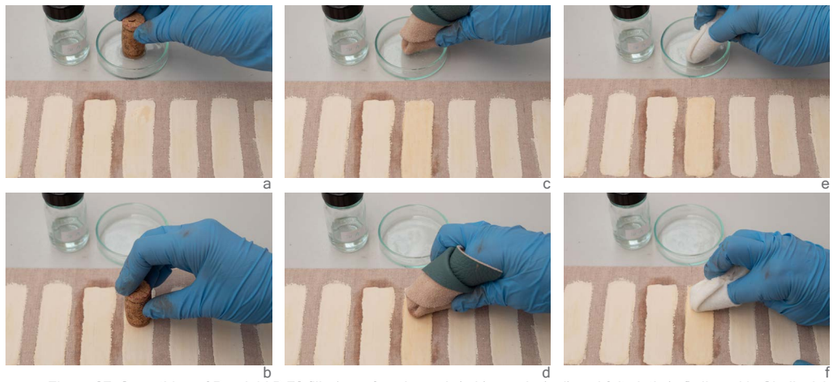


Figure 27: Smoothing of Paraloid B 72 filler's surface by cork (a,b), suede (c,d) and felt cloth (e,f) dipped in Shellsol A



Figure 28: Comparison of surface of filler applied by brush in raking light, unsmoothed and smoothed

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

Firstly, it should be noted that the sample of this type of filler could exhibit different properties, especially flexibility and adhesion to the support, if the filler were applied by brush in several thin layers. Unfortunately, the application of thicker filler by spatula did not have a positive influence on the results.
The filler showed a significant change in hardness, cohesion, and flexibility. After the accelerated aging tests, it became noticeably tougher and therefore more difficult to remove mechanically, although some aging cracks and shrinkage of the material occurred as well as a slight loss of adhesion to the textile support. However, the solubility in aromatic or polar solvents remained unchanged. Interestingly, the colour change was not as significant as when compared to other filler formulas.

1 WILSON, E. (1998). „Paraloid B-72 infilling systems for wooden artifacts“ in *ICOM: Ethnographic Conservation Newsletter*, n°18, pp. 9-11

PARALOID B 72 FILLER
CALCIUM CARBONATE

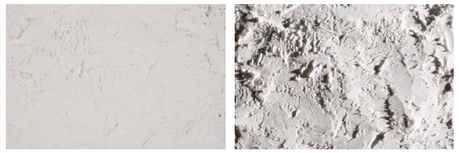
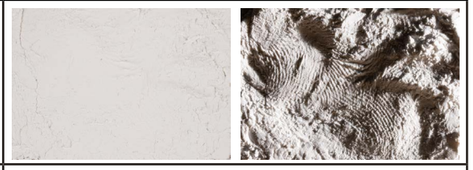
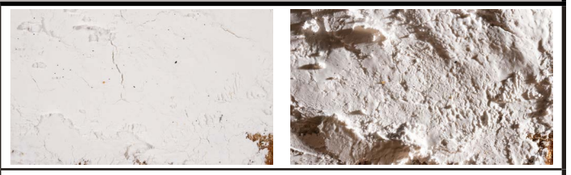
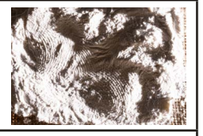
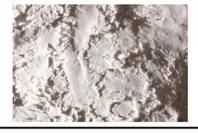
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change and shrinkage.			
colour change	L* 98.8 a* -0.5 b* 1.5 C* 1.6 h* 110.0	ΔE = 0.5	ΔE = 1.1 slightly darker	ΔE = 3.3 darker, yellower and redder the sample failed the tolerance
craquelure		No cracking developed. 	A few cracks appeared in the filler mass at the areas where thin layer of filler was applied. 	A few thin cracks appeared in the filler mass. 
surface dusting	Almost no material was captured; under the microscope, only a few larger particles of the filling material are observed, indicating a loss of cohesion of the unflattened surface of the sample.	Almost no material was captured; under the microscope, only a few larger particles of the filling material are observed, indicating a loss of cohesion of the unflattened surface of the sample.	The cotton swab is slightly white; this time not only a few larger particles which lost the cohesion to the surface of the sample are present but also the white dust of the filling material is observed.	Almost no material was captured; under the microscope, only a few larger particles of the filling material are observed, indicating a loss of cohesion of the unflattened surface of the sample.
hardness	The filler is quite tough; greater pressure must be applied to make a dimple.	The filler remains quite tough; greater pressure must be applied to make a dimple.	The filler became tougher compared to the unaged sample; stronger pressure must be applied to make a dimple.	The filler became tougher compared to the unaged sample; stronger pressure must be applied to make a dimple.
coherence	The cohesion is very good; it is difficult to scratch, does not powder, and can be disturbed only in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	very good	good	material slightly removed slightly loss of adhesion compared to the unaged samle	material slightly removed slightly loss of adhesion compared to the unaged samle
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water no White Spirit no toluene 5 rolls ethanol 5 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 5 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 5 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 5 rolls

Table 7: Paraloid B-72 filler bulked with calcium carbonate_evaluation of the properties based accelerated aging tests

PARALOID B 72 FILLER
CALCIUM CARBONATE : BOLOGNESE CHALK 1 : 1

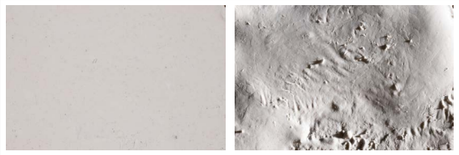
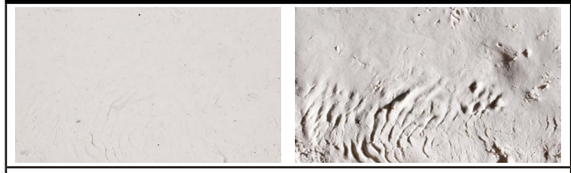
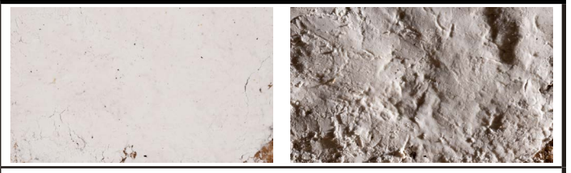
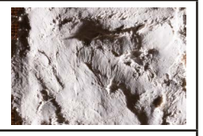
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change and shrinkage.			
colour change	L* 90.8 a* 0.4 b* 3.6 C* 3.7 h* 83.5	ΔE = 0.7	ΔE = 0.5	ΔE = 0.9
craquelure		No cracking developed. 	No cracking developed. 	No cracking developed. 
surface dusting	No material was captured on the cotton swab.	Only a very few larger particles were captured, indicating a loss of cohesion of the unflattened surface of the sample.	Only a very few larger particles were captured, indicating a loss of cohesion of the unflattened surface of the sample.	Only a very few larger particles were captured, indicating a loss of cohesion of the unflattened surface of the sample.
hardness	The filler is quite soft in the areas where a thin layer was applied; conversely, in areas where a thicker layer was applied, the filler is quite tough, requiring a lot of pressure to create a dimple.	The filler behaves similarly to the unaged sample, exhibiting contrasting characteristics between thin and thick layers.	The filler became significantly tougher compared to the unaged sample; in both thin and thick layers, a lot of pressure must be applied to create a dimple.	The filler became significantly tougher compared to the unaged sample; in both thin and thick layers, a lot of pressure must be applied to create a dimple.
coherence	The cohesion is very good; slightly easier to scratch compared to the sample bulked with caplcium carbonate only, when scraching it is slightly powdering.	The cohesion remains unchanged.	The cohesion remains unchanged.	The possibility to scratch is lowered, it is neither powdering, nor flaking.
adhesion to the support	very good	good	material slightly removed slightly loss of adhesion compared to the unaged samle	significantly more material removed compared to the privious sample loss of adhesion compared to the unaged samle
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water no White Spirit no toluene 5 rolls ethanol 10 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 10 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 10 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 10 rolls

Table 8: Paraloid B-72 filler bulked with calcium carbonate and bolognese chalk (1:1)_evaluation of the properties based accelerated aging tests

PARALOID B 72 FILLER
CALCIUM CARBONATE : KAOLIN 2 : 1

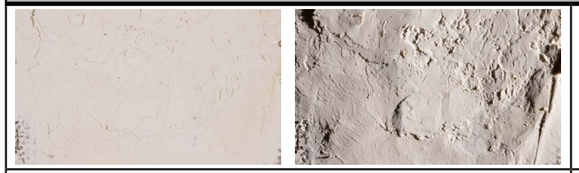
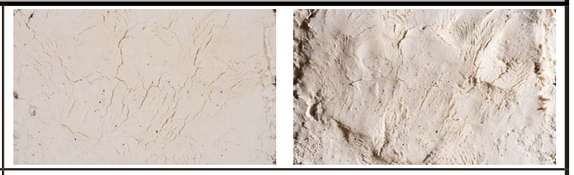
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	Cracking caused by drying whether a thick layer is applied; however in several thin layer application by brush, no dimensional change.			
colour change	L* 91.0 a* 0.8 b* 11.3 C* 11.3 h* 85.9	ΔE = 2.4 slightly lighter (caused by unconsistent application)	ΔE = 2.6 lighter (caused by unconsistent application)	ΔE = 2.5 lighter (caused by unconsistent application)
craquelure		No cracking caused by aging developed. 	No cracking caused by aging developed. 	No cracking caused by aging developed. 
surface dusting	The cotton swab is very slightly white; only a white dust made of the bulking material was captured.	The cotton swab is very slightly white; only a white dust made of the bulking material was captured.	The cotton swab is slightly more white compared to the unaged sample; only a white dust made of the bulking material was captured.	The cotton swab is very slightly white; only a white dust made of the bulking material was captured.
hardness	The filler is quite soft, significantly softer when compared to other formulations of this filler; the hardness remains consistent across both thick and thin layers.	The filler retains similar hardness properties as the unaged sample.	The filler became slightly tougher compared to the unaged sample; slightly more pressure must be applied to make a dimple. However, it is still much less when compared to other formulations of this filler.	The filler became slightly tougher compared to the unaged sample; slightly more pressure must be applied to make a dimple. However, it is still much less when compared to other formulations of this filler.
coherence	The cohesion is good; when scratched, it is powdering.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	some of the material removed lower adherence compared to the previous samples bulked with another filling material	remains similar compared to the unaged sample	significantly more material removed compared to the unaged sample significant loss of adhesion compared to the unaged samle	significantly more material removed compared to the unaged sample loss of adhesion compared to the unaged samle
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water no White Spirit no toluene 5 rolls ethanol 10 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 10 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 10 rolls	distilled water no White Spirit no toluene 5 rolls ethanol 10 rolls

Table 9: Paraloid B-72 filler bulked with calcium carbonate and kaolin (2:1)_evaluation of the properties based accelerated aging tests

3.4 ACRYLIC RESINS IN DISPERSION_PLEXTOL B 500

The process of producing acrylic resins from acrylic esters was described in the previous chapter. Basically, acrylic resins are polymers synthesized from acrylic monomers. These monomers typically include esters of acrylic and methacrylic acid, such as methyl acrylate, butyl acrylate, ethyl acrylate, and others. These are the starting materials that produce acrylic dispersions through a process called emulsion polymerization. In this process, the acrylic resin is dispersed in water. The addition of emulsifiers and stabilizers is crucial. Emulsifiers work to reduce the interfacial tension between the acrylic resin and water, allowing for the formation of stable droplets or particles. Additionally, emulsifiers and stabilizers help to control the size and distribution of the acrylic polymer particles. The reaction is often carried out at elevated temperatures under controlled conditions to achieve the desired molecular weight and particle size. After the desired polymerization is achieved, the acrylic dispersion may undergo post-polymerization steps to adjust its properties. The final acrylic dispersion is then typically filtered to remove any remaining impurities or oversized particles.[1]

The manufacture of dispersions requires relatively low investment and lends itself to easy variation of products by adding various additives, such as surfactants, plasticizers, etc., whose exact composition is often undisclosed. Therefore, a large number of products with similar or competing properties are available on the market. They became widely available during the 1950s and were also developed for use in the conservation field for various applications. Their increasing popularity was aided by greater film resistance to yellowing compared to PVAc dispersion applied films.[2] At the end of 2018, the world market accounted for 36,000,000 tons, with this number divided between vinyl and acrylic dispersions, the latter being predominant. In fact, the share of vinyl copolymers is 21%, while the ethylene vinyl acetates accounts for 15%. The dispersions of prue acrylics, which are used in restoration, have a 25% share. They have been recently replaced by styrene-acrylics, which are in the first place with 39% of the market. The acrylic market accounts for about 160,000 tons per year, with only a few tons suitable for use in the restoration field. Unfortunately, it is not surprising that production companies tend to focus on products that are more marketable than others. The development of new variants is rapid, and considerations for the restoration field are not always a top priority in industrial strategies. The composition of additives is a crucial consideration, influencing factors such as pH, glass transition temperature, film-forming temperature, solid content, particle size, and viscosity for their eventual use in conservation treatments.[3]

An example of these acrylic dispersions widely used in restoration is *Primal AC-33*® (Röhm & Haas, USA). It is the most famous of the vast family of Primal (found in the North American market under the name Rhoplex). It was developed in 1953 but is no longer in production since 2000. It contains 66% ethyl acrylate and 34% methyl methacrylate. It was one of the most studied products used by restorers at that time, although it is no longer part of the company‘s market strategies. It was replaced by *Primal E330S*, which is certainly an excellent binder for coatings, but its application is not satisfactory. The void left in the market was filled by several „false Primal variations“; thus, even today, *Primal AC-33* fakes are commercially available. For instance, a company called C. T. S. based in Italy proposed a substitute for this product named *Acril 33*®. It is intended as a 100% pure acrylic resin in aqueous dispersion characterized by excellent resistance to atmospheric agents, chemical stability, and high resistance to yellowing.[4] The average particle diameter is 0.15 microns, and it has a non-ionic surfactant character.[5]
In the restoration field, *Acril 33*® is used as an additive for injection and filling mortars; binder for pigments, glazes, whitewashes; adhesive; consolidant and fixative of paint layers; and as a medium for fillers on easel paintings.
The recipe is described by L. Fuster-Lopez and is as follows:

- *Acril 33* is prepared with distilled water in a ratio of 90:10.
- Afterward, calcium carbonate is gradually added as a filling material until the required consistency is achieved, approximately 1:1.

Because of the liquid consistency of the filler, application by brush is necessary. The best properties are achieved when the filler is applied in several layers, placing the next layer on the previous one once it is almost dried. This specific character of the putty is suitable for filling large losses. The filler is very flexible, making it adjustable to the tension and movement of the textile support. Excess filler over the original painting can be removed by low aromatic solvents or acetone. Additionally, distilled water can be used for the swelling and removal of the over-layers, which can be finished mechanically by a scalpel. The imitation of the surface texture is possible after the aqueous compound of the filler dries out. On the surface, it is possible to rip and scratch the craquelure with scalpels. Additionally, the surface could be swelled again by acetone, and more filler could be placed on top if required (for example, liquid filler is applied with a suitable brush to imitate the brushstroke character of the painting).
The filler, after accelerated aging, proved to be stable to UV radiation and unevenly increased temperature. It retains its flexibility and is resistant to weather effects.[6]

An important comparative study on acrylic dispersions used in the conservation field was conducted by the American researcher M. C. Duffy. The research considered five different products: Plextol B500, Rhoplex AC33, Rhoplex AC234 (similar to Primal, available in Europe), Lascaux 360 HV, and Lascaux 498 HV. The adhesives were examined in two possible applications: firstly, as thin pure films applied on a plastic board, allowed to dry, and then the adhesive films were detached from the support; secondly, as a lining adhesive by simultaneously lining the original and supporting canvas, activating the adhesive on a low-pressure table when in a wet condition, and then reactivating the dry film with toluene. Half of the samples underwent accelerated aging in an environmental chamber, while the second half remained under ambient conditions. The results were compared after 100 hours of aging. The parameters considered were: color change as a measure of yellowing; swelling by distilled water, isopropyl alcohol, and toluene to indicate solubility; and detachment force by peel strength to indicate reversibility.
The best results were obtained with Plextol B500, which appeared to be the most resistant to changes in peel strength over time. Unfortunately, Plextol B500 also showed the most discoloration among the tested adhesives. Therefore, the purpose of the adhesive application becomes a question. Since it is used as a lining adhesive and is hidden from light exposure, yellowing may not be a factor for consideration. The swelling ability was best achieved for all the samples with toluene; nevertheless, the long-term reliability of these materials appears questionable, considering the short aging exposure. [7]

PLEXTOL® B500

This dispersion was originally composed in Germany by Degussa from the producer Röhm. It is available also under the name Degalan B500.
The polymer contains 60% ethyl acrylate and 40%methyl methacrylate. The particles which constitute the dispersion have a diameter of 0.1-0.2 microns.[8]

The pH value of the dispersion is 9.5[9]. In a comparative study by Valls and Barber[10], the properties of liquid solutions and dry films were compared for several adhesives, including their gluing qualities as well as chemical and physical properties. Testing was conducted after accelerated drying and aging of the films in a climatic chamber, where they were exposed to stable conditions (50 ± 5% RH, 23º ± 2 ºC) and absence of light for seven days. One of the adhesives tested was Plextol B500, both alone and in combination with sturgeon glue. The study yielded interesting results, which can be found in the paper. However, in this case, the question of changes in pH values is highlighted. The pH of the samples was measured before aging in liquid solutions using pH paper strips and after aging on dry films using a pH contact meter. The pH of the dried film of Plextol dramatically changed to a value of pH 4.9. This is an important finding, as the pH values significantly changed due to the evaporation of ammonia, which is one of the constituents. This information should be taken into account when choosing the particular application.

Plextol B500 has gained fame after Merha‘s research in the 1970s. The resin was used for cold lining and nap bonding systems. In Merha‘s study, several resins were compared for this type of application (including Plexisol, Mowilith, Mowital, and Bedacryl, for example). The aim of the study was to develop a lining system where the adhesive material is only placed on the new lining support, rather than being applied directly to the original canvas. This approach helped avoid the saturation problems commonly associated with traditional methodologies used at the time. The nap-bonding system was proposed as the method for applying the adhesive. In this case, the adhesive is not freely applied but rather through a perforated screen. This method allows for a more controlled and reduced quantity of adhesive, ensuring the right amount necessary for proper and long-term bonding of the lining. The viscosity of the dispersion is thickened with a cellulose ether in a water solution (Klucel). Over the years, the system has slightly evolved to a method where a very fine network acts as a screen, allowing for the passage of a continuous film of uniform thickness. The lining adhesive is then activated on a cold table, which is a vacuum table without heating switched on. The process is supported by air fluctuation, and the adhesive is reactivated by a limited amount of solvent.[11]
Since that time, systems for cold lining have been further investigated and developed. Nowadays, there are several variants of cold lining systems and cold lining adhesives used in restoration practice. This includes not only the type of Plextol proposed here, but also techniques like mist-lining developed at SRAL in The Netherlands, among others.



Figure 29: Plextol B500
source: https://deffner-johann.de/en/plextol-b-500-1-l-en.html [3. 5. 2024]

1 Roehm GmbH Darmstadt. (1988). US 4771098A. United States Patent

2 HORIE, C. V. (2010). ‘Acrylic polymers‘, *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britain, Routledge, ISBN 0 7506 6905 5, pp.153-171

3 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Acrylic resins in dispersion“, in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 131-132

4 https://ctsconservation.com/fr/resines-cires-et-caoutchoucs/5985-acril-33-pack-size-1-kg.html [17/04/2024]

5 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Acrylic resins in dispersion“, in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 131-132

6 FUSTER LOPEZ, Laura. (2008). *El estuco en la restauración de la pintira sobre lienzo: criterios, materiales y procesos,* Spain: Universitad Politecnica de Valencia, ISBN 978-84-8363-221-5, pp. 102-103

7 DUFFY, M., C. (1989). „A study of Acrylic dispersions used in the treatment of paints“, in *Journal of the American Institute for Conservation*, JAIC Volume 28, p. 67-77

8 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Acrylic resins in dispersion“, in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 133-134

9 https://ctsconservation.com/en/resins-waxes-and-rubbers/4593-plextol-b-500-pack-size-1-kg.html [17/04/2024]

10 VALLS, M., P., BARBER, D., J. *Testing polymers in the adhesion of specimens with adhesive failures in “oil-commercial ground” contemporary painting.* Grupo Español de Conservación. International Institute for Conservation of Historic and Artistic Works, Ge-conservación nº 20, pp. 352-368

11 MEHRA, Vishwa, R. (1975). “Comparative Study of Conventional Relining Methods and Materials and Research Towards Their Improvement.” *Interim Report to the ICOM Committee for on Structural Supports of Canvas Paintings*, 4th Triennial Meeting, Venice, Paper No. 75/11/5

RECIPE FOR PLEXTOL B 500 FILLER

- Plextol B 500 in distilled water in ratio 2:1
- bulking agent

First of all the polyacrilic dispersion Plextol B 500 is diluted with distiled water. The ratio is 2 parts of Plextol B 500 to 1 part of distiled water(a). Mix the liquids thorouughly(b).

Sieve the filling material and add gradually to the Plextol B 500 solution(c,d). Mix it with wooden or glass stick(e) properly until no lumps of powder are left and each particle of bucking agent is encapsulated by the adhesive. The amount of bulking agent added depends on a particular consistency desired to be achieved. Recommended ratio is approximately 1 : 1 (adhesive : filling material)[1] (f), however based on trials approximately the ratio 1 : 2 is more sufficient to handle(g) and place the filler on a support(h).

The filler could be coloured by pigment if it is required. Pigment can be added both before and after mixing the filling material with the Plextol B 500 solution.

The filler is stored in a lidded container in a cold environment (refrigerator). It could be stored for several months if the filler is covered with a moisturized piece of cloth or tissue inside the container (without leaving any air gabs).

There is a wide range of bucking agents possible to be used as a filling material. Different kinds of fillers could be added to the Plextol B 500 solution alone or in a combination with another one in several ratios. The ones chosen for the trials were aluminium hydroxide and calcium carbonate combined with bolognese chalk and kaolin(i).



Figure 30a - i: Preparation of Plextol B500 filler

1 Recipe by Laura Fuster Lopez.

APPLICATION

In the publication by L. Fuster-Lopez, it is recommended to prepare the filler using a composition of Plextol B500 mixed with water and a bulking agent in a 1:1 ratio. However, based on the tests, the addition of a larger amount of filling material is possible, as no cracking appeared during or after drying. Another option could be to add a cellulose ether solution as a third component (for example, approximately 4% Klucel or Tylose in distilled water), which will adjust the viscosity of the desired filler[1]. The moderate viscosity of the filler indicates its potential for use in both small and large losses.

Depending on the viscosity of the filler, it can be applied using a brush, putty knife, or spatula. However, if the filler is more liquid, changes in dimensions could occur during drying as the water content evaporates.

The filler is highly flexible, making it adaptable to the tension and movement of the canvas support, which was evident for all tested filling materials (Fig. 30). The maximum flexibility is achieved when aluminum hydroxide serves as the bulking agent. Interesting properties are also obtained when the filling material is a mixture of calcium carbonate and kaolin.

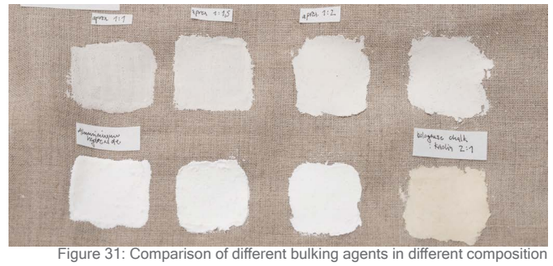
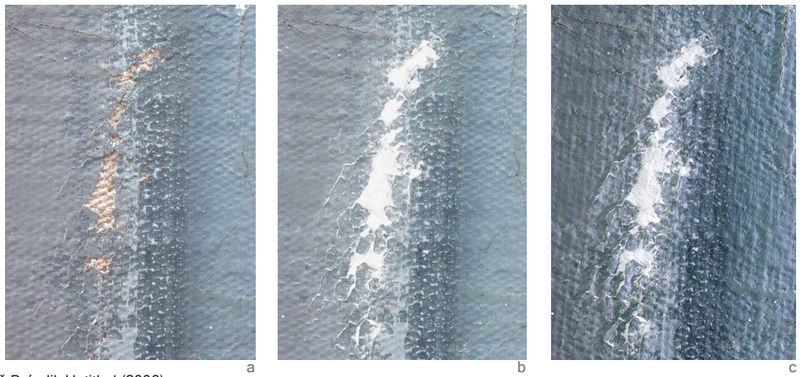


Figure 31: Comparison of different bulking agents in different composition

Any excess filler over the painting can be removed using distilled water, low aromatic hydrocarbons, or acetone, depending on the solubility and sensitivity to water or solvents of the painting.

The imitation of the texture can be achieved during the application of the filler using a brush or spatula, depending on the desired character of the painting. After drying, it is possible to rip or cut the craquelure using scalpels, or to moisten the surface of the filler again with distilled water, depending on each conservator's priorities.

Any type of retouching material may be used on both isolated or nonisolated filler surfaces.



CASE STUDY vol.2_Aleš Brázdil: Untitled (2006)
„In this case, a modern acrylic painting obtained several losses with missing paint and ground layer. Flaking and loose paint occurred around the damages; therefore, the affected areas were firstly consolidated, and the losses within the surrounding paint were accordingly isolated. The selection of the Plextol B500 filler was based on the character of the painting; being a relatively young artwork, a similar material for the fillings as the original paint constitution was sought. Since both materials are based on acrylic dispersion, this filler was deemed appropriate. Furthermore, the handling properties and application method by spatula, as well as the option for incision and imprinting of the textile, were considered significant advantages. As a bulking agent, aluminum hydroxide was chosen due to the increased flexibility it provides to the filler.

Figure 32: Aleš Brázdil: Untitled; macro-photographs in day light before infilling (a); and after filling in day (b) and raking light (c)
Work and photo credit: Jakub Donda

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

This filler exhibited slightly different properties when bulked with different materials.
The amount of dimensional loss during the drying process was especially the reason why calcium carbonate was not used as the sole bulking agent, but only in combination with Bolognese chalk or kaolin. While the former combination of bulking materials exhibited quite good properties except for coherence and adherence to the ground, the latter combination of calcium carbonate and kaolin exhibited incredibly great properties in all aspects, which remained unchanged.
The filler bulked with aluminum hydroxide seemed to be highly flexible; however, bendability tests on the old canvas after accelerated aging showed a significant loss of flexibility, as well as an increase in the occurrence of cracks.
A significant colour change occurred in all samples due to the migration of wax-resin adhesive residues from the old lining canvas, which was observed in the fourth mock-up.

1 The recipe is than on the bases as for Evacon R or Lascaux 498 HV filler on the following pages of the thesis.

PLEXTOL B 500 FILLER
ALUMINIUM HYDROXIDE

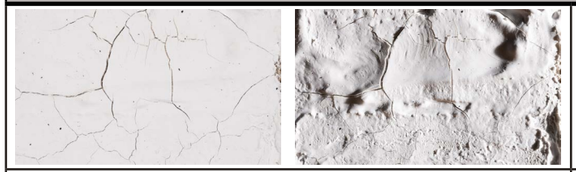
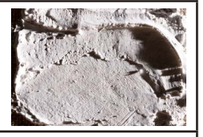
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change whether the filler is applied in thin layer one by one after drying.			
colour change	L* 98.7 a* 0.1 b* 0.4 C* 0.4 h* 67.2	ΔE = 0.7	ΔE = 0.9	ΔE = 6.5 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	Significantly more cracks developed mostly by extending the drying cracks. 	Significantly more cracks developed mostly by extending the drying cracks. 
surface dusting	No material was cought on the cotton swab.	No material was cought on the cotton swab.	No material was cought on the cotton swab.	No material was cought on the cotton swab.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass behaves very pliable and squishy.	The filler maintains its soft and pliable character, the same as was observed in the unaged sample.	The filler remains its soft and pliable character as the unaged sample.	The filler remains its soft and pliable character as the unaged sample.
coherence	The cohesion is very good; since the filler is soft, it can be scratched and sliced very easily into thin flakes without any powdering.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	very good	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -
change in reversibility	distilled water no White Spirit no toluene swelled after 10 rolls ethanol 10 rolls	distilled water no White Spirit no toluene swelled after 10 rolls ethanol 10 rolls	distilled water no White Spirit no toluene swelled after 10 rolls ethanol 10 rolls	distilled water slightly after 30 rolls White Spirit no toluene swelled after 10 rolls ethanol 10 rolls

Table 10: Plextol B500 filler bulked with aluminium hydroxide_evaluation of the properties based accelerated aging tests

PLEXTOL B 500 FILLER
CALCIUM CARBONATE : BOLOGNESE CHALK 1 : 1

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change whether the filler is applied in thin layer one by one after drying.			
colour change	L* 93.0 a* 0.0 b* 3.3 C* 3.3 h* 89.2	ΔE = 0.6	ΔE = 0.8	ΔE = 4.1 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	Significantly more cracks developed mostly by extending the drying cracks. 	No cracking caused by accelerated aging developed. 
surface dusting	The cotton swab is slightly white; only a white dust made of the bulking material was captured.	The cotton swab is less white white compared to the unaged sample; only a white dust made of the bulking material was captured.	The cotton swab is less white white compared to the unaged sample; a white dust made of the bulking material was captured, forming larger configurations.	Almost no material was picked up.
hardness	The filler is quit soft; only a little pressure is required to make a dimple.	The filler remains the same hardness as demonstrated by the unaged sample; only a little pressure is required to make a dimple.	The filler remains the same hardness as demonstrated by the unaged sample; only a little pressure is required to make a dimple.	The filler remains the same hardness as demonstrated by the unaged sample; only a little pressure is required to make a dimple.
coherence	The cohesion is good; when scratched, it is slightly powdering.	The cohesion remains unchanged.	Slightly loss of cohesion; the material exhibits powdering slightly more compared to the unaged sample.	Significantly loss of cohesion; the material exhibits powdering significantly more compared to the unaged sample.
adhesion to the support	very good	remains very good	remains very good	a lot of material removed in large particles significantly loss of the adherence compared to the unaged sample
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -
change in reversibility	distilled water: slightly after 30 rolls White Spirit: no toluene: swelled after 10 rolls ethanol: 10 rolls	distilled water: slightly after 20 rolls White Spirit: no toluene: swelled after 10 rolls ethanol: 10 rolls	distilled water: no White Spirit: no toluene: swelled after 10 rolls ethanol: 10 rolls	distilled water: slightly after 30 rolls White Spirit: no toluene: swelled after 10 rolls ethanol: 10 rolls

Table 11: Plextol B500 filler bulked with calcium carbonate and bolognese chalk (1:1)_evaluation of the properties based accelerated aging tests

PLEXTOL B 500 FILLER
CALCIUM CARBONATE : KAOLIN 2 : 1

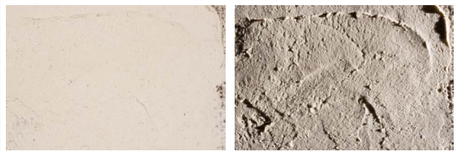
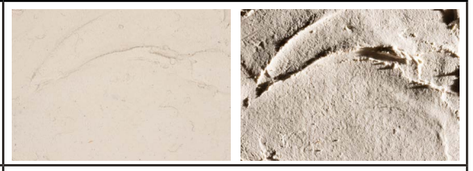
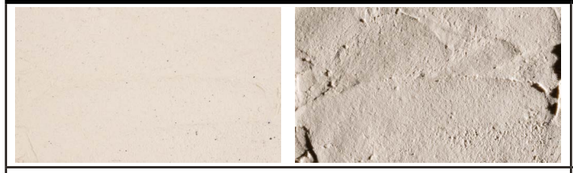
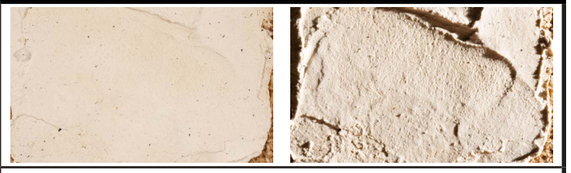
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change for both thin and thick layered application.			
colour change	L* 86.0 a* 0.7 b* 12.4 C* 12.4 h* 86.5	ΔE = 0.4	ΔE = 0.6	ΔE = 5.0 darker and yellower the sample failed the tolerance
craquelure		No cracking developed. 	No cracking developed. 	No cracking developed. 
surface dusting	No material was cought on the cotton swab.	No material was cought on the cotton swab.	No material was cought on the cotton swab.	No material was cought on the cotton swab.
hardness	The filler is quit soft; only a little pressure is required to make a dimple.	The filler remains the same hardness as demonstrated by the unaged sample; only a little pressure is required to make a dimple.	The filler remains the same hardness as demonstrated by the unaged sample; only a little pressure is required to make a dimple.	The filler became slightly less soft compared to the unaged sample; a little more pressure is required to make a dimple.
coherence	The cohesion is very good; since the filler is soft (slightly less than when bulked with aluminium hydroxide), it can be scratched and sliced very easily into thin flakes without any powdering.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	very good	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩
change in reversibility	distilled water — slightly after 10 rolls White Spirit — no toluene — swelled after 10 rolls ethanol — 10 rolls	distilled water — slightly after 10 rolls White Spirit — no toluene — swelled after 10 rolls ethanol — 10 rolls	distilled water — slightly after 15 rolls White Spirit — no toluene — swelled after 10 rolls ethanol — 10 rolls	distilled water — slightly after 15 rolls White Spirit — no toluene — swelled after 10 rolls ethanol — 10 rolls

Table 12: Plextol B500 filler bulked with calcium carbonate and kaolin (2:1)_evaluation of the properties based accelerated aging tests

3.5 VINYL ACETATE-DERIVED POLYMERS_PVAc and PVA

VINYL DERIVATIVES

From a structural point of view, ethylene and its corresponding polymer, polyethylene, are the simplest type of organic molecules - hydrocarbons. The name itself indicates the presence of two compounds in the molecule: carbon and hydrogen. Hydrocarbons can be divided into several classes based on their molecular structure: linear (open chain), cyclic (closed ring-shaped chain of at least three carbon atoms), saturated (containing only simple carbon-carbon bonds), unsaturated (containing double or triple carbon-carbon bonds), and aromatic (derived from the benzene C_6H_6 ring). Therefore, due to the constitution of these hydrocarbons consisting only of carbon and hydrogen, they could be considered, in some way, as the foundation and basis of all other more complex organic compounds.
The chemical process follows this path: a hydrogen atom from the aliphatic (saturated or unsaturated, open or cyclic) or aromatic hydrocarbon is replaced. The remaining structure is called an organic radical to which a series of different atoms (generally, a combination of at least two atoms) is attached, called a functional group. The compound derived by „functionalization“ is called a functional derivative, and the term „functional“ is then replaced by the specific name of the derivative.
For example, from the simplest linear saturated hydrocarbon, ethane, by removing a hydrogen atom, the ethyl radical is produced. In this case, if the removed hydrogen atom is replaced by an oxygen functional derivative (-O-), the resulting product is ethyl ether. This is an example of monomer derivation; when the polymer is derived, the resulting product is called polyethyl ether.
The significant importance in the production of derived polymers lies mainly in the retention of ethylene as the most common product, the monomer of the polymer polyethylene. These derivatives are considered as the precursors of a series of so-called vinyl derivatives. Therefore, the ethylene radical is commonly referred to as the vinyl radical, and the term „vinyl derivatives“ is more commonly used than „ethylene derivatives.“[1]

In the conservation field, for the purpose of treatment and considerations of adhesive properties, mainly three types of oxygen-containing vinyl derivatives are used: polyvinyl alcohol (PVA or PVAl), polyvinyl acetate (PVAc or PVAC), and polyvinyl acetal.
Polyvinyl acetate can be prepared by the direct polymerization of the vinyl acetate monomer. Furthermore, it serves as a starting point for the synthesis of the other two derivatives.
Due to the fact that polyvinyl alcohol cannot be prepared from its nominal monomer, vinyl alcohol, because of its instability, the acetate groups are instead removed from PVAc and replaced by hydroxyl groups attached to the carbon chain in a process called alcoholysis (which is essentially the same process as hydrolysis, but using alcohol instead of water). Depending on the completion of the reaction, there is a choice in the amount of acetate groups remaining in the molecule. This creates a structure that may be considered as a copolymer consisting of vinyl acetate and vinyl alcohol monomer units. Various methods are used to describe the content of vinyl alcohol groups; usually, the molar degree of hydrolysis is identified by its percentage of the description of the product. The proportion of alcohol groups in commercial polymers can range between 70 and 100%, with 100% indicating complete hydrolysis. Another variant is the saponification number which indicates the a certain number of acetyl groups remained in the chain.
In addition, polyvinyl acetals are manufactured by reacting polyvinyl alcohol with an aldehyde. The resulting product is essentially a terpolymer consisting of vinyl acetal, vinyl alcohol, and vinyl acetate monomers. Once again, the proportion of each compound group is indicated as a percentage of the content in the product.[2]

An important class of vinyl acetates used in the restoration field are ethylene-vinyl acetate copolymers, commonly known as EVA copolymers. These EVA copolymers are widely used in everyday life, such as in glues for wood in aqueous dispersion, or EVA is an important component in the bases of BEVA® 371 (which will be further discussed in a chapter on BEVA fillers).[3]

On the market, there are a wide variety of different types of these products. Basically, it depends on the composition of the side components, the type of polymerization and derivation, the degree of hydrolysis, and the form in which the product is delivered to the market. Vinyls can be found in the form of solid resins (bulk, granules, powder...) or dispersions. Furthermore, almost all products include various types. An important parameter is also the length of the starting polyvinyl acetate, which determines the natural size obtained: longer chains lead to higher viscosities and better mechanical properties.

POLYVINYL ACETATE RESINS

The solubility of solid polyvinyl acetate ranges from very polar solvents (alcohols) down to aromatic hydrocarbons (toluene). Polyvinyl acetate is a resin commonly available also in formulations in aqueous dispersion, generally stabilized at an acetic pH.
There is a big question of cross-linking of polyvinyl acetate (as well as polyvinyl alcohol) regarding the solubility of aged films. The cross-linking is increased by the presence of hydroxyl groups, which have a tendency to interact strongly with metal ions (Ca, Cu, Fe, Al), forming coordination complexes. In practice, these metal ions can act as cross-linkers of the polymer. Due to the hydroxyl groups being present in esterified form in polyvinyl acetate, it could be said that their interaction with metal ions is „deactivated.“ However, based on several studies, the aging of polyvinyl acetate produces numerous free -OH groups, ultimately slowly transforming the polyvinyl acetate macromolecule into polyvinyl alcohol. This is responsible for cross-linking and the fact that very aged polyvinyl acetate film, in contact with a pigment layer, is highly difficult to remove (it can only be swelled by prolonged exposure to an aqueous-alcoholic mixture). Therefore, it is important to consider these factors when applying the materials (both polyvinyl acetate and polyvinyl alcohol).
The development of acidity is another potential problem to be carefully evaluated. The hydrolytic decomposition of PVAc leads to the release of acetic acid in situ, which means directly in contact with the material on which the adhesive has been applied. There is a risk of solubilization and corrosion of materials sensitive to acidity (e.g., cellulose, gypsum, calcium carbonate, certain pigments, etc.).[4]
PVAc has a relatively low glass transition temperature (Tg), close to room temperature. The material can then become very soft, attracting and interacting with deposited dirt particles.

POLYVINYL ALCOHOL RESINS

Polyvinyl alcohol is a good adhesive, often used also as a consolidant for pictorial layers, due to its relative opacity compared to classic Paraloid or Primal acrylics, according to the study by M. Bicchieri.[5] First reports of its usage in conservation were in early 1950s for adhering textiles for backings, as an adhesive for parchament and as a heat-seal adhesive for paper.
The degree of hydrolysis determines the solubility of polyvinyl alcohol. It may be soluble in cold water when the degree of hydrolysis is lower than 80%. If the degree is higher than 90%, it is soluble in hot water. Among organic solvents, its solubility is very limited, with solubility observed in ethyl and methyl alcohols, and better solubility when mixed with water.
An interesting characteristic of polyvinyl alcohol is the amount of solid material soluble in water (or hydro-solvent mixture). It is possible to dissolve it up to 20%, however, the maximum working concentration is 10%. This is due to excessive viscosity increase, which poses a risk of irregular accumulation of the product on the surface (creating a glossy effect).
Prolonged exposure to light does not cause cross-linking, and therefore loss of solubility. However, there is unfortunately a progressive loss of mechanical resistance due to chain scission. The tendency to yellow is not significant, occurring only when heated to 100°C, leading to yellowing and cross-linking.
The development of cross-linking occurs, as was described above, in contact with metal ions, metallic salts, which are present in a some of the pigment contents.
Polyvinyl alcohols are prone to biological degradation and are susceptible to biological attack. Therefore, they must be treated with a preservative if they are to be stored for an extended period.[6]

The use of polyvinyl acetate and polyvinyl alcohol as a binding medium for fillers for paintings on canvas was not only described by Laura Fuster-Lopez. The types of resins she used are no longer on the market nowadays. The product Mowilith DMC2 was discontinued in production during the end of the 1990s. It consisted of polyvinyl alcohol with 35% of di-butyl maleate as a copolymer, which acted as an internal plasticizer. According to aging tests conducted by Down et al., Mowilith DMC2 turned out to be the most stable vinyl. As a polyvinyl alcohol, Mowiol 04-M1 was used. It is an internally plasticized copolymer of polyvinyl alcohol with a small amount of polyvinyl acetate by Hoechst, West Germany. Nowadays, it is being produced by several companies under the name Mowiol 4-88 in the market. It is partially hydrolyzed (86.7-88.7 mol% hydrolysis, ~630 polymerization) with no additional components disclosed according to applicable regulations.[7]. These products could be replaced by any other variants available on the market (for example, Rhodopas M, Elvacet, Vinnapas, or Rhodoviol, Elvarol, Poliviol, etc.). Possibly, the products by C.T.S and Kremer Pigmente GmbH & Co. KG, under the names polyvinyl acetate and polyvinyl alcohol, delivered as a powder or granules, are available too. The important values to consider are the additional components, pH, molecular weight, and the degree of hydrolysis (of polyvinyl alcohol).

The use of polyvinyl alcohol as a binding medium for filler was examined in a comparative study by Falvey in 1981. A variety of binding media were considered, and formulations containing synthetic binders were compared with those traditionally used, testing ease of handling, modeling, and minimal shrinkage tendencies. Mowiol 04-M1, produced by Hoechst of West Germany, gave the best results of all the binding media, both synthetic and traditional, that were tested. The putty has good practical handling characteristics similar to the traditional formulations but possesses improved aging characteristics.[8]

Another example of the use of polyvinyl alcohol filler in the treatment of contemporary paintings is by Giovanna Scicolone, who highlights its perfect consistency, adhesion to the support, stable flexibility, reversibility, and user-friendly application.[9]

Two types of polyvinyl alcohols were tested for the filler in the thesis. One with lower and one with higher degree of hydrolysis (Fig. _). The polyvinyl acetate as a medium for filler was not chosen to be tested because of the studies refearing about its instability, degradation and slow molecular change to the polyvinyl alcohol molecules. However, the recipes for both polyvinyl acetate and polyvinyl alcohol are remaining the same, only the solution of the PVAc and PVA is variable depending on the molecular weight and viscosity properties.



Figure 33: Two types of polyvinyl alcohol selected for testing

1 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Vinyl derivatives“, in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 87-90

2 HORIE, C. V. (2010). 'Vinyl Acetate-Derived Polymers', in *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britain, Routledge, ISBN 0 7506 6905 5, pp.137-147

3 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Vinyl derivatives“, in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, p. 95

4 DOWN, J., L., MACDONALD, M., A., TÉTREAULT, J., WILLIAMS, R., S. (1996). A*dhesives Testing at the Canadian Conservation Institute: An Evaluation of Selected Poly (Vinyl Acetate) and Acrylic Adhesives*, Studies in Conservation, Volume 41. pp. 19-44

5 BICCHIERI, M. (1992). *Alcool Polivinilico e restauro: il preché di una scelta e le metodologie d'uso*, CAB Newsletter n°3

6 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Vinyl derivatives“, in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 95-96

7 Product by Sigma-Aldrich® Solutions, specified on the website in safety data sheet: https://www.sigmaaldrich.com/CZ/en/product/aldrich/81381 [19/04/2024]

8 FALVEY, Diane. (1981). *The advantages of mowiol (polyvinyl alcohol): comparative studies of organic and synthetic binding media for fillers for paintings on canvas*. ICOM Committee for Conservation. 6th Triennial Meeting, Ottawa

9 SCICIONE, Giovanna, C. (1993). *Il restauro dei dipinti contemporanei. Dalle tecniche di intervento tradizionali alle metodologie innovative*. Nardini. Firenze

RECIPE FOR PVA FILLER

- 7-9% polyvinyl alcohol (PVA) solution in distilled water
- bulking agent

First of all the solution of polyvinyl acetate in water is prepared. The percentage of the solution depends on a specific kind of polyvinyl acetate but should be kept in a range between 7 -9%. The lower concentration of the solution creates smooth, elastic and easy to work with filler. Two types of polyvinyl alcohol were tested. The first one is named Poval™ 48-80 and it is produced by the Kuraray company[1]. It disposes of 79-81% degree of hydrolysis. The 9% solution in water(a) obtains high viscosity gel with adequate adhesive qualities. The second one disposes of a higher degree of hydrolysis. It is produced by C. T. S. Conservation[2], the degree of hydrolysis is between 87-89%. This type of polyvinyl alcohol was made as the 8% solution in water(b).

The measured amount of polyvinyl alcohol (PVA) is left to be swelled in distilled water(c). The proper delution of PVA practicals could take several hours and is impossible to dissolve it when it is left standing. To speed up the process it is effective to put the solution on a magnetic stirrer, with a slow increase of the temperature, and let it blend for a couple of hours(d).

Once the solution is diluted into a viscous gel(e) it is mixed with a bulking agent(f,g). To obtain a properly mixed filler it could be simplified by the stirring on glass or marble grinding slab(h,i). It is indeed convenient to stir the filling material with PVA solution on the grinding slab with a flat-edged putty knife(j) until no lumps of powder are left and each particle is encapsulated by the adhesive(k,l). The proportion of adhesive to bucking agent depends on the consistency of the filler which is proposed to be achieved[3](m).

The filler could be coloured by pigment if it is required. Pigment could be added both before and after mixing the filling material with PVA solution.

The mixture is stored in a lidded container in a cold environment (refrigerator). It could be stored for several months if the filler is covered with a moisturized piece of cloth or tissue inside the container (without leaving any air gabs).

There is a wide range of bucking agents possible to be used as a filling material. Different kinds of fillers could be added to the PVA solution alone or in a combination with another one in several ratios. The ones chosen for the trials were aluminium hydroxide and calcium carbonate both alone and combined with bolognese chalk and kaolin.



Figure 34a - m: Preparation of PVA filler

1 https://www.kuraray-poval.com/products/kuraray-poval?keyword=polyvinyl%20alcohol&device=c&network=g&gad_source=1&gclid=CjwKCAiA0bWvBhBjEiwAtEsoWzjDCZSU-1VgPIIUfuvK85WMJuSnlxkiOhppCeK6pxvGAKM4NQySihoC-I0QAvD_BwE [02/03/2024]

2 https://ctsconservation.com/en/resins-waxes-and-rubbers/4564-polyvinyl-alcohol-pva-pack-size-1-kg.html [02/03/2024]

3 Laura Fuster Lopez recommend the ratio of bucking agent to PVA solution 1 :1. The achieved consistency has the appearance of yoghurt.

APPLICATION

Depending on the consistency of the mixture, this filler can be used to fill either small shallow losses or large damages.

In cases where large losses need to be filled, the filler could be composed as a more liquid solution applied by brush in several thin layers. This process, casted in this way, will prevent the filler from shrinking, cracking, and changing dimensions during drying. Note that some bubbles could occur on the applied liquid layer; however, after drying, they dissipate.

In cases where the filler should be used to fill smaller losses, it is better to prepare the mixture in a more solid condition. Then, it may be applied by a metal, wood, or stone spatula to the proper position and leveled immediately.

To illustrate this, the differences in the liquidity of the formula are demonstrated in these two pictures by applying it on a textile (Fig.35). The ratio of the PVA solution to the bulking agent (in this case, calcium carbonate in mixture with Bolognese chalk 1:1) is noted in the second picture. The comparison of the appearance of wet and dry filler can be examined.



Figure 35: Comparison of different composition of binding medium and bulking agent applied on textile in wet and dry condition

The consistency of the filler obtained also depends on the type of PVA solution and its viscosity. Moreover, the type and degree of hydrolysis of the polyvinyl alcohol used for the basis of the formula can result in different handling and flexibility properties for the filler. Therefore, it is recommended to test the working features on a piece of Melinex sheet or textile before actual application to the loss on the original painting. Furthermore, the drying process should be observed, and any possible changes in dimension or shrinkage should be noted. If necessary, the mixture should be adjusted accordingly. However, the selection of the bulking agent could also significantly change the flexibility and drying properties. In Figure 36, a mixture of calcium carbonate with kaolin was used in a ratio of 2:1. The first row is made from a 9% Poval™ 48-80 solution, and the second one from an 8% PVA solution produced by C.T.S. Conservation.



Figure 36: Comparison of different composition of binding medium and bulking agent applied on textile

The excesses of the filler over the surrounding paint should be remove immediatly mechanicaly with the spatula or by cotton swab or a piece of cloth dipped in distilled water.

The filler surface could be smoothed by cork, balsa wood or piece of suede of felt cloth. The texturizing could be done at the time, the filler is still slightly wet by incision or layering more liquid filler over the surface, depending on the desired appearance and surrounding painting surface. The moulds or textile imprint could be pressed to the wet filler surface if it is required. Once the filler is dry, it could be reactivated by a little amount of distilled water, and the surface may be adjusted. In the cases, a large loss is being filled, for obtaining the filler to the same level, wide stone spatulas or roller with interlayer of melinex sheet could be used.

It is better to apply a separating layer over the surface before retouching, since the surface is quite hydrophobic. Depending on the components of this layer, the inpainting could be cast by water-based paints as well as the pigments binded in synthetic resin medium or commercial retouching paints.

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

The comparison between fillers bound in two different types of polyvinyl alcohol, namely hydrolyzed polyvinyl acetate, is an interesting aspect, but it could significantly vary when another material is used. The fillers with less hydrolyzed polyvinyl alcohol (Poval™ 48-80) tend to be more flexible and slightly more reversible than those with more hydrolyzed polyvinyl alcohol (C.T.S.).
Interestingly, all the fillers show quite strong resistance to discoloration, even on the old lining canvas with wax-resin adhesive residues, compared to the other tested fillers.
Surprisingly, flexibility is not the best property of PVA fillers, although they exhibit very good flexibility just after application. Both PVA fillers bulked with any material exhibited more or less significant loss of coherence and adhesion to the support.

PVA FILLER_POVAL™ 48-80
ALUMINIUM HYDROXIDE

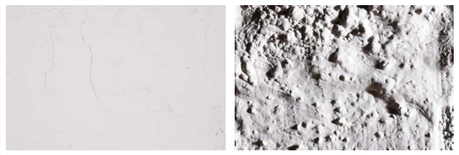
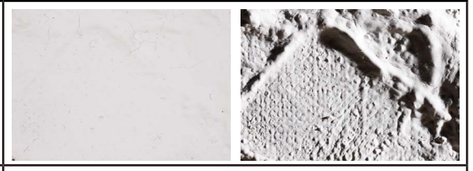
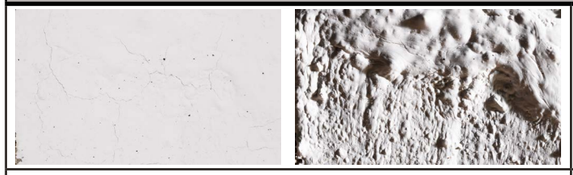
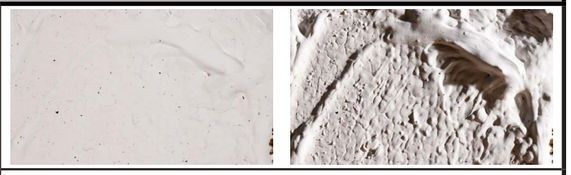
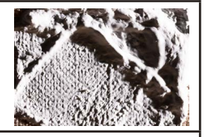
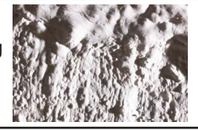
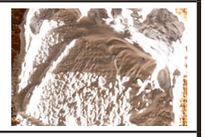
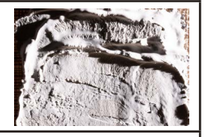
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The filler does not crack during drying; however, around 5% of shrinkage of the fisrt layer applied due to solvent evaporation.			
colour change	L* 99.5 a* 0.2 b* 0.2 C* 0.2 h* 43.3	ΔE = 0.3	ΔE = 0.2	ΔE = 2.9 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	No cracking caused by accelerated aging developed. 	Only a very few cracks caused by accelerated aging developed. 
surface dusting	No material was cought on the cotton swab.	No material was cought on the cotton swab.	No material observeable by human eye was cought on the cotton swab; under the microscope a very few particles of white dust made of bulking agent appears.	No material observeable by human eye was cought on the cotton swab; under the microscope a very few particles of white dust made of bulking agent appears.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass behaves very pliable and squishy.	The filler remains quite soft; when a slight pressure is applied, the filler mass behaves very pliable and squishy.	The filler remains quite soft; however, it lost its squishy and paliable character.	The filler became slightly tougher; it lost its squishy and paliable character.
coherence	The cohesion is very good; since the filler is soft, it can be scratched and sliced very easily into thin flakes without any powdering.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	a little amount of materila removed slightly loss of the adehernce	remains similar as the unaged sample	significantly more material removed significant loss of the adehernce compared to the unaged sample	significantly more material removed significant loss of the adehernce compared to the unaged sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls

Table 13: PVA [Poval™48-80] filler bulked with aluminium hydroxide_evaluation of the properties based accelerated aging tests

PVA FILLER_C.T.S.
ALUMINIUM HYDROXIDE

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition
macro photography day light | raking light		 
drying dimensional change	The filler does not crack during drying; however, around 5% of shrinkage of the first layer applied to solvent evaporation.	
colour change	L* 97.8 a* 0.5 b* 0.4 C* 0.7 h* 39.8	ΔE = 0.5
craquelure		No cracking caused by aging developed. 
surface dusting	No material was cought on the cotton swab.	The cotton swabs are sligthly white; under the microscope dust particles of filling material are visible.
hardness	The filler is quite soft; however, it does not attain the pliable and squishy character to the extent of the previous sample.	The filler remains quite soft; only a little pressure is required to make a dimple.
coherence	The cohesion is very good; since the filler is soft, it can be scratched and sliced very easily into thin flakes without any powdering; compared to the privious sample slightly more difficult to disturb th filler mass.	The cohesion remains unchanged.
adhesion to the support	good	remains good
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls

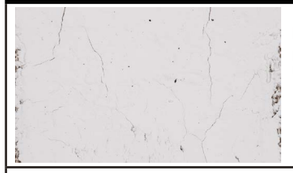
exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
 	 
ΔE = 0.6	ΔE = 2.6 darker and yellower the sample failed the tolerance
The drying cracks became slighty deeper and extended. 	The drying cracks became slightly deeper and extended. 
The cotton swab is sligthly white, approximately twice more times as the previous sample from stable studio environment; under the microscope dust particles of filling material are visible.	The cotton swab is sligthly white, approximately twice more times as the previous sample from stable studio environment; under the microscope dust particles of filling material are visible.
The filler remains quite soft; however, a slightly greater pressure is required to make a dimple in areas where a thick layer of filler was applied, in contrast to those with a thin layer.	The filler remains quite soft; however, a slightly greater pressure is required to make a dimple in areas where a thick layer of filler was applied, in contrast to those with a thin layer.
The cohesion remains unchanged.	The cohesion remains unchanged; only the flakes became sharper, since the filler is slightly tougher.
remains good	material slightly removed slightly loss of the adehernce compared to the unaged sample
ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls

Table 14: PVA [C.T.S.] filler bulked with aluminium hydroxide_evaluation of the properties based accelerated aging tests

PVA FILLER_POVAL™ 48-80
CALCIUM CARBONATE

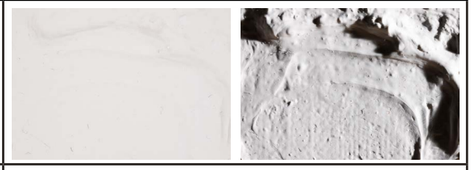
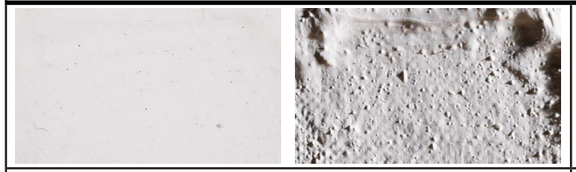
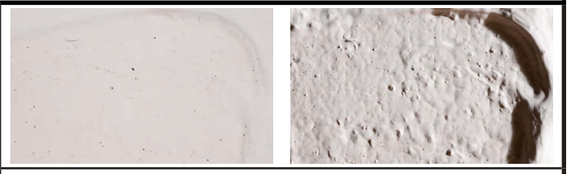
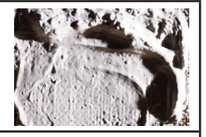
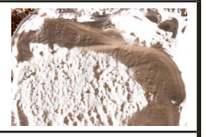
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The filler is slightly cracking during drying; however, around 5% of shrinkage due to solvent evaporation.			
colour change	L* 98.6 a* 0.0 b* 1.0 C* 1.0 h* 88.1	ΔE = 0.5	ΔE = 1.2	ΔE = 2.2 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	No cracking caused by accelerated aging developed. 	No cracking developed. 
surface dusting	No material was cought on the cotton swab.	No material was cought on the cotton swab.	No material was cought on the cotton swab.	No material was cought on the cotton swab.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is soft, whereas where a thick layer was applied, the filler is quite tough.	The filler maintains the same hardness, which varies depending on the thickness of the application.	The filler maintains the same hardness as the unaged sample, which varies depending on the thickness of the application.	The filler maintains the same hardness as the unaged sample, which varies depending on the thickness of the application.
coherence	The cohesion is very good; when scratched (a larger pressure applied compared to the samples bulked with alumoinium hydroxide) a very sufficient flaking are removed.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	very good	remains very good	remains very good	remains very good
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 10 rolls White Spirit no toluene no ethanol no	distilled water 10 rolls White Spirit no toluene no ethanol no	distilled water 10 rolls White Spirit no toluene no ethanol no	distilled water 10 rolls White Spirit no toluene no ethanol no

Table 15: PVA [Poval™48-80] filler bulked with calcium carbonate_evaluation of the properties based accelerated aging tests

PVA FILLER_C.T.S.
CALCIUM CARBONATE

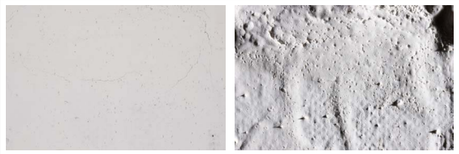
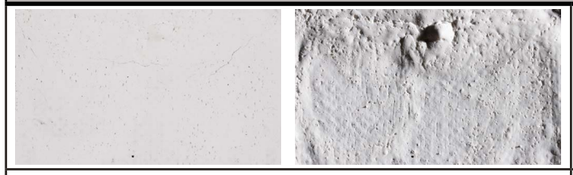
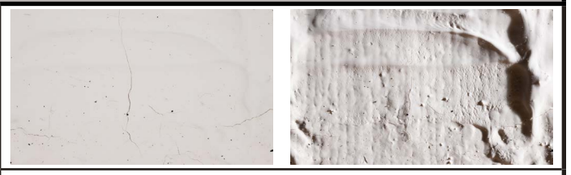
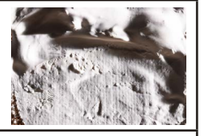
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The filler is slightly cracking during drying; however, around 5% of shrinkage due to solvent evaporation.			
colour change	L* 98.8 a* -0.1 b* 0.3 C* 0.3 h* 117.4	ΔE = 0.8	ΔE = 0.7	ΔE = 2.7 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	No cracking caused by accelerated aging developed. 	A few cracks caused by accelerated aging developed. 
surface dusting	No material was cought on the cotton swab.	The cotton swab is slightly grayish; only a very sufficient, almost unvisible (within the microscope observation) dust was captured from the surface.	The cotton swab is slightly grayish; only a very sufficient, almost unvisible (within the microscope observation) dust was captured from the surface.	The cotton swab is slightly grayish; only a very sufficient, almost unvisible (within the microscope observation) dust was captured from the surface.
hardness	The filler is quite soft; however, in areas where a thicker layer was applied, the filler is slightly tougher.	The filler maintains the same hardness as is discribed by the unaged sample.	The filler became slightly harder in thicker areas, while thin layers retained the same softness as the unaged sample.	The filler became slightly harder in thicker areas, while thin layers retained the same softness as the unaged sample.
coherence	The cohesion is very good; when scratched (a larger pressure applied compared to the samples bulked with alumoinium hydroxide) it is slightly powdering.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	very good	remains very good	material slightly removed slightly loss of the adehernce compared to the unaged sample	material slightly removed slightly loss of the adehernce compared to the unaged sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water — significantly after 5 rolls White Spirit — no toluene — no ethanol — no	distilled water — significantly after 5 rolls White Spirit — no toluene — no ethanol — no	distilled water — 5 rolls (10 rolls same as unaged) White Spirit — no toluene — no ethanol — no	distilled water — 5 rolls (10 rolls same as unaged) White Spirit — no toluene — no ethanol — no

Table 16: PVA [C.T.S.] filler bulked with calcium carbonate_evaluation of the properties based accelerated aging tests

PVA FILLER_POVAL™ 48-80
CALCIUM CARBONATE : BOLOGNESE CHALK 2 : 1

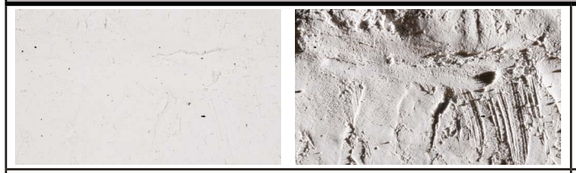
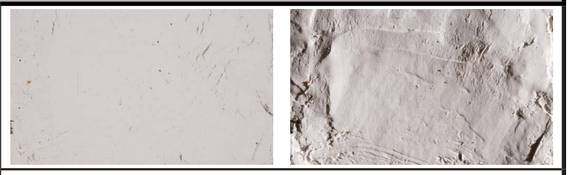
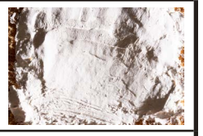
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The filler does not crack during drying; however, shrinkage due to solvent evaporation is lower compared to when it is bulked solely with calcium carbonate.			
colour change	L* 94.8 a* 0.0 b* 1.8 C* 1.8 h* 89.6	ΔE = 0.2	ΔE = 0.4	ΔE = 1.2
craquelure		No cracking caused by aging developed. 	No cracking developed. 	No cracking developed. 
surface dusting	The cotton swab is slightly white; not only white dust was picked up, but also microscopic particles of the filling material.	The cotton swab is slightly white; not only white dust was picked up, but also microscopic particles of the filling material.	The cotton swab is approximately twice as white as before aging, and the microscopic particles of the bulking material are forming larger configurations.	The cotton swab is approximately twice as white as before aging, and the microscopic particles of the bulking material are forming larger configurations.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is soft, whereas where a thick layer was applied, the filler is quite tough.	The filler maintains the same hardness, which varies depending on the thickness of the application.	The filler maintains its characteristic variable hardness even after aging.	The filler maintains its characteristic variable hardness even after aging.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	good	remains good	remains good	material slightly removed slightly loss of the adehernce compared to the unaged sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene no ethanol slightly after 20 rolls	distilled water 5 rolls White Spirit no toluene no ethanol slightly after 20 rolls	distilled water 5 rolls White Spirit no toluene no ethanol slightly after 20 rolls	distilled water 5 rolls White Spirit no toluene no ethanol slightly after 20 rolls

Table 17: PVA [Poval™48-80] filler bulked with calcium carbonate and bolognese chalk (2:1)_evaluation of the properties based accelerated aging tests

PVA FILLER_C.T.S.
CALCIUM CARBONATE : BOLOGNESE CHALK 2 : 1

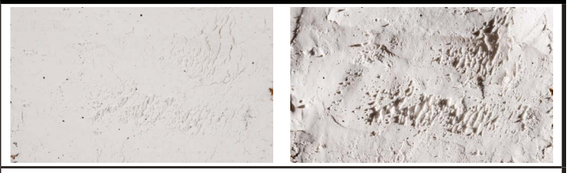
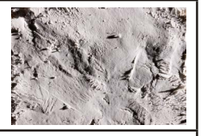
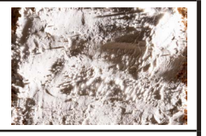
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The filler does not crack during drying; however, shrinkage due to solvent evaporation is lower compared to when it is bulked solely with calcium carbonate.			
colour change	L* 94.1 a* 0.1 b* 2.0 C* 2.0 h* 87.6	ΔE = 0.4	ΔE = 0.2	ΔE = 0.7
craquelure		No cracking caused by aging developed. 	No cracking caused by accelerated aging developed. 	No cracking caused by accelerated anging developed. 
surface dusting	The cotton swab is very slightly white; only white dust made of bulking material was picked up.	The cotton swab is very slightly white; only white dust made of bulking material was picked up.	The cotton swab is approximately twice more white compared to the unaged sample; only white dust made of bulking material was picked up.	The cotton swab is less white compared to the previous sample; only white dust made of bulking material was picked up in similar amount as the unaged sample.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is soft, whereas where a thick layer was applied, the filler is quite tough.	The filler maintains consistent hardness, which varies depending on the thickness of the application; furthermore, it is exhibiting increased brittleness and powdering of the material around the dimple.	The filler remains hardness characteristic as dicribed on the unaged sample; however the increased brittleness and powdering of the material around the dimple occurs.	The filler remains hardness characteristic as dicribed on the unaged sample; however the increased brittleness and powdering of the material around the dimple occurs.
coherence	The cohesion is very good; when scratched, it is slightly powdering.	The cohesion remains unchanged.	Very slightly loss oof cohesion, it is significantly more powdering when scrached, easily removable from the support both as a powder or in larger particles.	Very slightly loss oof cohesion, it is significantly more powdering when scrached, easily removable from the support both as a powder or in larger particles.
adhesion to the support	large amount of material removed significantly lower adherence compered to the other PVA fillers bulked with another material	remains similar as the unaged sample	remains similar as the unaged sample	even allmost all material removed significant loss of the adherence caused by aging process
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water significantly after 5 rolls White Spirit no toluene no ethanol no	distilled water significantly after 5 rolls White Spirit no toluene no ethanol no	distilled water significantly after 5 rolls White Spirit no toluene no ethanol no	distilled water significantly after 5 rolls White Spirit no toluene no ethanol no

Table 18: PVA [C.T.S.] filler bulked with calcium carbonate and bolognese chalk (2:1)_evaluation of the properties based accelerated aging tests

PVA FILLER_POVAL™ 48-80
CALCIUM CARBONATE : KAOLIN 3 : 1

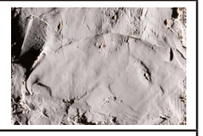
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The filler does not crack during drying; however, shrinkage due to solvent evaporation is lower compared to when it is bulked solely with calcium carbonate.			
colour change	L* 94.0 a* 5.4 b* 5.3 C* 5.3 h* 85.2	ΔE = 0.2	ΔE = 0.2	ΔE = 0.2
craquelure		No cracking caused by aging developed. 	No cracking developed. 	No cracking developed. 
surface dusting	The cotton swab is slightly white; not only white dust was picked up, but also microscopic particles of the filling material.	The cotton swab is slightly white similar to the unaged sample; not only white dust was picked up, but also microscopic particles of the filling material.	The cotton swab is approximately twice as white as the unaged sample; not only was more white dust picked up, but also a larger amount of microscopic particles of the filling material are present.	The cotton swab is slightly less white as the privious sample but more than the unaged sample; more white dust particles were picked up and just a few larger microscopic particles of the filling material are present.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is soft, whereas where a thick layer was applied, the filler is quite tough.	The filler maintains the same hardness, which varies depending on the thickness of the application.	The filler maintains its characteristic variable hardness even after aging.	The filler maintains its characteristic variable hardness even after aging.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	good	remains good	material slightly removed slightly loss of the adehernce compared to the unaged sample	material slightly removed slightly loss of the adehernce compared to the unaged sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene no ethanol slightly after 10 rolls	distilled water 5 rolls White Spirit no toluene no ethanol slightly after 10 rolls	distilled water 5 rolls White Spirit no toluene no ethanol slightly after 10 rolls	distilled water 5 rolls White Spirit no toluene no ethanol slightly after 10 rolls

Table 19: PVA [Poval™48-80] filler bulked with calcium carbonate and kaolin (3:1)_evaluation of the properties based accelerated aging tests

PVA FILLER_C.T.S.
CALCIUM CARBONATE : KAOLIN 3 : 1

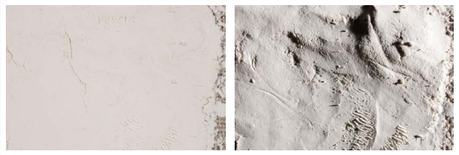
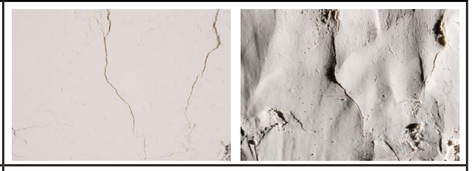
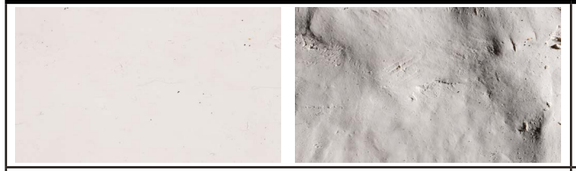
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	The filler does not crack during drying; however, shrinkage due to solvent evaporation is lower compared to when it is bulked solely with calcium carbonate.			
colour change	L* 94.0 a* 0.5 b* 5.7 C* 5.7 h* 85.4	ΔE = 0.3	ΔE = 0.5	ΔE = 0.7 slightly yellower
craquelure		No cracking caused by aging developed. 	No cracking developed. 	A few sufficient cracks caused by accelerated aging developed. 
surface dusting	Almost no material was picked up by the cotton swab; only a few larger particles of the bulking agent are observed.	Almost no material was picked up by the cotton swab; only a few larger particles of the bulking agent are observed.	The cotton swab is slightly grayish due to the presence of a larger amount of larger particles of the bulking agent; however, no dusting material was picked up.	The cotton swab is slightly grayish due to the presence of a larger amount of larger particles of the bulking agent; however, no dusting material was picked up.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is soft, whereas where a thick layer was applied, the filler is quite tough, but less tough than the previous sample.	The filler maintains the same hardness, which varies depending on the thickness of the application.	The filler is slightly softer compared to the unaged sample.	The filler is slightly softer compared to the unaged sample.
coherence	The cohesion is very good; when scratched, it is slightly powdering, easily removable from the support both as powder or in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	good	remains good	material slightly removed slightly loss of the adehernce compared to the unaged sample	more material removed compared to the privious sample loss of the adehernce compared to the unaged sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water significantly after 5 rolls White Spirit no toluene no ethanol no	distilled water significantly after 5 rolls White Spirit no toluene no ethanol no	distilled water significantly after 5 rolls White Spirit no toluene no ethanol no	distilled water significantly after 5 rolls White Spirit no toluene no ethanol no

Table 20: PVA [C.T.S.] filler bulked with calcium carbonate and kaolin (3:1)_evaluation of the properties based accelerated aging tests

RECIPE FOR PVA WITH TYLOSE FILLER

- 25 g solution of Tylose C300 in distilled water (cellulose ether)
- 5 g solution of PVA in distilled water
- 60 g bulking agent
- (pigment to colour)

First of all the solutions of 4% Tylose C300 and the PVA solution both in distilled water are prepared. The measured amount of Tylose is left to be swelled in distilled water overnight(a). The next day Tylose molecules are properly diluted and a gelled solution is obtained(b). Once again, two types of PVA were tested. The first one is named Poval™ 48-80 and it is produced by the Kuraray company[1]. It disposes of 79-81% degree of hydrolysis. The 9% solution in water obtains high viscosity gel with adequate adhesive qualities(c). The second one disposes of a higher degree of hydrolysis. It is produced by C. T. S. company[2], the degree of hydrolysis is between 87-89%. This type of polyvinyl alcohol was made as the 8% solution in water(d).

The proper mixing of the components of the filler glass or marble desk is convenient to be used. It is indeed easier to put the ingredients on the grinding slab and stir them with a small pallet knife then more vigorously with a larger flat-edged putty knife.

Firstly measure the proper amount of Tylose solution(h) and mix it with the measuered amount of PVA solution(i) until the even consistency is achieved. Weight the amount of filling material(j) and place it on the grinding slab. In the middle of the hill of powder pour the adhesive mixture(k). Stir the adhesive into the powder with a pallet and putty knifes(l) until no lumps of powder are left and each particle of bucking agent is encapsulated by the adhesive(m).

If the filler is supposed to be coloured it is recommend to mix the pigment with bucking agent first and just afterwards stir the mixture of powders with adhesive solution.

Store the filler in a lidded container and cold environment (refrigerator). For prolonging the storage of the prepared filler, place a moisturized piece of cloth or tissue directly on the mixture in the container without leaving any air gabs.

There are several possibilities of the filling materials which could be used. In the original recipe for Evacon R filler is recommended aluminium hydroxide and specified as Portafil® A40. It is a commercial product produced by Sibelco company. It is demanded to be a more stable version of aluminium hydroxide[3]. However it is not easily accessible for several countries. That was the reason aluminium hydroxide produced by Kremer Pigmente GmbH & Co. KG was chosen for the trials. The disadvantage is proclaimed to be its absorption moisture from the atmosphere[4]. Next to aluminium hydroxide, calcium carbonate and its mixture with bolognese chalk was tested as well.



Figure 37a - m: Preparation of PVA filler with Tylose C 300

1 https://www.kuraray-poval.com/products/kuraray-poval?keyword=polyvinyl%20alcohol&device=c&network=g&gad_source=1&gclid=CjwKCAiA0bWvBhBjEiwAtEsoWzjDCZSU-1VgPIIUfuvK85WMJuSnlxkiOhppCeK6pxvGAKM4NQySihoC-I0QAvD_BwE [02/03/2024]

2 https://ctsconservation.com/en/resins-waxes-and-rubbers/4564-polyvinyl-alcohol-pva-pack-size-1-kg.html [02/03/2024]

3 http://www.sibelco-specialty-minerals.eu/ssme/applications/32-portafill-a [02/03/2024]

4 SEYMOUR. Kate. (2013). *Fillers: Adaptation on Traditional and Commercial Products,* Lecture presented at NOVA, Lisbon

This recipe is an alternative to the PVA fillers described above, inspired by the Evacon R filler developed at Stichting Restauratie Atelier Limburg (SRAL), which will be described later. The reason for combining two bulking agents (whiting/powder and cellulose ether) was to create a more viscous filler with different flexibility, properties, and application qualities than the filler composed only of PVA in a water solution and filling material.

APPLICATION

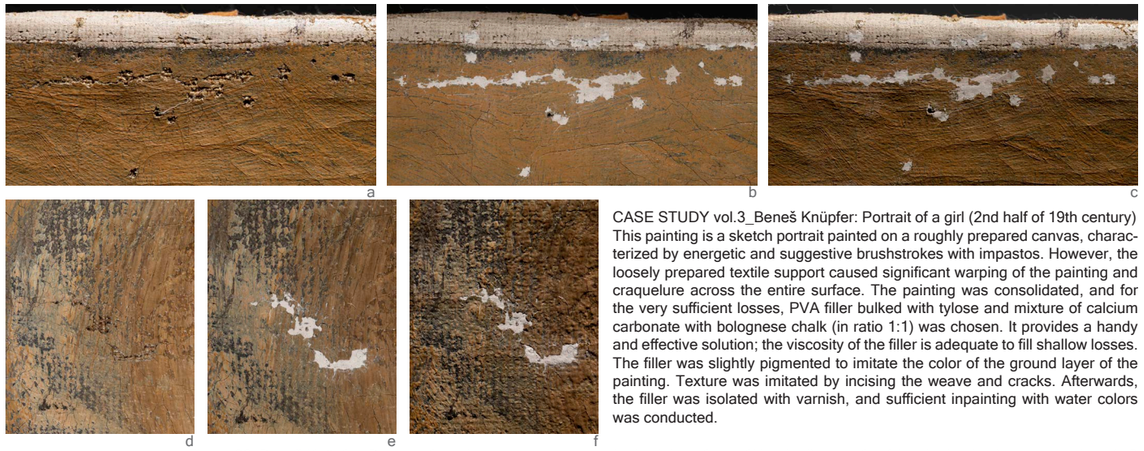
The filler can be used to fill either small shallow losses or larger damages. As previously described, the filler may be stored for a longer period only if kept wet. Unfortunately, one must monitor whether mold begins to grow due to the damp condition of the mixture. To prolong the storage of the filler, only clean tools should be used to remove the amount of filler needed for a particular work. Additionally, storing the filler in a cold environment, such as a refrigerator, could be beneficial.

The filler is obtained as a semi-solid mixture, therefore application with a metal, stone, or wood spatula is required. However, the consistency of the filler obtained also depends on the type of PVA solution and its viscosity. Moreover, the type and degree of hydrolysis of the polyvinyl alcohol used for the basis of the formula can result in different handling and flexibility properties for the filler. Therefore, it is recommended to test the working features on a piece of Melinex sheet or textile before actual application to the loss on the original painting. Furthermore, the drying process should be observed, and any possible changes in dimension or shrinkage should be noted. If necessary, the mixture should be adjusted accordingly.

The excesses of the filler over the surrounding paint should be removed immediately mechanically with the spatula or by cotton swab or piece of cloth dipped in distilled water.

The filler surface could be smoothed by cork, balsa wood or a piece of suede of felt cloth. The texturizing could be done at the time, the filler is still slightly wet by incision or layering more liquid filler over the surface, depending on the desired appearance and surrounding painting surface. The moulds or textile imprint could be pressed to the wet filler surface if it is required. Once the filler is dry, it could be reactivated by a little amount of distilled water, and the surface may be adjusted. In the cases, a large loss is being filled, for obtaining the filler to the same level, wide stone spatulas or roller with interlayer of melinex sheet could be used.

It is better to apply a separating layer over the surface before retouching, since the surface is quite hydrophobic. Depending on the components of this layer, the inpainting could be cast by water-based paints as well as the pigments binded in synthetic resin medium or commercial retouching paints.



CASE STUDY vol.3_Beneš Knüpfer: Portrait of a girl (2nd half of 19th century)
This painting is a sketch portrait painted on a roughly prepared canvas, characterized by energetic and suggestive brushstrokes with impastos. However, the loosely prepared textile support caused significant warping of the painting and craquelure across the entire surface. The painting was consolidated, and for the very sufficient losses, PVA filler bulked with tylose and mixture of calcium carbonate with bolognese chalk (in ratio 1:1) was chosen. It provides a handy and effective solution; the viscosity of the filler is adequate to fill shallow losses. The filler was slightly pigmented to imitate the color of the ground layer of the painting. Texture was imitated by incising the weave and cracks. Afterwards, the filler was isolated with varnish, and sufficient inpainting with water colors was conducted.

Figure 38: Beneš Knüpfer: Portrait of a girl; macro-photographs in daylight before infilling (a,d); and after filling in day (b,e) and raking light (c,f)
Work and photo credit: Marie Čádová

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

A significant difference between PVA fillers bulked not only with powder filling materials (such as calcium carbonate, chalk, aluminum hydroxide) but also with cellulose ethers (in this case Tylose C 300) is their reversibility. These fillers are much more soluble in a wide range of solvents both before and after the accelerated aging process. The fillers bound in less hydrolyzed polyvinyl alcohol (Poval™ 48-80) tend to dissolve more easily compared to those bound by more hydrolyzed polyvinyl alcohol (C.T.S.).
On the other hand, the disadvantage of these fillers compared to the previous ones bulked without the addition of Tylose is exhibited surface dusting and a higher amount of loss of adherence to the support.
The softness of the fillers is an advantage that remains unchanged over the accelerated aging process.
The resistance to colour change is slightly lower for all samples when applied on an old canvas with wax-resin lining adhesive residues.

PVA FILLER WITH TYLOSE C 300__POVAL™ 48-80
ALUMINIUM HYDROXIDE

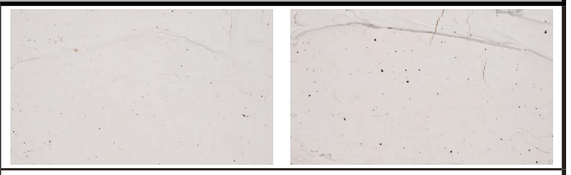
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No significant dimensional change occured.			
colour change	L* 98.3 a* 0.2 b* 0.0 C* 0.2 h* 349.5	ΔE = 0.3	ΔE = 0.4	ΔE = 2.8 darker and yellower the sample failed the tolerance
craquelure		No cracking caused aging developed. 	No cracking developed. 	No cracking developed. 
surface dusting	The cotton swab is white; a large amount of dust powder made of filling material was picked up.	The cotton swab is remains white; a large amount of dust powder made of filling material was picked up.	The cotton swab is remains white; a large amount of dust powder made of filling material was picked up.	The cotton swab remains white; a large amount of dust powder made of filling material was picked up.
hardness	The filler is quite soft; only a little pressure is required to make a dimple.	The filler remains the same softness compared to the unaged sample.	The filler maintains the same softness even after aging.	The filler maintains the same softness even after aging.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	good	remains good	remains good	large amount of material removed loss of the adehernce compared to the unaged sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water: significantly after 5 rolls White Spirit: very slightly after 30 rolls toluene: no ethanol: 5 rolls	distilled water: significantly after 5 rolls White Spirit: very slightly after 30 rolls toluene: no ethanol: 5 rolls	distilled water: significantly after 5 rolls White Spirit: very slightly after 30 rolls toluene: no ethanol: 5 rolls	distilled water: significantly after 5 rolls White Spirit: very slightly after 30 rolls toluene: no ethanol: 5 rolls

Table 21: PVA [Poval™48-80] filler bulked with tylose C 300 and aluminium hydroxide_evaluation of the properties based accelerated aging tests

PVA FILLER WITH TYLOSE C 300_C.T.S.
ALUMINIUM HYDROXIDE

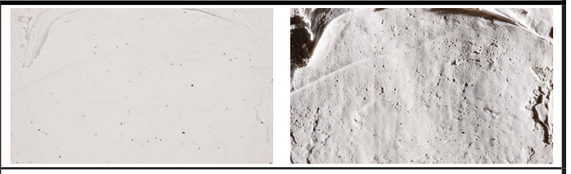
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No significant dimensional change occured.			
colour change	L* 98.0 a* 0.2 b* -0.1 C* 0.2 h* 344.7	ΔE = 0.4	ΔE = 0.2	ΔE = 2.9 darker and yellower the sample failed the tolerance
craquelure		No cracking caused aging developed. 	The drying cracks got by aging extended. 	No cracking developed. 
surface dusting	The cotton swab is white; a large amount of dust powder made of filling material was picked up.	The cotton swab remains white; a large amount of dust powder made of filling material was picked up.	The cotton swab is even whiter; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton.	The cotton swab is remains white, slightly less than the previous sample; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton.
hardness	The filler is quite soft; only a little pressure is required to make a dimple.	The filler remains the same softness compared to the unaged sample.	The filler maintains the same softness even after aging.	The filler maintains the same softness even after aging.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	significantly lower adherence compared to the previous PVA filler sample	large amount of material removed even larger loss of the adherence	large amount of material removed compared to the privious sample even larger loss of the adherence	large amount of material removed, similar as the privious sample even larger loss of the adherence
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water — significantly after 5 rolls White Spirit — slightly after 20 rolls toluene — very slightly after 25 rolls ethanol — 5 rolls	distilled water — significantly after 5 rolls White Spirit — slightly after 20 rolls toluene — very slightly after 25 rolls ethanol — 5 rolls	distilled water — significantly after 5 rolls White Spirit — slightly after 20 rolls toluene — very slightly after 25 rolls ethanol — 5 rolls	distilled water — significantly after 5 rolls White Spirit — slightly after 20 rolls toluene — very slightly after 25 rolls ethanol — 5 rolls

Table 22: PVA [C.T.S.] filler bulked with tylose C 300 and aluminium hydroxide_evaluation of the properties based accelerated aging tests

PVA FILLER WITH TYLOSE C 300_POVAL™ 48-80
CALCIUM CARBONATE

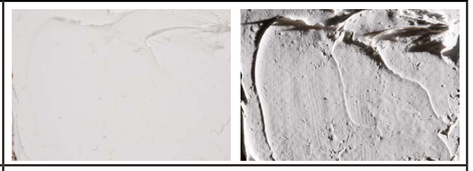
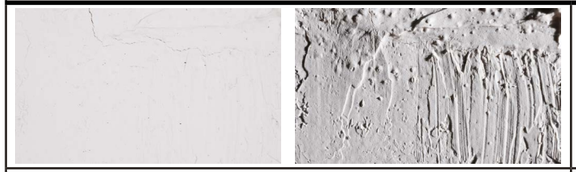
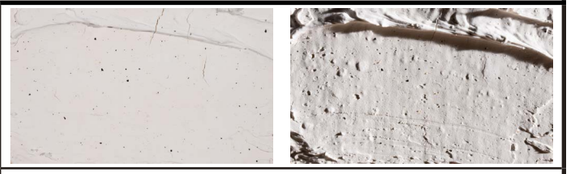
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	A slight dimensional change occured; very sufficient cracking occured in the filler mass.			
colour change	L* 96.9 a* 0.0 b* 0.8 C* 0.8 h* 91.2	ΔE = 0.6	ΔE = 0.4	ΔE = 2.3 darker and yellower the sample failed the tolerance
craquelure		No cracking caused aging developed. 	No cracking developed. 	No cracking developed. 
surface dusting	The cotton swab is sligthly grayish; A little amount of white dust was picked up.	The cotton swab is sligthly grayish; A little amount of white dust was picked up.	The cotton swab is slightly white; approximately twice as much white dust was picked up compared to the unaged sample.	The cotton swab is slightly white; approximately twice as much white dust was picked up compared to the unaged sample.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is soft, whereas where a thick layer was applied, the filler is quite tough.	The filler maintains the same hardness, which varies depending on the thickness of the application.	The filler maintains its characteristic variable hardness even after aging.	The filler maintains its characteristic variable hardness even after aging.
coherence	The cohesion is very good; when scratched a very sufficient powdering occurs, removable from the support both as a powder or in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	good	remains good	material slightly removed slightly loss of the adehernce compared to the unaged sample	good adherence no loss compaered to the previous sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls

Table 23: PVA [Poval™48-80] filler bulked with tylose C 300 and calcium carbonate_evaluation of the properties based accelerated aging tests

PVA FILLER WITH TYLOSE C 300_C.T.S.
CALCIUM CARBONATE

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition
macro photography day light | raking light		
drying dimensional change	A slight dimensional change occured; very sufficient cracking occured in the filler mass.	
colour change	L* 97.2 a* 0.1 b* 0.6 C* 0.6 h* 82.8	ΔE = 0.3
craquelure		No cracking caused aging developed. 
surface dusting	The cotton swab is sligthly grayish; A little amount of white dust was picked up.	The cotton swab is sligthly grayish; A little amount of white dust was picked up.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is soft, whereas where a thick layer was applied, the filler is slightly tougher.	The filler maintains the same hardness, which varies depending on the thickness of the application.
coherence	The cohesion is very good; when scratched a very sufficient powdering occurs, removable from the support both as a powder or in larger particles.	The cohesion remains unchanged.
adhesion to the support	significantly lower adherence compare to the previous PVA filler sample	remains similar as the unaged
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water significantly after 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls

exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
	
ΔE = 0.4	ΔE = 2.0 darker and yellower the sample failed the tolerance
A network of very sufficient cracks developed within the are of very thin layer of the filler. 	The drying cracks got deeper and extended by accelerated aging. 
The cotton swab is slightly white; approximately twice as much white dust was picked up compared to the unaged sample.	The cotton swab is even whiter; approximately three times more white dust was picked up compared to the unaged sample.
The filler maintains its characteristic variable hardness even after aging.	The filler maintains its characteristic variable hardness even after aging.
The cohesion remains unchanged.	The cohesion remains unchanged.
material slightly removed slightly loss of the adehernce compared to the unaged sample	more material removed compared to the privious sample loss of the adehernce compared to the unaged sample
ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
distilled water significantly after 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls

Table 24: PVA [C.T.S.] filler bulked with tylose C 300 and calcium carbonate_evaluation of the properties based accelerated aging tests

PVA FILLER WITH TYLOSE C 300_POVAL™ 48-80
CALCIUM CARBONATE : BOLOGNESE CHALK 1 : 1

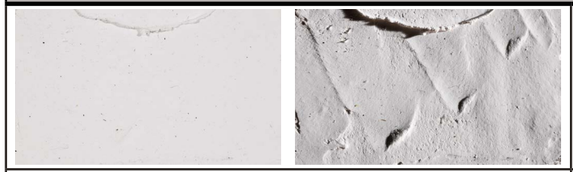
	stabile environment inside black box	63 days of day light exposition in relatively stabile environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macrophotography day light | raking light				
drying dimensional change	No dimensional change occured.			
colour change	L* 93.4 a* 0.5 b* 1.8 C* 1.9 h* 75.3	ΔE = 0.6	ΔE = 0.7	ΔE = 1.1 slightly darker and yellower
craquelure (question of thick and thin levels of filler)		No cracking caused aging developed. 	No cracking developed. 	No cracking developed. 
surface dusting	The cotton swab is slightly white; A few amount of white dust was picked up.	The cotton swab is slightly whiter; approximately twice much white dust was picked up compared to the unaged sample.	The cotton swab is slightly whiter; approximately twice much white dust was picked up compered to the unaged sample.	The cotton swab is slightly whiter; approximately twice much white dust was picked up compered to the unaged sample.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is soft, whereas where a thick layer was applied, the filler is quite tough.	The filler maintains the same variable hardness as the unaged obtained.	The filler maintains the variable hardness depending on the thickness of layer; however, the areas with the thicker layer of filler exhibit slightly softer character compared to the unaged sample.	The filler maintains the variable hardness depending on the thickness of layer; however, the areas with the thicker layer of filler exhibit slightly softer character compared to the unaged sample.
powdering	The cohesion is very good; when scratched a very sufficient powdering occurs, removable from the support both as a powder or in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the ground	significantly lower adherence compare to the previous PVA filler sample	large amount of material removed even larger loss of the adherence	large amount of material removed compared to the privious sample even larger loss of the adherence	large amount of material removed, similar as the privious sample even larger loss of the adherence
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in revesibility	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls

Table 25: PVA [Poval™48-80] filler bulked with tylose C 300 and calcium carbonate with bolognese chalk (1:1)_evaluation of the properties based accelerated aging tests

PVA FILLER WITH TYLOSE C 300_C.T.S.
CALCIUM CARBONATE : BOLOGNESE CHALK 1 : 1

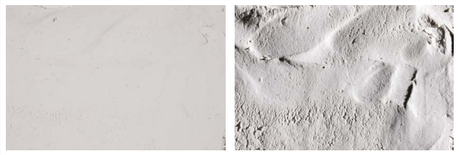
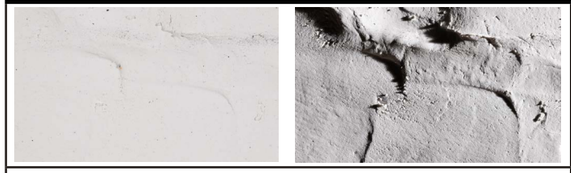
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change occured.			
colour change	L* 92.8 a* 0.4 b* 2.6 C* 2.6 h* 82.0	ΔE = 0.3	ΔE = 0.4	ΔE = 1.2 slightly yellower
craquelure		No cracking caused aging developed. 	No cracking developed. 	A few cracks caused by accelerated aging developed on both thin and thick layered filler. 
surface dusting	The cotton swab is white; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton.	The cotton swab is white; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton.	The cotton swab remains white; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton. No difference between aged and unaged samples.	The cotton swab remains white; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton. No difference between aged and unaged samples.
hardness	The filler is quit soft in both thick and thin layer in contrast to the previous sample; only a little pressure must be applied to make a dimple.	The filler maintains the same softness as demonstrated on the unaged sample.	The filler remains the same softness as demonstrated on the unaged sample.	The filler remains the same softness as demonstrated on the unaged sample.
coherence	The cohesion is very good; when scratched a very sufficient powdering occurs (slighlty more compared to the previous sample), removable from the support both as a powder or in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	significantly lower adherence compare to the previous PVA filler sample	large amount of material removed even larger loss of the adherence	large amount of material removed compared to the privious sample even larger loss of the adherence	large amount of material removed, similar as the privious sample even larger loss of the adherence
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water — significantly after 5 rolls White Spirit — slightly after 20 rolls toluene — no ethanol — 5 rolls	distilled water — significantly after 5 rolls White Spirit — slightly after 20 rolls toluene — no ethanol — 5 rolls	distilled water — significantly after 5 rolls White Spirit — slightly after 20 rolls toluene — no ethanol — 5 rolls	distilled water — significantly after 5 rolls White Spirit — slightly after 20 rolls toluene — no ethanol — 5 rolls

Table 26: PVA [C.T.S.] filler bulked with tylose C 300 and calcium carbonate with bolognese chalk (1:1)_evaluation of the properties based accelerated aging tests

3.6 VINYL AND ACRYLIC DISPERSIONS_EVACON R and LASCAUX 498 HV

The characteristics of vinyl and acrylic resins have already been described in previous chapters. Both resins are available as powders or granules, as well as in dispersions on the market. The process of creating the dispersions is similar for both types of synthetic resins. The preparation of acrylic dispersion was previously explained in a chapter dedicated to Plextol B 500, which is an acrylic dispersion. However, let me briefly explain it in comparison to vinyl dispersions once again.
The starting materials are emulsified with water. The emulsified monomer droplets are then mixed with an initiator, which is required for the polymerization reaction known as emulsion polymerization.[1] Basically, the initiator causes the monomers to polymerize and form polymer chains within the emulsion. Afterwards, surfactants and stabilizers are added to maintain the stability and distribution of the polymer particles, although the method of stabilization could differ.
The main differences are, of course, first of all the starting material, the type of resin. Acrylic dispersions are made from esters of acrylic and methacrylic acid, while vinyl dispersions are made from vinyl monomers including vinyl acetate (VAc) for polyvinyl acetate (PVAc) dispersions and vinyl chloride (VC) for polyvinyl chloride (PVC) dispersions. The materials used as initiators, emulsifiers, and stabilizers are different for both types of dispersions, as well as the additive components added after the polymerization process to adjust the properties of the resulting dispersion.

The use in conservation could differ for both types of dispersions. They could be used as adhesives, consolidating agents, coatings, final varnishes, mediums for paints, mediums for fillers, etc. There is a huge range of companies producing these materials, in different types, quantities, and with various additives which are not always specified and indicated in data sheets.

One of the most important comparative studies was done by the *Canadian Conservation Institute* in 1996[2]. They examined a wide range of vinyl and acrylic resins and compared their properties before and after accelerated aging (together after 20 years of aging). Unfortunately, the study was concentrated only on products in the American market. No study in such a large format has been conducted in the European context so far. For example, the tests were conducted for several types of *Paraloid (Acryloid), Rhoplex emulsions* (similar to the European variant *Plextol B500*), *Lascaux 360 HV, BEVA 371*, aqueous emulsions *CM Bonds M-2* and *M-3, Mowilith* types, *Elmer's glue types, Vinnapas dispersions EP1*, or *UHU All-purpose Clear Adhesive*, etc. Finally, 52 samples, 27 vinyls, and 25 acrylics, were made in two different series: one to be aged in the dark and one to be aged by light exposure (700-800 lux and 190 µW/lm-1, with UV). To compare the properties of various adhesives, five parameters were considered: pH, emission of volatile substances, mechanical tensile strength, flexibility, and color. Here is a brief summary of the results and conclusions reported in the study:

- The pH results showed that the PVAc adhesives were more acidic than the acrylic adhesives and that light aging tended to decrease the pH of both classes. The PVAc homopolymers were generally more acidic than the PVAc copolymers, and many acrylic adhesives containing butyl acrylate were found to be neutral.
- The analysis of volatile compounds from the PVAc and acrylic adhesives showed that they emitted various ester and residual solvent compounds. Only the PVAc adhesives released appreciable quantities of acetic acid, but any risk associated with these emissions decreases rapidly after the initial curing period of several weeks.
- In general, both the PVAc and acrylic adhesives became less flexible upon dark aging, and the PVAc adhesives were stronger and less flexible than the acrylic adhesives. PVAc copolymers displayed and retained more flexibility than PVAc homopolymers.
- The PVAc adhesives yellowed approximately twice as quickly as the acrylic adhesives, and light aging tended to make all the adhesives yellow more quickly than dark aging.

The question of releasing acetic acid and the change of pH down to over 4 must be taken carefully. Materials that produce this transformation should not be used on supports sensitive to acidity, such as textiles and paper. Furthermore, the volatile acid can attack parts of the work which are not in direct contact with the material[3]. This should be seriously taken into account when the material is chosen not only as a binding medium for fillers.

LASCAUX HV 498®
The characterization of this product is very close to Plextol B500. It is a dispersion of a thermoplastic acrylic polymer based on methyl methacrylate and butyl acrylate, thickened with acryl-butyl ester to reduce penetration. The film has a softening temperature between 68-76°C, and the pH value is stabilized at 8-9 and treated with preservatives.
It is dilutable with water, although after drying it becomes water-insoluble. It is permanently soluble in acetone, alcohol, toluene, and xylene, however insoluble in aliphatic solvents such as white spirit.[4]
On the market there is also a product named Lascaux 498-20X®. It is the same product but with 20% od xylene to reduce the penetration in the pictorial layer. It is especially suited for strip-lining, fabric marouflages and mounting. Mehra studies describe a possible use of this product for a lining system with reduced humidity for water-sensitive painting, reactivating with solvents.[5] It has the identical solubility, pH and softening temparature, but its drying is much faster.[6]



Figure 39: Lascaux 498 HV

1 Acrylic dispersions may also be prepared by the less widely used process of solution polymerization, although it is not as commonly preferred as emulsion polymerization. In this case, acrylic monomers are dissolved in a suitable solvent. The similar process is then undertaken with the initiators and the polymerization reaction. After the reaction, the solvent is often removed to obtain the acrylic resin in solid form. This product could be further modified, or the resulting solid resins can go directly to the market for specific applications, such as consolidants, adhesives, etc.

2 DOWN, J., L., MACDONALD, M., A., TÉTREAULT, J., WILLIAMS, R., S. (1996). A*dhesives Testing at the Canadian Conservation Institute: An Evalation of Selected Poly (Vinyl Acetate) and Acrylic Adhesives*, Studies in Conservation, Volume 41. pp. 19-44

3 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch III. Evaluation studies of synthetic adhesives", in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, p. 58

4 Information from Lascaux HV 498 product specification date sheet: https://www.kremer-pigmente.com/elements/resources/products/files/81002e.pdf [03/2024]

5 For more informations see the chapter about Plextol B500, page 29.

6 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Acrylic esters", in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, p. 135

An important comparative study on acrylic dispersions used in the conservation field was conducted by the American researcher M. C. Duffy. The research considered five different products: Plextol B500, Rhoplex AC33, Rhoplex AC234 (similar to Primal, available in Europe), Lascaux 360 HV, and Lascaux 498 HV. The adhesives were examined in two possible applications: firstly, as thin pure films applied on a plastic board, allowed to dry, and then the adhesive films were detached from the support; secondly, as a lining adhesive by simultaneously lining the original and supporting canvas, activating the adhesive on a low-pressure table when in a wet condition, and then reactivating the dry film with toluene. Half of the samples underwent accelerated aging in an environmental chamber, while the second half remained under ambient conditions. The results were compared after 100 hours of aging. The parameters considered were: color change as a measure of yellowing; swelling by distilled water, isopropyl alcohol, and toluene to indicate solubility; and detachment force by peel strength to indicate reversibility.
The best results were obtained with Plextol B500, which was already described in a chapter dedicated to Plextol B500. However, the results for Lascaux 498 HV are also very valuable. The peel strength values were significantly different for the non-aged and aged film. It appears that the adhesion to the support increases with aging, requiring more stress to separate bonded materials. The discoloration of Lascaux 498 HV was the second most measured among the examined adhesives, just after Plextol B500. The measured difference was 1.96 in Chroma values, which still remains relatively low. Particularly high values of swelling up to 50% were observed with toluene; however, slight swelling also occurred with water for the unaged film. Nevertheless, the long-term reliability of these materials appears questionable, considering the short-term aging exposure.[7]

EVACON R™
Evacon R is a water-based dispersion adhesive. It is a low molecular weight ethylene vinyl acetate copolymer emulsion which contains no surfactant additives and is resistant to hydrolysis. This property is achieved by the rearrangement of acetate groups, due to the presence of polyethylene blocks. There is also a very low presence of calcium carbonate in the composition of the glue, which assists in stability and acidity reduction. Evacon R™ has a neutral pH of 7-8, is non-plasticized[8], and remains water-soluble when dry. It was formulated in the UK by Conservation by Design Ltd. in 1983 for the conservation field.[9] A disadvantage of this product is that it is not easily available in other European countries, only in the UK market.

Evacon R is widely used in the paper conservation field, which also led the Czech National Archive to conduct a study on different types of glues used in practice. For the comparative study of the properties of Evacon R, the following commercial glues were included: Akrylep 545x1, Akrylep 545x2, Duvilax BD20, and Planatol Elasta. Samples were prepared in several sets for accelerated aging in a climatic chamber with higher humidity exposure. Afterwards, the adhesives were compared for aged and non-aged samples. The parameters considered were the influence of the type of application on the flexibility of the materials, microbiological degradation, change in color, pH value, solubility in organic solvents, and peel strength.
The results of the accelerated aging were very satisfactory, and the conclusion is to recommend this product for use in the conservation field despite some changes in properties after aging. Mostly, no significant degradation had occurred; only the change in color after aging was noted. In the higher humidity environment, the glue film darkened and yellowed. However, the values remained significantly lower than for the other tested glues. The best reversibility of the aged glue was obtained with water; after 30 minutes, the film was very uneven, swelled, and easily removable. With ethanol, acetone, and toluene, the film swelled after 30 minutes of exposure to these solvents, making it difficult to remove without leaving residues.[10]



Figure 40: Evacon R

Fillers based on Evacon R™ glue were composed at Stichting Restauratie Atelier Limburg (SRAL) in the Netherlands. These recipes consist not only of the binding medium (Evacon R™ glue) but also include cellulose ethers as components. While these materials are mostly known as binders or (low) adhesives, they can also act as a bulking agent when added to formulations and may assist in maintaining water solubility.
SRAL presented two types of Evacon R fillers. The first one, chosen for the accelerated aging tests, consists of Tylose C300 (using a 4% solution in water), Evacon R, and aluminum hydroxide (Portafl A40). It is noted that Tylose C300 could be replaced by another type of cellulose ether, such as Klucel G, Tylose MH300, or Methocel A4M, and likewise, Evacon R could be substituted with another EVA or PVA glue. This flexibility led to the inclusion of a filler based on Lascaux 498 HV in this study, as it is more readily available in European countries such as the Czech Republic.
Subsequently, there is an alternative filler reported by SRAL. After several tests by SRAL, it is also recommended due to its stability, flexibility, and resistance. The recipe is as follows:

- 15 mL Evacon R (EVA)
- 85 mL Water
- 60 g Mica (Phyllosilicates)
- 40 g Chalk: calcium carbonate (CaCO3)

Mix the Evacon R and water together. Then mix the Mica powder and the chalk. Combine all the ingredients until a stiff consistency is obtained. Note that this filler will be slightly more brittle than the above mixture as it has a higher portion of inert fill ingredients.[11]

7 DUFFY, M., C. (1989). „A study of Acrylic dispersions used in the treatment of paints", in *Journal of the American Institute for Conservation*, JAIC Volume 28, pp. 67-77

8 safety data sheet: https://shop13501.sfstatic.io/upload_dir/docs/Lim/CXD-MSDS-Evacon-2021-safety.pdf [21/04/2024]

9 BURG, J., M., Van den, SEYMOUR, K. (2024). *Painting conservation part 4: Filling Losses in Paint.* Cultural Heritage Agency of the Netherlands. Ministry of Education, Culture and Science. Amersfoort. p. 35

10 The Research Laboratory, 10th department of the Národní Archiv of The Czech Republic. (2003). *Vlastnosti lepidla Evacon-R™*

11 BURG, J., M., Van den, SEYMOUR, K. (2024). *Painting conservation part 4: Filling Losses in Paint.* Cultural Heritage Agency of the Netherlands. Ministry of Education, Culture and Science. Amersfoort. p. 41

RECIPE FOR EVACON R FILLER

- 25 g solution of Tylose C300 in distilled water (cellulose ether)
- 5 g Evacon R
- 60 g bulking agent
- (pigment to colour)

First of all the 4% solution of Tylose C300 in water is prepared. The measured amount of Tylose is left to be swelled in distilled water overnight(a). The next day Tylose molecules are properly diluted and a gelled solution is obtained(b).

The proper mixing of the components of the filler glass or marble desk is convenient to be used. It is indeed easier to put the ingredients on the grinding slab and stir them with small a pallet knife then more vigorously with a larger flat-edged putty knife.

Firstly the proper amount of Tylose solution is measured(d), afterwards on the scale tare button is clicked(e) and desired amount of Evacon R is measured to the same container(f). Both solutions are mixed thoroughly until the even consistency is achieved, into slightly white solution(g). Weight the amount of filling material and place it on the grinding slab. In the middle of the hill of powder pour the adhesive mixture (h). Stir the adhesive into the powder with a pallet and putty knives(i) until no lumps of powder are left and each particle of bucking agent is encapsulated by the adhesive(j).

If the filler could be coloured it is recommended to mix the pigment with bucking agent first and just afterwards stir the mixture of powders with adhesive solution.

Store the filler in a lidded container and cold environment (refrigerator). For prolonging the storage of the prepared filler, place a moisturized piace of cloth or tissue directly on the mixture in the container without leaving any air gabs.

There are several possibilities of the filling materials which could be used. In the original recipe is recommend the aluminium hydroxide and specified as Portafil® A40. It is a commercial product produced by Sibelco company. It is demand to be more stable version of aluminium hydroxide[1]. However it is not easily accessible for several countries. That was the reason aluminium hydroxide produced by Kremer Pigmente GmbH & Co. KG was chosen for the trials. The disadvantage is proclaimed to be its absorption moisture from the atmosphere[2]. Next to aluminium hydroxide, calcium carbonate and its mixture with bolognese chalk was tested as well.



Figure 41a - j: Preparation of Evacon R filler

1 http://www.sibelco-specialty-minerals.eu/ssme/applications/32-portafill-a [02/03/2024]

2 SEYMOUR. Kate. (2013). *Fillers: Adaptation on Traditional and Commercial Products,* Lecture presented at NOVA, Lisbon

APPLICATION

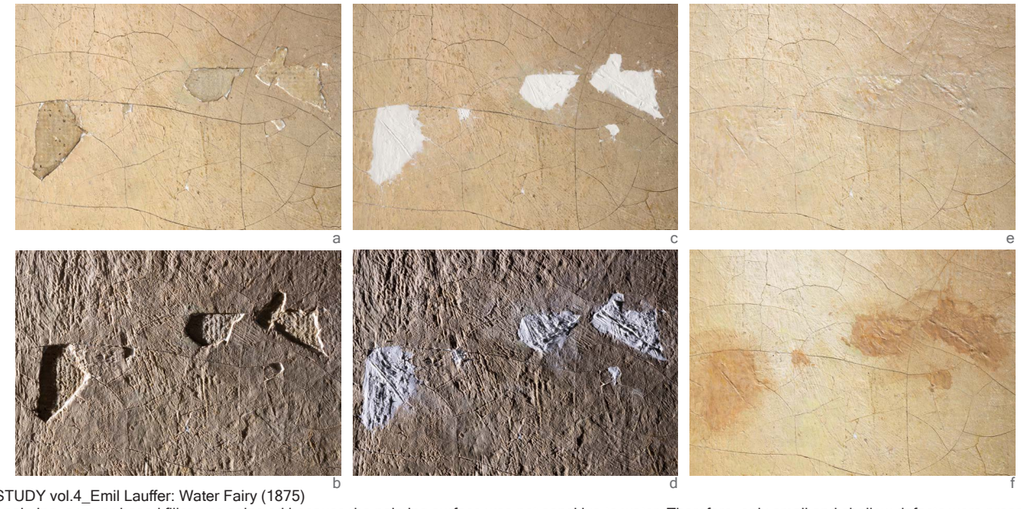
This filler is primarily designed for use as an infilling material for larger losses on a canvas painting. However, it can also be used for smaller damages. As already described, the filler may be stored for a longer period only if kept wet. Unfortunately, one must monitor whether mold begins to grow due to the damp condition of the mixture. To prolong the storage of the filler, only clean tools should be used to remove the amount of filler needed for a particular work. Additionally, storage in a cold environment, such as a refrigerator, could be beneficial.

The filler is obtained as a semi-solid mixture, therefore application with a metal, stone, or wood spatula is required.

The excesses of the filler over the surrounding paint should be removeed immediately mechanically with the spatula or by cotton swab or piece of cloth dipped in distilled water.

The filler surface could be smoothed by cork, balsa wood or a piece of suede of felt cloth. The texturizing could be done at the time, the filler is still slightly wet by incision or layering more liquid filler over the surface, depending on the desired appearance and surrounding painting surface. The moulds or textile imprint could be pressed to the wet filler surface if it is required. Once the filler is dry, it could be reactivated by a little amount of distilled water, and the surface may be adjusted. In the cases, a large loss is being filled, for obtaining the filler to the same level, wide stone spatulas or roller with interlayer of melinex sheet could be used.

It is better to apply a separating layer over the surface before retouching, since the surface is quite hydrophobic. Depending on the components of this layer, the inpainting could be cast by water-based paints as well as the pigments binded in synthetic resin medium or commercial retouching paints.



CASE STUDY vol.4_Emil Lauffer: Water Fairy (1875)
For this painting, a water-based filler was selected because the painting surface was not sensitive to water. Therefore, only small and shallow defects were present on the painting, requiring a filler with good working properties, easy handling, and good adjustability and flattening. For that reason, Evacon R filler bulked with a mixture of calcium carbonate and Bolognese chalk (1:1) was chosen. The filler was applied with a metal spatula and immediately flattened and leveled. Any excess over the surrounding painting was removed with a cotton swab dipped in distilled water (a thinned varnish layer was kept on the painting, therefore, no initial varnish layer was applied). Further texturing of the filler surface was done under raking light conditions. The crackle of the paint and the painting's technique, including the impastos and brushstroke character, were imitated by applying a more liquid filler with a brush and making incisions with the tip of a scalpel. The separating layer, consisting of 10% Regalrez 1094 dissolved in Shellsol D 40, was applied only on the fillers with a brush. The base for retouching was made using watercolors, and the final touches were applied using Gamblin retouching paints.

Figure 42: Emil Lauffer: Water Fairy; macro-photographs before and after filling in daylight (a,c) and raking light (c,d) ; after retouching in daylight (e) and UV luminescence (f)

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

All types of differently bulked fillers exhibited good properties, which remained more or less unchanged. However, the disadvantage of these fillers is the excessive surface dusting observed on all samples, both aged and unaged. Furthermore, the adhesion to the textile support is not the best compared to other fillers that were tested. A large amount of material was removed by Scotch Tape Tests, especially when bulked with calcium carbonate alone or in combination with bolognese chalk. The flexibility of the samples is also not the highlight of these fillers.
The advantage of this type of filler is the retained softness, especially the fillers bulked with aluminum hydroxide, which are very pliable and smooth. Another good characteristic is the solubility in solvents, which remained unchanged.
Interestingly, the resistance to colour change could be observed for fillers bulked with aluminum hydroxide and a mixture of calcium carbonate and Bolognese chalk. The filler bulked only with calcium carbonate became slightly yellower and darker when applied on the old canvas with residues of wax-resin lining adhesive.

EVACON R FILLER
ALUMINIUM HYDROXIDE

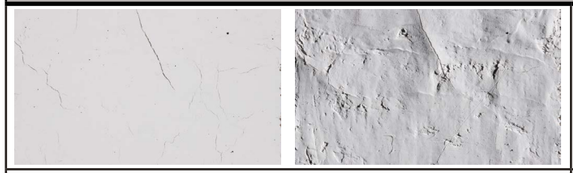
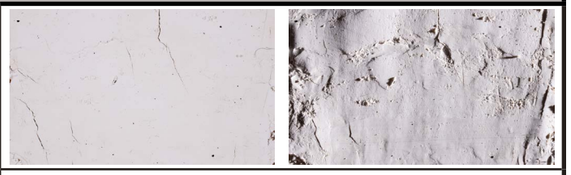
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	A slight dimensional change occured; very sufficient cracking occured in the filler mass.			
colour change	L* 98.9 a* 0.2 b* 0.5 C* 0.6 h* 71.3	ΔE = 0.1	ΔE = 0.1	ΔE = 1.3 slightly yellower
craquelure		No cracking caused aging developed. 	No cracking caused by accelerated aging developed. 	The drying cracks got slightly extanded. 
surface dusting	The cotton swab is slightly grayish; A little amount of white dust was picked up.	The cotton swab is slightly white; A little larger amount of white dust, approximately twice much compared to the unaged sample, was picked up.	The cotton swab is slightly white; A little larger amount of white dust, approximately twice much compared to the unaged sample, was picked up.	The cotton swab is slightly white; A little larger amount of white dust, approximately three times more compared to the unaged sample, was picked up.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass behaves very pliable and squishy.	The filler maintains its soft and pliable character, the same as was observed in the unaged sample.	The filler remains its soft and pliable character as the unaged sample.	The filler maintains its soft and pliable character as the unaged sample.
coherence	The cohesion is very good; when scratched a ver sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed	similar when compared to the unaged sample	remain similar when compared to the unaged sample	remain similar when compared to the unaged sample
flexibility	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls

Table 27: Evacon R filler bulked with aluminium hydroxide_evaluation of the properties based accelerated aging tests

EVACON R FILLER
CALCIUM CARBONATE

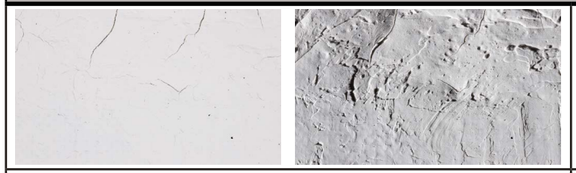
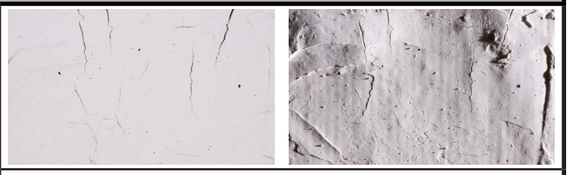
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	Slightly larger dimensional change occured, compared to the filler bulked with aluminium hydroxide; significant cracking occured in the filler mass.			
colour change	L* 97.0 a* -0.1 b* 0.6 C* 0.6 h* 95.8	ΔE = 0.1	ΔE = 0.4	ΔE = 2.6 darker and yellower the sample failed the tolerance
craquelure		No cracking caused aging developed. 	Only a slightly cracking caused by aging developed. 	The drying cracks got slightly extanded and new cracks caused by accelerated aging occured. 
surface dusting	The cotton swab is slightly white; only white powder dust was picked up.	The cotton swab is slightly white same as the unaged sample; only white powder dust was picked up.	The cotton swab is slightly whiter compared to the unaged sample (0,5 more times); only white powder dust was picked up.	The cotton swab is slightly white same as the unaged sample; only white powder dust was picked up.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass is little less pliable and squishy than the formulation mixed with aluminium hydroxide; however, on the thick layers it is little tougher.	The filler maintains its soft character, the same as was observed in the unaged sample.	The filler remains its soft and pliable character as the unaged sample, moreover, the thick layer of filler is even softer than before aging.	The filler remains its soft and pliable character as the unaged sample, moreover, the thick layer of filler is even softer than before aging.
coherence	The cohesion is very good; when scratched a ver sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed approximately the same as the filler bulked with aluminium hydroxide	similar when compared to the unaged sample	remains similar when compared to the unaged sample	remains similar when compared to the unaged sample
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls

Table 28: Evacon R filler bulked with calcium carbonate_evaluation of the properties based accelerated aging tests

EVACON R FILLER
CALCIUM CARBONATE : BOLOGNESE CHALK 1 : 1

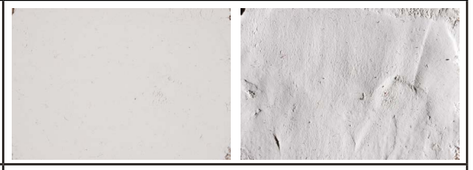
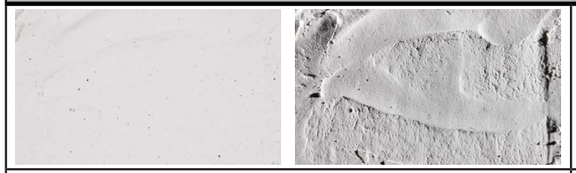
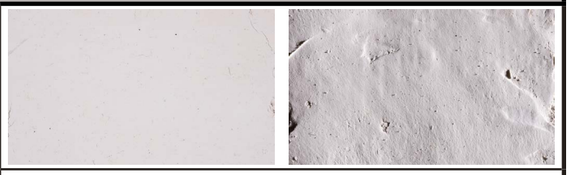
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimenasional change occured.			
colour change	L* 93.1 a* 0.3 b* 2.4 C* 2.4 h* 83.1	ΔE = 0.5	ΔE = 0.3	ΔE = 0.7 slightly yellower
craquelure		No cracking developed. 	No cracking developed. 	No cracking developed. 
surface dusting	The cotton swab is white; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton.	The cotton swab remains white; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton.	The cotton swab remains approximately as white as the one from the unaged sample; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton.	The cotton swab remains approximately as white as the one from the unaged sample; a large amount of dust powder made of filling material was picked up, filling the gaps between the threads of the cotton.
hardness	The filler is quite soft; only a slight pressure applied make a dimple.	The filler retains its soft character, the same as was observed in the unaged sample.	The filler remains its soft character as the unaged sample.	The filler remains its soft character as the unaged sample.
coherence	The cohesion is very good; when scratched a ver sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed approximately the same as the filler bulked with aluminium hydroxide	even lower adherence to the support compared to the unaged sample	even lower adherence to the support compared to the unaged sample almost all material removed	even lower adherence to the support compared to the unaged sample almost all material removed
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene slightly after 20 rolls ethanol 5 rolls

Table 29: Evacon R filler bulked with calcium carbonate and bolognese chalk (1:1)_evaluation of the properties based accelerated aging tests

RECIPE FOR LASCAUX 498 HV FILLER

- 25 g solution of Tylose C300 in distilled water (cellulose ether)
- 5 g Lascaux 498 HV
- 60 g bulking agent
- (pigment to colour)

First of all the 4% solution of Tylose C300 in water is prepared. The messured amount of Tylose is left to be swelled in distilled water overnight(a). The next day Tylose molecules are properly diluted and a gelled solution is obtained(b).

The proper mixing of the components of the filler glass or marble desk is convenient to be used(c). It is indeed easier to put the ingredients on the grinding slab and stir them with a small pallet knife then more vigorously with a larger flat-edged putty knife.

Firstly measure the proper amount of Tylose solution(d) and mix it with the measuered amount of Lascaux 498 HV(e) until the even consistency is achieved, into a slightly white solution. Weight the amount of filling material(f) and place it on the grinding slab. In the middle of the hill of powder pour the adhesive mixture(g). Stir the adhesive into the powder with a pallet and putty knifes(h) until no lumps of powder are left and each particle of bucking agent is encapsulated by the adhesive(i).

If the filler is supposed to be coloured it is recommended to mix the pigment with bucking agent first and just afterwards stir the mixture of powders with adhesive solution.

Store the filler in a lidded container and cold environment (refrigerator). For prolonging the storage of the prepared filler, place a moisturized piece of cloth or tissue diractly on the mixture in the container without leaving any air gabs.

There are several possibilities of the filling materials which could be used. In the original recipe for Evacon R filler is recommended aluminium hydroxide and specified as Portafil® A40. It is a commercial product produced by Sibelco company. It is demanded to be a more stable version of aluminium hydroxide[1]. However it is not easily accessible for several countries. That was the reason aluminium hydroxide produced by Kremer Pigmente GmbH & Co. KG was chosen for the trials. The disadvantage is proclaimed to be its apsorbtion moisture from the atmosphere[2]. Next to aluminium hydroxide, calcium carbonate and its mixture with bolognese chalk was tested as well.

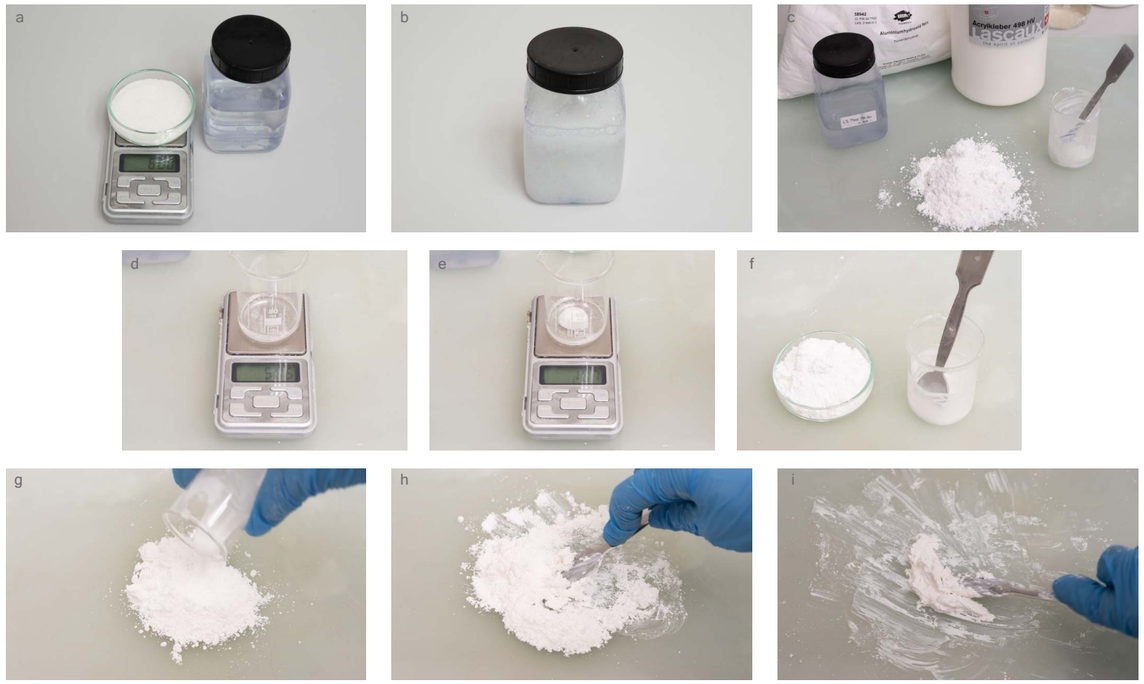


Figure 43a - i: Preparation of Lascaux 498 HV filler

1 http://www.sibelco-specialty-minerals.eu/ssme/applications/32-portafill-a [02/03/2024]

2 SEYMOUR. Kate. (2013). *Fillers: Adaptation on Traditional and Commercial Products,* Lecture presented at NOVA, Lisbon

This filler is an alternative to the Evacon R filler developed at The Stichting Restauratie Atelier Limburg (SRAL) in The Netherlands. The reason why it is included in the theses and testing trials, is a limited accessibility of the acrylic glue Evacon R, which is produced only in Great Britain. Acrylic glue Lascaux 498 HV was chosen for its similar properties and availability on the European market.

APPLICATION

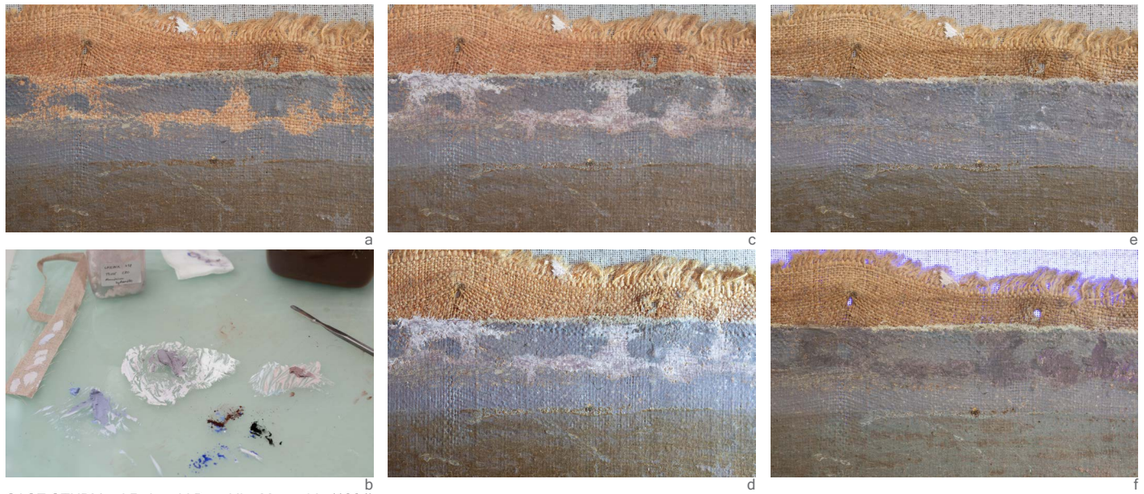
This filler could be used either to fill small shallow losses or larger damages. As already described, the filler may be stored for a longer period only if kept wet. Unfortunately, one must monitor whether mold begins to grow due to the damp condition of the mixture. To prolong the storage of the filler, only clean tools should be used to remove the amount of filler needed for a particular work. Additionally, storage in a cold environment, such as a refrigerator, could be beneficial.

The filler is obtained as a semi-solid mixture; therefore, application with a metal, stone, or wood spatula is required. It is a very suitable filler for coloring, especially when small shallow losses need to be filled. If it is pigmented sufficiently, no retouching is necessary. Note that the filler changes tone after drying as well as after varnishing, therefore tests of these two factors should be conducted before head, separate from the actual filling on the original painting.

The excesses of the filler over the surrounding paint should be removed immediately mechanically with the spatula or by cotton swab or piece of cloth dipped in distilled water.

The filler surface could be smoothed by cork, balsa wood or a piece of suede or felt cloth. The texturizing could be done at the time, the filler is still slightly wet by incision or layering more liquid filler over the surface, depending on the desired appearance and surrounding painting surface. The moulds or textile imprint could be pressed to the wet filler surface if it is required. Once the filler is dry, it could be reactivated by a little amount of distilled water, and the surface may be adjusted. In the cases, a large loss is being filled, for obtaining the filler to the same level, wide stone spatulas or roller with interlayer of melinex sheet could be used.

It is better to apply a separating layer over the surface before retouching, since the surface is quite hydrophobic. Depending on the components of this layer, the inpainting could be cast by water-based paints as well as the pigments binded in synthetic resin medium or commercial retouching paints.



CASE STUDY vol.5_Arnold Boecklin: Mermaids (1864)
In this case, there were very significant and shallow losses, primarily around the edges of the painting, which could have been mechanically stained. Therefore, the Lascaux 498 HV filler, combined with the bulking agents Tylose C 300 and aluminum hydroxide, was selected. This type of filler obtains very good mechanical and handling properties, allowing for effective filling of small shallow losses. The flexibility of aluminum hydroxide is a significant advantage, particularly suitable for canvas support, which experiences tension and motion. The filler was pigmented before and after application, and the texture of the canvas was scratched with scalpels to the wet filler. Subsequently, two initial varnish layers were applied with a small brush, followed by some gentle inpainting using Gamblin retouching paints.

Figure 44: Arnold Boecklin: Mermaids; illustrating photography of preparation of pigmented filler(b); macro-photography in daylight before filling(a); after infilling in day(c) and raking light(d); after retouching in daylight(e) and UV luminiscence(f)

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

Whether this filler is an alternative to the previous one, bound with Evacon R, firstly, the properties of this particular filler could be compared to the previous one. The most significant feature is its higher flexibility, as demonstrated in bendability tests when the filler is bulked with aluminum hydroxide or calcium carbonate. Furthermore, it is soluble in a wider range of solvents, all of which were tested, and the solubility remains unchanged.

However, dimensional changes during drying were observed, especially with very sufficient cracks occurring (which could be reduced when the filler is applied in several thin layers).

Surface dusting was observed for all the samples with different bulking agents, as well as a slight loss of adherence to the textile support.

The colour change was observed again only on samples applied on old canvas with wax-resin lining adhesive residues.

LASCAUX 498 HV FILLER
ALUMINIUM HYDROXIDE

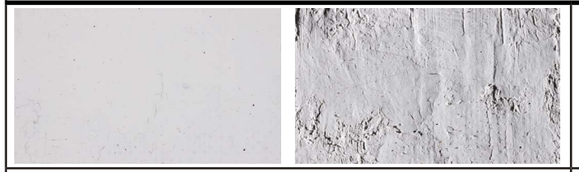
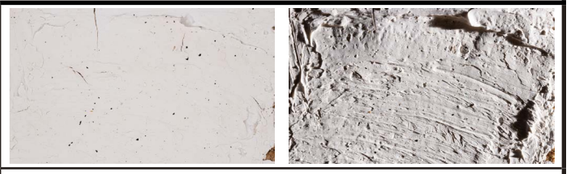
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimenasional change occured.			
colour change	L* 97.6 a* 0.1 b* -0.1 C* 0.1 h* 328.5	ΔE = 0.1	ΔE = 0.1	ΔE = 2.1 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by accelerated aging developed. 	Only a few very sufficient and hollow cracks caused by aging developed. 	No cracking caused by accelerated aging developed. 
surface dusting	The cotton swab is slightly grayish; Not only a little amount of white dust was picked up, but also a few larger particles of the filling material visible under the microscope.	The cotton swab is slightly grayish, same as the unaged sample; not only a little amount of white dust was picked up, but also a few larger particles of the filling material visible under the microscope.	The cotton swab is slightly grayish, same as the unaged sample; not only a little amount of white dust was picked up, but also a few larger particles of the filling material visible under the microscope.	The cotton swab is slightly white; compared to the unaged sample larger amount of white dust was picked up, the amount of larger particles of the filling material visible under the microscope remains the same.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass behaves very pliable and squishy.	The filler maintains its soft and pliable character, the same as was observed in the unaged sample.	The filler remains its soft and pliable character as the unaged sample.	The filler remains its soft and pliable character as the unaged sample.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed	even lower adherence to the support compared to the unaged sample	even lower adherence to the support compared to the unaged sample	even lower adherence to the support compared to the unaged sample
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit slightly after 20 rolls toluene slightly after 15 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 20 rolls toluene slightly after 15 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 20 rolls toluene slightly after 15 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 20 rolls toluene slightly after 15 rolls ethanol 5 rolls

Table 30: Lascaux 498 HV filler bulked with aluminium hydroxide_evaluation of the properties based accelerated aging tests

LASCAUX 498 HV FILLER
CALCIUM CARBONATE

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	A slight dimensional change occured, compared to the filler bulked with aluminium hydroxide; significant cracking occured in the filler mass.			
colour change	L* 96.6 a* -0.2 b* 0.3 C* 0.4 h* 130.3	ΔE = 0.2	ΔE = 0.4	ΔE = 3.8 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by accelerated aging developed. 	The drying cracks got slightly deeper and a network of very sufficient cracks developed. 	The drying cracks got slightly extanded by accelerated aging. 
surface dusting	The cotton swab is slightly white; A larger amount of dust obtained from filling material was picked up.	The cotton swab remains slightly white; A larger amount of dust obtained from filling material was picked up.	The cotton swab remains slightly white; A larger amount of dust obtained from filling material was picked up.	The cotton swab is slightly less white compared to the unaged sample; less amount of dust obtained from filling material was picked up.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass is little less pliable and squishy than the formulation mixed with aluminium hydroxide; however, on the thick layers it is little tougher.	The filler maintains its soft character, the same as was observed in the unaged sample.	The filler remains its soft character, the same as was observed in the unaged sample.	The filler remains its soft character, the same as was observed in the unaged sample.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed approximately the same as the filler bulked with aluminium hydroxide	even lower adherence to the support compared to the unaged sample	even lower adherence to the support compared to the unaged sample	even lower adherence to the support compared to the unaged sample
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit slightly after 20 rolls toluene slightly after 10 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 20 rolls toluene slightly after 10 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 20 rolls toluene slightly after 10 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 20 rolls toluene slightly after 10 rolls ethanol 5 rolls

Table 31: Lascaux 498 HV filler bulked with calcium carbonate_evaluation of the properties based accelerated aging tests

LASCAUX 498 HV FILLER
CALCIUM CARBONATE : BOLOGNESE CHALK 1 : 1

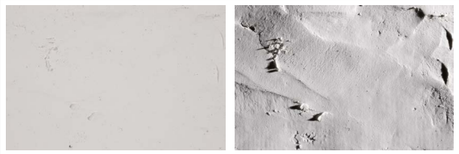
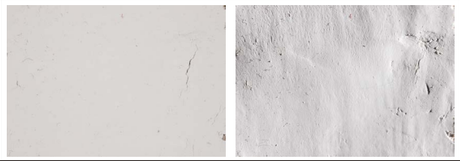
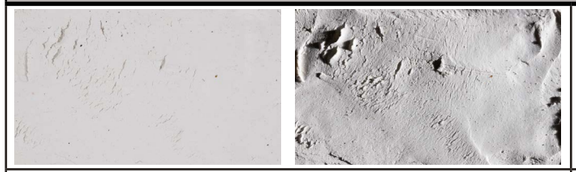
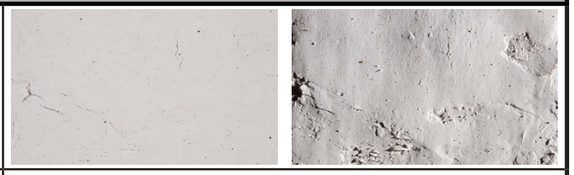
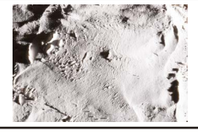
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	exposure for 62 cycles in the environmental humidity chamber old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimenasional change occured.			
colour change	L* 94.3 a* 0.0 b* 2.0 C* 2.0 h* 90.9	ΔE = 0.2	ΔE = 0.3	ΔE = 1.0 slightly yellower
craquelure		No cracking caused by accelerated aging developed. 	Only one crack caused by aging developed in the area with thicker layer of filler. 	Only a few cracks around the adges within the thicker layer of filler developed. 
surface dusting	The cotton swab is slightly white; large amount of white powder dust obtained from bulking material was picked up.	The cotton swab is slightly whiter compared to the unaged sample; larger amount of white powder dust obtained from bulking material was picked up.	The cotton swab is slightly whiter compared to the unaged sample, same as the previous one; larger amount of white powder dust obtained from bulking material was picked up.	The cotton swab is slightly whiter compared to the unaged sample, same as the previous one; larger amount of white powder dust obtained from bulking material was picked up.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass behaves very pliable and squishy.	The filler retains its soft and pliable character, the same as was observed in the unaged sample.	The filler remains its soft and pliable character as the unaged sample.	The filler remains its soft and pliable character as the unaged sample.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed approximately the same as the filler bulked with aluminium hydroxide	even lower adherence to the support compared to the unaged sample	even lower adherence to the support compared to the unaged sample almost all material removed	even lower adherence to the support compared to the unaged sample almost all material removed
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit slightly after 25 rolls toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 25 rolls toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 25 rolls toluene slightly after 20 rolls ethanol 5 rolls	distilled water 5 rolls White Spirit slightly after 25 rolls toluene slightly after 20 rolls ethanol 5 rolls

Table 32: Lascaux 498 HV filler bulked with calcium carbonate and bolognese chalk (1:1)_evaluation of the properties based accelerated aging tests

3.7 SYNTHETIC RESIN_AQUAZOL®

In the second half of the 1970s, The Dow Chemical Company received a series of patents on a new tertiary amide polymeric material based on the monomer 2-ethyl-2-oxazoline. It was quickly discovered that the new polymer exhibited some unusual physical and chemical properties. The first comprehensive review of Poly(2-Ethyl-2-Oxazoline) (PEOX) was published by Chiu and coworkers (Chiu, Thill, and Fairchock) in 1986. PEOX was developed as a water- and organic-soluble polymer. It was prepared by the ring-opening polymerization of the monomer 2-ethyl-2-oxazoline.[1]

Under the name Aquazol®, produced by US Polymer Chemistry Innovations since 1990, it has been on the market as a pressure--sensitive, hot-melt adhesive. Aquazol is non-toxic and biodegradable. It has been tested and tried on several materials to determine its solubility and compatibility with other materials, mainly by Wolbers' team. The fundamental properties that make the adhesive attractive for the conservation field are its solubility in water and in a wide range of solvents in terms of polarity: from methanol (Fd 30) to chlorinated hydrocarbons (Fd 67-70), and limited solubility in even lower polarity solvents, such as hydrocarbons (Fd 80-100). Furthermore, the option for heat-sealing at approximately 55°C has been validated. There are four types of Aquazol marked by numbers 5, 50, 200, and 500. These numbers refer to the molecular weight and also indicates the viscosity and gluing properties of the particular type of Aquazol:
Aquazol 5 ..... Mw 5 000 amu
Aquazol 50 ..... Mw 50 000 amu
Aquazol 200 ..... Mw 200 000 amu
Aquazol 500 ..... Mw 500 000 amu
The glass transition temperature is at 69-70°C for all types.[2]

To the conservation field was introduced by Richard Wolbers in the 1990s as a consolidant and replacement for glue with the commercial names PEOX and Aquazol®. Together with McGynn and Duerbeck, Wolbers introduced and published their research project on this product at the Williamsburg symposium in 1994. The purpose of the project was to present the results of accelerated light-aging tests on the resin and to describe a series of test applications to a selected group of painted objects. In the study, two types of Aquazol, 50 and 500, were aged by light exposure (The cast films were exposed to a 72-hour lamp "on" period, followed by a 72-hour dark period, and then a second 72-hour lamp "on" period. The total radiant exposure received was estimated to be 280 kJ m^{-2}.), the total exposure obtained was equivalent to approximately twenty four years of natural aging under standart museum exhibition condition. The samples were subsequently analyzed with size-exclusion chromatography (SEC), pH measurements, thermogravimetric analysis (TGA) and differential thermal analysis (DTA), re-solubilization tests, viscosity measurements (by Brookfield viscometer), colour measurements, infrared spectroscopy (FTIR) and tensile strength measurements. In an effort to evaluate the less tangible, but equally important, practical working or handling properties of Aquazol 50 and 500 solutions as consolidants, three painted wooden objects were chosen for testing. These objects had decorative materials that needed consolidation and moreover in some cases the possibility of filling gabs, carried out with aqueous solution of Aquazol at 10-25% by weight (and in some cases ethanol as co-solvent was used).
The summarized conclusion is as follows:

- When aging (viscosity, thermal, and SEC data after light aging) suggests that the polymer seems to depolymerize rather than cross-link, reducing the risk that it cannot be re-solubilized again.
- Color measurements before and after light aging indicated no significant difference in terms of discoloration. The exposed samples remained essentially transparent.
- No change in acidity was demonstrated: pH 6.4 before aging, pH 6.2 after aging. This value appears to be consistent with the nonionic character of the polymer.
- Subsequently, the same solubility was retained in the same solvents for unaged and light-aged samples.
- According to the FTIR spectrum tests, after aging, there is no new absorption band that can be attributed to oxidation products (indicating no gross chemical changes).
- The polymer seems to retain its plastic character even at low RH conditions.
- The material seems to behave as a weak adhesive, and therefore, it seems advisable to use it only when moderate adhesive forces are needed.[3]

After the preliminary tests by Wolbers, this material was further tested by a group of Italian conservation chemists from CESMAR 7. Samples were tested before and after accelerated aging by color analysis and FTIR. The tests showed sensitivity to UV radiation, in distinction to Wolbers' study. The radiation leads to chain scission effects, deducible from the evident formation of amides, which allows us to hypothesize a mechanism involving scission of the main chain and the formation of an amide and a terminal double bond. It follows that Aquazol can only be used as an adhesive and must not be exposed to the effects of UV radiation. However the degradation is still lower than another very often used adhesive Klucel G under the similar aging condition. [4]
Another study was conducted by L. Tocci, which focused on the mechanical properties of Aquazol. The test results indicated a potential risk associated with the use of Aquazol. At high relative humidity, a softening of the material can occur, leading to a consequent decrease in mechanical resistance.[5]

1 HORIE, C. V. (1996). „Miscellaneous Synthetic Thermoplastics", in *Materials for conservation: Organic consolidants, adhesives and coatings,* Great Britain: Hartnolls Ttd.,Bodmin, Cornwall, ISBN 0 7506 0881 1, p.196

2 https://www.kremer-pigmente.com/elements/resources/products/files/63901-63905e.pdf [12/03/2024]

3 WOLBERS, R. C., MCGYNN, M., DUERBECK, D. (1994). „Poly(2-ethyl-2-oxazoline): a new conservation consolidant". in *Painted Wood: History and Conservation, Proceedings of the Symposium in Williamsburg,* Virginia, pp. 514-527

4 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Polyethyloxagolines", in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 177-178

5 TOCCI, L. (2009). *Valutazione dell'Aquazol (PEOX - POLI 2-ETIL-2-OSSAZOLINA) utilizzato come consolitandte della tela di supporto dei dipinti,* Congresso Nazionale IGIIC „Lo Stato dell'Arte", Napoli

The properties and characterization of Aquazol, as described above, have led conservators to use it relatively often in modern and contemporary art, both as an adhesive and as a consolidant.[6] Furthermore, since approximately the 2010s, Aquazol has been widely tested as a binder for fillers. The material was originally proposed and composed as an alternative to animal protein glues. In some cases, traditional stuccos and putties demonstrate their limitations, mainly linked to their increasing rigidity; thus, Aquazol could be used as a binder instead of glue.

The study in 2011 by a cooperative team composed of Italian conservation researchers Aquazol 500 was tested as an compatible alternative to animal glue.[7] Aquazol 200 and 500 were selected for testing to see how the different degrees of curing might affect the final putty. Mixtures were prepared by combining the two Aquazol types in different percentages in different dispersants: water, alcohol and 50/50 water/acetone. Each type of mixture was divided into two parts, one of which contained the inert calcium carbonate and the other the gypsum. Paints of natural origin (Mastic), acrylic origin (Retoucher) and new generation (Regalrez® 1094) were used in the colour design tests on the different samples. Laboratory experiments, colourimetric tests and artificial aging tests were carried out to determine the physical and chemical properties of the material, such as workability, drying time, strength and, in addition, the colour stability of the above-mentioned grouts and colour restorations. The study showed that Aquazol 500 in 20% solution gives the filler with the best workability properties. The most suitable solvents are water and water and alcohol in a ratio of 80:20. The tensile test showed that the fillers based on Aquazol 500 have considerable strength.

Studies of the properties of Aquazol® based fillers have continued over the years to address the issues of aging and surface texture. Another study was carried out at the University of Madrid and presented at the RECH 6 conference.[8] The aim of the study was to investigate the properties and applications of Aquazol 200 based filler for moisture-sensitive easel paintings. Aquazol based filler was chosen from a wide palette of materials due to several reasons; some other materials introduce excess moisture to the painting during application, while others are problematic to handle when imitating the surface of paintings, such as brush strokes and impastos made by a palette knife. Aquazol 200 was selected because of its molecular weight, indicating binding properties, and also based on previous studies of Aquazol 500 fillers, which showed a relatively high possibility of cracking after drying. Aquazol 200 was diluted in a hydroalcoholic mixture (75% distilled water and 25% ethanol) to create a 10% solution. Calcium sulfate was chosen as a bulking agent. The preparation process was similar to that of traditional stucco. However, due to the viscosity of the binder concentration, the settling time of the solid material is much longer. Consequently, the preparation of the filler is slower. Once calcium carbonate is added, the glass bottle is covered to prevent the evaporation of solvents, and then left to decant. This process is repeated until the liquid becomes saturated. Two mock-ups were created with different types of surface adjustments: one textured with a stiff-bristled brush following the direction of the brushstrokes, and the other, with impastos, had the losses filled first and then leveled when dry, with additional filling applied with a spatula. After drying, these mock-ups underwent accelerated aging in a climatic chamber. The results were very promising; the material's cohesion remained stable during aging, and no cracking appeared on the surface of the fillers. Furthermore, the surface imitation was remarkable, and nearly invisible after retouching with Aquazol based watercolors (QoR®).

Another chapter involves the research into the possibilities for conservation of modern and contemporary art. The wide range of different materials, characterized by new textures, unvarnished surfaces, or matte finishes, has led conservation researchers to investigate fillers that could be used for retouching to sufficiently fill losses on painting surfaces[9]. In this case, the filler could be composed as a thermoplastic, full-bodied paint. The filler is prepared as a sheet and inserted into the loss in the correct position, either by heat setting or solvent regeneration. Many paint manufacturers produce full-bodied media that can be added to paints consisting of the same media. However, the preparation of this type of filler was tested using the studied Aquazol solution and described by the SRAL conservation department. The Aquazol mixture could be diluted both in water or in solvent solution, for actual possibility for filling in water sensitive materials of the painting.[10] Due to its instability to UV radiation, it is advisable to varnish the surface with a protective layer to prevent light efflorescence.



Figure 45: Aquazol® 50, 200, 500


Figure 46: Aquazol® 200

6 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Polyethyloxagolines", in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, p. 178

7 CALORE, R., FRIZZA, L., XACA-CAMIEC, M., RIZZIONELLI, L., STEVANATO, N., TISATO, F. (2011). *Aquazol 500. Una possible alternativa ecocompatibile alla colla animale nella preparazione degli stucchi per il restauro dei dipinti. Testpreliminari pe la stabilita, lavorabilita e comportamenti.* Atti del Congresso „Le fasi finali nel restauro delle opere policrome mobili", Trento

8 MORALES-MARTÍN, D., FESTA, Antonella, della, ORTIZ, A. S. (2021). *Moisture senstive easle paintings: A practical application of filling and texturing of losses with Aquazol® based filler.* RECH6 - 6th International Meeting on Retouching of Cultural Heritage, Valencia, Spain

9 FERNÁNDES-VILLA, S., G. (2015). *Filling as retouching: The use of coloured fillers - in the retouching of contemporary matte paintings.* RECH3: 3rd International Meeting on Retouching of Cultural Heritage, Complutence University, Madrid

10 BURG, J., M., Van den, SEYMOUR, K. (2024). *Painting conservation part 4: Filling Losses in Paint.* Cultural Heritage Agency of the Netherlands. Ministry of Education, Culture and Science. Amersfoor,. p. 48

RECIPE FOR AQUAZOL 200 FILLER

- 10% Aquazol 200 in distilled water + few drops of Ethanol 96%[1]
- bulking agent
- (pigment addiction)

First of all, the solution of Aquazol 200 in water is prepared. Weight 10g of Aguazol 200 and put it into a glass container with 100 ml of destiled water(a). Add a few drops of Ethanol for increasing the effectiveness of the dilution process(b). Left is over night, eventually mixing the solution after few a hours.

Sieve the filling material and add it gradually to the dissolved Aquazol solution(d). Mix properly with wooden or glass sticks(e). Add sufficient solid content to achieve a putty with the desired consistency(f). To check that you have the right consistency, brush or smear the filler mixture onto a glass plate or Melinex sheet(g) and allow to dry. Check the dried film for cracking. By the characterization of shrinkage add more 10% Aguazol solution of filling material(h,i).

In the case the filler is supposed to be coloured, mix the pigment powder (pigment with very sufficient particles is admired) into the filler. Check the proper colour of the filler after drying on a piece of melinex sheet of glass. The pigment proportion could be adjusted if it is necessary.

Store the filler in a lidded container in a cold environment (refrigerator).

Bulking agent could be chosen from a variety of filling materials. Calcium carbonate alone or in a combination with bolognese, champagne chalk or kaolin is recommended. Also aluminium hydroxide is a sufficient option.

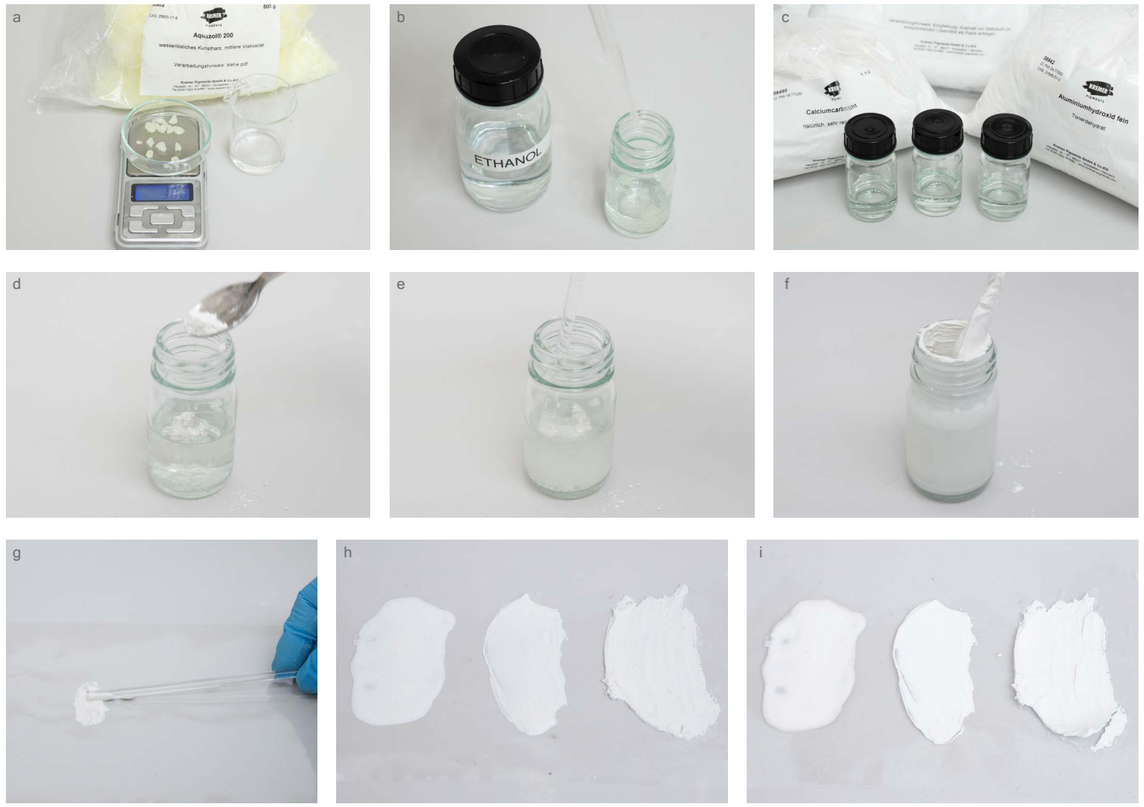


Figure 47a - i: Preparation of Aquazol® 200 filler

1 The proportion of the percentage of Aquazol® 200 in hydrosolvent solution was chosen after several tests and supported by the information in the newest publication about fillers for easel painting: *Painting conservation part 4: Filling Losses in Paint* by J. M. van den Burg and K. SEYMOUR (2024).

APPLICATION

Depending on the amount of bulking agent added to the Aquazol solution, the filler could be applied with a spatula (in the case the mixture is thicker) or with a brush (in the case the mixture is prepared in a more liquid solution). The choice of the thickness of the putty mainly refers to the particular type of loss in the paint.

In the case study by Simona Škorja from the National Gallery of Slovenia, 10 ml of Aquazol® 500 (chosen for its high viscosity) in a 10% ethanol solution was mixed with only 5 g of inner material (plus an unspecified compound of pigment mixture) to allow for brushing thin layers of filler into a loss. This was required to imitate the brushstroke character of the painting. The disadvantages of this type of filler are described as „not having equally good working properties and a certain loss of volume being observed“.[1]

For the trials, the ratios of the medium to bulking agent were tested in several compositions. The amount of inner material mostly depends on the particular filling material that is chosen. Moreover, every commercial company provides a slightly specific product which could be more or less hygroscopic. Tests of the proportion of the filling materials within the filler mixture are recommended to always be conducted before the actual filling of the original painting, simply by applying the filler on a piece of Melinex sheet and leaving it to dry.

Any excess filler over the original painting can be removed by distilled water or by organic solvent, such as ethanol or acetone, alone or in a less polar mixture.



CASE STUDY vol.6_František Viktor Mokrý: The Nude (around half of 20th century)
The deep losses in the paint were exposed to the lacquer layer of underpainting. The Aquazol filler was chosen because of the moisture sensitive surface, possibility for adjustment the surface and layering the filler to obtain the depth of the losses. Moreover, the Aguazol mixtures were also used as a local consolidant for a flaking paints. The filler was composed with the recipe above: 20% Aquazol 200 solution in distilled water with a small amount of ethanol, and calcium carbonate with Bolognese chalk (ratio 2:1). The filler was made as a thick mixture applied with a spatula. After drying, fillers were slightly swelled with distilled water to activate the surface, and the specific structure of impastos was created using a less thick filler (to the mixture, 20% Aquazol solution was added) applied with a brush. To adjust the significant hydrophilicity of the filling surfaces, a 10% Aquazol 200 in hydrosolvent solution (75% distilled water and 25% ethanol) was brushed over them. The retouching was done with a mixture of pigments using the same Aquazol 200 hydrosolvent solution that was used for the isolating layer. Afterwards, the retouching was locally isolated with varnish to protect them from UV radiation during daylight exposure.

Figure 48: František Mokrý: The Nude; macro-photographs before filling in day(a) and raking light(b); after filling in day(c) and raking light(d); after retouching in day light(e) and UV luminescence(f)

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

The disadvantage of these fillers is a dimensional change during the drying process which was observed for all of the samples with different bulking agents. However, it could be adjusted when the mock-ups of the filler are prepared just after mixing as described on the previous page. Therefore, the filler should be always pre-tested and rather applied in several layers than in one thick.
Interestingly, the solubility of some of the fillers became increased also in a solvent they were not soluble before aging. Overall the reversibility of the filler is very good both in terms of solubility and removability.
The disadvantage is the filler tends to shrink during aging and for all differently bulked fillers more cracking after aging occured (except of aluminium hydroxide). Moreover, the loss of the adhesion to the support slightly increased for all the samples after accelerated aging.
The best flexibility of the sample was exhibited during the bendability tests when filler was bulked with aluminium hdyroxide. When bulked with calcium carbonate, the bendability lowered, and furthermore when bulked with a combination of calcium carbonate and bolognese chalk or kaolin, it failed already by bending around the widest beaker.

1 ŠKORJA, Simona. (2017) *Use of coloured synthetic filler: The case of St. Nicholas, a baroque painting by Fortunat Bergant*, National Gallery of Slovenia. RECH4: 4th International Meeting on Retouching of Cultural Heritage. Croatia. pp. 120-127

AQUAZOL FILLER
ALUMINIUM HYDROXIDE

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition
macro photography day light | raking light		
drying dimensional change	A slight dimensional change occured; significant cracking developed in the filler mass during the process of drying; however the adjustment of the porportion of binding media and bulking agent could significantly change the result.	
colour change	L* 98.8 a* -0.1 b* 0.1 C* 0.2 h* 117.1	ΔE = 0.3
craquelure		No cracking caused by accelerated aging developed. 
surface dusting	The cotton swab is white; a large amount of dust powder obtained from the bulking material was picked up, filling the gaps between the threads of the cotton.	The cotton swab remains as white as the unaged sample; a large amount of dust powder obtained from the bulking material was picked up, filling the gaps between the threads of the cotton.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass behaves very pliable and squishy.	The filler remains its soft and pliable character, the same as was observed in the unaged sample.
coherence	The cohesion is very good; when scratched a ver sufficient flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed	even lower adherence to the support compared to the unaged sample
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm x	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm x
change in reversibility	distilled water — significantly after 5 rolls White Spirit — very slightly after 30 rolls toluene — no ethanol — 5 rolls	distilled water — significantly after 5 rolls White Spirit — very slightly after 30 rolls toluene — no ethanol — 5 rolls

exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
 	 
ΔE = 0.3	ΔE = 2.3 darker and yellower the sample failed the tolerance
Significantly more cracking developed; the drying cracks got deeper and extended and a network of very sufficient cracks caused by aging occured. 	No cracking caused by accelerated aging developed. 
The cotton swab remains as white as the unaged sample; a large amount of dust powder obtained from the bulking material was picked up, filling the gaps between the threads of the cotton.	The cotton swab is slightly less white compared to the other samples; A slightly less amount of dust powder obtained from bulking material was picked up, filling the gaps between the threads of the cotton.
The filler remains its soft and pliable character as the unaged sample.	The filler remains its soft and pliable character as the unaged sample.
The cohesion remains unchanged.	The cohesion remains unchanged.
even lower adherence to the support compared to the unaged sample almost all material removed	even lower adherence to the support compared to the unaged sample almost all material removed
ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -
distilled water — significantly after 5 rolls White Spirit — very slightly after 30 rolls toluene — slightly after 25 rolls ethanol — 5 rolls	distilled water — significantly after 5 rolls White Spirit — very slightly after 30 rolls toluene — slightly after 25 rolls ethanol — 5 rolls

Table 33: Aquazol 200 filler bulked with aluminium hydroxide_evaluation of the properties based accelerated aging tests

AQUAZOL FILLER
CALCIUM CARBONATE

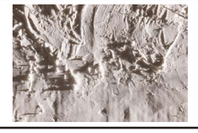
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	A slight dimensional change occured; significant cracking developed in the filler mass during the process of drying; however the adjustment of the portion of binding media and bulking agent could significantly change the result.			
colour change	L* 98.9 a* -0.6 b* 0.6 C* 0.8 h* 137.4	ΔE = 1.1 sligthly darker	ΔE = 2.4 darker the sample failed the tolerance	ΔE = 4.5 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by accelerated aging developed. 	Significantly more cracking developed; the drying cracks got deeper and extended and a network of very sufficient cracks caused by aging occured. 	Slightly more cracking caused by accelerated aging developed. 
surface dusting	The cotton swab is slightly white; a little amount of dusting filling material was cought, as well as a few microscopic particles of the material.	The cotton swab remains slightly white; a little amount of dusting filling material was cought, as well as a few microscopic particles of the material.	The cotton swab remains slightly white; a little amount of dusting filling material was cought, as well as a few microscopic particles of the material.	The cotton swab is slightly less white; only a little amount of dusting filling material was cought, as well as only a few microscopic particles of the material.
hardness	The filler is quite soft; when a slight pressure is applied, the filler mass behaves very pliable and squishy.	The filler maintains its soft and pliable character, the same as was observed in the unaged sample.	The filler remains soft, however is much less paliable and squishy compared to the unaged sample.	The filler remains soft, however is much less paliable and squishy compared to the unaged sample.
coherence	The cohesion is very good; when scratched a very sufficient (more than when bulked with aluminium hydroxide) flaking are disturbed, removable from the support in larger particles.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed approximately the same as the filler bulked with aluminium hydroxide	even lower adherence to the support compared to the unaged sample	even lower adherence to the support compared to the unaged sample almost all material removed	even lower adherence to the support compared to the unaged sample almost all material removed
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm x ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls

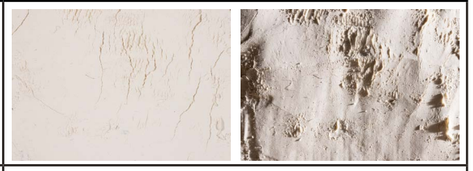
Table 34: Aquazol 200 filler bulked with calcium carbonate_evaluation of the properties based accelerated aging tests

AQUAZOL FILLER
CALCIUM CARBONATE : BOLOGNESE CHALK 2 : 1

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light		 	 	 
drying dimensional change	A slight dimensional change occured; significant cracking developed whether a thicker layer was applied; however the adjustment of the porportion of binding media and bulking agent could significantly change the result.			
colour change	L* 93.7 a* -0.1 b* 2.3 C* 2.3 h* 93.0	ΔE = 0.4	ΔE = 0.4	ΔE = 0.5
craquelure		No cracking caused by accelerated aging developed. 	Significantly more cracking developed; the drying cracks got deeper and extended. 	More cracking caused by accelerated aging developed. 
surface dusting	The cotton swab is slightly white; a larger amount of dusting filling material was picked up as well as a few microscopic particles of the material.	The cotton swab remains slightly white; a larger amount of dusting filling material was picked up, slightly more microscopic particles of the material were cought compared to the unaged sample.	The cotton swab remains slightly white; a larger amount of dusting filling material was picked up, slightly more microscopic particles of the material were cought compared to the unaged sample.	The cotton swab is only slightly grayish; almost no dusting material was picked up, only a few larger microscopic particles were cought.
hardness	The filler is soft; only a little pressure is required to make a dimple.	The filler is soft in the whole mass as the unaged sample.	The filler remains soft only in the areas where a thin layer of filler was applied; conversely, in thicker layers, the filler became slightly tougher.	The filler remains soft only in the areas where a thin layer of filler was applied; conversely, in thicker layers, the filler became slightly tougher.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles. Similar behaviour when compared to the privious sample.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed approximately the same as the filler bulked with aluminium hydroxide	even lower adherence to the support compared to the unaged sample	even lower adherence to the support compared to the unaged sample almost all material removed	even lower adherence to the support compared to the unaged sample almost all material removed
flexibility	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water 5 rolls White Spirit no toluene no ethanol 5 rolls

Table 35: Aquazol 200 filler bulked with calcium carbonate and bolognese chalk (2:1)_evaluation of the properties based accelerated aging tests

AQUAZOL FILLER
CALCIUM CARBONATE : KAOLIN 2 : 1

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition
macro photography day light | raking light		
drying dimensional change	A slight dimensional change occured; significant cracking developed in the filler mass during the process of drying; however the adjustment of the porportion of binding media and bulking agent could significantly change the result.	
colour change	L* 94.1 a* 0.2 b* 6.5 C* 6.6 h* 88.2	ΔE = 0.5
craquelure		No cracking caused by accelerated aging developed. 
surface dusting	The cotton swab is only a very slightly white; a little amount of dust obtained from the filling material was captured.	The cotton swab is only a very slightly white; a little amount of dust obtained from the filling material was captured.
hardness	The filler is quite soft; only in areas where a thicker layer was applied it is slightly tougher.	The filler remains the same character as the unaged sample.
coherence	The cohesion is very good; when scratched a very sufficient flaking are disturbed, removable from the support in larger particles. Similar behaviour when compared to the privious sample.	The cohesion remains unchanged.
adhesion to the support	quite low of adherence to the support a large amount of material is removed approximately the same as the filler bulked with aluminium hydroxide	even lower adherence to the support compared to the unaged sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene no ethanol 5 rolls

exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
	
ΔE = 0.6 slightly yellower	ΔE = 1.2 slightly darker
Significantly more cracking developed; the drying cracks got deeper and extended. 	Slightly more cracking developed; the drying cracks got deeper and extended. 
The cotton swab is slightly grayish; only a very little amount of dust obtained from the filling material was captured, significantly less than from the unaged sample.	The cotton swab is slightly grayish; only a very little amount of dust obtained from the filling material was captured, significantly less than from the unaged sample.
The filler remains soft; moreover, even the thick-layered areas have become softer compared to the unaged sample.	The filler remains soft; moreover, even the thick-layered areas have become softer compared to the unaged sample.
The cohesion remains unchanged.	The cohesion remains unchanged.
even lower adherence to the support compared to the unaged sample almost all material removed	even lower adherence to the support compared to the unaged sample almost all material removed
ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
distilled water significantly after 5 rolls White Spirit no toluene very slightly after 15 rolls ethanol 5 rolls	distilled water significantly after 5 rolls White Spirit no toluene very slightly after 15 rolls ethanol 5 rolls

Table 36: Aquazol 200 filler bulked with calcium carbonate and kaolin (2:1)_evaluation of the properties based accelerated aging tests

RECIPE FOR BULKED COLOURED PAINT_BODIED AQUAZOL

- 40% solution of Aquazol 50, 200 and 500 in proportion 1:1:1 in water or Ethanol 99,9%
- pigment

Firstly, prepare the solution of Aquazols. A mixture of all three types of Aquazol is required(a). Weigh equal amounts of Aquazols separately(b) and mix them together in a glass container. To achieve the 40% solution, add the measured amount of distilled water with a few drops of ethanol(c) to the container and shake it once it is lidded. Ethanol is added to the mixture to reduce surface tension. If the filler should be used for water-sensitive painting surfaces, the mixture of Aquazols could be dissolved in almost pure ethanol (99.9%). Leave it to be diluted overnight.

The next day, add the pigment component until the desired color of the filler is obtained(d,e,f). This reduces the need for retouching.

The formulation could be stored in a lidded container(g,h) or in sheets (and used as a thermoplastic filler) if the solution is poured onto a piece of silicone Melinex(i,j,k,l) and left to dry(m).

The filler dries to a semi-matte surface, which can be coated with Aquazol (or most other desired coatings) to increase gloss.



Figre 49a - l: Preparation of budied Aquazol®

APPLICATION

This bulked colour paints could be used for modern surfaces or to replace thin lacquer layers. According on the solvent Aquazol is dissolved at, it could be inserted also in the water- or solvent-sensitive surfaces. This type of budied Aquazol paint could be used as a filler for both small and large losses.

The application of this type of budied Aquazol filler depends on whether the filler is casted as a viscous liquid/semi-solid mixture or a sheet. For the first case, it is applied by brush(Fig.50f,g) or spatula into the losses. Any excess filler over the original painting can be removed by distilled water or by organic solvent alone or in a less polar mixture.

In the cases, the filler is casted as a thin sheet, the specific shape of the loss is cut from the sheet(Fig.50a) and is applied by reactivation of the adhesive properties. For this operation, for example, transparent tape could be used. A piece of tape is placed over the surrounding paint around the loss, and the shape of the loss is drawn on the tape. Then, the tape is carefully removed and placed on the filler sheet. This will simplify the cutting of the proper shape for the loss marked on the tape. Afterwards, the filler is inserted into the loss, reheated, and adhered with a flat-tipped spatula(fig.50e). Instead of reactivation by the heat, the regeneration by appropriate solvent or solvent mixture (ethanol, mixture of ethanol and hydrocarbon, etc.; Fig.50b) in combination with pressure(Fig.c) could be used to fix the filler into the position.

The filler may be smoothed by activating the surface with heat using a heated spatula within an interlaying layer of silicone Melinex sheet, or by placing the silicone Melinex sheet and applying pressure on the surface(Fig.50d) after it has been wetted with a piece of cloth dipped in an appropriate solvent or solvent mixture. The texturizing of the filler surface could be done by incision or by textile imprinting. For imprinting, the surface of the filler should be first reactivated by an appropriate solvent(Fig.50h), and then the imprinting can be cast(Fig.50i); or by heat reactivation, whereas the textile is first placed on the surface in the desired position and afterward, a heated spatula with a flat tip is applied with heat and pressure. Note that relatively high temperatures are required for the heat reactivation of the surface, therefore, this should be taken into account during application, and very precise work should be done.

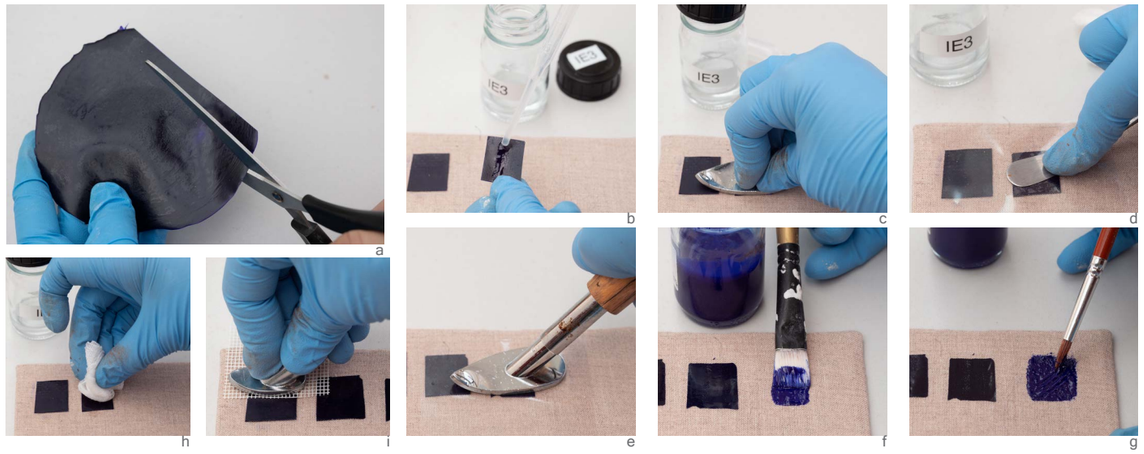


Figure 50a- i: Variants for application and texturing of budied Aquazol®

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

The main disadvantage of this filler is the dimensional change during the drying process, which was observed in samples applied by brush. However, when the filler is cast as a sheet (poured onto a piece of silicone Melinex sheet and left to dry) and then applied by heat or solvent reactivation, as described above, no dimensional change appears after insertion into the particular loss.
An interesting phenomenon of both fillers (water- and ethanol-based) is the extensive increase in glossiness after accelerated aging. Furthermore it became darker by aging (how is described in the properties of Aquazol at the beginning of this chapter). However, it could be different whenever the filler would be coated as recommended to protect against degradation caused by UV radiation.
The filler remains very flexible, with good coherence and adherence to the support.
Additionally, it retains its solubility in solvents in the same range as before accelerated aging.

BUDIED AQUAZOL
ULTRAMARIN DARK

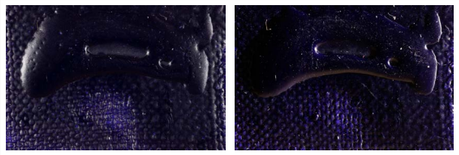
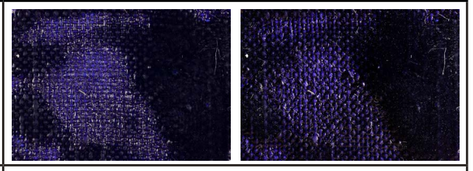
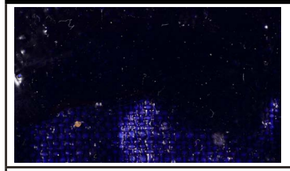
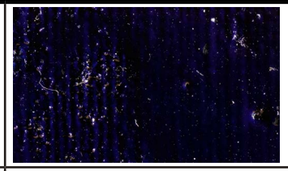
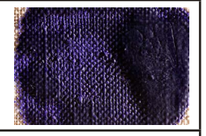
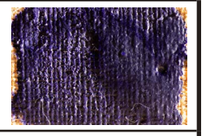
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	Significant dimensional change in terms of width and height when filler is applied by brush; No change whether filler is casted as a sheet and placed on the support.			
colour change	L* 21.5 a* 1.7 b* -5.6 C* 5.9 h* 286.8	ΔE = 7.6 darker and brighter the sample failed the tolerance	ΔE = 15.3 darker and brighter the sample failed the tolerance	ΔE = 14.3 darker and brighter the sample failed the tolerance
craquelure		Not a case. No cracking developed. 	Not a case. No cracking developed. 	Not a case. No cracking developed. 
surface dusting	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.
hardness	The filler is significantly tougher compared to the other ones; even with greater pressure, only a hollow dimple is made.	The filler remains the same hardness characteristic as the unaged sample.	The filler maintains the same hardness characteristic as the unaged sample even after aging.	The filler maintains the same hardness characteristic as the unaged sample even after aging.
coherence	The cohesion is very good; no disturbtion is make.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	very good no material is removed	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩
change in reversibility	distilled water: significantly after 5 rolls White Spirit: no toluene: no ethanol: significantly after 5 rolls	distilled water: significantly after 5 rolls White Spirit: no toluene: no ethanol: significantly after 5 rolls	distilled water: significantly after 5 rolls White Spirit: no toluene: no ethanol: significantly after 5 rolls	distilled water: significantly after 5 rolls White Spirit: no toluene: no ethanol: significantly after 5 rolls

Table 37: Aquazol 50, 200 an 500 budied with ultramarin dark_evaluation of the properties based accelerated aging tests

BUDIED AQUAZOL
RAW UMBER

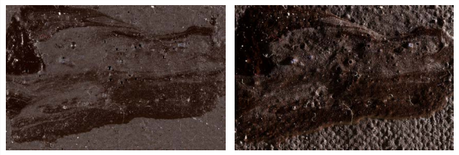
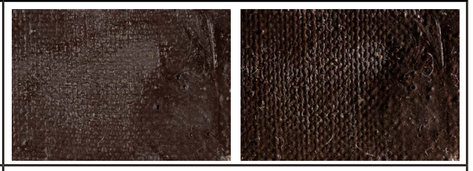
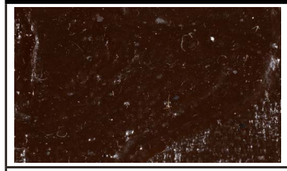
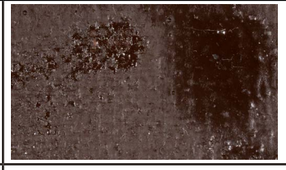
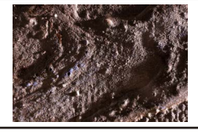
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	Significant dimensional change in terms of width and height when filler is applied by brush, larger compared to the previous one (dissolved in ethanol); No change whether filler is casted as a sheet and placed on the support.			
colour change	L* 24.5 a* 2.6 b* 1.0 C* 2.8 h* 20.2	ΔE = 0.5	ΔE = 10.1 darker and brighter the sample failed the tolerance	ΔE = 10.6 darker and brighter the sample failed the tolerance
craquelure		Not a case. No cracking developed. 	Not a case. No cracking developed. 	Not a case. No cracking developed. 
surface dusting	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.
hardness	The filler is significantly tougher compared to the other ones; even with greater pressure, only a hollow dimple is made.	The filler remains the same hardness characteristic as the unaged sample.	The filler maintains the same hardness characteristic as the unaged sample even after aging.	The filler maintains the same hardness characteristic as the unaged sample even after aging.
coherence	The cohesion is very good; no disturbtion is make.	The cohesion remains unchanged.	The cohesion remains unchanged.	The cohesion remains unchanged.
adhesion to the support	very good no material is removed	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩
change in reversibility	distilled water — significantly after 5 rolls White Spirit — no toluene — 10 rolls ethanol — significantly after 5 rolls	distilled water — significantly after 5 rolls White Spirit — no toluene — 10 rolls ethanol — significantly after 5 rolls	distilled water — significantly after 5 rolls White Spirit — no toluene — 15 rolls ethanol — significantly after 5 rolls	distilled water — significantly after 5 rolls White Spirit — no toluene — 15 rolls ethanol — significantly after 5 rolls

Table 38: Aquazol 50, 200 an 500 budied with raw umber_evaluation of the properties based accelerated aging tests

3.8 EMULSION WAX - RESIN - OIL FILLER

Traditional fillers, up to today, were mostly aqueous or thermoplastic in nature. Many complex recipes for fillers existed, and these almost rock-like cements can be found in many paintings. Typical aqueous systems include animal glue (skin or hide glue) mixed with a white inert mineral pigment (Chalk, Gypsum, Kaolin). Thermoplastic fillers historically consist predominantly of wax/resin mixtures to which a similar bulking agent is added. Additives such as drying oils are often found in old filling recipes. Both systems have numerous disadvantages, especially when considering long-term stability.

An example of this thermoplastic filler consists of wax and oil components. Helmuth Ruhemann introduced a wax-oil filler formula which had been widely used in the conservation field beyond the borders of Europe. Ruhemann was a German restorer who moved to Great Britain during the very early stages of the establishment of the Third Reich due to his Jewish origin. He worked for the National Gallery and Tate Britain as a restorer. Ruhemann is especially noted for his copious notes, detailed letters exchanged with other art historians, and the many photographs he kept of his restorative undertakings, all of which greatly broadened our understanding of art historical thinking in the early to mid-20th century. His attitude towards the conservation of artworks emphasized the role of the conservator as a connoisseur[1].
His formula consisted of: 60 grams gilders whiting
15 grams stand oil
20 grams animal glue in water, rather viscous
10 grams zinc white
5 grams beeswax
The recipe is following:

- Combine all ingredients on a hotplate warm enough to melt the wax, and knead together to a smooth consistency.
- Before filling a damage it is advisable to varnish the painting to prevent hair cracks from inadvertently filling with putty. Apply the putty to the hole with a small spatula, then use a small flat piece of balsa wood to push it home. Moisten the balsa wood slightly, and with circular motions wipe the surface of the filler flat and flush with the paint surface. In this way the putty fills the hole and finds the right surface more or less automatically. Where necessary, imprint canvas grain at this stage with a matching canvas grainer made of a thin layer of a resin which sets hard without losing all flexibility on fiberglass cloth.
- Allow the putty to dry, and then scrape with a scalpel until the edges of the damage appear sharp and the surface is smooth. The surface should be slightly lower than that of the surrounding paint to allow for the thickness of the inpainting.
- Insulate the surface of the filling with a thin coat of shellac, taking the greatest care not to go beyond the edges of the damage. Finally, where there is putty over the original paint, wipe it off with mineral spirits[2].

Another recipe for „Estuco de emulsion“ (emulsion filler) was described in a research thesis published by Laura Fuster Lopez. This recipe is a traditional one used not only in Spain. The emulsion filler consists of stand oil (with the possibility to vary the oil origin, also walnut or poppy seed oil could be chosen), animal glue (ideally rabbit skin glue), and chalk.
The preparation is as follows:

- The rabbit skin glue is left to swell in water for 24 hours. The hydrated glue is then melted in a water bath. Once it is melted, water is added in a proportion of 1:4, and the solution is properly mixed in the water bath.
- The chalk is then gradually added to the mixture little by little until the consistency similar to yogurt is achieved. It is important not to mix it vigorously; otherwise, bubbles will appear, which could cause the formation of small craters when the putty is inserted into the defect.
- For the next step, it is better to work on a flat plate (marble or glass grinding slab). The mixture is placed there, and the oil is gradually stirred into the glue-chalk mixture by single drops with a spatula until the desired consistency is achieved.

In history, lead white was usually added to the filler. However, it caused an increase in the irreversibility of the putty.
The preparation of the filler is pretty problematic, and it is difficult to handle and insert the filler into defects. Furthermore, the adjustment of the surface is also troublesome. It is important to put an isolating varnish layer on the painting before filling. The overlaid areas are removed by water. By aging, the irreversibility of the filler is very significant, as well as the shrinking of the filler due to drying and the influence of oxidation.[3]

A very similar variant of this filler, known as *composition filler* or simply „*compo*,“ emerged in the late 18th century. However, based on the medieval treatises, it is clear this filler was developed from the variants of press-moulded compositions of filler from that time. Compo is an oil-based putty consisting of animal glue, linseed oil, a natural resin (such as colophony), and chalk (either calcium carbonate or sulphate). It conducts a soft and malleable texture when warm, but unfortunately, on aging, it hardens to an extent that it becomes extremely difficult to dissolve or remove mechanically. Originally used for infilling carved elements in frames, as well as addressing losses or voids in panel and canvas paintings and wooden sculptures, compo gained widespread commercial availability during the late 19th century and remained on the market until the 20th century. Interestingly, its composition is very similar to window putty used to hold glazing in frames.[4]

There are several variations of this kind of thermoplastic filler used around the world. One particular variant was introduced in Czechoslovakia and has since become one of the most traditional fillers, with alternatives widely used in the Czech Republic to this day. The formula was developed by Bohuslav Slánský (1900-1980), often considered as the founder of „the czech restoration school“, as introduced in a chapter dedicated to glue chalk filler. This filler was originally developed as an alternative of putty for paintings which obtained wax-resin lining. The content of this filler is based on the similar materials compatible with the lining adhesive mixture and due to a huge amount of painting treated with this type of lining it has been widely used till nowadays.

The original recipe consisted of a mixture of glue (or gelatine), chalk, and oil or resin. A 10% gelatine solution in water was swelled with chalk in a proportion of 1:4, combined with dammar resin, beeswax, and polymerized linseed oil. The mixture was prepared in a water bath. Firstly, the gelatine solution with chalk was warmed separately, and wax together with resin or oil was melted in a metal can. The waxy component was then added to the gelatine-chalk mixture and mixed until a thick, properly mixed consistency of the putty was achieved.
The filler was recommended for the restoration of paintings on canvas, especially because of its proposed flexibility, allowing the canvas to be removed from the stretcher and rolled onto a tube. The disadvantages of the filler, as described by Slánský, included difficulties with surface adjustment, sharpening, and removal of the residues that covered the painting itself. These issues should be promptly addressed with turpentine.[5]. The filler quickly became very popular and for a huge number of restorers, it was the first choice.

During the 1990s, Professor Karel Stretti (1943-2018), head of the restoration studio at The Academy of Fine Arts, along with his assistants from the restoration studio, improved the filler formula. He reduced the amount of wax-resin-oil mixture by half compared to the previous one. With this adjustment, it became possible to use water to remove overlaid residues of the filler.

This recipe for the thermoplastic filler is still widely used and taught at the restoration studio at the Academy in Prague. The formula and its preparation are described in the following pages.

COMPONENTS OF THE EMULSION WAX-RESIN-OIL FILLER
GELATINE
Gelatine is purified form of glue[6].


Figure 51: Gelatine

BEESWAX
Beeswax is obtained from the hives of honey bees and is usually purified by melting (melting point: 63°C) and filtering. It is a complex mixture of at least 284 compounds, principaly hydrocarbons, esters, and free fatty acids. Its composition can be modified by heat treatment or fractionation and the discolouring is achieved by heating above 85°C. Beeswax is slightly soluble in a small range of solvents (such as chloroform and tetrachloromethane). The solubility increases considerably with temperature. Presuambly it yellow by the oxidation influence, it can remain soluble over millennia (in Egyptian thombs). Beeswax has been widely used, mixed with natural resin and fillers, for relining paintings. Additionally, beeswax has been utilized for consolidation, similar to paraffin wax, and as a matting agent for varnishes.[7]


Figure 52: Dammar resin

DAMMAR RESIN
Dammar is a hydrocarbon triterpenoid resin obtained from various species of the Dipterocarpaceae family. Like other natural resins, dammar is composed of a mixture of similar molecules, with proportions varying from sample to sample. In its natural state, dammar contains approximately 10% dammar wax, which dissolves only in hydrocarbon solvents. Dammar is a hard, brittle resin that is easily scratched and has little flexibility. Its low molecular weight enables the preparation of mobile solutions in a wide range of solvents, both non-polar and polar. During exposure to ultraviolet light in air, each molecule of dammar absorbs about two molecules of oxygen, increasing the polarity of solvents needed for dissolution.[8]


Figure 53: Beeswax whittened

POLYMERIZED LINSEED OIL (STAND OIL)
Triglycerides are the esters of glycerol with a wide range of fatty acids. The differences between types of oils lie in the composition of the fatty acid components. Most fatty acids consist of linear carbon chains with 18 carbon atoms. The drying of the oil, leading to polymerization into a solid, occurs through oxidative cross-linking. This process is initiated by the double bonds, thereby increasing the reactivity of the fatty acid with oxygen proportional to the number of double bonds present. Alkyd resins are formed by reacting (heating) drying oils with a polyhydric alcohol (glycerol) and an organic acid (such as phthalic anhydride). A polymer with a much higher molecular weight than the oil is produced. The number of cross-links, and therefore the amount of unsaturation required for film insolubilization, is reduced. This improvement enhances resistance to oxidation, degradation, and yellowing.
Polymerized linseed oil, also known as stand oil, is made by heating raw linseed oil at a high temperature to cause it to polymerize, or cross-linking. This process creates more viscous oil. They are widely used in the production of oil-based paints, varnishes and coatings.[9]



Figure 54: Linseed stand oil
source: https://www.kremer-pigmente.com/en/shop/mediums-binders-glues/73201-linseed-stand-oil-450-p.html [cit. 03/05/2024]

1 https://www.hki.fitzmuseum.cam.ac.uk/archives/helmutruhemann [09/03/2024]
2 JESSELL, B 1977 *Helmut Ruhemann's Inpainting Techniques* JAIC Vol 17 No 1 pp 01-08
3 FUSTER-LOPEZ, Laura. (2008). *El estuco en la restauración de la pintura sobre lienzo: criterios, materiales y procesos,* Spain: Universitad Politecnica de Valencia, ISBN 978-84-8363-221-5, pp. 87-88
4 BURG, J., M., Van den, SEYMOUR, K. (2024). *Painting conservation part 4: Filling Losses in Paint*. Cultural Heritage Agency of the Netherlands. Ministry of Education, Culture and Science. Amersfoort, p. 15
5 SLÁNSKÝ, Bohuslav. (1955). „Tmelení defektů v obazech“, in *Technika malby, část II: průzkum a restaurování obrazů,* 2nd edn, Prague: Paseka, ISBN 80-7185-623-1, p. 206
6 Glue properties are described on page 21.
7 HORIE, C. V. (2010). „Natural Resins“, *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britan, Routledge, ISBN 0 7506 6905 5, pp.160-161
8 HORIE, C. V. (2010). „Natural Resins“, *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britan, Routledge, ISBN 0 7506 6905 5, pp.153-157
9 HORIE, C. V. (2010). „Natural Resins“, *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britan, Routledge, ISBN 0 7506 6905 5, pp.161-166

RECIPE FOR TRADITIONAL CZECH EMULSION WAX/RESIN FILLER

- 10 g gelatine
- 100 ml distilled water

- 1:4 solution of gelatin in destil water : bulking agent by volume

- 15 g mixture of resin dammar and whiten beeswax in proportion 1:1
- 15 g polymerized linseed oil

The first step is to prepare the 10% gelatine in water solution(a,b). The measured amount of the gelatine is added to the measured amount of the distilled water and left to swell overnight. The gelatine particles swell during several hours, enhancing their adhesive properties. The next day in the water bath, the gelatine is dissolved into a slightly viscous solution(c). It's important to note that the water in the water bath should not be boiling; ideally, the temperature should be around 60°C, as otherwise the gelatine may lose its adhesive properties. Once the solution is dissolved, the filling material is gradually added while still kept in the water bath. It is highly recommended to add the filling materials after sieving to avoid creating lumps and blobs(d). The recipe recommends adding a mixture of stone chalk and Bolognese chalk in a proportion of 1:1. This part of the process requires patience, as it is difficult to add the entire amount of chalk at once; a slower addition results in a better outcome(e,f).

Next, the wax-resin-oil mixture is prepared. To dissolve the damar resin, increase the temperature of the water bath slightly to approximately 80°C. First, place the measured amount of bleached beeswax(h) into an iron container (for example, a perfectly cleaned tomato puree tin) and allow it to melt(j). Then, add the measured amount of damar resin(g,k). Crushing the damar resin into a powder will speed up the melting process. Once the wax-resin mixture is completely melted(l), gradually add the measured amount of polymerized linseed oil. It is helpful to prepare and measure the proper amount of polymerized linseed oil in advance for easy addition(i,m). Adding the oil into the wax-resin mixture is noticeably simplified this way. When the entire wax-resin-oil mixture is dissolved(n), it is gradually added into the warmed mixture of chalks and gelatine water(o,p,q,q,r).

Regarding the choice of bulking agents:
The original recipe combines two kinds of chalk and recommends testing and evaluating different proportions to find the most suitable one. Typically, lime white and Bolognese chalk are used in the Czech area. Other possibilities include composing the filler from different types of chalk such as champagne, mountain chalk, or chalk from Ruegen, etc. In tests, calcium carbonate and aluminium hydroxide were also mixed into the filler solution individually.



Figure 55a - r: Preparation of Emulsion wax-resin-oil filler

APPLICATION

The emulsion filler obtains a very compact, dense, and solid consistency. It is possible to add more 10% gelatin solution in distilled water if necessary, but it is not recommended. For simplifying the application, it is convenient to slightly warm up the filler in water bath. This can be done using a water bath or by warming a small amount of the filler, which will be inserted, in the conservator's hand, as it is certainly recommended.

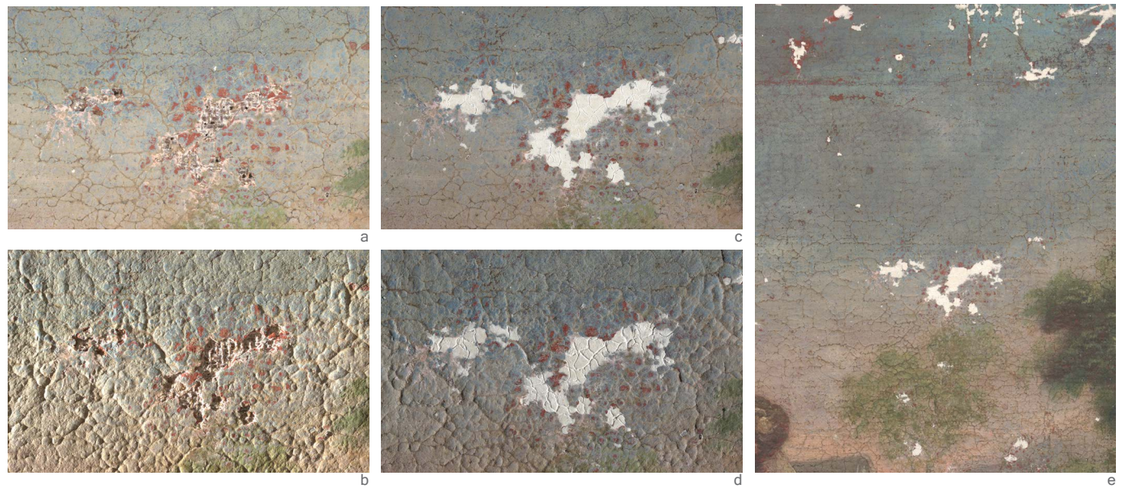
The emulsion filler is sufficient to cover smaller losses. Filling huge defects with this filler is very problematic. If a large area is covered with the filler, cracking and shrinking could widely appear due to the intermolecular tension.

Any excess of the filler is removed mechanically by scalpel or spatula or by a wet cotton swab.

The surface could be leveled by a slightly wet cork or suede cloth. Additionally, a piece of felt cloth or agate could be used to smooth the surface of the filler.

The surface can be further modified and adjusted by brushing the liquid filler (adding more 10% gelatin in water solution) to reconstruct the appearance of brushstrokes and impastos. Additionally, scalpels and spatulas could be helpful for creating the craquelure effect on the painting surface by incision to the dry filler. The filler is thermoplastic; therefore, imprinting the texture may be done by reactivating the surface with a heated spatula. Texturing the surface by textile imprint or flexible mold to obtain the surrounding paint structure is possible.

The surface of the filler could be isolated by an initial varnish before retouching. All retouching material could be used because of the good adhering character of the filler.



CASE STUDY vol.7_Unknown artist: Rachel hiding the idols of her father Laban (first half of 18th century)
This Baroque painting has undergone several treatments already. Certain signs were present on the painting; for example, it underwent two linings with different adhesive materials (glue-starch paste and wax-resin lining), and old fillers were found in the damages. Both lining canvases were removed, as well as the inadequate filler, which had aged into a very stone-like material. However, due to the presence of residues of the wax-resin lining adhesive in the structure of the painting, it was decided to infill the losses with a traditional filler containing materials existing in the painting. Therefore, the wax-resin-oil emulsion filler was applied to the losses by spatula, and after drying, the specific craquelure was scratched by scalpels and needles onto the surface. Fillers were sealed before inpainting by dammar resin varnish, and retouching was done firstly with watercolors and finally with Gamblin retouching paints.

Figure 56: Unknown artist: Rachel hiding idols of her father Laban; macro-photographs before infilling in daylight(a) and raking light(b); after filling in day (c,e) and raking light(d)
Work and photo credit: Pavel Geryk

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

The dimensional changes of this filler can be observed during the drying process. To prevent this, thin layers of the filler can be applied one by one after it has almost dried.
The filler exhibits more dimensional changes during accelerated aging processes; shrinkage and cracking significantly appear when it is bulked with calcium carbonate and aluminum hydroxide. Additionally, the adherence of these two fillers is worse and decreases with aging when compared to the filler bulked with a combination of chalks. There is almost no surface dusting, and the hardness remains almost unchanged.
However, the filler is quite tough, and after aging, it becomes even tougher. This phenomenon corresponds with the research described at the beginning of this chapter, referring to stony-like material into which this filler could be transformed.
Moreover, the removability and reversibility of this filler are not very sufficient, the worst when compared to the other filler formulas.

TRADITIONAL CZECH EMULSION WAX/RESIN/OIL FILLER
LIME WHITE : BOLOGNESE CHALK 1:1

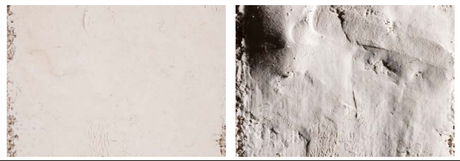
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	Only slightly, better to apply in several thinner layers.			
colour change	L* 86.4 a* 0.4 b* 7.5 C* 7.5 h* 86.7	ΔE = 0.5	ΔE = 2.8 darker and yellower the sample failed the tolerance	ΔE = 3.2 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	No cracking caused by aging developed. 	No cracking caused by aging developed. 
surface dusting	No material was captured on the cotton swab.	No material was captured on the cotton swab.	The cotton swab is slightly grayish; only a little amount of dusting filling material was captured.	The cotton swab is slightly grayish; only a little amount of dusting filling material was captured.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is quite soft, whereas a thicker layer was applied, the filler is slightly tougher.	The filler exhibits similar hardness depending on its thickness as the unaged sample; however, where a thin layer was applied, the filler is quite soft, whereas when a thick layer was applied, the filler is significantly tougher.	The filler exhibits similar hardness to the unaged sample in areas with thin layers; however becomes even tougher than the previous sample in areas with thick layers.	The filler exhibits similar hardness to the unaged sample in areas with thin layers; however becomes even tougher than the previous sample in areas with thick layers.
coherence	Because the filler is quite tough, it is difficult to disturb. When larger pressure is applied, the mass crumbles off the support in larger particles.	The filler remains the same character as demonstarted on the unaged sample.	The filler maintains the similar character as the unaged sample, only it crables within much larger practicles from the support, it became slightly more fragile.	The filler maintains the similar character as the unaged sample, only it crables within much larger practicles from the support, it became slightly more fragile.
adhesion to the support	good no material is removed	remains good	only a little material is removed slightly loss of adherence compared to the unaged sample	only a little material is removed slightly loss of adherence compared to the unaged sample
flexibility	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water slightly after 10 rolls White Spirit no toluene no ethanol no	distilled water slightly after 10 rolls White Spirit no toluene no ethanol no	distilled water slightly after 15 rolls White Spirit no toluene no ethanol no	distilled water slightly after 15 rolls White Spirit no toluene no ethanol no

Table 39: Emulsion wax-resin-oil filler bulked with dolomitic and bolognese chalk (1:1)_evaluation of the properties based accelerated aging tests

TRADITIONAL CZECH EMULSION WAX/RESIN FILLER
CALCIUM CARBONATE

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	Yes, sufficient drying cracks on both thin and thick layered application, much larger cracks appeared in the thick layers of filler.			
colour change	L* 94.4 a* 0.3 b* 4.8 C* 4.8 h* 86.7	ΔE = 0.5	ΔE = 1.3 slightly darker and yellower	ΔE = 2.4 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	No cracking caused by aging developed. 	Slightly more cracking developed; the drying cracks got deeper and extended. 
surface dusting	No material was captured on the cotton swab.	No material was captured on the cotton swab.	The cotton swab is slightly grayish; only a little amount of dusting filling material was captured.	No material was captured on the cotton swab.
hardness	The filler exhibits different hardness depending on its thickness; where a thin layer was applied, the filler is quite soft, whereas a thicker layer was applied, the filler is slightly tougher.	The filler became tougher in the areas of a thicker layer, but remains soft in the thin-layered areas.	The filler became tougher for both thin and thick layered areas compared to the unaged sample.	The filler became even tougher in the thick layered areas compared to the previous sample.
coherence	Because the filler is quite tough, it is difficult to disturb. When larger pressure is applied, the mass crumbles off the support in larger particles.	The filler remains the same character as demonstarted on the unaged sample.	The filler remains the same character as demonstarted on the unaged sample.	The filler maintains the similar character as the unaged sample, only it crables within much larger practicles from the support, it became slightly more fragile.
adhesion to the support	good no material is removed	remains good	only a little material is removed slightly loss of adherence compared to the unaged sample	more material is removed compared to the privious sample loss of adherence compared to the unaged sample
flexibility	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water slightly after 15 rolls White Spirit no toluene no ethanol no	distilled water slightly after 15 rolls White Spirit no toluene no ethanol no	distilled water slightly after 20 rolls White Spirit no toluene no ethanol no	distilled water slightly after 20 rolls White Spirit no toluene no ethanol no

Table 40: Emulsion wax-resin-oil filler bulked with calcium carbonate_evaluation of the properties based accelerated aging tests

TRADITIONAL CZECH EMULSION WAX/RESIN FILLER
ALUMINIUM HYDROXIDE

	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	Yes, sufficient drying cracks in thick layered application, no cracking whether a very thin layer of filler is applied.			
colour change	L* 96.4 a* 0.1 b* 4.1 C* 4.1 h* 86.2	ΔE = 0.5	ΔE = 1.5 slightly darker and yellower	ΔE = 2.4 darker and yellower the sample failed the tolerance
craquelure		No cracking caused by aging developed. 	Significantly more cracking developed; the drying cracks got deeper and extended as well as new cracks occured. 	Slightly more cracking developed; the drying cracks got deeper and extended. 
surface dusting	No material was captured on the cotton swab.	No material was captured on the cotton swab.	No material was captured on the cotton swab.	No material was captured on the cotton swab.
hardness	The filler is quite soft; only a little pressure is required to make a dimple.	The filler maintains quite soft similar to the unaged sample.	The filler maintains quite soft similar to the unaged sample.	The filler remains quite soft, similar to the unaged sample, only in areas with a thinner layer; whereas in areas with a thick layer, it becomes slightly tougher.
coherence	The filler is slightly less tough compared to the other samples binded in the same medium. When larger pressure is applied, the filler slightly flakes and the mass crumbles off the support in larger particles.	The filler remains the same character as demonstarted on the unaged sample.	The filler remains the same character as demonstarted on the unaged sample.	The filler maintains the similar character as the unaged sample, only it crables within much larger practicles from the support, it became more fragile.
adhesion to the support	good no material is removed	remains good	only a little material is removed slightly loss of adherence compared to the unaged sample	more material is removed compared to the previous sample loss of adherence compared to the unaged sample
flexibility	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -	ø 17 cm x ø 11 cm - ø 9 cm - ø 7 cm -
change in reversibility	distilled water slightly after 15 rolls White Spirit no toluene no ethanol no	distilled water slightly after 15 rolls White Spirit no toluene no ethanol no	distilled water slightly after 20 rolls White Spirit no toluene no ethanol no	distilled water slightly after 20 rolls White Spirit no toluene no ethanol no

Table 41: Emulsion wax-resin-oil filler bulked with aluminium hydroxide_evaluation of the properties based accelerated aging tests

3.9 PIGMENTED WAX- RESIN FILLER

Wax-resin fillers were widely used in conservation in the past. The principal reason for choosing these fillers was their properties such as thermoplasticity, flexibility, ease of texturizing, and handling. The history of wax-resin fillers dates back to the 12th century (and likely even earlier, with centuries of use). One of the earliest manuscripts on painting techniques, which briefly mentions fillers for defects in artworks, is *Il Libro dell'Arte* by Cennino Cennini from 1395. In this treatise, he mentioned two types of fillers based on lead white, as well as a wax-resin-based putty consisting of mastic, fresh wax, and sifted powdered stone.[1] This filler was recommended for use in mending stones but presumably was also used for treating other types of artworks.
Another example of pigmented wax filler can be found in *Vasari on Technique* from 1550. Vasari described how to prepare wax for making models for sculptures. The wax is melted over a fire and mixed with animal fat, turpentine, and black pitch to make it more malleable, tenacious, and flexible. The possibility of coloring this formula is described, easily achieved by adding ground pigment powder to the mixture when it is melted.[2] It is assumed that such a material was likely used to repair losses in both panel and canvas paintings. A very common type of filler was based on beeswax and resin from mainly coniferous trees (such as mastic, colophony, or dammar resin). The beeswax was heated, and resin powder was added and melted thoroughly. These fillers were often augmented with pigment compounds. The filler was inserted as a heated mass, which helped fill the defect and also consolidate the flaking paint around the losses. These fillers were very popular due to their easy preparation, smooth flow into voids, availability of ingredients, and resistance to humidity. Primarily, they were used for treating panel desks, although they could be found on many artworks on different supports.[3]
With the beginning of the 19th century, more comprehensive discussions were made on (and not only, of course) the account of restoration techniques and materials. Numbers of treatises could be found referring also to the materials for putties on the works of art. One example where the pigmented wax-resin filler is described is in a French manuscript on painting techniques where there is a chapter dedicated to preservation and restoration by Simone Horsin-Déon from 1851. He provides several options for the formulas, including also gilder's putty („glue of skin and white of Spain") and pure beeswax („nothing but natural virgin wax"). The wax-resin filler is „a compound of wax and resin dissolved together, to which ochre is added in order to color it and give it body".[4]
Typically in middle Europe, where wax resin formulation for lining canvases were widley used, the reason for similar materials add to the restoration treatment act a role in the decision to choose the proper filler for the exact case. Those fillers were made from a mixture of beeswax and filling materials (chalk or different kinds of pigments). Later the mixture was improved by mixing the wax part of the filler with damara resin. The filler was stored in a thick stick and inserted to the defects in painting by hot spatulas or needles[5].

The phenomenon of the development of the substitution of traditional products by synthetic ones could be observed from the half of the 20th century, not only in the conservation field. A rapid growth in development came hand in hand with technology and transportation expansion during and within a few years after World War II, especially in the oil refining industry. The driving force for the growth in technology and in the number and size of refineries worldwide was the growing demand for automotive gasoline and aircraft fuel. Oil refining produced by-products based on polyethylene glycols, which are further adjusted to paraffin or microcrystalline waxes. In the late 1950s, several companies began to cooperate with those oil refineries and started to produce new products which could be used also for restoration practices. The aim was to replace the traditional beeswax-resin (colophony or dammar) mixtures with those semi-synthetic waxes. Waxes are mainly considered to be problematic, because it is difficult to remove them and they could cause several types of damages both on easel paintings and frescoes. They were used in variable applications. In the case of frescos, up to the beginning of the 20th century, wax or wax-resin mixtures were applied on the wall paintings to create a protection layer, which was totally water-proof, although, on the other hand, stopped any circulation of the humidity going naturally through the wall[6]. However, the most widespread application of these wax-resin mixtures is definitely in the case of lining of painting by the technique called wax-resin lining or Dutch lining. Numerous studies were made on the account of the discussion about the invasiveness of this lining method. The main problem is the penetration of waxy components not only inside the original canvas but also to the ground and paint layers. It could be observed, the wax residues on the front side of the painting, which are very difficult to remove. Furthermore, during the lining, often the impastos brushstrokes got flattened and the penetration of the mixture caused an overall also inevitable colour change of the picture[7]. In view of the problematic behaviour of waxes, these synthetic waxes were developed. These brand new products were distributed on the market under the names Polywax, Polydiol, or Carbowax. Their use in filler formulas was suggested by Heinz Alhhöfer in 1959. He recommended preparing the filler the same way as the one from beeswax-chalk filler. It consisted of 3 parts of Polywax 12000 and 2 to 3 parts of chalk. The possibility of adding Polywax 1000 in order the five better pliability to the mixture is mentioned. Whereas Polywax is soluble in water, it could be polished very easily with water.[8] These fillers, apart from having physical properties similar to waxes, were said to adhere well to canvases and old fills, be reversible with water, miscible with other wax-based and thermoplastic fillers, and resistant to chemical agents and environmental fluctuations.[9]
From the late 20th century, commercial formulations for wax-resin fillers have been available from several art supplies companies. These fillers are usually composed of waxes (both natural and microcrystalline, or in combination of these), synthetic resins, and are bulked with pigments in different colors and tones. On the market, there are products such as BAO® sets of wax-resin stick fillers (originally composed for filling defects in wood) or Gamblin pigmented wax/resin sticks.

The Gamblin pigmented wax/resin filler formula consisted of beeswax, microcrystalline wax, resin, and pigments. One of the original components, the resin Laropal A80, is no longer manufactured from 2008. That led *The Buffalo State College Art Conservation program* to adjust and improve the mixture. In 2011, they conducted a survey of different synthetic resins which could replace the previous one and further tested also different waxes. The conclusion of the investigation was a new formula consisting of beeswax, microcrystalline wax, resin Laropal A81, and pigments. Gamblin produces this filler in twelve different shades and as a series of grays. This formula is widely used in the USA; however, it is also available in the European market.[10] The formulation could also be mixed by the conservators themselves.

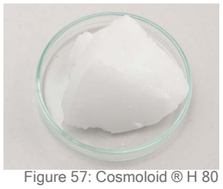
The phenomenon of blooming, especially in some of the heavy metal-containing pigments, appears due to the content of beeswax. That prompted Catarina Pires to investigate the adjustment of the formula as her research thesis project at NOVA University of Lisbon, Portugal. The filler named NOVA-PWR has been field-trialed and reported in 2021. The materials selected have not shown any degradation phenomenon after rigorous testing. Microcrystalline wax Cosmoloid H80 was chosen as the wax content, synthetic low molecular weight hydrogenated hydrocarbon resin Regalrez 1126 as the resin content, and champagne chalk, kaolin, and aluminum hydroxide (alone or in combination) are recommended as filler materials. The amount of pigments added is moderated to achieve the desired visual properties of the filler.[11].

BEESWAX

Characterization of beeswax and its properties are described in the previous chapter.

MICROCRYSTALIINE WAX

Polyethylene (PE) is made by the polymerization of ethylene gas. When the chains in PE are highly regular, they can pack closely together to form crystals. These crystals form within the amorphous polymer mass. Wax can be considered as a low molecular weight version of polyethylene, with two main forms available: paraffin and microcrystalline[12]. Paraffin is defined as aliphatic alkane with low molecular weight and microcrystalline wax is composed mainly of highly branched or cyclic alkanes in irregular molecules and has a higher molecular weight.[13]
Cosmoloid® H 80 is a brand name for a series of microcrystalline wax formulations supplied by several companies, such as Kremer Pigmente GmbH & Co. KG. It has been recommended as an inert material with a suitable degree of hardness[14]. The melting point is between 80-85 °C. It has also been considered highly stable against chemical degradation. When aging, there are no yellowing phenomena due to oxidation because the chains are saturated (they do not contain double bonds), and there are no impurities present, unlike in natural waxes.[15]


Figure 57: Cosmoloid ® H 80

SYNTHETIC RESINS

Laropal® A 81 is a pale, yellowing-resistant urea aldehyde thermoplastic resin, soluble in almost all solvents (but not in water), and compatible with practically all coating raw materials. Its main uses include combination with other resin binders and the production of all-purpose pigment pastes. The softening temperature ranges between 80-95°C.[16]


Figure 58: Laropal ® A 81


Figure 59: Regalrez ® 1126

Regalrez® is a registered trademark that characterizes a series of hydrogenated aliphatic resins, and the index number refers to different properties. While Regalrez 1094 is more commonly used as a final varnish, Regalrez 1126 has been used as a blend consolidant for wood[17]. Regalrez 1126 was chosen due to its higher molecular weight, higher glass transition T (Tg), and higher softening point. Regalrez resins have been reported to be photochemically stable[18], UV stable[19], and resistant to change under accelerated environmental conditions[20]. They also have high compatibility with microcrystalline waxes.

1 CENNINI, Cennino. (1395). *Il Libro dell'Arte*, Padova, Italy, p.105

2 VASARI, Gorgio. (1907). *Vasari on Technique: being the introduction to the three arts of design, architecture, sculpture and painting, prefixed to the Lives of the most excellent painters, sculptors and architects*, J. M. Dent & co., London, pp. 148-149

3 BURG, J., M., Van den, SEYMOUR, K. (2024). *Painting conservation part 4: Filling Losses in Paint*. Cultural Heritage Agency of the Netherlands. Ministry of Education, Culture and Science. Amersfoort. p. 15

4 HORIS-DÉON, Simone. (1851). *De la conservationet de la restauration des tableaux*. Hector Bossagne, Paris, p. 51

5 SLÁNSKÝ, Bohuslav. (1955). „Tmelení defektů v obraze", in *Technika malby, část II: průzkum a restaurování obrazů,* 2nd, Prague, Paseka, ISBN 80-7185-623-1, p. 207

6 CATHER, S., HOWARD, E. (1986). *The use of wax and wax-resin preservatives on English mediaeval wall painting: rationale and consequences*, Case Studies in Conservation of Stones and Wall Paintings, Pre.prints of the IIC 11th International Congess, Bologna, pp. 48-63

7 KECK, C., K. (1977). *Lining adhesives: their history, uses and abuses*, Journal of the American Institute for Conservation, Vol. 17, N. 1, Taylor & Francis, Ltd. , pp. 45-52

8 ALTHÖFER, Hein. (1959). "The Use of Polyethylene Glycols in the Field of Painting Restoration." in *Studies in Conservation*, Vol. 4, p. 33

9 FUSTER LOPEZ, Laura. (2012). 'Filling': in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings,* USA and Canada: Rouledge, ISBN 978-0-7506-8199-5, p. 590

10 MCINTYRE, Chritine. (2011). *Development of a pigmented wax/resin fill formulation for the conservation of paintings*, Art conservation department, Buffalo stage collage, USA

11 PIRES, Catarina, Nunes, Aníbal, Rocha. (2021). *An invastigation on the suitability and stability of a new pigmented wax-resin formulation to be used in the conservation of painting,* Master disertaion, NOVA School of Science and Technology, NOVA University of Lisbon, Portugal

12 Most waxes are derived from fractions of crude oil. Crude oil is refined into various products, including ethylene. During the refining process, ethylene is obtained from the cracking of hydrocarbon molecules found in crude oil.

13 HORIE, C. V. (2010). Hydrocarbons, *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britan, Routledge, ISBN 0 7506 6905 5, pp.125-128

14 HORIE, C. V. (2010). Hydrocarbons, *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britan, Routledge, ISBN 0 7506 6905 5, p. 128

15 CREMONESI, Leonardo Borgioli, Paolo, 2019, Ch IV. Synthetic film-forming substances used in restoration: Polyethylene, *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 82-85

16 https://www.kremer-pigmente.com/elements/resources/products/files/67204e.pdf , Kremer Pigmente GmbH & Co. KG, 67204 Laropal® A 81 [19/03/2024]

17 CREMONESI, Leonardo Borgioli, Paolo, 2019, Ch IV. Synthetic film-forming substances used in restoration: Aliphatic resins, *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 153-161

18 MCGLINCHEY, W. Ch., RIE, E., R., de la. (1990). *New synthetic resins for picture varnishes*, Studies in Conservation, Vol. 35, N. 1, Pre-print of the Contribution to the Brussels Congress, pp. 168-173

19 WHITTEN, J. (1995). *Low-Molecular-Weight Resins for Picture Varnishes*, In AIC Paintings Specialty Group Postprints, American Institute for Conservation 23rd Annual Meeting, Saint Paul, Minnesota, Washington, DC, pp. 124-129

20 GOTZ, von der, M., PROCTOR, R., G., WHITTEN, J., MAYER, L., MYERS, G., HOENINGSWALD, A., SWICKLIK, M. (2012). "Varnishing as Part of the Conservation Treatment of Easel Paintings." In *Conservation of Easel Paintings*. 2nd ed., edited by Joyce Hill Stoner, and Rebecca Rushfield. New York: Routledge, pp. 635–657

RECIPE FOR GAMBLIN PIGMENTED WAX/RESIN FORMULA

- 3 parts beeswax
- 1 part microcrystalline wax (in the tested series Cosmoloid H 80 was used)
- 1 part synthetic resin Laropal A 81
- 5 parts pigment

*all parts measured by weight

Firstly, put the measured amount of beeswax into a glass container and place it into the water bath/on a hot plate(e). The temperature should be approximately 75°C. After melting, add the measured amount of microcrystalline wax Cosmoloid H 80(f). During the melting process, put the measured amount of resin Laropal A 81 into a mortar(b) and crush it(c) into a fine powder(d). After melting the wax mixture, add the resin content and slightly increase the temperature to approximately 90°C. Allow it to melt, which takes a couple of minutes. After perfect melting and mixing of these components, gradually add the measured amount of pigment(g) and mix it properly(h).

Prepare the silicone form beforehand(a) and pour the hot mixture into the grooves(i). The ready-to-use filler sticks will be obtained(j). Additionally, it could be cast as a sheet.

Allow it to cool down in the form, and afterwards, store the sticks/sheets in a dry place at room temperature.



Figure 60a - j: Preparation of Gamblin pigmented wax /resin formula

APPLICATION

The pigmented wax-resin filler is a thermoplastic filler; therefore, it has a specific way of application in contrast to other water-based fillers. The filler is usually cast as a thin stick (Fig.61; however, it could also be prepared as a sheet; for more details, see chapter *3.10 Pigmented wax-resin filler with BEVA*); its thickness depends on the priorities of the conservator and the purpose of the particular treatment. It is very helpful to have several sticks of different colors or tones prepared for immediate application in a studio. This type of filler is suitable for both small and large losses.



Figure 61: Gamblin PWR stored as sticks

For the application, a heated spatula is used. The filler stick is placed above the loss, and by the heat, the filler is melted and flows into the loss(Fig.62a). Depending on the character of the loss and its dimensions, small-tipped(Fig.62b) or larger flat heated spatulas may be used(Fig.62e). Moreover, the larger flat-tipped spatulas are used for adjustment, leveling, and flattening the surface of the filler.

Any excess of the filler over the original painting is removed by an appropriate solvent (Fig.62c; low aromatic hydrocarbon). If the painting is varnished before the infilling process, the initial varnish should not be affected by the removal of the residues of the filler(Fig.62d).

The texturing of the filler surface could be done by several options. If the surface should be flat, a silicone Melinex sheet is placed on top, and the heated spatula is used to flatten and smooth the surface(Fig.62f). It is left on the surface till the filler is cold(Fig.62g). In cases where a matte surface is required, a piece of baking paper could be placed on the surface instead of a silicone Melinex sheet, and the same process is applied. Incision of the craquelure could be done by heated needles or different instruments which are warmed beforehand. However, this type of filler is very suitable for texture imprinting by textiles or molds. The imprinting material is placed on the filler surface, and appropriate heat is applied[1].

Water-based retouching is not possible to be used because of the hydrophobic surface of the filler. All synthetic retouching resins will adhere well to this surface as well. However, mostly the filler is prepared with pigment to match the color of the surrounding paints.

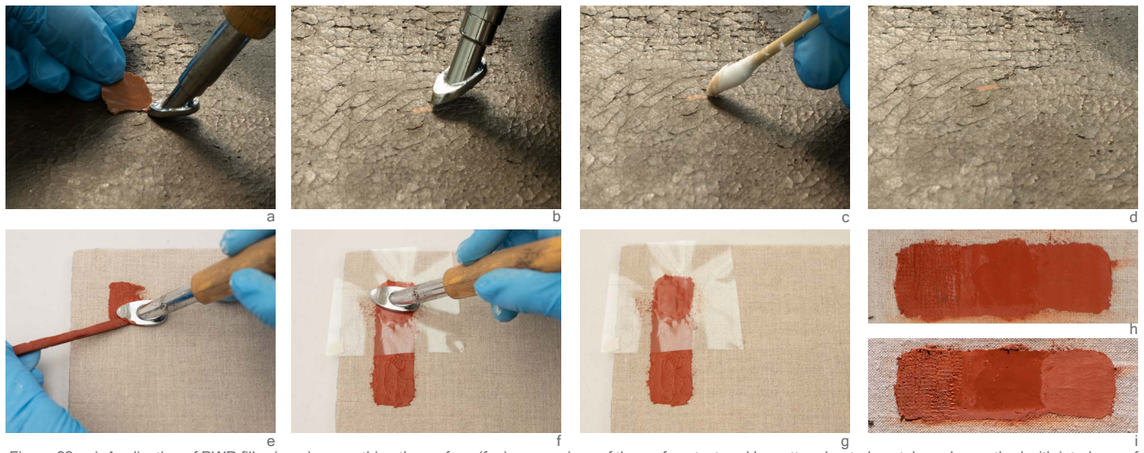


Figure 62a - i: Application of PWR filler (a - e); smoothing the surface (f ,g); comparison of the surface textured by pattern heated spatula and smoothed with interlayer of silicon Melinex sheet and baking paper, photographies in day light(h) and raking light(i)

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

The filler obtained very good properties before aging; however, some of them significantly changed after the accelerated aging process. Probably due to the high temperatures in the environmental chamber, the wax component dissolved from the filler into the textile support. This caused a significant dimensional change in terms of the height of the applied filler.
Additionally, the loss of the wax binding component caused the filler to become more fragile and lose its excellent flexibility properties. Moreover, it slightly lost its glossy character and became duller, resulting in an optical darkening.
However, the filler remained very easily soluble in a wide range of solvents, and the changes in properties occurred only for the fillers that were exposed in the environmental chamber.

Therefore, it is highly important and recommended to carefully consider the selection of this filler, considering where the art object will be exposed and what temperatures could be reached in that particular environment.

1 More information about the imprinting of textiles and moulds is in following chapter *4.2 Methods for filler reintegration and texturation*.

GAMBLIN PIGMENTED WAX/RESIN FILLER

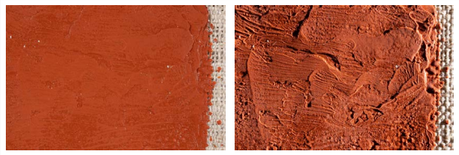
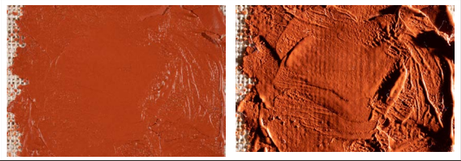
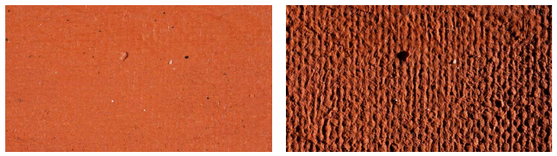
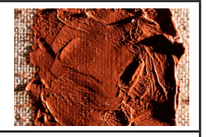
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change observed.			
colour change	L* 40.3 a* 28.2 b* 28.3 C* 39.9 h* 45.1	ΔE = 1.9 darker and duller	ΔE = 2.9 darker and duller the sample failed the tolerance	ΔE = 3.3 darker and duller the sample failed the tolerance
craquelure		Not a case. No cracking developed. 	Not a case. No cracking developed. 	Not a case. No cracking developed. 
surface dusting	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.
hardness	The filler is very soft; a very little pressure make a deep dimple.	The filler remains very soft.	The filler maintains very soft, similar to the unaged sample.	The filler is only slightly less soft, similar to the unaged sample.
coherence	Since the filler is very soft and adjustable it is very easy to scratch it, however, that is not indicated by the loss of cohesion.	The filler remains the same character.	The filler has become slightly more fragile due to the dissolution of the wax component into the support.	The filler has become slightly more fragile due to the dissolution of the wax component into the support.
adhesion to the support	very good no material is removed	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -	ø 17 cm ∩ ø 11 cm x ø 9 cm - ø 7 cm -
change in reversibility	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol 5 rolls	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol 5 rolls	distilled water slightly after 20 rolls White Spirit 5 rolls toluene 5 rolls ethanol 5 rolls	distilled water slightly after 15 rolls White Spirit 5 rolls toluene 5 rolls ethanol 5 rolls

Table 42: Gamblin pigmented wax-resin filler_evaluation of the properties based accelerated aging tests

RECIPE FOR NOVA-PWR FORMULA

- 1,5 part microcrystalline wax Cosmoloid H 80
- 1 part Regalrez 1126

- 1-2 parts bulking agent

*all parts measured by weight

The filler material could be chosen according to the preferences of the conservator. Trials by Caterina Pires explored various materials and their combinations. The tested materials included champagne chalk, calcium carbonate, kaolin, aluminum hydroxide, and several kinds of pigments. The recommended combination is champagne chalk with pigment in a 1:1 proportion. For this trial, the chosen combination was Bolognese chalk with a pigment mixture of Indian oxide red and gold ochre in a 1:1 proportion, relative to the binder medium(a).

The filler is prepared either in a water bath or on a hot plate.

Firstly, place the measured amount of microcrystalline wax into a glass beaker and put it into the water bath/on a hot plate(d). The temperature should be approximately 75°C. During the melting process, place the measured amount of resin Regalrez 1126 into a mortar(b) and grind it into a fine powder(c). After the wax has melted(e), slightly increase the temperature to approximately 90°C. Slowly add the resin content(f), allowing it to melt, and maintain for 20-25 minutes(g). Then, gradually add the weighted mixture of chalk and pigments(h), incorporating them while stirring the heated mass(i).

Pour the hot mixture between two metal plates covered with silicone Melinex. Use a warm iron to heat up the plates and melt the filler into a fine, even plate(j). Another option is to cast the filler as a stick.

Allow it to cool down in the form and then store the sheets/sticks in a dry place at room temperature.



Figure 63a - j: Preparation of NOVA-PWR filler

Another possible documentation of the procedure of preparation of the filler mixture on a hot plate processed by Catrina Pires.



Figure 64: Process of preparation NOVA-PWR on hot plate.
source: Pires, Catarina, (2021): 25

APPLICATION

The pigmented wax-resin filler is a thermoplastic filler; therefore, it has a specific way of application in contrast to other water-based fillers. The filler could be cast both as a stick or as a sheet. It is very helpful to have several sticks/sheets of different colors or tones prepared for immediate application in a studio(Fig.65a). This type of filler is suitable for both small and large losses.

The application process is the same as described above for the Gamblin pigmented wax filler formula. Therefore, only a brief explanation is provided (for detailed information, see the application of Gamblin filler). The heated small-tipped or larger flat-tipped spatula is used depending on the character of the loss(Fig.65b). larger flat-tipped spatulas are also used for adjustment, leveling, and flattening the surface of the filler. Any excess of the filler over the original painting is removed by an appropriate solvent (low aromatic hydrocarbon) and the texturing of the filler surface could be done by several options[1](Fig.65c).

Water-based retouching is not possible to be used because of the hydrophobic surface of the filler. All synthetic retouching resins will adhere well to this surface as well. However, mostly the filler is prepared with pigment to match the color of the surrounding paints.

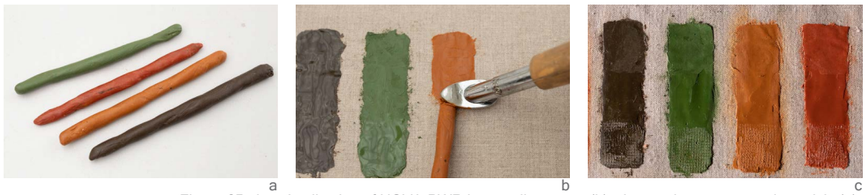


Figure 65a,b,c: Application of NOVA-PWR in a textile support(b) whereas it was prepared as sticks(a); comparison of different surfaces achieved by texturing or smothing(b)

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

The filler obtained very good properties before aging; however, some of them significantly changed after the accelerated aging process. Probably due to the high temperatures in the environmental chamber, the wax component dissolved from the filler into the textile support. This caused a significant change in the appearance of the filler. The surface became swollen, the wax component was absorbed into the support, and the residues of the filler components became bloated and exhibited a tumefied character.
However, in contrast to the previous pigmented wax resin filler, this one has not lost its flexibility. The filler also, like the previous one, slightly lost its glossy character and became duller.
On the other hand, the filler remained very easily soluble in a wide range of solvents, and the changes in properties occurred only for the fillers that were exposed in the environmental chamber.

Therefore, it is highly important and recommended to carefully consider the selection of this filler, considering where the art object will be exposed and what temperatures could be reached in that particular environment.

1 More information about the imprinting of textiles and moulds is in following chapter *4.2 Methods for filler reintegration and texturation*.

NOVA-PWR
NOVA formulation of pigmented wax/resin filler

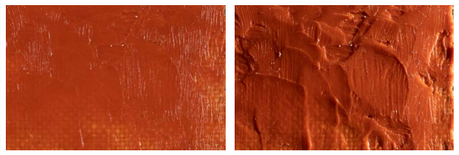
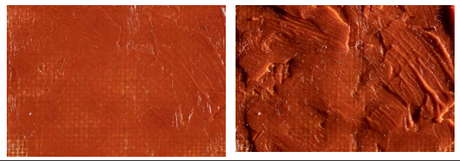
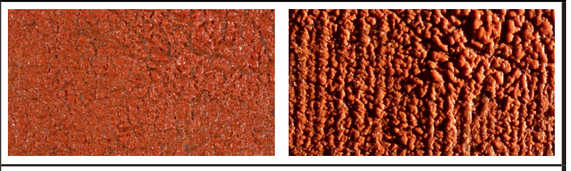
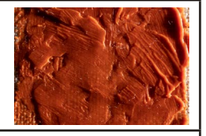
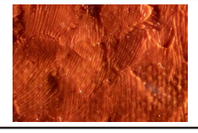
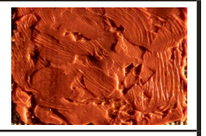
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change observed.			
colour change	L* 35.7 a* 32.8 b* 33.0 C* 46.5 h* 45.2	ΔE = 0.5	ΔE = 17.0 lighter and duller the sample failed the tolerance	ΔE = 18.4 lighter and duller the sample failed the tolerance
craquelure		Not a case. No cracking developed. 	Not a case. No cracking developed. 	Not a case. No cracking developed. 
surface dusting	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.
hardness	The filler is very soft; a very little pressure make a deep dimple.	The filler remains very soft.	The filler maintains very soft even after aging.	The filler maintains very soft even after aging.
coherence	Since the filler is very soft and adjustable it is very easy to scratch it, however, that is not indicated by the loss of cohesion.	The filler remains the same character.	The filler has become significantly more fragile due to the dissolution of the wax component into the support.	The filler has become significantly more fragile due to the dissolution of the wax component into the support.
adhesion to the support	very good no material is removed	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩
change in reversibility	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol no	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol no	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol slightly after 20 rolls	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol slightly after 20 rolls

Table 43: NOVA-PWR filler_evaluation of the properties based accelerated aging tests

3.10 PIGMENTED WAX-RESIN FILLER WITH BEVA

The development and history of pigmented wax-resin fillers were already described in a previous chapter. However, a very important role in this family of fillers is played by the acting material, which is widely used in the restoration field in a number of different applications. It is no wonder then that it could serve as a high-quality filling medium with a long history of use and testing overall.

In 1970, the history of a rapidly expanding adhesive began in the USA. That year, an American conservator, Gustav A. Berger, now recognized as one of the most innovative thinkers in the restoration field, presented the first work related to a brand-new adhesive he developed, called Gustav Berger's Original Formula 371, known as BEVA 371.
The original formula was created by Gustav Berger and William Russell in 1969 as a synthetic lining adhesive for use on vacuum hot tables. In 1967, Gustav A. Berger began a research program with support from the Samuel H. Kress Foundation to investigate new adhesives for the lining and consolidation of paintings. He was encouraged by William Suhr, the chief restorer of the Frick Collection in New York, to develop a lining adhesive that would be „stronger than wax, free of the hazards found with aqueous glue-paste, adhere to oil paint, and be reversible."[1]
The formulation was published in 1972, and in the following years, Berger further studied the product, considering many observations that arose from all parts of the world. Therefore, the formulation of BEVA and its components has undergone a number of changes since its commercialization. Additionally, Berger formulated modifications of the product to adapt it to various needs, such as cold lining and gel application. Consequently, he published several papers about the new modifications and methods of using the BEVA formula from the 1970s until the millennium.[2]

The principal component in BEVA 371 is an EVA copolymer. This class of vinyl acetates was briefly mentioned in a chapter dedicated to polyvinyl alcohol fillers. Let's discuss its characterization a little deeper.
Ethylene-vinyl acetate copolymers, commonly known as EVA copolymers, are prepared by copolymerizing the main monomer, ethylene, with vinyl acetate as a co-monomer. In practice, this means that polyethylene is further plasticized by the presence of vinyl acetate. This plasticizing also results in a considerable increase in solubility. EVA copolymers have a range of properties depending on the ratio of ethylene to vinyl acetate in the polymer. Due to the presence of vinyl acetate, EVA is more stable in terms of resistance to cross-linking caused by photo-oxidation than polyethylene. These EVA copolymers are widely used in everyday life, such as in glues for wood in aqueous dispersion.[3]

There are two different EVAs present in the formulation of BEVA 31:
Elvax 150® (DuPont™) and A-C 400® (Honeywell)
The key to EVA-based adhesives, is the combination of high and low molecular weight (mass) components, or, a base polymer and a tackifying resin, respectively. The tackifiers present in BEVA 371 are Laropal K 80® and Cellolyn 21®. EVA-based adhesives also contain a wax component, which is often added to control the melt viscosity and setting speed[4].

The original formula was patented by Gustav Berger and produced under license by Lascaux. However, the production got in the center of a legal dispute, which led Berger to revoke the license to the Swiss company. Lascaux is still producing slightly modified formula under the name Heat-Seal Adhesive 375.[5] Today two patented variants of Beva 371 are sold – one in the USA via Conservators Products Company (CPC), New Jersey and one in Europe via CTS, Italy.

CPC collaborated with Berger in the 1990's to reformulate the commercial product after Laropal K80 was discontinued in the production. Their formula, since 2008, has contained an unspecified aldehyde ketone resin, and is sold under the trade mark BEVA 371b. This product can be distinguished from the original formulation by its slightly yellower tone[6]. Starting at the 2014 productions, part of the keton resin was replaced by Laropal A81, which allowed to reduce the straw-yellow colour to a negligible level. From 2018, C.T.S. completely replaced the ketone resin with Laropal A81, and BEVA 371 is now crystal clear again[7].

It is not surprising that BEVA 371 belongs to the category of the most imitated products in the history of conservation. Its popularity worldwide has led numerous researchers to study its properties, applications, and aging. It still holds a central position in debates on lining techniques and remains a subject of criticism. Questions and doubts regarding the stability of BEVA 371 can be found addressed by Berger himself in his most recent book „Conservation of Paintings: Research and Innovations" (2000). However, according to Down et al.'s comparative study from the Canadian Conservation Institute (which was previously mentioned and described in chapters dedicated to PVA and Plextol B500 fillers), BEVA 371 still maintains its position as the most stable, reversible vinyl product, with properties retained over time.[8]

1 BERGER, Gustav, RUSSEL, William. (2000). *Conservation of Paintings: Research and Innovations*, Archetype Publications, University of California, USA, ISBN 9-7818-7313-237-1

2 Three examples of Berger's publications in Studies in Conservation: *Heat-seal lining of a torn painting with BEVA 371* (1975); *Unconventional treatments for unconventional paintings* (1976) and *More unconventional treatments for unconventional art* (1990)

3 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Vinyl derivatives", in *The synthetic resins used in the treatment of the polychrome works of art,* De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, p. 95

4 PLOEGER, Rebeca, McGLINCHEY, Chis W., RIE, E. René de al. (2015). *Original and reformulated BEVA 371: Composition and assessment as a consolidant for painted surfaces,* The International Institute for Conservation of Historic and Art

5 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Vinyl derivatives", in *The synthetic resins used in the treatment of the polychrome works of art,* De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, p. 103

6 BURG, Julia M. Van den, SEYMOUR, Kate. (2023). *Consolidation of Paint and Ground, Painting conservation, part 3*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 60

7 CREMONESI, Leonardo Borgioli, Paolo. (2019). „Ch IV. Synthetic film-forming substances used in restoration: Ethylene-vinylacetate copolymer (EVA)", in *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilmversum, ISBN 9789082936131, pp. 103-106

8 DOWN, J., L., MACDONALD, M., A., TÉTREAULT, J., WILLIAMS, R., S. (1996). *Adhesives Testing at the Canadian Conservation Institute: An Evaluation of Selected Poly (Vinyl Acetate) and Acrylic Adhesives*, Studies in Conservation, Volume 41. pp. 19-44

BEVA© 371 was formulated in a numerous of different variants available. It is produced as a BEVA 371 granules (dilutable to the desired concentration by conservators), BEVA 371 gelled in solvents (the granules pre-dissolved in 60% toluene and naphtha's) and BEVA 371 film[9]. The softening temperature of BEVA is below its melting temperature. That provides the significant property of the adhesive, by heating to approximately 65-70°C it becomes tacky but does not flow. The penetration of the adhesive into substrates is though reduced and nap bonds are permitted to be formed. The melt temperature of the higher molecular weight components is around 115°C. BEVA 371 was developed as a strong adhesive and consolidating material for canvas paintings. It is widespreadly used for consolidation, lining (both double and strip lining) and applying facing on easel painting. It could also be applied on other materials such as paper, stone, plaster, etc. Furthermore, the composition of BEVA 371 gives the opportunity to become a basis for wax-resin filler.
The Conservator's Products Company also produces BEVA Gesso in two forms: Gesso-V (Vermiculite) and Gesso-P (Paintings). Both were introduced in the 1990s in the USA and production slowly spread to Europe as well. The formula of Gesso-P is undisclosed but likely consists of hydrogenated hydrocarbon resins and a dispersion of ethylene-vinyl acetate copolymer. It includes chemically inert mineral powder (calcium carbonate), a pH buffer, oxidation inhibitors, UV stabilizers, and vinyl resin. It can be applied in both thick and thin films; thickness can be increased by adding more calcium carbonate. Different types of losses can be filled using various approaches for application, such as hand-building the texture, casting a small textured fill, and imprinting the texture in-situ. BEVA Gesso-V has a rougher consistency more similar to sand, with a content of Mica powder. It casts a highly elastic film with good adhering ability to wood, cardboard, canvas, mosaics, plastics, metal, etc.[10]

Already in 1975, Berger described the possible application of BEVA 371 in combination with whiting (1 part BEVA 371 and 2 parts bulking agent) or with a mixture of calcium sulfate and kaolin. The recipe is as follows[11]:
- Take one cup of BEVA 371 solution from the can.
- Add an equal amount of xylene. Heat in a double boiler until dissolved.
- Add two capfuls of naphtha to the above mixture, heat in a double boiler stirring occasionally.
- Depending on the amount of gesso needed for the job, take one or two cups of the final mixture and pour guilder's whiting slowly into the mixture, while stirring, until the consistency of soft gesso is reached.
- Spread some of this soft gesso on a slab or a piece of mylar for grinding.
- Keep the ground gesso in a closed jar.
- Prior to use, warm the BEVA gesso in a double boiler.

This BEVA Gesso could be inserted into losses and used to mend small tears in canvas from the back side of the painting. Once it is turned around, the canvas with the same density and weave could be primed over the filler. The BEVA Gesso could replace epoxy fillers, thus preventing the excessive spread of the epoxy resin.[12]

During the 1980s, the BEVA-chalk filler was introduced (after several trial tests) by German conservator Heinz Althöfer and his associates[13]. It consisted of BEVA 371 and filling material. Since then, several adjustments and improvements of the BEVA filler have been developed and tested as a stable thermoplastic filler for conserving easel paintings. Ready-to-use sheets of BEVA gesso could be prepared from BEVA 371 and kaolin (in ratios of 2:1 or 1:1) by spreading the mixture on a silicon-coated Mylar/Melinex sheet and then flattening the substance to the desired thickness. The filler can then be reactivated with a hot spatula and applied to the area of loss. The use of kaolin, rather than chalk, results in smoother and softer surfaces.[14]

The toxicity of the filler, due to the presence of solvents (toluene/naphtha) in the filler and their long retention, led to criticism of the filler at some point. This was one reason for further adjustment of the formula by Stichting Restauratie Atelier Limburg (SRAL). In their recipe, the solvents are allowed to evaporate from BEVA 371, and moreover, the wax-resin part of BEVA is diluted by adding microcrystalline wax[15]. Two variants of this type of BEVA 371 filler were tested in the thesis.



Figure 66: BEVA® 371
source: https://www.kremer-pigmente.com/en/shop/mediums--binders-glues/87030-beva-371-hot-sealing-adhesive.html
[cit. 03/05/2024]



Figure 67: BEVA® Gesso-P
source: https://www.kremer-pigmente.com/en/shop/ready--made-colors/87060-beva-artist-gesso-p.html
[cit. 03/05/2024]

9 Berger also developed an aqueous dispersion (BEVA D-8) and as a gel mixture of EVA, acrylic resin, and cellulosic materials named BEVA Gel.

10 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 30

11 BERGER, Gustav, RUSSEL, William. (2000). *Conservation of Paintings: Research and Innovations*, Archetype Publications, University of California, USA, ISBN 9-7818-7313-237-1, p. 335

12 BERGER, Gustav. (1975). *Heat-seal lining of a torn painting with BEVA 371*, Studies in Conservation, Vol. 20, N. 3. pp. 131-135

13 ALTHÖFER, H., ed. (1985). *Restaurierung Moderner Malerei: Tendenzen, Material, Technik*, Callwayv

14 FUSTER LOPEZ, Laura. (2012). 'Filling': in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings,* USA and Canada: Rouledge, ISBN 978-0-7506-8199-5, p. 592,

15 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 44

RECIPE FOR BEVA FILLER

3 parts BEVA 371b
1 part microcrystalline wax (for the mocups used Cosmoloid H80)
2 parts Aluminium hydroxide[1] ($Al2O3$) or 7 parts Kaolin
1 part pigment for colouring

*all parts by volume

Alternative of the recipe:

90 g BEVA 371b
60 g microcrystalline wax (for the mock-ups used Cosmoloid H80)
60 g Kaolin
4 g Titanium white (or another type of pigment)
26 g Chalk, calcium carbonate ($CaCO3$)

The preparation process is the same for both recipes. Both were mixed and applied on mock-up canvases for the trials. From a very subjective point of view, the second one with the exact amount of grams of each component is recommended. It is, though, easier to measure and adjust.

Firstly, measure the appropriate amount of BEVA into a jar and leave it to evaporate the solvent overnight. The BEVA will lose a little of the weight and volume; nevertheless, the amount is not going to be adjusted. Work with the pre-measured amount from the first day.

The process of mixing and melting the components is done on a hot plate or in a water bath.

The measured and evaporated amount of BEVA is melted by warming it in a glass jar(b) or metal dish(k) in a water bath or on a hot plate. After melting(l), add the measured amount of microcrystalline wax(m) and leave it to properly melt(n). The temperature of the bath or plate should be around 90°C. During melting, mix the mixture thoroughly but do not let it bubble.

Gradually sieve the filling material (or the mixture of different materials) with pigments(c,d;o,p). Mix it perfectly until a thick paste is obtained(e;q).

Place the hot filler paste between two silicone Melinex or silicone paper sheets(i,g) and flatten it in a hot press or between two aluminum metal sheets placed on a hot plate or table with a slight press of iron(h). The temperature required is around 85-90°C.

The filler is stored as ready-to-use sheets(i;r) in stable environment.

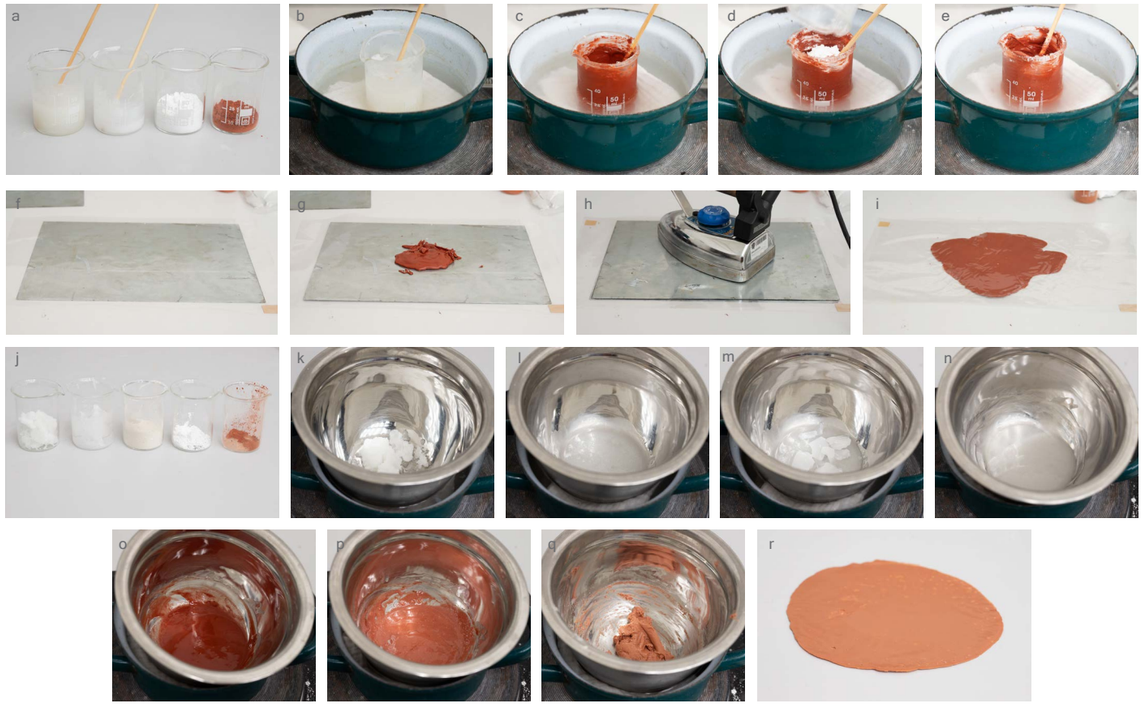


Figure 68a - r: Optional preparation of BEVA filler

1 At the recipe from SRAL Portafil A40 is recommended. It is a commercial type of aluminium hydroxide.

APPLICATION

The BEVA filler is a variant of pigmented wax resin filler which, due to its thermoplastic character, has a specific way of application in contrast to other water-based fillers. The filler is usually cast as a thin sheet; its thickness depends on the priorities of the conservator and the purpose of the particular treatment. It is very helpful to have several sheets of different colors or tones prepared for immediate application in a studio(Fig.69). The BEVA filler is suitable for both small and large losses.



Figure 69: BEVA filler sheets pigmented in different colours
source: Van den Burg, J. M., Seymour, K. (2024): 44

For the application, a heated spatula is used. The filler sheet is placed above the loss, and by the heat, the filler is melted and flows into the loss(Fig.70a). Depending on the character of the loss and its dimensions, small-tipped or larger flat heated spatulas may be used. Moreover, the larger flat-tipped spatulas are used for adjustment, leveling, and flattening the surface of the filler. Additionally, another option is to prepare really thin filler sheets and cut specific patterns from them for the loss. For this operation, for example, transparent tape could be used. A piece of tape is placed over the surrounding paint around the loss, and the shape of the loss is drawn on the tape. Then, the tape is carefully removed and placed on the filler sheet. This will simplify the cutting of the proper shape for the loss. Afterwards, the filler is inserted into the loss, reheated, and adhered with a flat-tipped spatula.

Any excess of the filler over the original painting is removed by an appropriate solvent (Fig.70c; low aromatic hydrocarbon). If the painting is varnished before the infilling process, the initial varnish should not be affected by the removal of the residues of the filler.

The texturing of the filler surface could be done by several options. If the surface should be flat, a silicone Melinex sheet is placed on top, and the heated spatula is used to flatten and smooth the surface. It is left on the surface till the filler is cold. In cases where a matte surface is required, a piece of baking paper could be placed on the surface instead of a silicone Melinex sheet, and the same process is applied. Incision of the craquelure could be done by heated needles or different instruments which are warmed beforehand. However, this type of filler is very suitable for texture imprinting by textiles or molds. The imprinting material is placed on the filler surface, and appropriate heat is applied[1](Fig.70e,f,g).

Water-based retouching is not possible to be used because of the hydrophobic surface of the filler, though acrylic colours do bind well to the surface. All synthetic retouching resins will adhere well to this surface as well(Fig.70h).



CASE STUDY vol.8_Portrait of Prague Archbishop Antonín Václav Vokoun (half of 18th century)
This painting was highly damages and a number of losses were present both in paint and support layer. The structural works within tear mending, inserting patches and intarzies and lining of the canvas was conducted before infilling. The BEVA filler was selected for the possible work in both small and large losses, prefect working ability and texturizing properties. Especially for the bottom missing part, imitative reintegration was desired. The adjusting of the filler surface was made by transferring the texture of the paint surface through the silicone moulds. Several different moulds were obtained and imprint by reheating the filler with hot air pen and heated spatula. The retouching was afterwards done by free pigments bound with Paraloid B-72 and the finals were made by Gambin retouching paints. The final varnish was sprayed.

Figure 70: Portrait of Prague Archbishop Antonín Václav Vokoun; application of filler(a,b,c,d); macro-photographs after filling in daylight (a,g) and raking light(f); after retouching in daylight(h)

PROPERTIES EVALUATION BASED ON ACCELERATED AGING TESTS

This filler is significantly the most resistant one from the category of pigmented wax resin fillers. Furthermore, no changes in properties occurred after accelerated aging processes.
The filler retains its high degree of flexibility, softness, coherence, adhesion to the textile support, and solubility in both low aromatic hydrosolvent and aromatic more polar solvents, with resistance to water.

1 More information about the imprinting of textiles and moulds is in following chapter *4.2 Methods for filler reintegration and texturation*.

PWR - BEVA© FILLER
KAOLIN

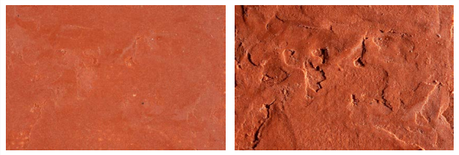
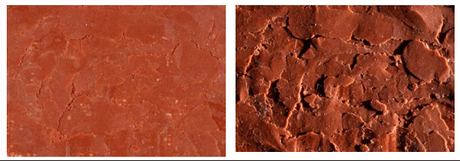
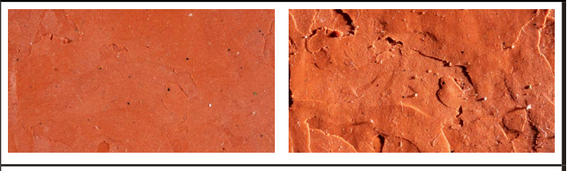
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change observed.			
colour change	L* 40.0 a* 23.8 b* 20.2 C* 31.2 h* 40.3	ΔE = 0.3	ΔE = 0.4	ΔE = 0.6
craquelure		Not a case. No cracking developed. 	Not a case. No cracking developed. 	Not a case. No cracking developed. 
surface dusting	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.
hardness	The filler is very soft; a very little pressure make a deep dimple.	The filler remains very soft.	The filler maintains very soft even after aging.	The filler maintains very soft even after aging.
coherence	Since the filler is very soft and adjustable it is very easy to scratch it, however, that is not indicated by the loss of cohesion.	The filler remains the same character.	The filler remains the same character.	The filler remains the same character.
adhesion to the support	very good no material is removed	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩
change in reversibility	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol slightly after 10 rolls	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol slightly after 10 rolls	distilled water no White Spirit 10 rolls toluene 5 rolls ethanol 10 rolls	distilled water no White Spirit 10 rolls toluene 5 rolls ethanol 10 rolls

Table 44: BEVA wax-resin filler bulked with pigment mixture and kaolin_evaluation of the properties based accelerated aging tests

PWR - BEVA© FILLER
KAOLIN : CALCIUM CARBONATE 2.3 : 1

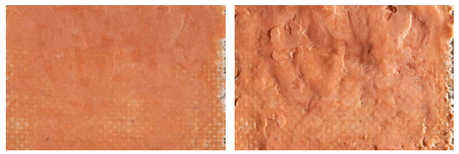
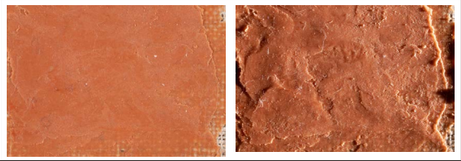
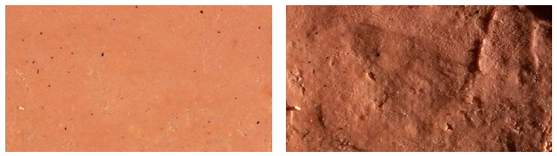
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light				
drying dimensional change	No dimensional change observed.			
colour change	L* 50.5 a* 23.3 b* 25.1 C* 34.2 h* 47.1	ΔE = 0.3	ΔE = 0.4	ΔE = 0.8 slightly darker
craquelure		Not a case. No cracking developed. 	Not a case. No cracking developed. 	Not a case. No cracking developed. 
surface dusting	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.
hardness	The filler is very soft, even softer compared to the previous sample; a very little pressure make a deep dimple.	The filler remains very soft.	The filler maintains very soft even after aging.	The filler maintains very soft even after aging.
coherence	Since the filler is very soft and adjustable it is very easy to scratch it, however, that is not indicated by the loss of cohesion.	The filler remains the same character.	The filler remains the same character.	The filler remains the same character.
adhesion to the support	very good no material is removed	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩
change in reversibility	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol slightly after 20 rolls	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol slightly after 20 rolls	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol 20 rolls	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol 10 rolls

Table 45: BEVA wax-resin filler bulked with pigment mixture, kaolin and calcium carbonate_evaluation of the properties based accelerated aging tests

PWR - BEVA© FILLER
ALUMINIUM HYDROXIDE

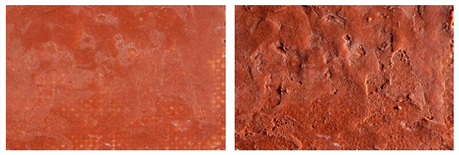
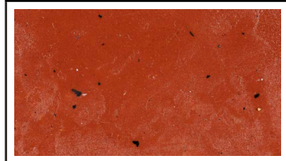
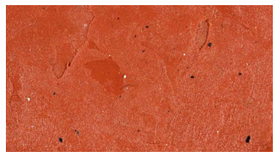
	stable environment inside black box	3 months of exposure to light efflorescence within UV radiation in relatively stable environment at restoration studio condition	exposure for 62 cycles in the environmental humidity chamber new canvas with skin glue isolation	 old canvas with residues of wax-resin lining adhesive
macro photography day light | raking light		 	 	 
drying dimensional change	No dimensional change observed.			
colour change	L* 39.0 a* 24.3 b* 20.0 C* 31.5 h* 39.5	ΔE = 0.6 slightly darker	ΔE = 1.9 darker and brigther however that probably caused by penetration by sample placed next to this one	ΔE = 2.8 darker and brigther however that probably caused by penetration by sample placed next to this one
craquelure		Not a case. No cracking developed. 	Not a case. No cracking developed. 	Not a case. No cracking developed. 
surface dusting	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.	Not a case. No material was captured.
hardness	The filler is very soft; a very little pressure make a deep dimple.	The filler remains very soft.	The filler maintains very soft even after aging.	The filler maintains very soft even after aging.
coherence	Since the filler is very soft and adjustable it is very easy to scratch it, however, that is not indicated by the loss of cohesion.	The filler remains the same character.	The filler remains the same character.	The filler remains the same character.
adhesion to the support	very good no material is removed	remains very good	remains very good	remains very good
flexibility	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩	ø 17 cm ∩ ø 11 cm ∩ ø 9 cm ∩ ø 7 cm ∩
change in reversibility	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol slightly after 10 rolls	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol slightly after 10 rolls	distilled water no White Spirit 5 rolls toluene 5 rolls ethanol 10 rolls	distilled water no White Spirit 10 rolls toluene 5 rolls ethanol 10 rolls

Table 46: BEVA wax-resin filler bulked with pigment mixture and aluminium hydroxide_evaluation of the properties based accelerated aging tests

4. FURTHER ADJUSTMENTS OF FILLERS

The loss compensation consists of a three-stage process: applying and leveling of the fill material, texturing of the filler, and color reintegration. The proper selection, use, and application of filling materials determine the success of visual compensation for losses. Matching colors alone will not be enough to integrate the missing parts if the surface has not been properly leveled, textured, and isolated.[1]

The successful infilling part of the conservation treatment is crucial for the aesthetic and visual reintegration of defects presented on the artwork, and it is important to pay attention to this phase. It is crucial to choose the proper filler based on its composition, as well as to carefully consider the process of application and texturization of the filler. Precision in the application of the filling material in the loss is essential for a beneficial result of the treatment. This process involves two stages: the preparation of the loss and the selection of the filling material, with a clear idea of the further reintegration, leveling, texturizing, and inpainting of the losses and how they will be presented.[2]

The infilling is usually done as one of the final parts of the treatment. It mostly takes place after the structural work and cleaning of the painting have been completed and before the pictorial reintegration is conducted. However, depending on the specific artwork, the structural work could be done after filling, or temporary fillers could be inserted. By structural work, we understand activities such as lining, tear mending, integration of canvas patches, and inlays. The decision on the treatment sequence depends on the actual type, condition, and requirements of the artwork, or in other cases, it is influenced by time-dependent factors.[3]

4.1 APPLICATION OF FILLER

The preparation of losses and defects varies depending on the particular painting. In cases where structural damage affects both the paint layer and canvas support, canvas reintegration is conducted before filling. There are several variants of these treatments. If tears occur, tear mending is performed. If there are losses in the canvas, they could be sewn or a new canvas could be inserted (known as intarsia). The selection of materials used for this phase may already indicate the selection of the filler.[4] While filling losses in the paint layer, it is advisable to prepare the losses before filling begins. Proper preparation involves consolidating the loss and surrounding loose or flaking paint. In some cases, isolation of the canvas and surrounding paint is required to limit the penetration of binding material into the support, ground, or paint layer. This could potentially cause a loss of adhesive and cohesive properties of the filling material. In cases where losses were previously filled, it is important to completely remove any residues of old putty. If some old material remains in the loss, it could affect the properties of the new filler; moreover, adhesion to the old filler may not be sufficient and the filler could fall apart.

Prior to the application of the filler, the conservator should make a decision about pictorial reintegration. The material and method of retouching should be clear before fillings are applied. Basically, inpainting is divided into two categories: imitative (deceptive) retouching and visible retouching (sfumato, neutro). This influences how the filler is applied, whether it is leveled with the surrounding original material or slightly lowered. This is indicated by the reintegration method; for example, thin glazes may compose a retouching, or several thick layers of paint may be required. Depending on the choice of pictorial reintegration, application and texturizing of the filler are selected.

Application methods were described for each filler in a dedicated chapter. To summarize briefly, fillers can be applied using spatulas (made from metal, wood, cork, bamboo, bone, teflon, agate, etc; Fig.71) or various types of brushes. The choice of application method usually depends on the viscosity of the filler and the type of loss being filled. Overall, it is usually better to apply the filler in several layers, especially for deeper losses, to significantly reduce the potential for cracking and shrinkage of the material. The thin layers of filler are applied one by one after the previous one is dried, or it could be slightly reactivated by wetting the filler surface with a small amount of appropriate solvent. In the case of thermoplastic fillers, they must be applied while warm, often using hot spatulas or needles (Fig.72). Excess filler material should be removed immediately with a spatula. The remaining residues may be removed after drying using a wet cotton swab skein or piece of cloth moistened with an appropriate solvent or distilled water. It is important not to forget that the inert bulking material is abrasive, so the swabs and cloth must be changed often to prevent abrasion of the surrounding paint. It is advisable to first apply the filler onto a Melinex sheet, glass plate, piece of textile (canvas), or a piece of wood. This allows observation of solvent (water) evaporation, loss on drying, or adjustment of the filler by adding more pigment to achieve the desired color, or more bulking agent if the filler is too liquid and difficult to handle. These trials can be retained for future reference and as a personal sample reference file.



Figure 71: Spatulas form different materials suitable for application of solven-based fillers



Figure 72: Heated spatula with different tips suitable for application of thermoplastic fillers

1 FUSTER LOPEZ, Laura. (2012). 'Filling': in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings,* USA and Canada: Rouledge, ISBN 978-0-7506-8199-5, p. 586

2 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, pp. 48-49

3 FUSTER LOPEZ, Laura. (2008). *El estuco en la restauración de la pintura sobre lienzo: criterios, materiales y procesos*, Spain: Universitad Politecnica de Valencia, ISBN 978-84-8363-221-5, pp. 63-72

4 FUSTER LOPEZ, Laura. (2012). 'Filling': in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings,* USA and Canada: Rouledge, ISBN 978-0-7506-8199-5, pp. 586-597

4.2 METHODS FOR FILLER REINTEGRATION AND TEXTURATION

No matter how perfect the colour matching can be, the loss of original material will always remain visible if the underlying infill is not sufficiently merged in level and texture with the surrounding surface.[5] The texture of the painting surface is one of the most characteristic properties of a work of art. It varies greatly depending on numerous factors, such as the origin and texture of the fabric support, the properties of the ground layer, whether it is thin or thick, applied by brush or palette knife, etc. Furthermore, the typology of painting technique is crucial. Paintings from the Baroque period are absolutely different from those made in the Expressionistic style of the late 19th century. Not only the technique of building up the pictorial layers, but also the characterization of the expressive or deliberate language of the artistic approach. A painting may have both a smooth and flattened surface or thick impastos with passionate brushstrokes. Moreover, one painting could exhibit both (and several other) attitudes. Last but not least, the damage caused by aging of the artwork could be significantly present. Extensive craquelure of different types (primary, secondary, caused by a bend or puncture from both front and back sides of the painting) could occur. All these types of surface modifications of the painting are characteristic for each artwork. To conduct successful infilling and inpainting, it is essential to maintain the typical features of the surrounding surface of the painting.



a b c

Figure 73: Painting surface characteristic: expressive impastos(a), passionate brushstrokes (b) and secondary craquelure(c)

Before adjusting the surface of the filler to match the texture of the surrounding paint, it is useful to flatten it. This action will simplify any subsequent work. Flattening and leveling the filler can be achieved by scraping off any excess with a scalpel or a wet cotton swab or piece of cloth. To achieve a smooth surface on the filler, a piece of balsa wood or a wine cork dipped in distilled water or an appropriate solvent can be rotated over the surface. This system will provide better adherence to the supporting material (canvas, adjusting properly to the loss and comparing the filling material. The use of raking light could be very helpful in assessing the level of the fill (Fig.74). With raking light, it is more effectively visible whether more material is needed to create a flat surface or whether excess material needs to be removed. For this operation, optical instruments such as the Midi LED Lamp by Aspherilux or a common LED headlamp may be useful (Fig.75). Always avoid any abrasive contact with the original paint around the loss. Any residues present on the surrounding area can be removed, as described earlier, using a skein of cotton swab or a piece of cloth. As a general rule, paying greater attention to the preparation of the filler surface will result in more effective work with surface adjustment and texturing.



Figure 74: Use of raking light during adjustment and leveling filler



Figure 75: Options for raking light devices: Midi LED Lamp by Aspherilux and LED headlamp

Several methods could be applied, considering the desired appearance, whether it is required to match the original surrounding areas or to provide a differentiated texture that will allow restored areas to be perceptible. Moreover, the method chosen depends on whether the texturing is done on the damp or dry filler and the type of texture desired. For a proper understanding of the particular texture of the painting, including the painting's technique and the condition of the painting within the system of craquelure, it is helpful to observe the painting closely using magnifying glasses, microscopes, and/or macro-photography, both in daylight and with raking light. However, this observation typically forms part of the initial examination of the artwork before the actual restoration treatment begins.[6]

5 SEYMOUR, Kate. (2017). *Fillers: Adaptations on Traditional and Commercial Products,* Lecture Presented at NOVA, Lisbon

6 This chapter is based on a research by Laura Fuster-Lopez published in 2008 in the chapter 3.1. Métodos de estructuratión in book *El estuco en la restauración de la pintira sobre lienzo: criterios, materiales y procesos,* pp. 125-151 Spain: Universitad Politecnica de Valencia, p, ISBN 978-84-8363-221-5

This table categorizes the methods and suggests the appropriate instruments to achieve the desired texture on the surface of the filler.

filler characteristic	method		instruments	achieved texture
wet and soft filler	brushstrokes and drips by fluid filler		brushes, scalpels, spatulas	original brush strokes and impastos so-called „orange peel“
	imprint		different textiles obtaining similar pattern as the original weave	original canvas weave
dry filler	smoothing		piece of cork, suede or felt cloth, agate, sandpaper, scalpel, etc.	smooth surface
	brushstrokes and drips by fluid filler		brushes, scalpels, spatulas	original brush strokes and impastos so-called „orange peel“
	incision		scalpels, needles, sharp spatulas, dental instruments	craquelure cracks, rifts, scratches
	imprint	textile patterns	different textiles obtaining similar pattern as the original weave	original canvas weave
		flexible moulds	natural materials: latex, alginates, etc.	all different types of textures present on the original painting‘s surface
			synthetic materials: silicones, etc.	
	alternative methods for structuration		acrylic medias applied by brush	irregular roughness
			heated spatula with different surfaces	textiles with different weave

Table 47: Surface adjustment and texturing methods

I. IMITATION OF THE PAINTING TECHNIQUE BY THE FLUID FILLER

The imitation of the surface of the painting based on the author‘s technique applied to a particular artwork could be done both during the application of the filler itself and after drying. For correct and effective imitation, it is necessary to properly understand the technique of the painting, characteristics of the ground layer, underpainting, layering system of the paint, glazes, features of impastos, and brushstrokes, etc.

Much of this work could already be prepared during infilling the losses. For example, if the surface of the painting features significant brushstroke application, the final layer of the filler could be applied by brush. If necessary, the filler mixture could be adjusted by adding the liquid part used for its preparation to achieve an appropriate consistency, similar to yoghurt (or, if only a slight adjustment is required, a small amount of distilled water or an appropriate solvent may be used). If the filler is being adjusted after drying and leveling, the surface could be activated by gently touching it with a wet cotton swab or piece of cloth. Afterward, the same system with the fluid filler is conducted. An important factor to consider during the application of the fluid filler is cleaning the brush from any filler residues after each application. Otherwise, the filler may begin to dry on the brush, causing the bristles to thicken. However, before starting a new application, the brush should be thoroughly dried; otherwise, any remaining liquid may alter the consistency.

In cases where the technique of the painting is typical for its impasto character, it is highly helpful to understand how the impastos were made and what instruments were used. Afterwards, the imitation could be done using the same application system. For such cases, different types of spatulas, knives, needles, putty knives, or the back side of the brush may be required. It mainly depends on how the material is applied with the particular tool. Preparation through some trials and mock-ups may also be helpful to conduct alongside.

The characteristics of painting techniques are diverse, with thousands of different approaches to creating and building up a painting. There is a wide range of tool variants and their usage that can achieve the desired texture. There is no limit to investigation and creativity in finding the proper tools for the particular case.



Figure 76: Imitation of the brushstroke character of the painting by fluid filler applied by brush
source: Fuster-Lopez, Laura, (2008): 130

II. SMOOTHING AND POLISHING OF THE SURFACE

In some cases, it is not only necessary to achieve a flat surface of the filler (as described above), but also to obtain a perfectly smooth and polished-like surface. For these instances, the smoothing of the surface may be done first with cork or a piece of balsa wood, and then with a piece of suede or felt cloth. Additionally, a piece of nylon or polyester textile could be used, as suggested in K. Nicolaus‘ study[7]. Gentle pressure is applied to rotate the materials over the surface of the filler, with the cloth piece adjusted around an index finger. Both materials could be slightly dipped in distilled water or solvent. After this process is completed to achieve a polished and glossy appearance, agate or cuttlefish bone could be used to finish the smoothing. Again, gentle pressure is applied as the tool is rotated several times over the surface of the filler.



Figure 77: Materials for smoothing surface of filler

When flattening and smoothing wax-resin or BEVA fillers, it is necessary to place a sheet of silicone-covered Melinex(Fig.78a) over them; otherwise, they may stick to the material, especially when a little heat is applied. The Melinex sheet is removed after a short time, once the filler has cooled. Conversely, if a glossy surface is not desired, a piece of backing paper(Fig.78b) could be placed over the filler‘s surface, and heat (slightly lower than the melting point) applied by running a heated spatula over it. This process will yield a matte surface for the filler.[8]



a b c

Figure 78a,b,c: Methods for smoothing surface of thermoplastic filler:
interlayer from silicone Melinex sheet(a) for glossy surface and baking paper(b) for matte surface; comparison of the results of smoothing(c)

III. INCISION

From the beginning of the restoration discipline itself, and according to the treatises of the time, the texturing of the filling material was carried out to improve integration with the pictorial fabric during the retouching phase. These texts mostly describe how to reproduce the warp and weft of the support by means of an incision system. An example is the following citation from Vincente Poleró[9]:

„Easy in every way, and no less fruitful in good results, is the imitation of the threads of the canvas, following the same direction marked by the color. This procedure most convincingly proves its excellence in the almost absolute impossibility of detecting the restorations of the painting, if by chance they have been executed correctly.

The same knife used to scrape the stucco, assuming it has a blunt tip, can be used to mark the directions of the threads of the canvas on all those stucco points, simply by carefully observing those of the original fabric. The less forceful the knife is driven, the greater the certainty of success, because even though at first glance it seems it is not making an impression, it is making one. However, the lines draw themselves as soon as the painting is varnished...“

In current times, the reproduction of the weave system and characteristics of the fabric is usually achieved by imprinting a similar canvas texture, as will be described next. Incision is mainly used for the imitation of lifts, cracks, and craquelure in the painted layer. For this operation, different types of scalpels, spatulas, needles, and dental instruments are typically used (Fig.79). This type of texturing is usually done when the filler is dry on a properly smooth surface. However, it could already be prepared during the application of the filler and adjusted more sufficiently after drying.

For successful results, it is necessary to have a deep understanding of the type and characteristics of the cracks and rifts, whether they were caused primarily by the artistic technique or secondarily by a hit, pressure, humidity, etc. This understanding will significantly improve the operation and resulting appearance (Fig.80).

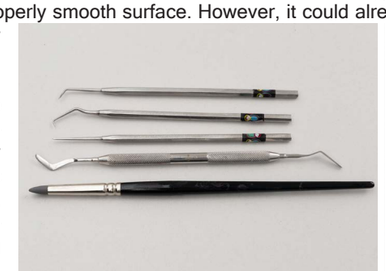


Figure 79: Tip pointed tools for incision



Figure 80: Example of incision imitating craquelure

7 NICOLAUS, Knut. (1999). *Manual de restauración de cuadros*, Ed. Könemann, Spain, pp. 244-245

8 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 46

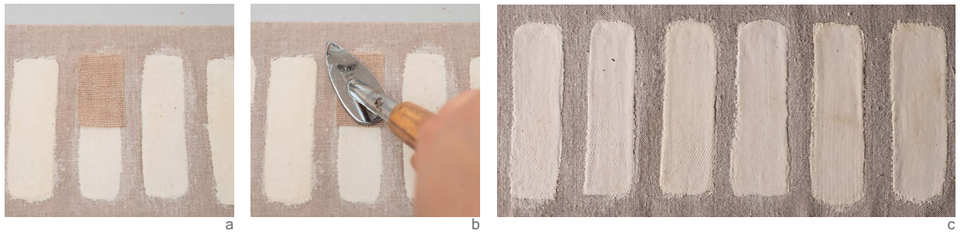
9 MACARRÓN, A (Ed.) (2018). *Arte de la Restauración y otros textos sobre conservación de cuadros*. Sevilla: Athenaica. pp. 94-95

IV. TEXTILE IMPRINT

Probably the most basic, widespread, and easiest way to imprint the texture of the textile support is by imprinting a texture of a textile with the same or highly similar properties of the weave system as the original one. It is important to respect the direction of the weft and warp threads of the original fabric (Fig.81). Upon closer inspection, it could be detected due to the reversal system of the imprint. Naturally, by imprinting the textile, the result is a negative of the weave. However, the system is very fast and effective, and in most cases, when observed from a distance, it is not detectable. On the contrary, it helps to maintain the pictorial integrity of the fillers.In this imprinting system, it is possible to work with both wet and dried filler. When the filler is still slightly damp, the textile is placed over the surface in the appropriate weft direction and pressed onto it with a spatula or agate (Fig.83). Another method could be made with thermoplastic fillers. In this case, the imprinting is done once the filler is dry, leveled, and smooth. The textile, in the appropriate weft direction, is placed over the filler, and a heated spatula is used to activate the filler material and press the textile texture onto the surface(Fig.82). In both cases, it is important not to apply too much pressure, otherwise, the leveled surface of the filler may be damaged. Additionally, for both methods, it is important to remove the textile once the filler is dried or cold; otherwise, the texturizing could become damaged or the filler itself could shift inside the loss.



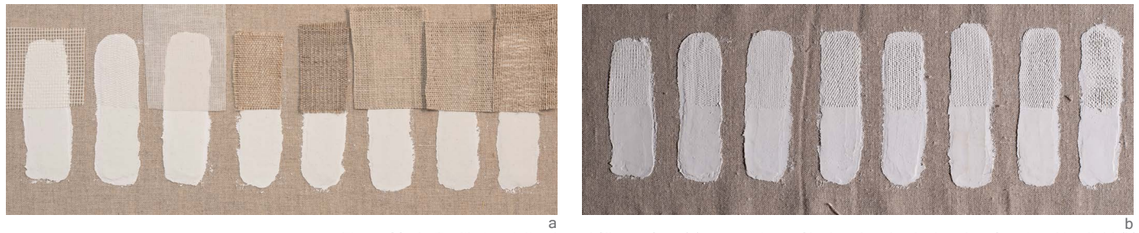
Figure 81: Different types of textile suitable for imprinting



a b c

Figure 82a,b,c: Texturing the surface by imprintment of textile (a) to thermoplastic filler by heated spatula(b); comparison of textured and untextured surface in raking light (c)

There are not a lot of historical treatises referring to this type of texturizing. For example, a text by J. Merimee from 1830 recommends that, for texturizing the filler in cases where the weave of the canvas is distinct in the painting‘s character, a piece of textile with the same texture is placed and pressed onto the wet filler[10]. And much later recommendation is proclaim by G. Berger. He suggested imprinting the texture by nylon or polyester textile to the wet filler[11].



a b

Figure 83a,b: Textile imprinting to wet filler surface (a); comparison of textured and untextured surface in raking light (b)

V. FLEXIBLE MOULDS

Texturizing the surface of the filler using flexible molds is the only system that leads to the perfect imitation of the surface of a particular painting. The mold is obtained in a negative form from the original painting. The exceptional surface texture is then transferred to the filler surface in a positive form. This way, the same surface is properly achieved.

The materials for preparing these flexible molds were originally intended for other specializations and disciplines than conservation, mostly medical and dental. However, the precision of these materials is highly distinctive, which led conservators and restorers to try their application for this purpose as well. The results are perfect; it is possible to reproduce the surface texture unbelievably precisely. Not only the artist‘s technique, such as brushstrokes and impastos, or the texture of the original canvas weave, is achieved, but also the defects and changes presented in the artwork, like craquelure and lifts, etc.

However, the preparation of the flexible form is quite difficult and time-consuming. Therefore, they are used in cases of larger defects that require reconstruction, where equal and uniform texture is necessary. For smaller defects, it is better to use different methods for texturizing, as described above.

10 MERIMEE, J., F., L. (1830). *De la peinture a l'huile*. Mme. Huzard Libraire, in facsmilie EREC, Paris (1981). in MACARRÓN, A., M. (1997). *Historia de la Conservación y de la Restauración*, Ed. Tecnos, Madrid, p. 139

11 BERGER, G., A. (1995). „Inpainting media and varnishes which do not discolour. Part I: preparation for inpainting“ in *The picture restorer*, n°8, pp. 5-8

The system of imprinting depends on the nature of the filler. Different processes are required for thermoplastic fillers and other types. In the case of fillers based on animal or synthetic glue, which are not thermoplastic or do not require high temperatures for activation, the mould is imprinted onto a surface that is still slightly wet and left until the filler is dry. For cases where thermoplastic filler is used, the putty is first inserted and adjusted to the correct position and level with the surrounding painting. After it dries, the mould is placed on the surface in the correct position, and a heated spatula or micro fan is used to activate the filler and press the mould to achieve the desired texture. In cases where defects are large, it is possible to moderate the pressure evenly by imprinting the mould onto the filler on vacuum hot or cold tables or in an envelope system. The imprint of the texture is then achieved by negative pressure forces, or a roller could also be used to increase the pressure over the mould.

The materials chosen for this operation could be both of natural (latex, gelatine, alginate) and synthetic origin (synthetic gelatine, silicone rubbers). The criteria for the selection of the material are as follows[12]:

- It is flexible enough to obtain a thin and easily removable form at an angle of 90°C.
- It is compatible with the filler material, and good contact can be achieved.
- It is inert, non-toxic, and therefore harmless to the painting film and coating.
- It is not sticky, and no adhesion will occur to the original painting.
- It achieves high precision in capturing details on the painting‘s surface.
- It possesses sufficient hardness for imprinting under pressure onto the filler surface.
- It is temperature-resistant.
- It dries appropriately quickly at room temperature.
- Transparent color is an advantage but not required.

The simplified schema illustrates the process of preparing the flexible mould and its imprinting on the surface of the filler:

1. Painting surface with an isolation varnish layer.
2. Pouring of the moulding material onto the painting.
3. Setting and drying of the mould.
4. Removing the mould.
5. Application of the filler.
6. Imprinting of the texture obtained on the mould.
7. Isolation of the filler surface.
8. Chromatic reintegration of the filler and final varnish application.

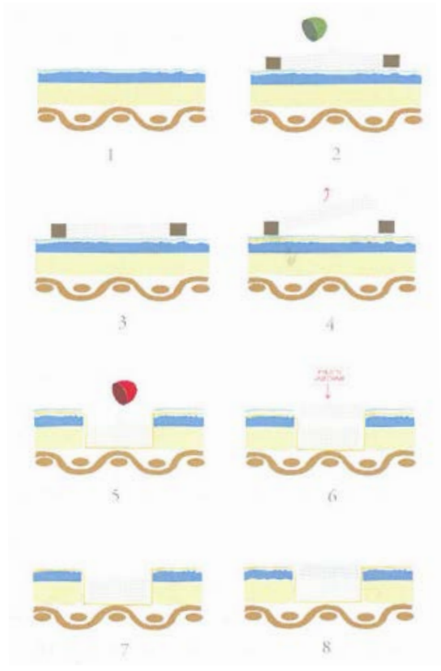


Figure 84: Schema of moulding
source: Fuster-Lopez, Laura (2008): 142

NATURAL MATERIALS

Several natural materials were used for transferring painting surface texture to the filler through the method of flexible molding before synthetic materials, mostly silicone, began to be adopted from other disciplines into the restoration field. These materials are more affordable, easier to prepare, and their reproduction is relatively sufficient.

Latex
It is a natural product obtained from the milkweeds of several trees, most commonly from the Pará rubber tree (Hevea brasiliensis). It is a very complex material (an emulsion of alkaloids, starches, sugars, oils, proteins, tannins, resins, and gums) soluble in water. Several additives, such as preservatives (stabilizers), vulcanizing agents (which simplify the process of thickening), and stabilizers, are added to the latex to adjust its properties. However, latex shrinks by approximately 8% upon drying unhindered. Therefore, for mould

12 Crf. GREEN, J., SEDDON, J., ibid.; LEMOT, M.,: *Étude de l'alteration des peintures á structure pavimenteuse: traitment d'un cas. Dossier de restauration: Marine avec Jonas recraché par la baleine, Gaspar Dughet (1615-1675). Recherche sur les élastoméres solicones pour le moulage des surfaces peintes.* IFROA, 1991, pp. 98-117

preparation, a small amount of ammonia is added.[13] Therefore, an isolation layer should be applied to the surface of the painting from which the mold is taken (due to the presence of ammonia). The molds can be used several times, but during storage, it is important to place an isolation layer (talc, etc.) between the sheets to prevent them from sticking together.
The preparation according to Castellano and Aristegui study[14]:

1. The latex mold is prepared by applying several thin layers on top of each other when each layer is not completely dry. It is mentioned that a small amount of sawdust could be added to the latex to achieve better consistency.
2. The filler is applied to the loss in several thin layers to prevent shrinkage and cracking.
3. Talcum powder is poured onto the surface of the filler; since it will be applied for several hours, it could become stuck to it.
4. The mold is made when the last layer of filler is not completely dry. The consequential shrinkage of the materials is taken into account.
5. The mold is left on the surface of the filler until it is completely dry. A certain weight could be placed over the mold to prevent its possible movement and to better support imprinting.
6. The mold is then removed.

Gelatin
Organic gelatins are the immediate predecessors of the synthetic polymers produced by the chemical industry. These natural materials have a low melting point and are therefore prepared in a water bath. A viscous material is achieved. It is a very economical and easily prepared option for moulding. However, the mechanical resistance is quite low; nevertheless, it can be reheated several times and applied again. Unfortunately, this material rapidly deteriorates due to microorganisms. The addition of formalin or potassium dichromate is possible to prevent biological deterioration; however, these materials render the gelatin insoluble again.

The moulds could be prepared from both animal or plant gelatines. The recipes are already present in medieval treatises[15]. There are two examples:

Variation I. plant origin
agar-agar powder ..... 180 g
destilled water ..... 1 l
glycerol ..... 1 360 g
preservative ..... few drops

Variation II. animal origin
surgeon glue ..... 150 g
destilled water ..... 250 g
glycerol ..... 200 g
talc powder ..... 40 g
preservative ..... few drops

Also, synthetic gelatines[16] are produced and could be used for moulding texturization. However, to prepare them, it is required to melt them at 100°C. They dry quite quickly; therefore, the operation should be fast, and the material is placed on the original painting while still very warm. This could cause several damages. Furthermore, the texture obtained is not as satisfactory as with different materials. Therefore, this material is not recommended.

Alginate
Alginic acid is a natural polysaccharide present in brown algae. It is hydrophilic and forms a viscous gum when hydrated. When combined with metals such as sodium and calcium, its salts are known as alginates.[17] They are used as gelling agents, stabilizers, and, crucially, are the main component of dental molding pastes in stomatology, making them one of the most common forming materials.

It is a well-affordable material, inert, and non-toxic, which obtains very sufficient and precise forming and imprinting ability. It is produced as a powder. When mixed with water (approximately in a ratio of 1:2.5 by weight), a liquid solution is obtained which solidifies into a viscous solid material after a few minutes.[18] There is a wide range of products available on the market, usually characterized by their specific color or smell, but they dry as a white semi-flexible material. The disadvantage is that as the material dries, it loses its flexibility. For this reason, work should be done quickly; otherwise, the mould may not be usable. Therefore, several studies[19] recommend the use of this mould for its fast work, excellent handling, and resulting texture attainment, as the preparation for a more stable and reusable mould.

SILICONE RUBBERS

„The casting of surface texture, using silicone molds taken from the original painting, may offer a solution that is simple, quick, safe, and aesthetically pleasing.“
These are words said by J. Green and J. Seddon in their study, which was one of the first significant research on imprinting the texture of the original painting.[20] The aim of their research was to compare different filler materials with surface adjustment. They tested four silicone rubber mixtures (*Reposil Light, Reposil putty, Silastic 504, Vinagel 116*), which were applied to the original painting, then removed after drying, and imprinted onto samples made of various types of fillers[21]. These important observations were made:

- The materials used for taking impressions should be flexible, forming a thin film that can be easily peeled back from the surface.
- The drying rate of the filler should not be too critical and should be easily established, primarily to judge the right moment when it is still soft enough to receive the impression (though not too wet, yet not too dry).
- The casting material should not undergo dimensional changes, as this would not produce the right impression and could damage the paint surface from which it is taken.

This study was one of the first and most comprehensive research endeavors on the usage of silicone molds. While somewhat limited and brief, it laid the foundation for further exploration in this area. Some of the products are still available, but several new ones have appeared, along with case studies showcasing their application.

For example, a study conducted by Marques and Carlyle, presented at RECH3 Conference.[22] In this case study, a portrait painting from the 19th century was treated. The most significant defect was a long missing strip of both painting and canvas (approximately 9 x 66 cm) along the bottom edge of the painting. A textured replacement strip was crafted with BEVA® Gesso-P, as this material could be cast over a silicone mould, made from two componental Duplosil®, of the painting's surface texture in a thin, even, and flexible film. The study refers to several possibilities for texturizing the filler.

- For filling large losses (in this case, the long missing strip), a barrier film was created to protect the painting from silicone oils in the moulding material. This barrier film closely conformed to the painting's surface with the use of a vacuum cold table. Subsequently, a diluted filler was spread in a thin, even film into the uniform thickness mold created. The resulting films formed a flexible textured strip with the same thickness as the combined paint and ground layer. It was incorporated with the painting during Mist Lining, where it was adhered directly to the lining canvas.
- When it is necessary to fill smaller losses, the same system of textured fills can be used. The filler is then cut into the required shapes for the particular losses and applied using the same, but more fluid, filler formula to adhere the filler to the loss.
- Another option is to apply the filler to the loss, and before it completely dries out, place the silicone mould on top of the filler surface and weight it until it completely dries out. In cases where the silicone mold is sensitive to the solvents that are components of the filler, a protective layer could be applied to the mould surface first (for example, 10% Paraloid B-72 in acetone).

In this particular case, the texturing by silicone mould was made on a solvent-based filler and the texture was imprinted during the drying process of the filler. There are also options to use the thermoplasticity of the particular filler. In these cases, it is important to select the silicone material, from which the mould is prepare, resistant to higher temperatures.

An example of this situation was presented at the RECH4 Conference two years later by Ana Oplak[23]. In this case, the commercial filler BEVA® Gesso-P was selected. Texturing was performed twice in some cases to achieve a proper result. Firstly, moulds were made from Zetaplus™ silicone by applying them to the undamaged paint surface, pressing them onto the painting with a roller, and allowing them to dry. Several 2 mm thick patches were made, approximately 15 x 20 cm in size. Then the moulds were placed on the surface of fillers applied to losses while they were still slightly wet, weighted down, and left to dry. For those where the texture was not totally successfully achieved, the fills were textured again when dry using heat and pressure by heating a spatula pressed onto the silicone mould. To achieve sufficient texturing, the temperature had to be raised to approximately 120 °C. The disadvantage of this method is that the silicone moulds could only be used several times before they began to deform.

In these two case studies, commercial BEVA Gesso-P was selected as a filler material. However, those methods could be used as well on the other types of commercial filler, or which is a basis of this thesis, on the studio made ones.
In the excellent book *Mixing and Matching: Approaches to Retouching Paintings*, edited by R. Ellison et al., one study dedicated to texturing fills using silicone molds is published.[24] In this case, the filler was prepared in the studio and is a wax-resin-based filler made from beeswax, dammar resin, and champagne chalk. The thermoplasticity of the filler is utilized for molding texturing. A silicone mold was prepared from a two-part compound material consisting of silicone rubber and catalyst. The recommended silicone rubber solutions are produced by *Bentley Chemicals Ltd.* under the trade name *Rhodorsil® RTV 3040*. The material was chosen for forming firm, but flexible, transparent molds. The imprinting of the texture onto the silicone mold is recommended to be undertaken after the painting surface is cleaned but before an intermediate varnish coat and retouching are applied. The selected area should be on the part of the painting that most closely resembles the texture of the missing part.
The process is as follows:

- A thin varnish could be applied to this selected area to protect the painting from direct contact with the silicone. The silicone solution should be mixed right before application, poured onto the painting surface, and left to dry. A piece of Melinex sheet could

13 HORIE, C. V. (2010). Hydrocarbons: Rubbers, *Materials for conservation: Organic consolidants, adhesives and coatings,* 2nd, Great Britan, Routledge, , ISBN 0 7506 6905 5 pp. 130-132

14 CASTELLANO, E., ARISTEGUI, B. (1990). „Utillización de modeles de látex para la reconstrucción de texturas en la pintura contemporánea“. in *Grupo Español de Trabajo sobre Conservation y Restauración de Arte Contemporáneo.* ICRBC. Madrid pp. 75-80

15 NAVARRO, J., L. (2000). *Maquetas, modelos y moldes: materiales y técnicas para dar forma a las ideas.* Butterworth-Heinemann, Oxford. p. 78

16 NAVARRO, J., L. (2000). *Maquetas, modelos y moldes: materiales y técnicas para dar forma a las ideas.* Butterworth-Heinemann, Oxford. p. 239

17 https://en.wikipedia.org/wiki/Alginic_acid [03/05/2024]

18 MC CABE, J., F. (1988). *Materials de aplicación dental.* Salvat. Barcelona, p. 29

19 AAVV,(2002). „Utilització de l'alginato com a material de reproducció en la restauració del retaule do Sant Bernat i San Bernabé de l'església de Santa Maria de Montblanc“ in *Unicum (Revista de la Escuela Superior de Conservación y Restauración de Bienes Culturales de Cataluña),* n°1 pp. 46-49

20 GREEN, Jan, SEDDON, Joan. (1981). *A study of materials for filling losses in easel paintings, and their receptiveness to casting of textures*, ICOM Committee for Conservation, 7th Triennial Meeting, Ottawa, Canada

21 Together 29 filler formulas were tested. They were made from several types of commercial pastes, acrylic dispersions and synthetic resins solutions bulked with calcium carbonate, as well as traditional fillers based on glue and gelatine.

22 MARQUES, R., CARLYLE, L. (2015). *Further developments on the use of BEVA® Gesso-P infills and solutions for reintegration of a large loss*, III. International Meeting on Retouching of Cultural Heritage, Postrints RECH3, Bilbao, Portugal, pp. 165-171

23 OBLAK, Ana. (2017). *Dealing with unsuitable retouchings: the steps toward successful reintegration*. IV. International Meeting on Retouching of Cultural Heritage, Postrints RECH4, Split, Croatia, pp. 112-117

24 FOLKES. Simon, REDDINGTON, Sophie. (2010). „Texturing fills using silicone mould“ in Ellison, R., Smithen P., Turnbull, R. *Mixing and Matching: Approaches to Retouching Paintings*, Archetype Publications Ltd., London, Great Britain, ISBN 978-1-904982-50-0, pp.158-162

be placed on top of the mold, which will slightly protect the silicone surface during ironing, and it is advisable to mark orientation lines for the position of the mold.
- The filler is inserted into the loss, left to dry, and then an equally thick and smooth surface is achieved by cork abrasion. A wine cork is cut at an angle, sanded to be smooth, dipped in white spirit, and rotated on the surface of the filler until the level of the filler exactly matches that of the surrounding paint.
- Once the filler is prepared, the silicone mold is placed on top of it in the appropriate position. The heating spatula is warmed to approximately 80-90°C, and the surface of the mold is evenly ironed. The temperature may be adjusted depending on the thickness of the mold, but it can't be too high; otherwise, the filler will start to flow due to excessive heat.

Since it was described in previous paragraphs, it is obvious, there is a wide variety of different silicone rubbers available on the market which are suitable for the texture casting. These two-component silicones are used in everyday life, such as dental or food industries. The important properties of the silicone, which should be taken in account during selection are: non-toxicity, neutral pH value, solvent--free content, thickening and drying time, fluidity and thickness of the solution, ability to adjust to the painting surface and temperature resistance. In some cases, the transparent colour could be an advantage for more comfortable handling, but it is not required.
The most commonly used two-component silicone mould materials in conservation are[25]:
- Optosil / Xantopren (Heraeus Kulzer) https://www.kulzer.com/en/en/products/optosil-xantopren.html
- Aquasil (Dentsply/Sirona) https://www.dentsplysirona.com/en-us/shop/categories/restorative/indirect-restoration.html
  This company produces also Aquasil silicone gun, which could significantly simplify the process of application.
- Peakosil (Neosil Corporation) http://www.neosil.co.kr/?lang=e
- Rebound 25 Silicone Rubber (Smooth On) https://www.smooth-on.com/products/rebound-25/
- CHT silicones (Smart Chemistry with Character; MM) https://cht-silicones.com/products/moulding_rubbers/MM913

Based on the mentioned studies, the summarization of the process of imprinting the painting texture on the filler, within the preparation of the silicone moulds system, is as follows:

- The painting is prepared for infilling after the structural work, such as tear mending, inserting patches, lining, etc., is done (in most cases). Additionally, the consolidation of flaking and loose paints is conducted, and cleaning of the surface, including varnish removal or thinning, is achieved.
- The material for molding is selected based on the criteria mentioned above (Fig. 85a).
- The selection of the fragment of the painting's surface for molding is made in terms of compatibility with the surface texture of the missing part. The selected part of the painting could be temporarily coated to ensure no staining or transfer of material to the painting (Fig. 85b).
- The two-component silicone mould kit is properly mixed and applied to the surface (Fig. 85c). Place a sheet of Melinex on top of the silicone. Place some weight (for example, a glass or metal block) over it to ensure that the mold is evenly thick and as thin as possible. This will help spread the pressure and heat equally when imprinting onto the filler.
- Mark the directional indicator on the Melinex or silicone mould before removing (Fig. 85d). If more silicone moulds are made from the same painting, it is advisable to mark them with the specifications of the painting part whose texture they obtain.
- Provide the surface of the silicone mould with an isolating coating if required.
- Insert the filler into the losses using the required method.



a b c d

Figure 85a,b,c,d: Preparation of silicone mould on a surface of a painting

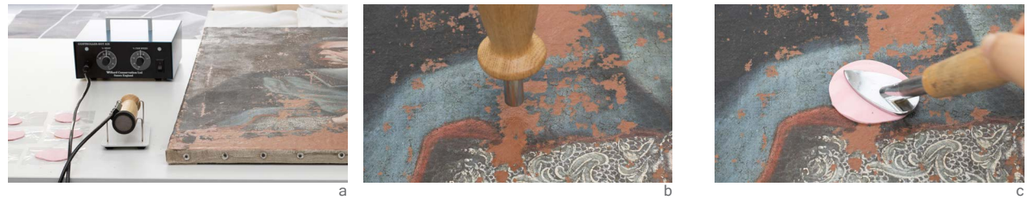
- Smooth the surface of the filler with a spatula, piece of balsa wood, or cork to achieve a level surface that exactly matches the surrounding paint. This step is crucial for the success of the final result.
- Carefully remove any excess bulking filler with a spatula and a cotton swab or piece of cloth slightly dampened with an appropriate solvent (or distilled water).

VARIATION I
- If the filler is still wet but not fluid, place the silicone mould in the appropriate direction and position on the surface of the filler. If the filler dries too quickly, excess filler can be removed after molding.
- Place a weight over the mould (a glass or metal block) and leave it there until the filler dries.

VARIATION II
- Allow any solvent to evaporate from the filler until it is completely dry.
- Place the silicone mould in the appropriate direction and position on the surface of the filler.
- Reactivate the filler by applying heat, using a heated spatula (Fig. 86c). The temperature depends on the type of filler and the thickness of the mold. It should be tested on a mock-up before actual treatment on the original painting.

25 Indicated in BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, p. 54

- Place the warm spatula on top of the silicone mould (or Melinex sheet) and evenly iron the surface. Ensure there is no direct contact between the spatula and the original painting.
- Another option for reactivation is to warm up the filler surface using a hot air pen (produced, for example, by Willard Conservation Ltd.; Fig. 86a). Set the appropriate fan speed and temperature based on the information provided in the product file. Warm up the surface of the filler and then directly place the silicone mould in the required position and weigh it down (Fig. 86b).
- Leave the silicone mould on the filler until it is cold, then carefully remove it.



a b c

Figure 86a,b,c: Imprinting the silicone mould to a surface of a filler by heat reactivation

VI. ALTERNATIVE METHODS FOR STRUCTURATION

Next to all these methods described above, there are several more variants which could be used for texture imitation.

ACRYLIC MEDIUMS

There is a wide range of acrylic mediums on the market. They are usually used by artists to adjust and enhance the impasto appearance of the painting. Additionally, they can be used for texturizing fillers. There are two options: one involves mixing the product with pigment to achieve the desired color, and these formulas are then used as bulked color paints or so-called bodied filling mediums. The mixture is applied to the losses with the same technique as the surrounding paint to imitate the surface texture. In this case, we could refer to this method as filling and retouching in one step.

The second option is to apply the medium on the filler after pictorial chromatic reintegration but before the final varnish is applied. The medium is applied to imitate the brushstrokes or impastos present on the surrounding paint. After drying, the medium becomes transparent, which makes the reintegration and retouching visible under this transparent texture film. Additionally, a piece of fabric can be imprinted onto the wet medium to imitate canvas or any other texture. After coating the entire painting surface, the medium is appropriately integrated, and the losses are sufficiently undetectable.[26]

There are several commercial products on the market produced as acrylic mediums or gels. For example, *Liquitex Acrylic Gel Medium* and *Acrylic Gel Medium* by *Spectrum Oil Colors*[27], or *Regular Gel Medium Matte* by *Golden Paints*[28].



Figure 87: Liquitex Acrylic Gel Medium source: https://www.atlantisart.co.uk/liquitex-matte-gel-237ml/



Figure 88: Regular Gel Medium Matte source: https://goldenartistcolors.com/resources/top-10-uses-for-soft-gel-gloss

PATTERN HEATED SPATULAS

Primarily for the imitation of textile textures, heated spatulas are produced with several different tips (or heads) available. These can be screwed onto the spatula instrument, and then, by the application of heat and pressure, the texture is imprinted onto the filler surface. They can be used for both thermoplastic or water-based fillers. The texture is imprinted after the filler is inserted and leveled to match the surrounding paint. When thermoplastic fillers are textured, it is required to apply a slightly lower temperature than the melting point to prevent the filler from moving or changing position. When water-based fillers are textured, it is better to slightly wet them before the imprinting process is done.

Several different tips for heated spatula are produced by *C.T.S. Conservation*[29], *Deffner & Johann*[30] or *IN SITU: Museum and Archive Services*[31].



Figure 89: Different types of tips for heated spatula source: Fuster- Lopez, Laura (2008): 151

26 BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, pp. 48

27 https://www.atlantisart.co.uk/liquitex-acrylic-mediums/ [09/05/2024]

28 https://goldenartistcolors.com/products/golden-artist-acrylics/gel-paste-mediums [09/05/2024]

29 https://ctsconservation.com/en/index.php?fc=module&module=leoproductsearch&controller=productsearch&cate=848&q=heat%20spatula&limit=12&leoproductsearch_static_token=0e51c58425b39e6ffd39acdecca6fb06 [08/03/2024]

30 https://deffner-johann.de/en/spatula-tip-014-for-rcm-heated-set-digital.html [08/03/2024]

31 https://www.insituconservation.com/en/products/heated_spatulas/themernomeni_spatoula [08/03/2024]

4.3 ISOLATION OF A FILLER'S SURFACE

Before the first phase of chromatic reintegration, it is important to control the absorbency of the filler. To moderate it, a separating layer is usually applied. This layer should meet the main criteria: it should reduce the porosity and, therefore, the absorbency of the filler. This reduction facilitates the application of retouching. In cases where the retouching is unsuccessful and it becomes necessary to rework or remove it and start over, the filler is isolated. Therefore, no damage to the filler or textured surface should occur.

For this operation, several materials exist which could be used. However, sometimes it is not necessary to apply any additional material on the filler; only smoothing of the surface is sufficient (of course, not for textured fillers). The smoothing of the surface may be done with a piece of suede or felt cloth, adjusted around an index finger. Additionally, agate or cuttlefish bone could be used as well. Gentle pressure is applied to rotate the materials over the surface of the filler[32]. If a mixture of natural or synthetic resin in solvent is selected, it is called coating, varnish layer, separating layer, or initial varnish layer. Different materials could be used in this case, usually approximately 10-15% resin in solvent (or solvent mixture). It is important to select the material properly; several criteria should be taken into account:

- The solution of resin in solvent should be compatible with the filling material.
- The solvent used for dissolving the resin should not be dangerous to the components of the filler and surrounding painting (less polar solvents are therefore used).
- Already the suggestion of retouching medium or media and the final varnish components should be clear and compatible with the initial varnish. It is beneficial to select an initial varnish that is distinct in solubility from the retouching medium so that unsuccessful attempts at retouching may be reworked or removed without disturbing the varnish layer. Likewise, it may be beneficial to use an initial varnish and retouching medium that are chemically distinct from the final varnish so that it is potentially removable without disturbing the underlying layers of varnish or retouching.

However, the initial varnish layer changes the surface tension of the material, and therefore, it should be taken into account that the application of retouching could be more difficult. Especially in cases where water-based retouching is preferred to be applied as an opaque base color for the following retouching consisting of translucent glazing layers. In these cases, ox gall could be used to reduce the surface tension, or the water-based retouching is applied before the initial varnish layer (although it could cause some difficulties during removing the retouching described above).

Initial Varnish	Retouching Medium	Final Varnish
Paraloid B72	• Paraloid B72	• Laropal A81 • Regalrez 1094 • Dammar • MS3
	• Laropal A81 (Gamblin)	• Regalrez 1094 • MS3 • Laropal A81 (brush after some months) or sprayed
	• Golden PVA colours (soluble in white spirits)	• Regalrez 1094 • Dammar • MS3 (as a spray varnish)
Laropal A81	• Laropal A81 (Gamblin)	• Regalrez 1094 • Spray Laropal A81
	• Golden MS3	• Regalrez 1094 • Laropal A81 (brush after some months or sprayed)
MS3	• Laropal A81 (Gamblin)	• Regalrez 1094 • Laropal A81 (sprayed)
	• Golden PVA colours	• Regalrez 1094 • MS3 (sprayed)
Dammar	• Laropal A81 (Gamblin) • Golden PVA colours	• Regalrez 1094 • Laropal A81 (sprayed)

Table 48: Compatibility of varnishing and retouching materials in terms of layering their layering
source: Van den Burg, J. M., Seymour, K. (2022): 62

32 The process was already discribed in a chapter *4.2 METHODS FOR FILLER ADJUSTMENT AND TEXTURATION: II. SMOOTHING AND POLISHING OF THE SURFACE* on several pages above.

In some cases, the initial varnish is applied before infilling (mostly when the painting surface is sensitive and the application of filler within the excess removal could be precarious) by brushing or spraying it. Although, the initial varnish could be applied only around the loss on the surrounding paint, and after the adjustment of the filler, it is removed. Another option is that the initial varnish is applied over the whole painting surface within the infilled parts after the fillers are accomplished, again could be sprayed or applied by brush. When only the fillers are being separated, the initial varnish could be applied by a thin round pointed brush when small defects are present or a bigger flat pointed one when large losses are treated. Sometimes it is a mixture of all those possibilities. It is always important to treat every single artwork specifically, depending on the character of the particular exceptional one.

The Table __ suggests materials used for initial varnish, retouching medium, and final varnish, which are possible to be combined. As described above, these phases, within the materials used for each other, are like „communicating vessels".[33]

4.4 INPAINTING AND RETOUCHING

It was mentioned several times before that the retouching media and the approach to chromatic reintegration should be more or less clear before the selection of the filler and separating layer is applied. The methods of retouching, or inpainting, vary according to personal preference, as well as the media, pigments and techniques used are each chosen to suit the individual object. There is a wide range for both water-based and resin-based retouching media, which could be prepared in the studio or bought as a retouching medium for pigments or retouching paints. However, the examination of both studio-made and commercial products was not the aim of this research. Nevertheless, there are several other studies focusing on this topic which are noteworthy. There are, for example, two recommendations:

- Brochure titled *Varnishing and Inpainting/Retouching: Painting Conservation, part 3*, edited by Julia M. Van den Burg and Kate Seymour, published two years ago in 2022 by the Cultural Heritage Agency of the Netherlands.

- Book titled *Mixing and Matching: Approaches to Retouching Painting,* edited by Rebecca Ellison, Patricia Smithen, and Rachel Turnbull, published in 2010 by Archetype Publications Ltd. in association with the Icon Painting Group and the British Association of Painting Conservator-Restorators.

33 BURG, Julia M. Van den, SEYMOUR, Kate. (2022). *Varnishing and Inpainting/Retouching, Painting conservation, part 3*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands, pp. 48-49

5. CONCLUSION

The aim of this thesis was to describe different possibilities of fillers that could be used as infilling materials for losses in paint and ground layers of paintings on textile support. This work opens the door to a very deep closet filled with materials offered for conservation treatments. The fillers could vary in their composition, which could subsequently determine their particular use and application. There is a wide range of both natural and synthetic (or semi-synthetic) materials produced and available on the market. The selection of the particular filler and the components it is prepared from should be decided based on the basic requirements, which include inertness, reversibility (or rather removability), ability to resist environmental changes, and compatibility with the particular work of art. It is important to approach every single artwork individually, based on a proper understanding of the exceptional piece of art, with a responsibility to the treatment and its consequences that are going to be retained in the constitution of the artwork. The conscious and thoughtful selection and deeper knowledge of the chemical and handling properties of the material inserted into the painting are key at any stage of each conservation treatment.

Attitudes towards the evaluation of proper materials can vary worldwide. Historical practices and the availability of materials on the market play a significant role in determining approaches. Furthermore, approaches can also vary geographically. The selection of filler formulas for this thesis was made under the influence of Central European restoration attitudes, with overlap to conservation practices in Southern and Western Europe. Understanding the infilling media is essential when treating artwork, considering the possible materials found in the artwork due to previous conservation treatments. The problematic of filling the defects in artworks is old the same as the art production itself. Already in a historical treatises several approaches could be found. Usually the work, of what we nowadays call restoration, was undertaken by the artist himself. The materials used for the putties were mostly the one which were available in the artist‘s workshop and therefore white lead, chalks, waxes, resins, but also flour or honey. More specific information about the putties formulations could be found from the 19th century when more complex attitude to the restoration appears world widely. From that time a numerous of recipes for the fillers are available retorator‘s handbooks based on natural materials and also commercial putties appeared on the market. With the 20th century and worldwide research a wide range of new materials, synthetic or semi-synthetic, were developed, the composition of fillers began to rapidly vary. Alongside new alternatives, more commercial putties were produced and started to be extensively sold on the market. However, these commercial ready-to-use putties were not the focus of this thesis and were only briefly mentioned. However, a wide range of materials, some of which are no longer used, were described in this study. Furthermore, there is another deep closet full of fillers and putties that could be inserted into losses in paintings on other supports, such as wood, copper, metal, plastic, etc. I did not open these doors; however, it would also be very interesting to investigate this filler‘s chapter, too.

The selected fillers were described within their chemical and physical properties, historical usage practices, and slightly geographical considerations, along with the examination of their aging based on worldwide research. The particular filler recipes were then specified, in detail described and enhanced with photo documentation of the suggested preparation process. In addition to this practical aspect, the application possibilities were described, particularly for the use of each filler on original paintings, illustrated through case studies that demonstrate the possible approach and selection of the filler. These case studies were not all conducted personally by me; some of them were carried out by other students in the restoration studio at the Academy of Fine Arts in Prague, a big thank to them.

Moreover, each filler was also examined in terms of aging and reactivity to environmental changes and light efflorescence within the natural UV radiation. For this part of the thesis, accelerated aging tests were conducted in an environmental chamber. The testing was designed to simulate non-museal conditions. The evaluation of the results was then carried out on each filler sample, comparing both the unaged and aged samples, as well as between different compositions and bulking agents used for the particular binding medium.

The mock-ups for the accelerated aging tests were prepared on both new and old canvases, simulating one of the possibilities for the condition of the original painting, which could have residues of different materials used in historical treatments, such as after treatment within wax-resin lining. The filler samples applied on these mock-ups exhibited more extensive degradation after the accelerated aging tests, whether the wax residues penetrated the fillers and changed the colour and visual appearance. This phenomenon could be observed on almost all of the testing fillers with the only exception for polyvinyl alcohol based fills. Furthermore, in some cases the wax residues built up a barrier between the filler and canvas and the adhesion was therefore lost. Beside this, most of the selected fillers sufficiently demonstrated stability and removability; however, each must be properly observed in terms of its particular application and use for every individual work of art.

The thesis also includes chapters about the application methods and further adjustment of the filler surface. This is an important phase of the infilling process because, even if the filler formula is prepared and inserted correctly into the loss, but the surface is not adjusted to imitate the surrounding painting, the pictorial reintegration will never be invisible and sufficient. In these chapters, different possibilities for filler integration are described and should be selected based on the particular requirements and desired achievements of the treatment purpose. Additionally, it would be important to discuss chromatic reintegration and materials used for inpainting and retouching. However, this topic was not in the capacity to cover in this particular thesis. Although two publications on this topic were recommended, many others exist as well.

The process of infilling losses in the ground and painted layers of paintings on textile support is deeply complex, and it is important to pay sufficient attention to it, as it will be paid back afterwards. If the filler is prepared, applied, and adjusted in the best possible way, the following inpainting is significantly simplified, as well as the final varnishing and the overall visual character of the work of art. However, this topic is very wide and a lot of the possibilities were not covered. Therefore, any further investigation and research may be conducted, which could significantly enhance and deepen the knowledge of the spectacular world of art conservation.

„The successful application of fillers hinges on their ability to become visually indistinguishable from the original material of the artwork. This demands precision, expertise, and a nuanced approach to restoration. By seamlessly integrating fillers into the surrounding surface, the restorer ensures that the viewer‘s focus remains on the artwork‘s aesthetic qualities, rather than its conservation history.“

„The true mark of a successful restoration is its invisibility. When done with care and expertise, restoration treatments should seamlessly integrate with the original artwork, leaving no discernible trace of intervention. This allows viewers to experience the artwork as it was intended by the artist, without distraction or interruption.“

Cesare Brandi „Theory of Restoration“



Figure 90: Filler samples after the evaluation of accelerated aging tests and examination of any change in properties

6. MATERIALS USED IN THE PRACTICAL PART OF THE THESIS

material	suppliers
chalk of Bolognese	studio storage
calcium carbonate	Kremer Pigmente GmbH & Co. KG
kaolin	Kremer Pigmente GmbH & Co. KG
aluminium hydroxide	Kremer Pigmente GmbH & Co. KG
Lime white	KITTFORT®
rabbit skin glue	GRAC spol s. r. o.
Paraloid™ B 72	Kremer Pigmente GmbH & Co. KG
Plextol B 500 Lascaux	Kremer Pigmente GmbH & Co. KG
Poval™ 48-80	Kuraray Co., Ltd.
polyvinyl alcohol (alcoolo polivinilico)	C. T. S. Conservation
Tylose C 300	Ceiba®
Evacon R	Conservation Resources Ltd.
Lascaux 498 HV	Kremer Pigmente GmbH & Co. KG
Aquazol® 50	Kremer Pigmente GmbH & Co. KG
Aquazol® 200	Kremer Pigmente GmbH & Co. KG
Aquazol® 500	Kremer Pigmente GmbH & Co. KG
pigment ultramarin dark	Kremer Pigmente GmbH & Co. KG
pigment raw umber	Kremer Pigmente GmbH & Co. KG
beeswax whitten	Kremer Pigmente GmbH & Co. KG
polymerized linseed oil (stand oil)	Kremer Pigmente GmbH & Co. KG
dammar	studio storage
Cosmolid® H 80 (microcrystalline wax)	Kremer Pigmente GmbH & Co. KG
Laropal® A 81	Kremer Pigmente GmbH & Co. KG
Regalrez® 1126	Kremer Pigmente GmbH & Co. KG
pigments (eisenoxide red, light ochre, green earth)	studio storage
BEVA® 371b	C. T. S. Conservation
Ethanol 99,9%	PENTA Chemicals unlimited® , VERCON s. r. o.
Ethanol 96%	PENTA Chemicals unlimited® , VERCON s. r. o.
distilled water	studio strage

Table 49: Materials used in practical part of thesis within the suppliers

7. LIST OF CASE STUDIES

case study vol.1 23
Augustus Cordus: Predella with the Last Supper from Loket (1579)
oil painting on panel
owner: State castle Loket
restoration treatment conducted by Alena Študlarová and Sára Syslová

case study vol.2 45
Aleš Brázdil: Untitled (2006)
acryl painting on canvas support
private owner
restoration treatment conducted by Jakub Donda

case study vol.3 73
Beneš Knüpfer: Portrait of a girl (second half of 19th century)
oil painting on canvas support
owner: National Gallery in Prague
restoration treatment conducted by Marie Čádová

case study vol.4 89
Emil Lauffer: Water Fairy (1875)
oil paniting of canvas support
owner: National Gallery in Prague

case study vol.5 97
rnold Boecklin: Mermaids (1864)
oil painting on canvas support
private owner

case study vol.6 107
František Viktor Mokrý: The Nude (around half of 20th century)
oil painting on canvas support
private owner

case study vol.7 125
Unknown artist: Rachel hiding the idols of her father Laban (first half of 18th century)
oil painting on canvas support
owner: Archbishopric of Olomouc
restoration treatment conducted by Pavel Geryk

case study vol.8 145
Portrait of Prague Archibishop Antonín Václav Vokoun (half of 18th century)
oil painting on canvas support
owner: Museum of Silver in Kutná Hora

8. LIST OF FIGURES

Figure 1: Stratigraphy of painting
source: Van den Burg, J. M., Seymour, K. (2024): 5 6

Figure 2: Schema of the application of a filler to a painting stratigraphy
source: Fuster-Lopez, Laura (2008): 53 7

Figure 4: Location of fillers in the structure of a canvas painting: (1) geometric centre of forces in a painting; (2) different behavior of filler and paint under tension
source: Fuster-Lopez, L., et. al, (2008):181 8

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source: Fuster-Lopez, L., et. al, (2008):181 8

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ABDEL-MAKSOUD, G., SOBH, R., TAREK, A., SAMAHA, S., H. (2020). „Evaluation of Montmorillonite (MMT)/polymer Nanocomposite in Gap Filling of Archaeological Bones“, in *Egyptian Journal of Chemistry*, Vol. 63

AGULLI, G., SILVA, L. (2005). *Treatment of lacunae*, Gestalt psychology and Cesare Brandi. From theory to practice, III. International Meeting of Retouching of Cultural Heritage, Postprints RECH3, Bailao

ALTHÖFER, Heinz. (1981). *Historical and ethical principles of restoration*, ICOM Committee for Conservation 6th Triennial Meeting, Ottawa, Canada

ALTHÖFER, H., ed. (1985). *Restaurierung Moderner Malerei: Tendenzen, Material, Technik*, Callwey

ALTHÖFER, Hein. (1959). “The Use of Polyethylene Glycols in the Field of Painting Restoration.” in *Studies in Conservation*, Vol. 4

AAVV. (2002). „Utilización de l‘alginato com a material de reproducción en la restauració del retaule do Sant Bernat i San Bernabé de l‘església de Santa Maria de Montblanc“ in *Unicum (Revista de la Escuela Superior de Conservación y Restauración de Bienes Culturales de Cataluña)*, n°1

BAILAO, A. CARDEIRA, L. (2017). *Mixing and Matching: A survey of retouching materials*. RECH4 Postprint, 4th International Meeting on Retouching of Cultural Heritage, Croatia

BERGER, Gustav, RUSSEL, William. (2000). *Conservation of Paintings: Research and Innovations*, Archetype Publications, University of California, USA, ISBN 9-7818-7313-237-1

BERGER, G., A. (1995). „Inpainting media and varnishes which do not discolour. Part I: preparation for inpainting“ in *The picture restorer*, n°8

BERGER, Gustav. (1975). *Heat-seal lining of a torn painting with BEVA 371*. Studies in Conservation, Vol. 20, N. 3

BRANDI, Cesare. (1963). *Theory of Restoration*. Nardini Editore, Istituto Centrale per il Restauro

BURG, Julia M. Van den, SEYMOUR, Kate. (2024). *Filling Losses in Paint, Painting conservation, part 4*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands

BURG, Julia M. Van den, SEYMOUR, Kate. (2023). *Consolidation of Paint and Ground, Painting conservation, part 3,* p. 60, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands

BURG, Julia M. Van den, SEYMOUR, Kate. (2022). *Varnishing and Inpainting/Retouching, Painting conservation, part 2*, Cultural Heritage Agency of the Netherlands, Amersfoort, The Netherlands

CALORE, R., FRIZZA, L., XACA-CAMICE, M., RIZZIONELLI, L., STEVANATO, N., TISATO, F. (2011). *Aquazol 500. Una possible alternativa ecocompatibile alla colla animale nella preparazione degli stucchi per il restauro dei dipinti. Test Preliminari per la stabilità, lavorabilità e comportamenti*. Atti del Congresso „Le fasi finali nel restauro delle opere policrome mobili“, Trento

CATHER, S., HOWARD, E. (1986). *The use of wax and wax-resin preservatives on English medieval wall painting: rationale and consequences,* Case Studies in Conservation of Stones and Wall Paintings, Pre.prints of the IIC 11th International Congress, Bologna

CASTELLANO, E., ARISTEGUI, B. (1990). „Utilización de modelos de látex para la reconstrucción de texturas en la pintura contemporánea“. in *Grupo Español de Trabajo sobre Conservación y Restauración de Arte Contemporáneo*. ICRBC. Madrid

CENNINI, Cennino. (1395). *Il Libro dell‘Arte*, Padova, Italy

CIATTI, Marco. (2010). *Le fasi finali nel restauro tra teoria e pratica, alcune riflessioni*, proceeding of Conference CESMAR7, Trento 2009 2010, Italy

CHIANTORE, O., RAVA, A. (2005). „1.2 New materials in contemporary art“ in Conserving Contemporary Art: Issues, Methods, Materials and Research, The Getty Conservation Institute, Getty Publications, Los Angeles, USA

CRAFT, Meg, Loew, SOLZ, Julie, A.. (1998). *Commercial vinyl and acrylic fill materials*, Journal for American Institute for Conservation, JAIC, vol. 37

CREMONESI, Leonardo Borgioli, Paolo. (2019). *The synthetic resins used in the treatment of the polychrome works of art*, De Kunstkliniek Veer & Veer, Hilversum, ISBN 9789082936131

ČERVEŇÁK, Jan. (2021). „Údržba památkových objektů“ webinar by *Společnost pro údržbu památkových objektů*

DOWN, J., L., MACDONALD, M., A., TÉTREAULT, J., WILLIAMS, R., S. (1996). *Adhesives Testing at the Canadian Conservation Institute: An Evaluation of Selected Poly (Vinyl Acetate) and Acrylic Adhesives*. Studies in Conservation, Volume 41

DUFFY, M., C. (1989). „A study of Acrylic dispersions used in the treatment of paints“, in *Journal of the American Institute fo Conservation*, JAIC Volume 28

FALVEY, Diane. (1981). *The advantages of Mowiol (polyvinyl alcohol): comparative studies of organic and synthetic binding media for fillers for paintings on canvas*. ICOM Committee for Conservation. 6th Triennial Meeting, Ottawa

FELICIANO, Anes, at al. (2019). *The Conservation of a Late Renaissance Tiled Stove: A Non-Aqueous Approach, Recent Advances in Glass and Ceramics Conservation*, Interim Meeting of the ICOM-CC Working Group, London, England

FELLER, R., L. (1978). *Standards in the evaluation of thermoplastic resins*. ICOM

FERNÁNDES-VILLA, S., G. (2015). *Filling as retouching: The use of coloured fillers - in the retouching of contemporary matte paintings*. RECH3: 3rd International Meeting on Retouching of Cultural Heritage, Complutense University, Madrid

FOLKES. Simon, REDDINGTON, Sophie. (2010). „Texturing fills using silicone mould“ in Ellison, R., Smithen P., Turnbull, R. *Mixing and Matching: Approaches to Retouching Paintings*, Archetype Publications Ltd., London, Great Britain, ISBN 978-1-904982-50-0

FOX, Marilyn. (2001). *Searching for a filler of my dreams: An Odyssey in gabs and glues*. Yale Peabody Museum of Natural History, Platform Presentation at the Society of Vertebrate Paleontology Annual Meeting, Bozeman, Montana

FUSTER LOPEZ, Laura. (2012). ‘Filling‘: in Rushfield, R., Stoner, J., H., et, *Conservation of easel paintings*, USA and Canada: Rouledge, ISBN 978-0-7506-8199-5

FUSTER LOPEZ, Laura, MECKLENBURG, Marion F., CASTELL, M., and GUEROLA, V. (2008). „Filling materials for easel paintings: when the ground reintegration becomes a structural concern.“ in *Preparation for Painting: The Artist’s Choice and its Consequences,* edited by Townsend, J. H., Doherty, T., Heydenreich, G., and Ridge, J., London: Archetype Books.

FUSTER LOPEZ, Laura. (2008). *El estuco en la restauración de la pintura sobre lienzo: criterios, materiales y procesos*, Spain: Universidad Politécnica de Valencia, ISBN 978-84-8363-221-5

GOTZ, von der, M., PROCTOR, R., G., WHITTEN, J., MAYER, L., MYERS, G., HOENIGSWALD, A., SWICKLIK, M. (2012). “Varnishing as Part of the Conservation Treatment of Easel Paintings.” In *Conservation of Easel Paintings*. 2nd ed., edited by Joyce Hill Stoner, and Rebecca Rushfield, New York: Routledge

GREEN, J., SEDDON, J., ibid.; LEMOT, M. (1991). *Étude del‘altération des peintures á structure pavimenteuse: traitement d‘un cas. Dossier de restauration: Marine avec Jonas recraché par la baleine, Gaspar Dughet (1615-1675). Recherche sur les élastomères silicones pour le moulage des surfaces peintes*. IFROA

GREEN, J., SEDDON, J. (1981). *A study for materials for filling losses in easel paintings and their receptiveness to casting the textures*, ICOM Committee for Conservation 6th Triennial Meeting, Ottawa, Canada

HORIE, C. V., (2010), *Materials for conservation: Organic consolidants, adhesives and coatings*, 2nd, Great Britain, Routledge, p.228-230, ISBN 0 7506 6905 5

HORIE, C. V. (1996). *Materials for conservation: Organic consolidants, adhesives and coatings*, Great Britain: Hartnolls Ttd.,Bodmin, Cornwall, ISBN 0 7506 0881 1

HORIS-DÉON, Simone. (1851). *De la conservationet de la restauration des tableaux*. Hector Bossagne, Paris

JACKSON, Julia A., ed. (1997). „Chalk“. in *Glossary of geology*, 4th ed. Alexandria, Virginia: American Geological Institute. ISBN 0922152349

JESSELL, B. (1977). *Helmut Ruhemann’s Inpainting Techniques,* JAIC, Vol 17, No°1

KECK, C., K. (1977). *Lining adhesives: their history, uses and abuses*, Journal of the American Institute for Conservation, Vol. 17, N. 1, Taylor & Francis, Ltd.

MACARRÓN, A (Ed.) (2018). *Arte de la Restauración y otros textos sobre conservación de cuadros*. Sevilla: Athenaica

MAYER, Ralph. (1991). *The artist's handbook of materials and techniques*, 5th, New York, ISBN 0-670-83701-6

MARQUES, R., CARLYLE, L. (2015). *Further developments on the use of BEVA® Gesso-P infills and solutions for reintegration of a large loss*. III. International Meeting on Retouching of Cultural Heritage, Postrints RECH3, Bilbao, Portugal

MC CABE, J., F. (1988). *Materiales de aplicación dental.* Salvat. Barcelona

MCGLINCHEY, W. Ch., RIE, E., R., de la. (1990). *New synthetic resins for picture varnishes*, Studies in Conservation, Vol. 35, N. 1, Pre-print of the Contribution to the Brussels Congress

MCINTYRE, Chritine. (2011). *Development of a pigmented wax/resin fill formulation for the conservation of paintings*, Art conservation department, Buffalo stage collage, USA

MEHRA, Vishwa, R. (1975). "Comparative Study of Conventional Relining Methods and Materials and Research Towards Their Improvement." in *Interim Report to the ICOM Committee for on Structural Supports of Canvas Paintings*, 4th Triennial Meeting, Venice, Paper No. 75/11/5

MELO, M., J., BRACCI, S., CAMAITI, M., CHIANTORE, O., PIACENTI, F. (1999). „Photodegradation of acrylic resins used in the conservation of stone", in *Polymer Degradation and Stability*. Torino, Italy

MERIMEE, J., F., L. (1830). „De la peinture a l'huile. Mme. Huzard Libraire", in facsmilie EREC, Paris (1981). in MACARRÓN, A., M. (1997). *Historia de la Conservación y de la Restauración*, Ed. Tecnos, Madrid

MORALES-MARTÍN, D., FESTA, Antonella, della, ORTIZ, A. S. (2021). *Moisture sensitive easel paintings: A practical application of filling and texturing of losses with Aquazol® based filler.* RECH6 - 6th International Meeting on Retouching of Cultural Heritage, Valencia, Spain

NAVARRO, J., L. (2000). *Maquetas, modelos y moldes: materiales y técnicas para dar forma a las ideas*. Butterworth-Heinemann, Oxford

NICOLAUS, Knut. (2005)."Types of demage and how they are caused" in *Restoration of Painting*, Könemann, ISBN 3895089222

NICHOLSON et al., (2002), *Detection of bone glue treatment as a major source of contamination in ancient DNA analyses.* American Journal of Physical Anthropology

OBLAK, Ana. (2017). *Dealing with unsuitable retouchings: the steps toward successful reintegration.* IV. International Meeting on Retouching of Cultural Heritage, Postrints RECH4, Split, Croatia

PIRES, Catarina, Nunes, Aníbal, Rocha. (2021). *An investigation on the suitability and stability of a new pigmented wax-resin formulation to be used in the conservation of painting*, Master dissertation, NOVA School of Science and Technology, NOVA University of Lisbon, Portugal

PLOEGER, Rebeca, McGLINCHEY, Chis W., RIE, E. René de al. (2015). Original

SCICIONE, Giovanna, C. (1993). *Il restauro dei dipinti contemporanei. Dalle tecniche di intervento tradizionali alle metodologie innovative*. Nardini. Firenze

SEYMOUR. Kate. (2013). *Fillers: Adaptation on Traditional and Commercial Products*, Lecture presented at NOVA, Lisbon

SLÁNSKÝ, Bohuslav. (1955). *Technika malby, část II: Průzkum a restaurování obrazů*, 2nd, Prague, Paseka, ISBN 80-7185-623-1

ŠKORJA, Simona. (2017) *Use of coloured synthetic filler: The case of St. Nicholas, a baroque painting by Fortunat Bergant*. National Gallery of Slovenia. RECH4: 4th International Meeting on Retouching of Cultural Heritage. Croatia

TOCCI, L. (2009). *Valutazione dell'Aquazol (PEOX - POLI 2-ETIL-2-OSSAZOLINA) utilizzato come consolitandte della tela di supporto dei dipinti,* Congresso Nazionale IGIIC „Lo Stato dell'Arte", Napoli

VALLS, M., P., BARBER, D., J. *Testing polymers in the adhesion of specimens with adhesive failures in "oil-commercial ground" contemporary painting*. Grupo Español de Conservación. International Institute for Conservation of Historic and Artistic Works, Ge--conservación nº 20

VASARI, Gorgio. (1907). *Vasari on Technique: being the introduction to the three arts of design, architecture, sculpture and painting, prefixed to the lives of the most excellent painters, sculptors and architects*, J. M. Dent & co., London

WHITTEN, J. (1995). *Low-Molecular-Weight Resins for Picture Varnishes*, AIC Paintings Specialty Group Postprints, American Institute for Conservation 23rd Annual Meeting, Saint Paul, Minnesota, Washington, DC

WILSON, D., M. (1998). „Further uses for Paraloid B-72: Infilling systems for gilded, painted and lacquered wood", in *Wooden Artifacts Conservator*, Watertown, MA, WAG Postprints, Alexandria, Virginia

WILSON, E. (1998). „Paraloid B-72 infilling systems for wooden artifacts" in *ICOM: Ethnographic Conservation Newsletter*, n°18

WOLBERS, R. C., MCGINN, M., DUERBECK, D. (1994). „Poly(2-ethyl-2-oxazoline): a new conservation consolidant". in *Painted Wood: History and Conservation*, Proceedings of the Symposium in Williamsburg, Virginia

WOLFE, Julie, O'CONNOR, Talitha. (2005). „Properties of fillers in putties based on Acryloid B-72", in *Objects Specialty Group Postprints*, Vol. twelve, American Institute for Conservation of Historic & Artistic Works, Washington, DC