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An investigation on the suitability and stability of a new pigmented wax-resin infill formulation to be used in the conservation of paintings

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Dissertation submitted in partial fulfillment of the requirements for the Master's degree in Conservation and Restoration

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An investigation on the suitability and stability of a new pigmented wax-resin in-fill formulation to be used in the conservation of paintings

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Resumo

As formulações de cero-resina pigmentadas (CRP) têm vindo a ser utilizadas para preencher e reintegrar lacunas em pinturas e outros objetos pelo menos desde o século XVIII. Estas formulações consistem em misturas de uma cera e de uma resina, às quais são adicionados uma carga / material inerte (como o carbonato de cálcio) e / ou pigmentos. A possibilidade de adicionar pigmentos diretamente à mistura é uma das maiores vantagens deste material, uma vez que permite que o preenchimento e a reintegração cromática sejam, potencialmente e quando a pintura o permite, realizados numa única etapa. Por outro lado, os preenchimentos com CRP podem receber texturas (através, por exemplo, de moldes de silicone) e ser esculpidos (por exemplo, para recriar pinceladas ou outras características topográficas da superfície), para além de serem facilmente removíveis mecanicamente ou com solventes de baixo índice aromático.

Um dos materiais comumente utilizado nas formulações tradicionais de cero-resina e, mais recentemente, presente nas formulações produzidas comercialmente pela *Gamblin Conservation Colors*, é a cera de abelha. A cera de abelha tem, no entanto, evidenciado desenvolver *bloom* (uma fina camada esbranquiçada que surge na superfície e altera a sua aparência e legibilidade), bem como corroer os suportes metálicos por vezes utilizados em pinturas a óleo.

Encontrar um material adequado para substituir a cera de abelha que pudesse ser combinado com uma resina sintética estável, tornou-se o foco de estudos recentes realizados na Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa (Lisboa, Portugal). Os resultados mais promissores foram alcançados com dois

materiais sintéticos: a cera microcristalina Cosmoloid H80 e a resina hidrocarbonada hidrogenada Regalrez® 1126. O principal objetivo do presente projeto de investigação consistiu em confirmar a adequabilidade destes materiais na composição de uma formulação de CRP inerte e estável, com boas propriedades físicas, visuais e de manuseamento.

A primeira parte da investigação centrou-se em compreender qual a influência dos materiais (Cosmoloid H80, Regalrez® 1126, cargas e pigmentos), e da sua presença em diferentes proporções, nas propriedades físicas e visuais das formulações, e ainda no seu comportamento em termos de preparação e aplicação.

A segunda parte consistiu na avaliação da estabilidade das formulações das CRP em estudo a flutuações de temperatura e humidade relativa, uma vez que estas podem influenciar o desenvolvimento de *bloom*, e porque as ceras são, em geral, sensíveis à temperatura. Os resultados foram avaliados através de fotografia macro, microscopia digital, medições de dureza, e Espectroscopia no Infravermelho por Transformada de Fourier no modo de Reflexão Total Atenuada (FTIR-ATR), e foram comparados com os obtidos para as formulações de CRP produzidas pela *Gamblin Conservation Colors*. Por último, foi testada uma pequena gama de vernizes e materiais de reintegração cromática para verificar a respetiva compatibilidade com as formulações de CRP.

A terceira e última parte da investigação procurou compreender de forma mais realista como é que as formulações CRP podem ser aplicadas em diferentes situações. Para tal, foram utilizadas, como casos de estudo, duas pinturas pertencentes ao *Stichting Restauratie Atelier Limburg* (Maastricht, Países Baixos).

Os resultados mostraram que as formulações de CRP não desenvolvem *bloom* quando sujeitas a flutuações de humidade relativa e/ou temperatura. Para além disso, quando expostas a temperaturas até 60° C, não apresentam alterações significativas ou amolecimento visível, mantendo qualquer textura previamente aplicada.

As formulações CRP provaram ser particularmente úteis nos casos em que é necessário reconstruir em detalhe uma textura/pincelada ou quando estão em causa áreas monocromáticas em que, simultaneamente ao preenchimento da lacuna, é possível fazer uma reintegração de cor precisa. Tendo-se comprovado a compatibilidade das CRP em estudo com alguns dos vernizes e materiais de reintegração cromática mais comuns, verificou-se que estes materiais podem também ser reintegrados cromaticamente e/ou ser ajustados com velaturas de cor mais ou menos transparentes.

O presente trabalho resultou numa apresentação oral e em duas publicações:

Artigo apresentado e aceite para publicação, *6th International Meeting on Retouching of Cultural Heritage (RECH 6)*, “**A new pigmented wax-resin formulation for infilling and reintegrating losses in paintings: testing its workability in two case studies**”, Catarina Rocha Pires, Leslie Carlyle, Kate Seymour e Susana França de Sá. Editorial Universitat Politècnica de València, Espanha, 4 a 6 de Novembro de 2021.

Artigo aceite para publicação, *Practical Approaches to Technical Research - Special Issue of the Journal of the American Institute for Conservation (JAIC)*, “**An investigation into the suitability and stability of a new pigmented wax-resin formulation for infilling and reintegration of losses in paintings**”, Catarina Rocha Pires, Leslie Carlyle, Kate Seymour, Isabel Pombo Cardoso e Susana França de Sá.

Palavras-chave: Cero-resinas pigmentadas; Cosmoloid H80; Regalrez® 1126; preenchi-mento; reintegração; aplicabilidade; estabilidade

Abstract

Pigmented wax-resin (PWR) formulations have been used to infill and reintegrate losses in paintings and other objects at least since the 18th century. These formulations consist of mixtures of a wax and a resin, to which an inert material (such as chalk) and/or pigments are added. The possibility of adding pigments directly to the mixture is a significant advantage for it enables infilling and colour reintegration to be done in a single step. PWR infills can also receive texture and be sculpted (e.g., to recreate brushstrokes or other topographical features) and are easily removable mechanically or with low-aromatic solvents.

One of the most common materials present in traditional PWR formulations, produced either by conservators themselves or, more recently, by Gamblin Conservation Colors, is beeswax. Beeswax has, however, been reported to develop bloom (a thin whitish layer on the surface) and to corrode metal supports where used in oil painting.

Finding an appropriate replacement material for beeswax which could be combined with a stable synthetic resin, became the core of recent studies conducted at the NOVA School of Science and Technology (Lisbon, Portugal). The most promising results were achieved with two synthetic materials: Cosmoloid H80 microcrystalline wax and Regalrez[®] 1126 hydrogenated hydrocarbon resin. Establishing the best formulations and confirming their suitability as an inert and stable infill material, with good physical, optical and handling properties, was the aim of this research project.

The first part focusses on understanding how the materials (Cosmoloid H80, Regalrez[®] 1126, inert fillers and pigments) and their presence in different proportions

influences not only the physical and visual properties of the formulations, but also their behaviour in terms of preparation and application.

The second part entails an evaluation of the stability of the NOVA-PWR formulations (PWR developed at NOVA, containing Cosmoloid H80, Regalrez® 1126, inert fillers and pigments) to fluctuating temperature and relative humidity, because these are considered possible factors in the development of bloom, and because waxes are, in general, temperature sensitive. Results were assessed with macro photography, digital microscopy, hardness measurements and ATR-FTIR spectroscopy, and were compared to those obtained for Gamblin Pigmented Wax/Resin formulations. Finally, a small range of varnishes and inpainting materials was tested for its compatibility with the PWR formulations.

The third and final part of the research aims at understanding realistically how the PWR formulations can be applied in different situations. For that purpose, two paintings belonging to the *Stichting Restauratie Atelier Limburg* (Maastricht, The Netherlands) were used as case studies.

Results showed that the NOVA-PWR formulations do not develop bloom when subjected to fluctuations in relative humidity and/or temperature. In addition, they do not exhibit any significant changes or softening when exposed to temperatures as high as 60° C, maintaining any texture previously applied. PWR formulations proved to be particularly useful where a detailed reconstruction of texture/brushstrokes was required or in monochromatic areas where an accurate colour match can be achieved at the same time as infilling the loss. Found to be compatible with some of the most common varnishes and inpainting materials, NOVA-PWR infills can also receive inpainting or be adjusted with coloured glazes.

This work resulted in one oral presentation and two publications:

Paper presented and accepted for publication, *6th International Meeting on Retouching of Cultural Heritage (RECH 6)*, “**A new pigmented wax-resin formulation for infilling and reintegrating losses in paintings: testing its workability in two case studies**”, Catarina Rocha Pires, Leslie Carlyle, Kate Seymour & Susana França de Sá. Editorial Universitat Politècnica de València, Espanha, 4 - 6th November 2021.

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Keywords: Pigmented wax-resin; Cosmoloid H80; Regalrez® 1126; infilling; reintegration; suitability; stability

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Abbreviations

ATR	Attenuated Total Reflection
ATR-FTIR	Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy
cm	Centimetres
FCT-NOVA	Faculty of Science and Technology – NOVA University of Lisbon
NOVA-WR	Wax-Resin mixture made at NOVA University of Lisbon (containing Cosmoloid H80 and Regalrez® 1126)
NOVA-PWR	Pigmented Wax-Resin made at NOVA University of Lisbon (containing Cosmoloid H80 and Regalrez® 1126 with fillers and/or pigments)
FT-IR	Fourier Transform Infrared Spectroscopy
g	Grams
Gamblin-PWR	Gamblin Pigmented Wax/Resin (containing beeswax, BeSquare™ 195 microcrystalline wax and Laropal® A81 resin)
GC-FTIR	Gas Chromatography Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography Mass Spectrometry
PWR	Pigmented Wax Resin
RH	Relative Humidity
T	Temperature
T _g	Glass transition temperature
WR	Wax-Resin

General introduction

The work presented in this dissertation aimed to produce a stable and workable pigmented wax-resin (PWR) formulation to be used for infilling and reintegrating losses in paintings.

PWR formulations have been used to infill losses in paintings and other objects at least since 1757 (Pernety, 1757). However, until recently, formulations for pigmented and unpigmented wax-resin infills were prepared by individual conservators. In 2014, Robert Gamblin introduced Gamblin Pigmented Wax/Resin (Gamblin-PWR), currently the only commercial source for this material (Gamblin Conservation Colors, n.d.). One of the principal components in the traditional formulations, and in Gamblin-PWR sticks, is beeswax. This natural product has two main drawbacks: it can be corrosive to metal substrates (specifically copper) and can develop a whitish surface defect referred to as bloom.

Since there are many advantages to using wax-resin infills (detailed below), projects to explore replacing beeswax with a synthetic wax were initiated at the NOVA School of Science and Technology (Lisbon, Portugal) (Vega, 2016 and González, 2018). These projects paved the way for the present research. Vega's most successful PWR formulation contained a mixture of Techniwax 9426 (a microcrystalline wax¹) and Regalrez® 1094 (a hydrogenated hydrocarbon resin)² (Vega, 2016). González continued the research in an effort to find a replacement microcrystalline wax for Techniwax 9426, which was not easily available in the small amounts that conservators

¹ Microcrystalline waxes are chemically modified waxes obtained from the distillation of petroleum fractions, which are produced from the processing of crude oil. Presently, they are widely used as substitutes for beeswax as well as for new applications (Vega, 2016 p. 25).

² In a ratio of 5:1 or 5:2 (wax:resin) (Vega, 2016).

would need. Cosmoloid H80³ was selected to be used in combination with Regalrez[®] 1126 (González, 2017). After literature research and initial trials with the resulting material, the decision for the present investigation was to continue studying the possibilities of the PWR containing Cosmoloid H80 and Regalrez[®] 1126.

This dissertation is divided into three main parts: Part I reports on an extensive literature search, both on recipes for wax-resin infills used by conservators since 1757 and on the advantages and disadvantages described. Part II details an investigation to evaluate the workability, suitability, and stability to different environmental conditions of the PWR formulations containing Cosmoloid H80 and Regalrez[®] 1126, as well as their compatibility with a range of varnishes and inpainting media used in conservation. The last part, detailed in Appendix VII, involved practical applications of the selected PWR formulations in two case studies: an oil painting on canvas (possibly 17th century); and an acrylic painting on canvas (circa 2002), both belonging to the *Stichting Restauratie Atelier Limburg*, in Maastricht, The Netherlands.

³ Carlyle suggested that an exploration should be made of Cosmoloid H80 since it is widely available to conservators and has had a long history of use. It proved to be a viable substitute for Techniwax 9426 and González carried out her project under the supervision of Vega and Pombo Cardoso (González, Project Report 2017).



Pigmented wax-resins used for infilling and reintegration: an overview of the recipes used and their advantages and disadvantages

1. Background and history of use

Mixtures of waxes and resins have been employed in painting conservation as consolidants (Smithen, 2006, p. 173), as adhesives (Berger, 1972, p. 614) and adhesives for lining paintings (Hackney, et al., 2012, p. 415), as well as for infilling paint/ground losses and their reintegration (see references in Table 1). This thesis focusses on the use of PWR formulations specifically for infilling and reintegrating losses in paintings.

1.1. Reintegration: infilling and retouching

Infilling is part of a process for paint/ground loss compensation. Infilling supplies a replacement material for missing paint and, where necessary, the underlying ground. The fill material brings the loss in plane with the surrounding paint. Fuster-López outlines this process and identifies three-stages: “applying and levelling the infill material, texturing the filler (either to match the original surrounding areas, or to provide a differentiated texture that will allow restored areas to be perceptible), and colour integration” (Fuster-López, 2021, p. 604).

Inpainting or retouching following infilling consists of re-colouring or reintegrating “missing or damaged paint films to a state that is consistent with the remaining original” (Digney-Peer, et al., 2012, p. 607). The most important properties of the materials used in reintegration are explained below.

1.2. Required properties of infilling and retouching materials

Fuster-López states that “the choices of filler and its manipulation depend both on the aim of the intervention – to achieve an imperceptible or visually detectable result – and on the type of loss” (Fuster-López, 2021, p. 604). She presents a list with the most important properties of the infill materials that influence the success of an intervention (p. 605):

- “fills must be reversible;
- filling materials (including the chemical, physical, and mechanical properties of the binders and the inerts) must be compatible with the original materials of the work of art and with the materials to be used in subsequent conservation treatments;
- filling materials should not be overly responsive to environmental changes or the stresses in the laminate structure of paintings”.

In her PhD thesis, Fuster-López (2006) also states that the infill material should be capable of being textured, should be stable to relative humidity and temperature fluctuations, be mechanically removable (or at least removable with mild aliphatic solvents), and have long term physical and chemical stability. Proper stiffness, minimum dimensional response and adhesive strength should also be considered, the latter being very important when it comes to influencing the “cohesion of fillers as well as their adhesion to the underlying substrate” (Fuster-López, 2021, p. 623).

As will be shown, infilling and colour reintegration can, when specific materials are applied and the loss enables it, be done at the same time. Mixtures of wax, resin, filler and pigment, without the need for any solvents, can be used for this purpose. These mixtures, which fulfill the properties mentioned above, are referred to as pigmented wax-resin (PWR) infills.

1.3. An overview of pigmented wax-resin formulations

Recipes of wax-resin and pigmented wax-resin formulations found in the literature are compiled in table 1. Below are the main observations taken from the interpretation of the recipes, focusing on the materials used.

- Wax is used alone, mixed with chalk and sometimes pigments, or together with a resin. The wax referred to in most recipes is beeswax, although it started being discredited in the 1970s, when other materials such as polyethylene glycols,

ethylene acrylic acid copolymers, paraffin wax and, more recently, microcrystalline wax, were introduced. Beeswax received attention again in the 1980s, was mentioned by some authors in the 1990s and is still listed as an ingredient as late as 2019. Beeswax is present in the commercial formulation produced by Gamblin Conservation Colors;

- Where included, the resin can be natural (dammar resin, colophony) or synthetic (cyclohexanone-aldehyde resins, or ketone, polyvinyl, alkyd, aldehyde and hydrocarbon resins) or a mixture of both (e.g., colophony and Alkydal⁴ used by Schneider in 1981);
- The filler does not vary a lot in the recipes; chalk (calcium carbonate) is listed most of the times. Some authors specify the use of Champagne chalk, Bolognese chalk, or "brown" or "finely ground chalk", while others simply list "chalk." Other fillers in use are kaolin, Portafill® A40 (an aluminium hydroxide, used at SRAL) and fumed silica (Kemp, 2009);
- Additional materials were listed as well, depending mostly on the purpose of the infill. These include: oils (e.g. stand oil, linseed oil, volatile oil, drying or non-drying oil); glues (Seccotine⁵ glue, sturgeon glue, skin glue or just "glue"); Japanese paper (to be used when infilling losses in paintings on cardboard); insect repellent (wormholes in wood) and even antioxidants;
- Pigments are mentioned but most of the time as an optional additive where a coloured filler is required or if the infill is used for reintegration;
- Preparation of the infill mixture, where given, is mostly done on hot/warm metal surfaces and the application is made with metal instruments (e.g., spatulas) that could be heated or, more recently, with thermostatically controlled heated spatulas or wax-carving pencils (e.g., Gamblin Conservation Colors);
- Authors refer to ways to remove excess material, which most of the times include using white spirit or turpentine with cotton swabs or with silk;
- Ways to work the surface are commonly included, such as smoothing with polishing stones, or texturing it with spatulas, scalpels or using silicone moulds to imprint texture.

⁴ Synthetic alkyd resin 50% + linseed oil 50% (Schneider, 1981, p. 44 and 45)

⁵ Brand name for refined liquid fish glue.

Table 1. Overview of the wax-resin recipes used for infilling and reintegrating losses

Author/Institution where used	Year	Wax(s)	Resin(s)	Other material(s)	Proportion of materials	Purpose	Application	Reference
Pernety	1757	Wax (type not mentioned)	Pitch of resin (type not mentioned)	Bricks pounded and sifted	Not mentioned	Infilling	Not mentioned	Pernety, 1757, p. 406
Fratel	1770	Wax (type not mentioned)	Not included	Oil paint	Wax and oil paint in equal proportions	Infill and reintegrate oil paint losses	With a palette knife	Ollendorf, 1999 in von Lenthe, 2019, p. 9
Prange	1828	Wax (type not mentioned)	Not included	Not mentioned	Not mentioned	Infilling disturbing cracks	Not mentioned	Wagner, 1988 in von Lenthe 2019, p. 9
Lucanus	1829	Wax (type not mentioned)	Not included	Chalk/chalk paste	Not mentioned	Infilling	Everything dissolved in turpentine	Lucanus 1929, p. 62 in von Lenthe, 2019, p. 9
De Montabert	1834	Melted wax (type not mentioned)	Not included	Volatile oil	Not mentioned	Infilling	Wax applied with a warm knife and smoothed with a polishing stone	Paetzold 1994, p. 47 in von Lenthe, 2019, p. 9
Hample	1846	Fresh yellow wax	Not included	Linseed oil, brown chalk, finely ground chalk or lead white	2:1:1:1 (wax:oil:brown chalk:white chalk)	Infilling	Not mentioned	Hampel 1846, p. 29 in von Lenthe, 2019, p. 10
Déon	1851	Virgin natural wax	Not included	Not mentioned	Not mentioned	Infilling losses in panel paintings	Not mentioned	Déon, 1851, pp. 20-21
		Wax (type not mentioned)	Resin (type not mentioned)	Not mentioned	Not mentioned	Infilling losses in panel paintings	Not mentioned	
Prager	1927	Wax (type not mentioned)	Resin (type not mentioned)	Drying or non-drying oil, dyes and pigments	Not mentioned	Infilling losses in wood, stone, cast iron	Not mentioned	Paetzold 1994, p. 48 in von Lenthe, 2019, p. 10

Author/Institution where used	Year	Wax(s)	Resin(s)	Other material(s)	Proportion of materials	Purpose	Application	Reference
Kudrjawzew	1954	Wax (type not mentioned)	Resin (type not mentioned)	Dry pigments	Not mentioned	Infilling and re-touching	Different coloured wax-resins mixed together to form varying colour tones	Kudrjawzew 1954, p. 137 in von Lente, 2019, p. 10
Brachert	1955	Melted wax (type not mentioned)	Not included	Stand oil and Champagne chalk	Not mentioned	Infilling	Not mentioned	Brachert, 1955 in von Lenthe, 2019, p. 10
		Melted wax (type not mentioned)	Resin (type not mentioned) or colophony	Champagne chalk	Not mentioned	Infilling	Not mentioned	
Althöfer	1959	Polyethylene glycols (Polywax, Polydiol and Carbowax)	Not included	Chalk, pigments, beeswax	3:2/3 (Polywax 12000:chalk)	Infilling and re-touching	Not mentioned	Althöfer, 1959 in Fuster-López, 2012, p. 590
Ruhemann	1968	Beeswax or re-lining wax	Not included	Gilder's whiting or pigment, drying oil, seccotine glue and zinc white	Not mentioned	Infilling losses in easel paintings	Mixture executed on a warm surface and pressed into the losses with a small metal modeling spatula or scalpel; excess removed with silk humidified in water or turpentine; smoothing of the surface with talcum powder	Ruhemann, 1968, p. 241
Kelly	1973	Beeswax	Not included	Insect repellent	Not mentioned	Infilling wormholes in wood	Wax applied with a heating spatula	Kelly 1979, p. 194, in von Lenthe, 2019, p. 10
Emile-Mâle	1976	Wax (type not mentioned)	Not included	Chalk; pigments	Not mentioned	Infilling and re-touching modern pictures	With a heated spatula and pallet	Emile-Mâle 1976, p. 88

Author/Institution where used	Year	Wax(s)	Resin(s)	Other material(s)	Proportion of materials	Purpose	Application	Reference
Canadian Conservation Institute	1980s	Beeswax	Ketone Resin N	Pigment; chalk	4:1 (wax:resin)	Infilling and re-touching losses in paintings	Not found	Vega, 2016, p. 25; Fuster-López, 2021, p. 618
Schneider	1981	Beeswax	Colophony and Alkidal (synthetic resin 50% + linseed oil 50%)	Methylcellulose; zinc white with glue + French chalk; English whiting, zinc white; pigment (if required)	1:1:1:2 (beeswax and colophony: alkidal:Methylcellulose: zinc white with glue) + 1:1:1 (chalk:whiting: zinc white)	Infilling losses in oil paintings on canvas	Applied in thin layer with a flexible spatula	Schneider, 1981, p. 44
		Beeswax	Colophony and Alkidal	Methylcellulose; Japanese paper (shredded); 10% solution of sturgeon bladder	1:1:2:4 (beeswax and colophony: alkidal:methylcellulose: Japanese paper)	Infilling losses in paintings on cardboard	Applied in thin layer with a flexible spatula	Schneider, 1981, p. 45
Leegenhoeck-Wade	1983	Beeswax	Not included	Calcium carbonate	Not mentioned	Infilling losses in paintings on copper	Not mentioned / not found	Leegenhoeck-Wade, 1983 in Vega, 2016, p. 22
Althöfer	1985	Beeswax	Dammar resin	Champaign chalk	3:2:1 (wax:resin:chalk)	Infilling losses in contemporary paintings	With a thermic spatula and a pre-heated dentist spatula and smoothened with a swab soaked in white spirit	Althöfer, 1985, p. 108
SRAL	1990-today	Paraffin wax (in BEVA 371/BEVA 371b)	Ketone resin (in BEVA 371)/aldehyde resin (in BEVA 371b)	Kaolin/Portafill 40/chalk; polymer fraction (EVA), plasticizer, solvent (in BEVA 371/BEVA 371b)	Varying proportions depending on the purpose of the material	Infilling and re-touching losses in paintings	To apply the filler a small metal dental tool can be heated and pressed over the silicon coated Melinex® on top of the filler	Seymour, pers. comm., 2019; Brites, Carlyle, & Marques, 2015, p. 75

Author/Institution where used	Year	Wax(s)	Resin(s)	Other material(s)	Proportion of materials	Purpose	Application	Reference
Garrel	1992	Beeswax	Not included	Not found	Not found	Infilling losses in paintings on copper	Not found	Garrel 1992 in Vega, 2016, p. 22
Gänsicke & Hix	1997	Ethylene acrylic acid copolymers A-C 540 and 580	Polyvinyl Acetate AYAC	Antioxidants Irganox 1076 or 1035; fillers	Not mentioned	Infilling losses in translucent materials	Not mentioned	Gänsicke & Hix, 1997, p. 24
Nicolaus	1999	Beeswax	Not included	Champagne chalk or Bolognese chalk	Not mentioned	Infilling losses in paintings	Mixture prepared on a metal plate and applied with a spatula	Nicolaus, 1999, p. 241
		Beeswax	Not included	Pigment	Not mentioned			
		Beeswax	Dammar resin	Champagne chalk or Bolognese chalk	3:1 (wax:resin)			
		Beeswax	Colophony	Venice turpentine; chalk	3:1:1 (wax:resin:turpentine)			
Kemp	2009	Microcrystalline wax	Not included	Fumed silica	Not mentioned	Infilling large-crystal translucent marbles	Not mentioned	Kemp, 2009, p. 70
		Beeswax	Resin (type not mentioned)	Dry pigments	Not mentioned	Infilling losses in marble	Not mentioned	Kemp, 2009, p. 74
Folkes & Reddington	2010	Beeswax	Dammar resin	Chalk	3:1 (wax:resin)	Infilling complex surfaces	Applied with a thermostatically controlled heated spatula; cotton wool swabs with white spirit to remove excess; texturing done with previously prepared silicone moulds	Folkes & Reddington, 2010, pp. 159-161

Author/Institution where used	Year	Wax(s)	Resin(s)	Other material(s)	Proportion of materials	Purpose	Application	Reference
Buffalo State College (NY)	Before 2011	Beeswax	Laropal® K-80	Not found	Not found	Infilling	Not found	McIntyre, 2011
McIntyre	2011	Beeswax	Laropal® A-81	Pigment + chalk (?)	4:1 (wax:resin)	Infilling and re-touching	Wax and resin mixed in a double boiler on a hot plate; applied with spatulas	McIntyre, 2011, p. 20
Gamblin	2014	Beeswax	Laropal® A-81	Dry pigments + chalk	4:1 (wax:resin)	Infilling and re-touching	Applied with a wax-carving pencil	Gambin Conservation Colours, n.d.; McIntyre, 2011
Vega	2016	Techniwax 9426	Regalrez® 1094	Pigment + chalk	4:1 (wax:resin)	Infilling and re-touching	Wax and resin mixed in a double boiler on a hot plate; applied using a 'wax carving pencil'	Vega, 2016
González	2018	Cosmoloid H80	Regalrez® 1126	Pigment + chalk	1,5:1 (wax:resin)	Infilling and re-touching	Wax and resin mixed in <i>bain marie</i> in a hot plate	González, 2017
Von Lenthe	2019	Beeswax and Cosmoloid H-80	Not included	Chalk and pigment	1:3:2,5 (beeswax:Cosmoloid H80:chalk)	Infilling and re-touching	Prepared in a hot plate and applied with heated spatulas	Von Lenthe, 2019, p. 2

2. Advantages and disadvantages of pigmented wax-resin for infilling and reintegrating

A chronological summary of the advantages and disadvantages as reported in the literature is presented below.

2.1. Advantages

One of the first mentions of the advantage of adding resin to wax fills was by Prager in 1927 who stated that the resin improves the adhesion properties of the wax fills, while adding oil can improve its plasticity (Paetzold 1994, p. 48 cited in von Lenthe, 2019, p. 10).

In 1954, in the reports from the Tretyakov Gallery, Moscow, Kudrjawzew states that fill materials with wax, resin and pigments have good adhesion in flat losses, enough cohesion and can be easily structured (Kudrjawzew 1954, p. 137 in von Lente, 2019, p. 10). In 1968, Ruhemann, in his well-known work *The Cleaning of Paintings: Problems and Potentialities*, mentions wax-resin mixtures as being one of the “easily-removable paint media” for retouching and that the colour, especially of a wax and MS2A⁶ resin, darkened far less than oil paint (Ruhemann, 1968, p. 242)

In 1985, in his book on the restoration of contemporary paintings, Althöfer refers to mixtures of beeswax, dammar resin and chalk (in a ratio of 3:2:1) as having a long tradition in restoration, being easily removable, having good adhesion in different substrates (natural or synthetic), and having a thermoplastic behaviour that enables them to be reactivated and used to create impasto. He also refers to the fact that these mixtures do not change in dimension after application and that they can be easily textured or smoothed (Althöfer, 1985, p. 110).

In 1997, Gänsicke & Hirx list the advantages of wax-resin mixtures: their relative ease and speed of application, the fact that they always remain removable and do not penetrate the original material (Gänsicke & Hirx, 1997).

In 2011, McIntyre conducted research on pigmented wax-resin infills during her master's project in the conservation department at Buffalo State College, where she outlines the advantages of using waxes as infill materials. She notes that the thermoplastic and adhesive properties of waxes make them ideal fill materials which are

⁶ Brand name for a polycyclohexanol resin.

easily reversible by mechanical removal or with solvents such as xylene. She also states that waxes are noted for having indefinite shelf life if stored in proper conditions (cool and dry environments), and as being water resistant and chemically stable. Another advantage is the fact that it is possible to add pigments to the melted wax, which will increase the density of wax and enable easier inpainting (McIntyre, 2011). McIntyre's PWR formulation was adopted by Gamblin Conservation Colors for the production of their Pigmented Wax/Resin sticks.

In Fuster-Lopéz's chapter, "Infilling", in the *Conservation of Easel Paintings* (2021), she provides an overview of the materials used and includes wax and wax-resin fillers (Fuster-Lopéz, 2021, p. 607). Fuster-Lopéz states that by the beginning of the 20th century, "wax fillers were used mainly in the north of Europe due to their ease of use, superior reversibility to oil and lead mixtures, and availability" (p. 607). She also mentions the suitability of pigmented wax fills for losses in materials that might undergo "dimensional expansion and contraction with climate shifts" such as in wood panel paintings, since these materials show little to no shrinkage after application and have the additional benefit of filling and colouring losses at the same time (p. 618).

In 2014, Gamblin's Pigmented Wax/Resin sticks became commercially available. The reasons why they are "ideal for filling losses in paintings" are listed on the website for Gamblin Conservation Colors. One advantage cited is that the material is easy to manipulate by using moderately heated tools and that it is possible to impress or sculpt the texture of the canvas on the material to make it match the adjacent surface. Another important advantage is that, since the wax-resin is placed in the area of loss only, there is no residue left on the surrounding paint. Gamblin's website also notes that, while their product is hard and somewhat brittle, it resists deformation at room temperature, is moisture resistant, and accepts inpainting and varnish readily (Gamblin Conservation Colors, n.d.)

Vega, in his master's thesis, outlined advantages for wax-resin formulations when used as infills for paintings on copper substrates (Vega, 2016, p. 24):

- They are non-aqueous materials, which can be especially important when used on paintings on copper as they are likely to stay relatively impermeable to moisture;

- They are thermoplastic materials, whose rheology changes with heat. They can be introduced in the loss after being melted or softened with heat, which means that they can be applied in the form of a fluid or a slightly warm paste;
- A very thin layer is easily achievable, and it is unlikely to shrink or crack; on the other hand, very thick infills can be applied in one single layer, unlike other infill materials which need to be applied in layers to achieve the same thickness;
- Texture can be created on the infill while it is still warm just by shaping it, or when cold by carving or using solvents with low aromatic content (e.g., white spirits);
- They can be easily removed mechanically or by using solvents with low aromatic content (e.g., white spirits).

2.2. Disadvantages

In 1985, after listing some of the advantages of beeswax, dammar resin, and chalk mixtures, Althöfer also states that the material is difficult to apply given its immediate solidification and the lack of viscosity, and that it tends to form cracks in large losses. After experimenting with the recipe on a variety of substrates, Althöfer concludes that wax-resin-filler materials should only be used for the reintegration of small losses as he found that the larger ones tend to break and lose their adhesion to the substrate.

Nicolaus (1999) gives detailed information on their production and application and states that “at room temperature, a wax-resin filler with higher proportion of filling material and pigment will be firm, hard and brittle” (p. 241), which he writes, could lead to flaking in the case of strong movements in the canvas. He concludes that “wax fillers are not suitable for filling a paint layer with a matte surface or for large defective areas in picture layers on textile supports” (p. 241).

Amongst the disadvantages outlined by McIntyre (2011) is the heat sensitivity of these materials which can make them much softer at high ambient temperatures, and therefore easy to scratch and retain dirt. She also recognises that wax-resin infills may crack or become susceptible to bloom. McIntyre mentions the risk that they can make inpainting too glossy, since wax fills are non-absorbent, as opposed to gesso fills that absorb a portion of the inpainting medium. According to McIntyre this characteristic can make pigmented wax/resin fills inappropriate for paintings that are unvarnished or have a matte varnish.

As detailed in table 1, all the recipes motioned by these authors have one common ingredient: beeswax. One of the main focuses of this dissertation consisted in assessing if a formulation containing a microcrystalline wax instead of beeswax would show improved properties in terms of heat sensitivity and shrinkage or cracking.

However, most importantly and as will be discussed further in Part II, one of the issues addressed in Vega's master's research (2016) was the concern that pigmented wax-resin infills could develop bloom (see section 2.2.1. below). This was also held to be related to presence of beeswax and was not expected to happen with formulations containing synthetic waxes, for example, microcrystalline wax. Vega tested this hypothesis with promising results. Another primary issue for Vega's research was the role of acidic components in beeswax which were found to be corrosive to copper supports. Vega found that replacing beeswax with a microcrystalline wax (in this case, Techniwax 9426) changed the acid value of the formulation to zero.

2.2.1. Bloom – a beeswax related concern

Although beeswax is “generally considered to be stable and chemically resistant, there are several factors that affect its properties” (Cízová, et al., 2019, p. 1), with its tendency to bloom being one of the main concerns when it comes to its use as an infilling material. According to Bartl et al., “the term ‘wax bloom’ is used to describe a whitish efflorescence that develops on the surface of beeswax objects under specific conditions” (Bartl, et al., 2015, p. 509), and which is visually disturbing. The chemical composition of the whitish efflorescence on pure beeswax has been studied by means of GC–MS and GC–FTIR, and was found to be mainly composed of linear unsaturated hydrocarbons that naturally occur in beeswax, together with a small amount of saturated hydrocarbons (Bartl, et al., 2013, p. 292; Bartl et al., 2015, p. 509). Von Lenthe points out that some of these components have a plasticising role in the wax, which is why beeswax can become more brittle after these materials migrate to the surface (von Lenthe, 2019, p. 18).

The causes and mechanisms behind the formation of bloom are however, “still a matter of discussion” (Bartl, et al., 2015, p. 509), although they are mostly considered to be physicochemical processes rather than chemical reactions (Bartl, et al., 2013, p. 292). As early as 1940, Bisson defined wax bloom as a migration of components to the surface as a result of the molecular rearrangement in the wax occurring at higher

temperatures (Coggshall & Morse, 1984 in von Lenthe, 2019, p. 19). More recently, it was posited that “alkenes could be dispersed in amorphous regions of beeswax at ambient temperature” and would crystallize by a decreasing of temperature below a ‘critical’ temperature, which has been empirically estimated to be between 12 and 16°C (Bartl, et al., 2013, p. 292).

Shrinkage at lower temperatures and the recrystallisation of beeswax were also suggested as possible causes for bloom since this might promote the diffusion of molecules to the surface of the material (Bartl, et al., 2013, p. 292). Results from research conducted by Bartl et al. (2015) have shown that at lower temperatures the solid phase of the wax is well ordered and that at higher temperatures it starts to “exhibit a high degree of conformational disorder and molecular mobility” (p. 512), facilitating the migration of unsaturated chains (which are present for prolonged periods at higher temperatures) to the surface of material, “where they eventually crystallize, forming the ‘wax bloom’ effect” (p. 512).

Manufacturers of artist’s coloured wax pencils, such as Prismacolor and Derwent, mention the possibility of their wax-based materials developing ‘wax bloom’ and give advice to artists on how to prevent it and remedy it. In their website accessed in 2019, in the section Derwent Lightfast FAQs: What is wax bloom and what causes it?, and Can bloom occur with Derwent Lightfast pencils?, the manufacturer mentions that “wax bloom is a natural oxidation process of wax-based materials (...) [that] appears as a cloudy white film over a drawing or colour lay down (...) especially prevalent in warmer climates and for artists who apply greater pressure when working...”. Regarding the causes of bloom, Derwent note that its occurrence is related to “melting point and humidity” and that “working in a non-humid environment will always prevent bloom”. The manufacturers advise artists to wipe away the bloom with a soft tissue or a clean, dry cloth and spray the drawing with a fixative to seal out air.



Testing to develop a stable pigmented wax-resin formulation for infilling and reintegrating losses in paintings

1. Main goals and summarised methodology

Part II details a multifaceted exploration of PWR formulations containing Cosmoloid H80 (wax) and Regalrez® 1126 (resin), in different proportions, together with pigments and fillers. These new formulations, which were developed at the NOVA School of Science and Technology (NOVA University of Lisbon), are referred to as **NOVA-PWR**. Multiple tests and environmental trials were conducted on a wide variety of samples of NOVA-PWR (circa. 600 samples), as well as four different formulations from Gamblin Pigmented Wax/Resin (**Gamblin-PWR**) for comparison. This was done in order to meet three main goals:

- The first was to understand how the materials in the NOVA-PWR (wax, resin, pigments and fillers) and their presence in different proportions could influence not only **visual and physical properties** (such as hardness, opacity/translucency and flexibility/bendability) but also behavior in terms of **preparation and ease of application**. In addition, the formulations were characterised using Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR). At this point, Gamblin-PWR were used mainly as references for the standard working properties of a PWR infill;
- The second goal was to evaluate the **stability** of the NOVA-PWR formulations **to changes/fluctuations in temperature and relative humidity**, as well as to

high temperatures of 50°C and 60°C⁷ and radiant heat. This was done to ensure that the infills made with the NOVA-PWR formulations would not develop bloom, lose/change texture, soften/deform or exhibit shrinkage/cracking in the tested conditions. Since bloom was expected to develop on the Gamblin-PWR, due to the presence of beeswax, subjecting NOVA-PWR and Gamblin-PWR samples to the same environmental conditions and comparing the results was considered an efficient way to evaluate whether the NOVA-PWR would develop bloom. Evaluation of possible visual, physical, and molecular variations of the samples resulting from the trials was to be done through macro photography, digital microscopy, hardness measurements and ATR-FTIR.

- The third goal was to assess the **compatibility of the NOVA-PWR to a selection of varnishes and inpainting media** commonly used in conservation which could be used in combination with the NOVA-PWR, if varnishing or inpainting on top of the infill were required.

The methodology used is summarised in Figure 1 below.

Following the characterisation and study of the stability of the NOVA-PWR detailed in this part of the dissertation, the most successful NOVA-PWR formulations were applied to two paintings (case studies) at the *Stichting Restauratie Atelier Limburg*. This is presented in Appendix VIII.

⁷ A maximum temperature of 60°C was chosen because, according to Ankersmit and Stappers, “if sunlight falls directly on a dark surface the local temperature can reach up to 60 °C (140 °F)” (Ankersmit & Stappers, 2009, p. 80).

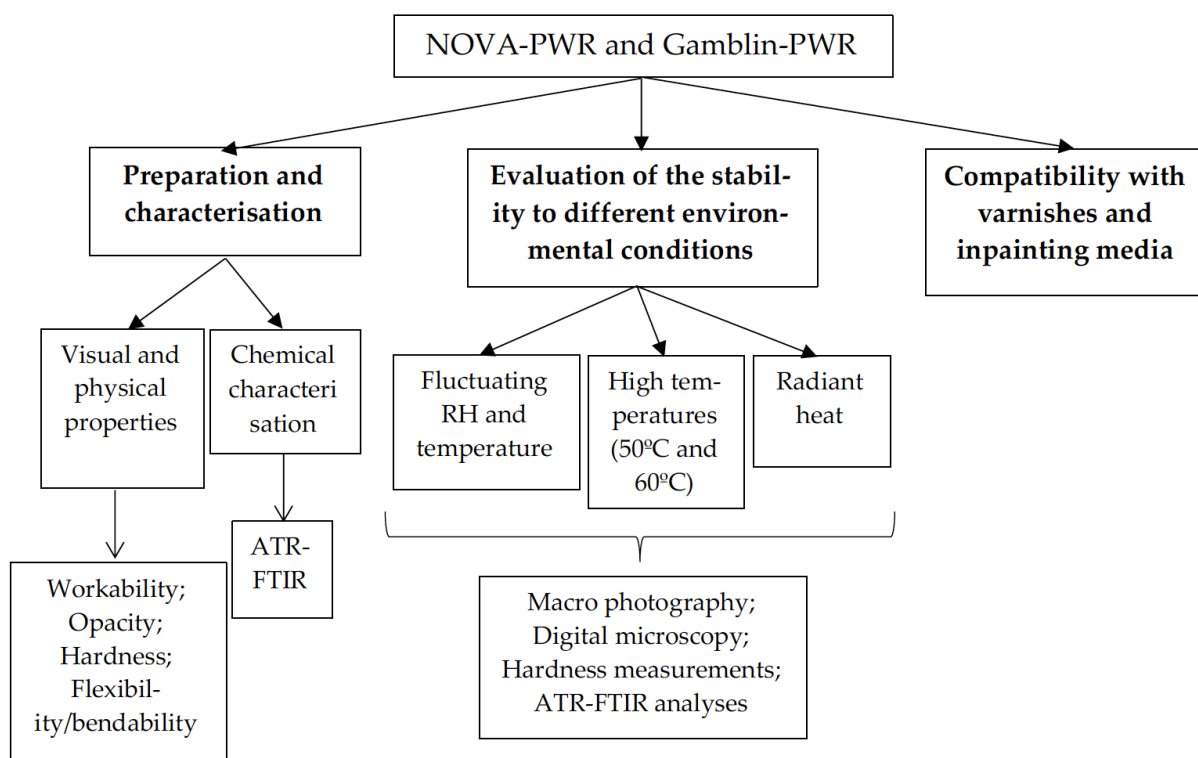


Figure 1. Diagram of Research Methodology

2.1. Materials

The materials (Suppliers, Appendix I) used to prepare the NOVA-PWR samples were:

- **Wax:** Cosmoloid H80 (microcrystalline wax)
- **Resin:** Regalrez® 1126 (hydrogenated hydrocarbon resin)
- **Inert fillers:** Champagne chalk, kaolin and Portafill® A40 (aluminum hydroxide)
- **Inorganic pigments:** titanium white, chrome oxide green and burnt umber.

2.1.1. Cosmoloid H80

Cosmoloid is a brand name for a series of microcrystalline wax formulations, supplied by companies such as Kremer Pigmente GmbH & Co. KG, Talas, C.T.S and Zeus, and manufactured by Astor (now The International Group, Inc.). Cosmoloid waxes have been used in conservation for several purposes, for example as substitutes to beeswax. Cosmoloid H80 has been recommended by Velson Horie as being an inert material with a suitable degree of hardness (Horie, 1990 in Sommermeyer, 1996 in von Lenthe, 2019, p. 21). It has also been considered highly stable against chemical

degradation (Matteini, et al., 2016 in Von Lenthe, 2019, p. 21), being a highly cross-linked synthetic wax with a very fine crystal structure that has no functional groups on which oxidation processes can take place.

The table below summarises the production and chemical and physical properties of Cosmoloid H80 given by different suppliers. This table is meant to provide a relatively comprehensive understanding of this product, while further information can be found in Appendix II.

Table 2. Information on the properties of Cosmoloid H80 given by the suppliers

Supplier	Kremer Pigmente (2018)	Talas (2008)	C.T.S. (2011)
Product information	“hydrocarbon wax with a microcrystalline structure (...) [consisting] mainly of branched-chain and naphthenic hydrocarbons (...) [and that] during the production from paraffins, the sulphur components are removed catalytically”	“a blend of petroleum waxes, combining freely with other waxes and resins”	“as all the microcrystalline waxes, C80 is formed by a mix of saturated hydrocarbons with straight and branched chains, obtained from oil refinement”
Form	Solid	Off-white solid	White pearls
Melting point	-	82°C	83-94°C
Flash point	-	>170°C	-
Acid value	0	-	-
Density	0.85 - 1.05 g/cm ³	-	-
Viscosity	-	15 mPas at 100°C	8.5-12.5 mm ² /s at 120°C
Solubility	-	-	Soluble in aliphatic and aromatic hydrocarbons

2.1.2. Regalrez® 1126

Regalrez® 1126⁸ is a synthetic low molecular weight (LMW) hydrogenated hydrocarbon resin, currently produced by Eastman Chemical Co. This resin has been reported to be photochemically stable (de la Rie & McGlinchey, 1990), UV stable (Whitten, 1995, p. 2) and resistant to accelerated environmental conditions (von der Goltz, et al., 2012). It has high compatibility with waxes (United States of America

⁸ Regalrez® 1126 was chosen over Regalrez® 1094 for its higher molecular weight, higher glass transition temperature (T_g) and higher softening point. This is developed further in Appendix II.

Patent Nr. 5332613, 1994), making it easily mixed with beeswax or microcrystalline waxes (Piena, 2001, p. 66). Moreover, it is soluble in low aromatic solvents (Chercoles, et al., 2011, p. 35). The main properties of Regalrez® 1126 are presented in the table below (Table 3). Additional information can be found in Appendix II.

Table 3. Properties of Regalrez® 1126

	Molecular weight	T _g	Softening point	Density at 21°C (kg/L)	Solubility
Regalrez® 1126	1250 g/mol (Kremer Pigmente, n.d.)	67° C (Kremer Pigmente, n.d.)/ 65° C (Chercoles et al., 2011)	124° C (Kremer Pigmente, n.d.)	0.97 kg/L (Kremer Pigmente, n.d.)	Soluble in low aromatic solvents (Chercoles et al., 2011); “Completely insoluble in polar solvents, including oxygenated solvents such as alcohols, ketones and ethers” (Whitten and Proctor, 1998 in von der Goltz, et al., 2012, p. 644.)

2.1.3. Dry pigments and fillers

As noted in Part I, one of the main advantages of wax-resin mixtures is that pigments and fillers can be added to them, allowing for infilling and retouching to be done in one step. To test the effect of adding pigments/ fillers in different proportions to the wax-resin binder, a set of three pigments and fillers was selected. One criterion for the choice of pigments was that they should be present in the Gamblin-PWR set, which was used for comparison in several of the tests and trials. In addition, the pigments chosen should be thermally stable (since heat was going to be used to make the formulations and it would be one of the parameters evaluated in all the trials) and lightfast.

Since one of the main purposes of this research is to understand if the NOVA-PWR formulation eliminates the possibility of bloom, two of the pigments chosen were in the sticks from Gamblin Conservation Colors that develop bloom inside the metallic box in which they are sold: **chrome oxide green** and **burnt umber**. **Titanium white** was included since it is one of the most popular white pigments used either alone or in mixtures with other pigments. Even though none of the Gamblin-PWR contain fillers, the intention behind including a set of fillers in this study was related to the possibility of the wax-resin formulations being used solely as an infilling material, on top of which inpainting is done (in a separate step). Furthermore, fillers are

added in combination with pigments in order to change or improve some of the properties of the PWRs such as making the mixtures bulkier, slightly different in colour or more matte. Two of the inert fillers chosen are widely available in conservation – **calcium carbonate**⁹ (in this case, Champagne chalk, which is the finest grade of the material) and **kaolin**¹⁰. The other filler – **Portafill® A40**¹¹, an aluminum hydroxide – is routinely used at SRAL¹², for its very white colour and very fine particles. The three fillers were used when testing the formulations in terms of their workability, opacity, and hardness. Only Champagne chalk was used for the trials that followed for it was the filler showing the most promising results in terms of compatibility with the NOVA-PWR mixtures and in terms of the visual results obtained (further detailed in section 4.1.2). Champagne chalk was added to the wax-resin mixtures both alone and in combination with each of the three pigments. A table with the main properties of the pigments and fillers used in this research is provided in Appendix III.

2.1.4. Gamblin Pigmented Wax/Resin

As explained above, the commercial **Gamblin Pigmented Wax/Resin** formulations were used as the gold-standard in terms of workability for the new formulations being investigated, but were also used for comparison, mainly in terms of possible development of bloom and heat sensitivity. With that purpose, four Gamblin-PWR formulations were included in this study: the sticks labelled “Neutral Base” (an unpigmented stick), “Titanium White”, “Burnt Umber” and “Chrome Oxide Green”. Besides the already mentioned pigments, Gamblin-PWR contain beeswax, BeSquare™ 195¹³ microcrystalline wax and Laropal® A81¹⁴ resin (Fuster-López, 2021, p. 618).

⁹ CaCO₃ (Kremer Pigmente, 2020c)

¹⁰ Al₂Si₂O₅(OH)₄ (Eastaugh, et. al, 2008, p. 882)

¹¹ Al(OH)₃ (Sibelco, 2018)

¹² Personal communication with Kate Seymour and Arnold Truyen (2020)

¹³ BeSquare™ 195 is a hydrotreated microcrystalline wax, with a melting range between 89.4 and 93.9°C and a relative density of 0.9 to 1 g/cm³ (Baker Hughes, 2010).

¹⁴ Laropal® A81 is a “low molecular weight resin with chemical composition based on urea-aldehyde compounds (...) formed through a condensation reaction between urea, formaldehyde and another aliphatic aldehyde (isobutyraldehyde)”, commonly used as a varnish on easel paintings since the late 90s (Farmakalidis, et al., 2017, p. 2). Laropal® A81 has a softening range between 80 and 95°C, a Tg of 57°C, an acid value of ≤ 3 mg KOH/g, and a density of 1.11g/cm³ (Kremer Pigmente, n.d. (b)).



Figure 2. Sets of Gamblin Pigmented Wax/Resin (Gamblin Conservation Colors, n.d.)

2.2. Evaluation Methods

To evaluate the PWR, both visually and in terms of their physical properties and at a molecular level, the following methods and equipment were used:

- Byko opacity charts for opacity evaluation, according to the “International standard for the determination of hiding power in paints and varnishes - ISO 6504-3:2019” (International Organization for Standardization, 2019);
- Shore D durometer for hardness measurements, according to the “Standard Test Method for Rubber Property - ASTM D2240 – 15” (American Society for Testing and Materials, 2021);
- Macro photography;
- Digital microscopy;
- Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) to characterise the PWR samples and find their characteristic bands, as well as at to identify possible spectral changes after the environmental trials.

Methods and equipment are detailed in Appendix I.

3. Sample preparation for the NOVA-PWR formulations

This section focuses on the preparation of the NOVA-PWR formulations that were used throughout the entire research, either when simply tested for their workability (section 4) or when transformed into samples for the environmental trials (section 5). The Gamblin-PWR did not require any preparation since the prefabricated sticks were simply melted to be made into into samples.

3.1. Preparation of the NOVA-PWR formulations

The steps in preparing the NOVA-PWR formulations were as follows:

- 1- Weighing the desired amount of Cosmoloid H80 wax (figure 3a) and placing it in a glass beaker;
- 2- Melting the wax by placing the glass beaker on a hot plate (an aluminum sheet can be placed between the beaker and the hot plate). The temperature required to melt the wax was approximately 70°C-75°C (temperature was monitored with a digital thermometer - see equipment Appendix I and figure 3b);
- 3- Weighing the desired amount of Regalrez® 1126 resin (figure 3c) and grinding it in a mortar with a pestle to achieve a very fine powder (figure 3d). This proved to be a crucial step that greatly helped in mixing the resin with the wax, accelerating both the melting and the mixing process;
- 4- Pouring the powdered resin, little by little, into the glass beaker after the wax was completely molten. To facilitate the melting of the resin, which has a higher melting point than that of the wax, the temperature was increased to 85°-90°C. To facilitate the mixing of both components, a magnetic stirrer was used in the beaker at this stage;
- 5- Waiting until the wax and resin are completely mixed together (figure 3e), while both heat and stirring were on. This step lasted up to 30 minutes, depending on the amount of resin added and the temperature used (the higher the temperature, the faster the melting of the resin). At this point the formulation with wax and resin alone was completed;
- 6- For formulations which included a pigment and / or filler, the desired amount of pigment / filler was poured in gradually, while stirring with the heat on. Both Champagne chalk and kaolin had been filtered through a fine mesh strainer previously (figure 3f) to ensure that no big solid particles would be added to the mixture. It was not necessary to use the strainer for the other pigments and Portafill® A40, due to their already small particle sizes;

- 7- The PWRs were then either poured onto a Melinex[®] sheet to solidify prior to being tested for workability; or made into samples by pouring into different moulds. See the next section (3.2.) and Appendix IV for sample preparation.



Figure 3. Steps in the preparation of the NOVA-PWR infills (each image is explained in the text above)

3.2. Preparation of sample pieces for testing

Sets of samples of different formats, either without or with a substrate, were made from mixtures following the preparation method presented above. The purpose of each set varied (e.g., some were made to be exposed in the environmental chamber, while others were made to evaluate specific properties of the mixtures, such as hardness or flexibility/bendability). A summary of each set follows, while details on the preparation are given in Appendix IV.

3.2.1. Samples without substrates:

- 1) Rectangles (34 x 23 x 1 mm) were prepared where half the surface was imprinted with a canvas texture. Texture was present to assess changes that might occur due to softening of the material. A total of 72 rectangles were prepared using 24 different NOVA-PWR formulations (both with and without pigment/filler). These samples were intended for exposure to fluctuating relative humidity and fluctuating temperature (**Trial 1**).

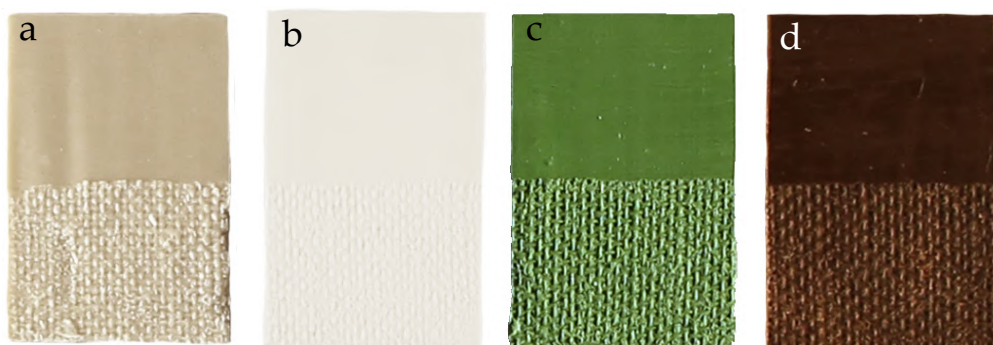


Figure 4. NOVA-PWR test samples: a) with Champagne chalk; b) with titanium white; c) chrome oxide green; d) with burnt umber. Note: texture was not applied to the samples with wax-resin alone

- 2) Rectangles were prepared with the same dimensions as above, with a glossy side, a matte side, and a circular protrusion in the centre. The glossy and matte sides were to assess the development of bloom and the central protrusion was made to assess any changes in texture (like the canvas texture above). The precise profile of the central protrusion made it easier to assess any changes due to softening of the materials. In total, 450 samples of 18 different NOVA-PWR formulations and from 4 different Gamblin-PWR sticks were prepared. These samples were intended for exposure to fluctuating relative humidity (**Trial 2**), and fluctuating temperature (**Trial 3**), and for exposure to varying temperatures: 50°C (**Trial 4**), 60°C (**Trial 5**), and radiant heat (**Trial 6**). A batch of three samples of each PWR formulation was used as control and stored in ambient conditions (see footnote 18, p. 49).

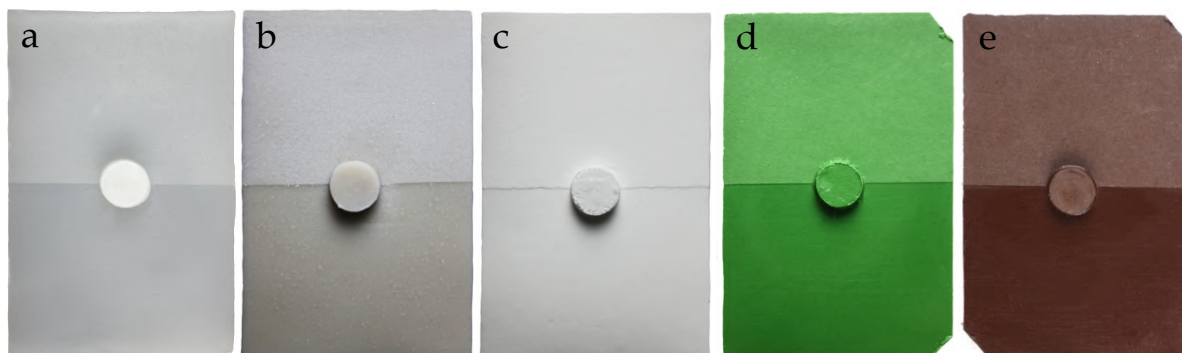


Figure 5. NOVA-PWR test samples: a) unpigmented; b) with Champagne chalk; c) with titanium white; d) with Champagne chalk and chrome oxide green; and e) Gamblin-PWR with burnt umber

- 3) Circular samples (3,5 cm diameter and 6 mm thick), intended for hardness measurements before, during and after exposure in the environmental chamber (**Trials 2 to 5 above**). In total, 230 circular samples of NOVA-PWR and Gamblin-PWR were made (same formulations as above).

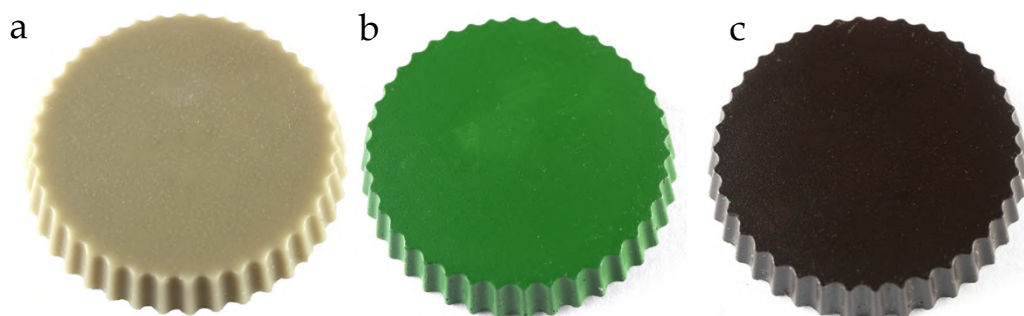


Figure 6. Examples of NOVA-PWR test samples used for hardness measurements: a) with Champagne chalk; b) with chrome oxide green; c) with burnt umber

3.2.2. Test samples with substrates

In addition to the samples without substrates, it was considered essential to apply the different NOVA-PWR and Gamblin-PWR infills in a realistic context. This was done in two different ways with two different purposes, as explained below:

- 4) NOVA-PWR formulations with three different fillers applied on pieces (8 cm x 6 cm) of linen canvas previously sized with Plextol B500. These were made to test the formulation's flexibility and ability to bend without breaking (section 4.2.1.2.). The aim was to choose the best formulation for use in the first case study (Appendix VIII). Their method of preparation is described in Appendix VIII, as it was the same as used for the insert, using a heat press. These samples were not subjected to any environmental trials;

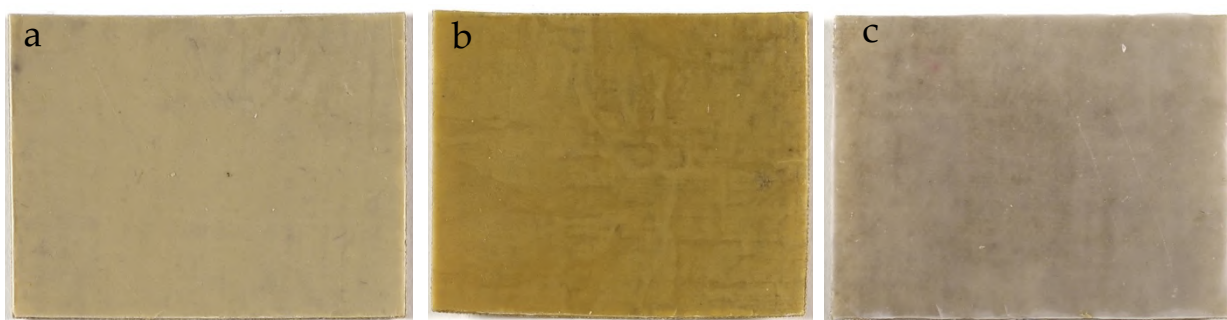


Figure 7. Examples of NOVA-PWR test samples applied on pieces of sized linen canvas: a) with Champagne chalk; b) with kaolin; c) with Portafill® A40

- 5) 18 NOVA-PWR and 4 Gamblin-PWR formulations were applied to losses in three model paintings that had been made in 2011 for Dina Reis' master's thesis project¹⁵ (Reis, 2011) (figure 8a). The losses were created with a hole punch (diameter of approximately 1 cm). All varnish and preparation layers were removed, leaving only the animal sized canvas (figures 8b and 9a.). The PWR formulations were applied and levelled to surface of the painting, having an approximate thickness of 0.5mm (figures 8c and 9b-d). One of the model paintings was used in **Trial 2**, the other in **Trial 3**, and the final was used as a control.

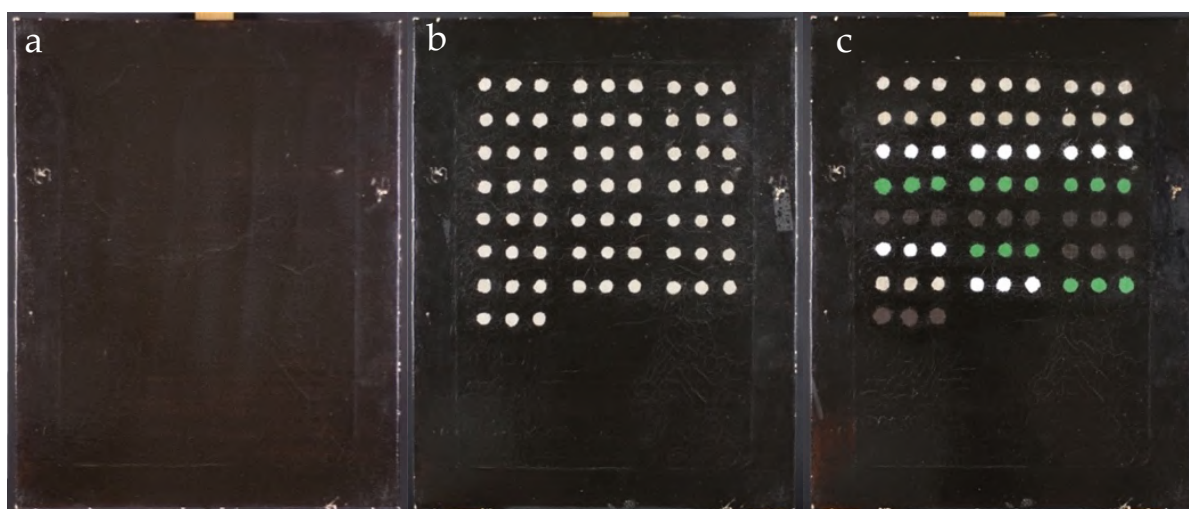


Figure 8. Model painting used for fluctuating temperature trials: a) before; b) with circular losses made with a hole puncher; c) with losses filled with the 22 PWR (NOVA and Gamblin) formulations

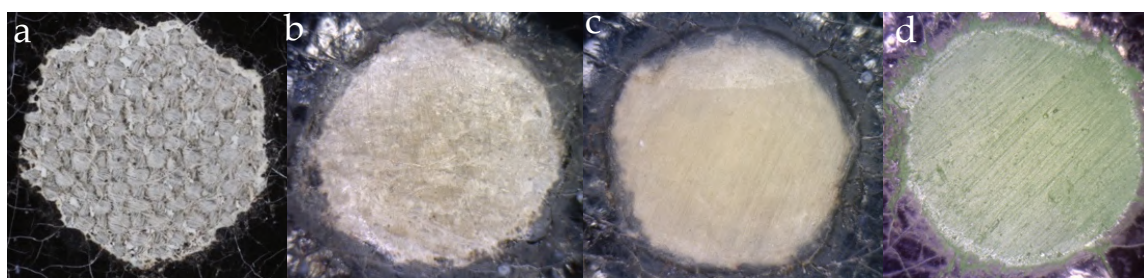


Figure 9. a) Loss on model painting before filling; Losses filled with NOVA-PWR: neutral (unpigmented) (b), with Champagne chalk (c) and with chrome oxide green (d)

¹⁵ Further information on the model paintings and their composition can be found in Appendix IV.

4. Characterisation of NOVA-PWR formulations (containing Cosmoloid H80 and Regalrez® 1126)

One of the main purposes of characterising the formulations was to select the most promising ones for evaluation in terms of their stability to different environmental conditions. Therefore, the NOVA-PWR were characterised, not only in terms of their optical and physical properties, but also at a molecular level.

4.1. Optical and physical properties

Initially, only unpigmented mixtures of Cosmoloid H80 and Regalrez® 1126 were tested (4.1.1), so that results were not masked by the presence of pigments or fillers. These unpigmented mixtures of the NOVA-WR formulations were tested mostly for their workability and hardness. Afterwards (section 4.2.1.), a set of three pigments and three fillers were added to the unpigmented mixtures which were the most promising, and these were then tested for their workability, hardness, and opacity. For comparison purposes, a neutral (unpigmented) Gamblin-PWR and three pigmented ones were tested following the same methods.

4.1.1. Wax:resin (WR) ratios without pigments/fillers

The first step consisted of applying the different NOVA-WR formulations (with Cosmoloid H80 and Regalrez® 1126 in different ratios) on two substrates: polyester film (Melinex®) and pieces of stretched canvas. Two different application methods were used: 1) melting directly onto the substrate using a Whipmix wax-carving pencil (see Appendix I); and 2) first melting on a small hot plate and transferring the warm NOVA-WR to the substrate with a metal spatula.

Workability took the following factors into consideration: the ability and ease of application in thin and thick layers; the ability and ease of sculpting and creating three-dimensional features (e.g., reproducing impasto), and the feel of each mixture while being manipulated. The temperature required for melting each formulation was also assessed. This was evaluated by slowly increasing the temperature of the small hot plate on which the formulations were being melted and closely observing changes in the material. These practical observations do not aim to replace specific melting temperature values for each formulation (for example by using Differential Scanning

Calorimetry, which was beyond the scope of this research), but rather aim to provide information of practical use in the conservation studio.

Hardness was assessed both organoleptically, i.e., by means of feeling while the formulations were being applied, and with a Shore D durometer (see Equipment, Appendix I).

Table 4. Observed and measured properties of different ratios of Cosmoloid H80 and Regalrez® 1126, compared with those of the unpigmented Gamblin-PWR, labelled “Neutral Base”

Formulation		Observed melting temperature (°C)	Workability	Hardness (organoleptically assessed)*	Hardness (measured with a Shore D durometer)
Cosmoloid H80	Regalrez 1126				
1 part	1 part	60-65	Yes	4	41.5 ± 0.9
1.5 parts	1 part	60-65	Yes	3	40.0 ± 0.8
2 parts	1 part	58-62	Yes	3	37.0 ± 0.6
2.5 parts	1 part	58-62	Yes	2	36.0 ± 0.8
3 parts	1 part	58-60	Yes	2	34.0 ± 0.6
3.5 parts	1 part	57-60	+/-	2	32.0 ± 0.9
4 parts	1 part	56-59	+/-	1	31.0 ± 0.8
4.5 parts	1 part	55-59	+/-	1	30.5 ± 0.7
5 parts	1 part	55-57	No	1	29.5 ± 0.7
1 part	1.5 parts	65-67	+/-	5	47.5 ± 1.6
1 part	2 parts	67-69	No	6	48.0 ± 2.7
Gamblin-PWR “Neutral Base”		57-60	Yes	2	32.5 ± 0.8

***1 = Very soft; 2 = Soft; 3 = Medium soft; 4 = Medium hard; 5 = Hard; 6 = Very hard**

The most promising results in terms of hardness and workability, i.e., the closest results to that of the Gamblin-PWR, were obtained with the ratios of 2:1 and 1.5:1 (Cosmoloid H80:Regalrez® 1126, by weight). Of the two, the ratio of 2:1 was the closest to the Gamblin-PWR “Neutral Base”. For this reason, it was the ratio chosen to be tested with pigments and fillers in the first environmental trial conducted in this research. As will be seen in chapter 5.2., some unexpected results were observed with the samples using this ratio, which is why, in the trials that followed, three different Cosmoloid H80:Regalrez® 1126 ratios were always tested simultaneously (1:1, 1.5:1 and 2:1, by weight).

4.1.2. Wax:resin:pigment/filler ratios

After studying the properties of the Cosmoloid H80-Regalrez[®] 1126 mixtures alone, the three different pigments (titanium white, chrome oxide green and burnt umber) and the three inert fillers (Champagne chalk, kaolin and Portafill[®] A40) were added to the most successful mixture in terms of workability and hardness: **1.5 parts of Cosmoloid H80 to 1 part of Regalrez[®] 1126 (by weight)**.

Pigments were added in three different proportions, and fillers were added in different ratios, generally higher than those of the pigments (Table 5). As well, a mixture of each pigment and Champagne chalk (1 part of pigment to 1 part of chalk) was added to the Cosmoloid H80-Regalrez[®] 1126 binder mixture (1 part of pigment + Champagne chalk to 1 part of binder), with the aim of evaluating the physical and optical differences between adding the pigment alone or in combination with a filler (bulking agent). Champagne chalk was the filler chosen because it showed the most promising results in terms of miscibility and visual appearance.

Opacity was evaluated based on the International standard for the determination of hiding power in paints and varnishes: ISO 6504-3:2019 (International Organization for Standardization, 2019). The different PWR formulations were applied both as thin and thick films on Melinex[®]. Each Melinex[®] sheet was then placed on top of a Byko Opacity 2A Test Chart and photographed. Ideally, the thin films of PWR would have been applied with a fixed distance applicator to ensure that all of them had the same thickness. However, since this equipment was not available, films were made using the Whipmix Wax Carving Pencil (Appendix I), with a flat end tip to spread the material as evenly as possible creating a very thin film. With this method, although a completely uniform thickness could not be achieved, the PWRs were applied consistently by one operator. Instead of measuring opacity of the paint films with reflectometry, in accordance with the ASTM D2805–11:2018 (American Society for Testing and Materials, 2018), opacity evaluation could only be done for this study through visual comparison between the different formulations. Therefore, the results are presented as a practical evaluation only (future research on the effect the ratio of binder to pigment/inert filler on opacity of the formulations would require access to reflectometry).

Hardness was measured for samples with 1 part of pigment/filler to 1 part of Cosmoloid H80-Regalrez[®] 1126 binder mixture (by weight). This established a basis

of comparison to evaluate how the addition of each specific pigment and filler would change the hardness of the PWR. The selected NOVA-WR formulation of wax-resin alone (1.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126) was 40.0 ± 0.8 (Table 4). The properties of the selected NOVA-WR with the addition of pigments and fillers were compared with Gamblin's Pigmented Wax/Resin: labelled "Titanium White", "Chrome Oxide Green" and "Burnt Umber" (Table 5). The ratio of pigment/filler to binder in the Gamblin-PWR was obtained via personal communication with Robert Gamblin.

Table 5. Observed and measured properties of the NOVA-PWR formulations containing three different pigments and three different fillers compared to the Gamblin-PWR formulations. Note that the parts of filler/pigment given are per 1 part of the binder (which consists of a mixture of 1.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126, by weight). The weight (in grams) of each component is given per 10g of the binder.

	Pigment/filler	Parts of pigment/filler to 1 part of binder, by weight (10g of binder)	Miscibility of components	Workability	Opacity (1 to 10)*	Average hardness (measured with a Shore D durometer)
Gamblin-PWR	“Titanium White”	1	-	Yes	9	36 ± 0.6
	“Chrome Oxide Green”	1	-	Yes	10	38.5 ± 0.8
	“Burnt Umber”	0.6	-	Yes	10	43 ± 0.6
NOVA-PWR	Titanium white	0.125 (1.25g)	Yes	Yes	4	-
		0.25 (2.5g)	Yes	Yes	6	-
		0.5 (5g)	Yes	Yes	7	-
		1 (10g)	Yes	Yes	9	48.5 ± 1
	Chrome oxide green	0.125 (1.25g)	Yes	Yes	5	-
		0.25 (2.5g)	Yes	Yes	8	-
		0.5 (5g)	Yes	Yes	8	-
		1 (10g)	Yes	Yes	10	49.5 ± 0.7
	Burnt umber	0.125 (1.25g)	Yes	Yes	4	-
		0.25 (2.5g)	Yes	Yes	6	-
		0.5 (5g)	Yes	Yes	8	-
		1 (10g)	Yes	Yes	10	50.0 ± 1.0
	Calcium carbonate	0.25 (2.5g)	Yes	Yes	2	-
		0.5 (5g)	Yes	Yes	3	-
		1 (10g)	Yes	Yes	4	51.0 ± 0.7
		2 (20g)	Yes	+/-	4	-
	Kaolin	0.25 (2.5g)	+/-	Yes	2	-
		0.5 (5g)	+/-	Yes	3	-
		1 (10g)	+/-	+/-	4	49.0 ± 0.6
		2 (20g)	No	No	-	-
	Portafill® A40	0.5 (5g)	+/-	Yes	1	-
		1 (10g)	+/-	Yes	1	50.0 ± 0.8
		2 (20g)	+/-	+/-	2	-
	Titanium white + Champagne chalk (1:1)	0.5 (2.5g of pig. + 2.5g of chalk)	Yes	Yes	8	49.5 ± 0.7
	Chrome oxide green + Champagne chalk (1:1)	0.5 (2.5g of pig. + 2.5g of chalk)	Yes	Yes	9	49.5 ± 0.9
	Burnt umber + Champagne chalk (1:1)	0.5 (2.5g of pig. + 2.5g of chalk)	Yes	Yes	6	51.0 ± 0.9

*1 – the most transparent; 10 – the most opaque

The main conclusions after preparing and applying the different PWR mixtures with pigments and fillers are as follows:

- All the mixtures with one exception were viable. The exception was 1 part of NOVA-WR binder to 2 parts of kaolin (by weight). In this case, there was not enough binder for all the filler and the mixture became crumbly and impossible to work with;
- Kaolin and Portafill® A40 did not mix as well with the binder as Champagne chalk did;
- Opacity/hiding power of the mixtures was directly related to the refractive index of the pigment/filler added (see Appendix III), as expected. Pigments have much higher hiding power than the fillers in mixtures with the same ratios;
- Champagne chalk, when added to each of the pigments, lowered the opacity of the mixture when compared with the pigments used alone. This was especially visible in the mixture with Champagne chalk and burnt umber;

Tables 6 and 7 include images from the different PWR formulations applied on a Melinex® sheet and placed on top of the Byko opacity charts. The images are meant to illustrate the opacity values given for every formulation in table 5.

Table 6. Opacity tests of PWR mixtures containing titanium white, chrome oxide green and burnt umber. The binder in all formulations (except Gamblin-PWR) consists of a mixture of 1.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126, by weight.

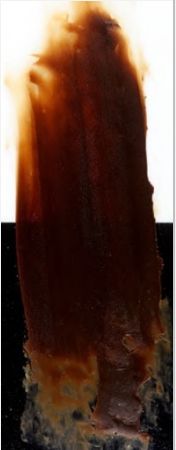
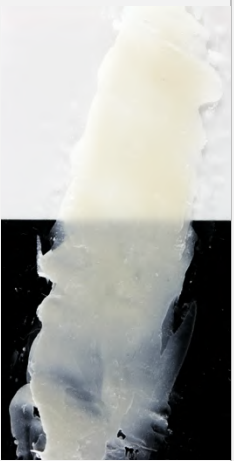
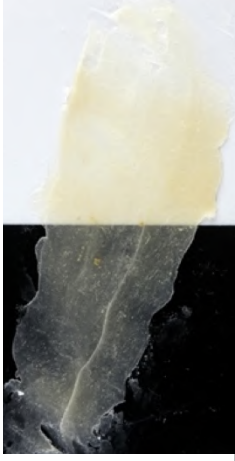
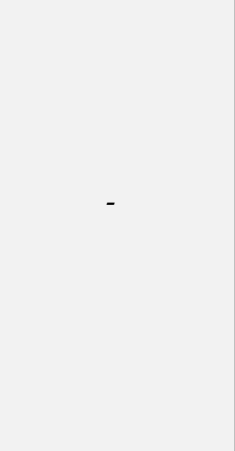
Parts of pigment to 1 part of binder, by weight (10g of binder) →	0.125 parts (1.25g)	0.25 parts (2.5g)	0.5 parts (5g)	1 part (10g)	Pigment + chalk (1:1) 0.5 parts (2.5g of pigment + 2.5g of chalk)	Gamblin PWR
Titanium white						
Chrome oxide green						
Burnt umber						

Table 7. Opacity tests of wax-resin mixtures containing Champagne chalk, kaolin and Portafill® A40. The binder in all formulations consists of a mixture of 1.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126, by weight.

Parts of filler to 1 part of binder, by weight (10g of binder) →	0.25 parts (2.5g)	0.5 parts (5g)	1 part (10g)	2 parts (20g)
Champagne chalk				
Kaolin				Not possible to make the mixture
Portafill® A40				

4.1.2.1. Bendability tests for NOVA-PWR formulations with fillers

Bendability tests were conducted to help choose the best formulation intended for a large insert needed in the first case study (Appendix VIII). It was necessary to establish if the Cosmoloid H80-Regalrez[®] 1126-filler formulation would be flexible enough to withstand bending without breaking. Bending tests would also give important information to determine whether such infills would fail if it was necessary to roll a painting for transport.

Not having access to a mandrel or plunger of defined dimensions, used for the ASTM E290-14 - Standard Test Methods for Bend Testing of Material for Ductility (American Society for Testing and Materials, 2014), 11 cylinders (laboratory beakers) with different diameters were used as the bending surfaces. Two different ratios of Cosmoloid H80:Regalrez[®] 1126 (2:1 and 1.5:1, parts by weight), combined with three different inert fillers (Champagne chalk, kaolin and Portafill[®] A40, in different amounts) were applied on small pieces of a linen canvas previously sized with Plextol B500.

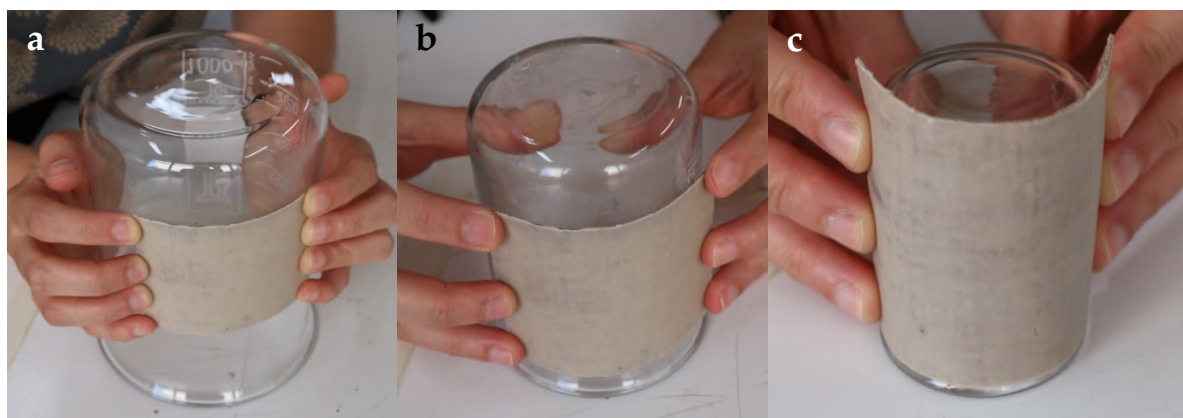


Figure 10. NOVA-PWR sample with Champagne chalk during bending tests on cylinders with the following diameters: 13 cm (a), 6 cm (b) and 4 cm (c). The NOVA-PWR mixture is on the outside of the bend.

These trials were performed manually (always by the same person applying the same amount of pressure) with one sample from each formulation tested. The results, while certainly not as objective as using the ASTM standard, were enough to provided broad indications of the behaviour of the samples. The observations are compiled in Table 8.

Table 8. Observations based on the manual bending tests.

Sample			Cylinder diameter									
Binder	Filler	Parts of filler to 1 part of binder (10g of binder)	22.5 cm	18 cm	13 cm	12 cm	10 cm	9 cm	7 cm	6 cm	4 cm	2 cm
1.5 parts of Cosmoloid H80 to 1 part of Re-galrez® 1126, by weight	Chalk	0.5 (5g)										x
		1 (10g)								x		
		2 (20g)							x			
	Kaolin	0.5 (5g)								x		
		1 (10g)							x			
		2	-									
	Porta-fill® A40	0.5 (5g)								x		
		1 (10g)					x					
		2 (20g)		x								
2 parts of Cosmoloid H80 to 1 part of Re-galrez® 1126, by weight	Chalk	0.5 (5g)										x
		1 (10g)								x		
		2 (20g)								x		
	Kaolin	0.5 (5g)									x	
		1 (10g)						x				
		2 (20g)	-									
	Porta-fill® A40	0.5 (5g)								x		
		1 (10g)								x		
		2 (20g)		x								



Cylinder diameter at which cracks become visible in the infill

These tests showed that the greater the amount of filler added, the less flexible or less capable of withstanding bending without breaking is the formulation. There was not a clear indication of the influence of the amount of wax in the binder in terms of the flexibility of the final material. Among the fillers tested, Champagne chalk was, in general, the one showing the most promising results, being the filler present in the mixtures capable of bending the most, the ones with 0.5 parts of Champagne chalk to 1 part of wax:resin binder only started to crack when bent around a cylinder with a diameter of 2 cm (figure 11).

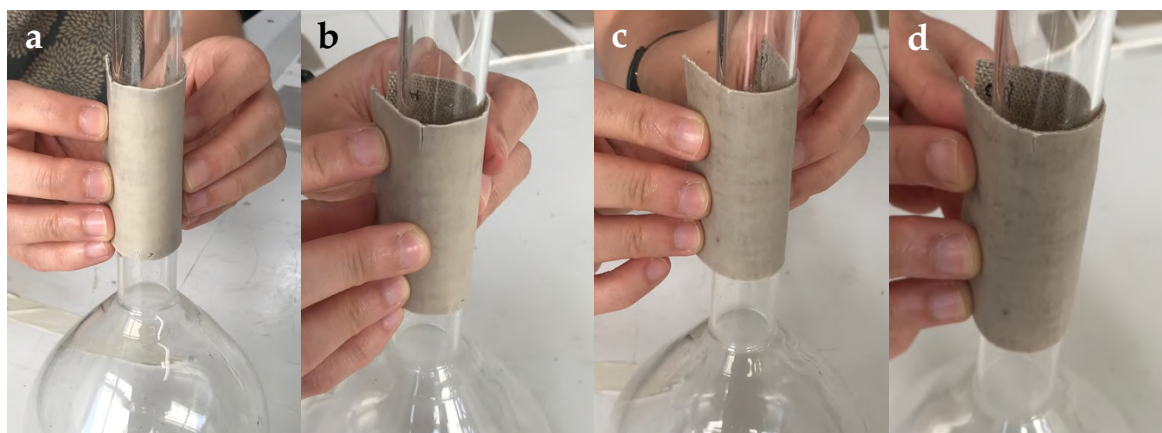


Figure 11. PWR with 0.5 parts of chalk to 1 part of binder being bent around a cylinder with 2 cm diameter; Cosmoloid H80:Regalrez® 1126 ratios: a) and b) 1.5:1; c) and d) 2:1 (parts by weight)

4.2. Characterisation of the PWR with ATR-FTIR

In terms of the molecular characterisation of the PWR mixtures, ATR-FTIR proved to be useful and very sensitive to changes in the wax:resin ratio.

The individual ingredients of the mixtures were also analysed and compared. In the case of the NOVA-PWR, Cosmoloid H80 and Regalrez® 1126 were analysed as reference materials. As for the Gamblin-PWR, the information available when the analyses were conducted indicated only that they contained beeswax, a microcrystalline wax and Laropal® A81. For this reason, Cosmoloid H80, already used and analysed for the NOVA-PWR, and a purified virgin beeswax were used as the reference for the microcrystalline wax and the beeswax, respectively. More recently, in the second edition of *Conservation of Easel Paintings* (2021), Fuster-López states that the microcrystalline wax present in the Gamblin-PWR formulations is BeSquare 195 (Fuster-López, 2021, p. 618), even though that information is still not available in Gamblin's website. Laropal® A81, from Kremer Pigmente, was also analysed and used as a reference.

See Appendix VI for tables with the main bands identified in the spectra and a possible attribution found in the literature.

4.2.1. NOVA-WR

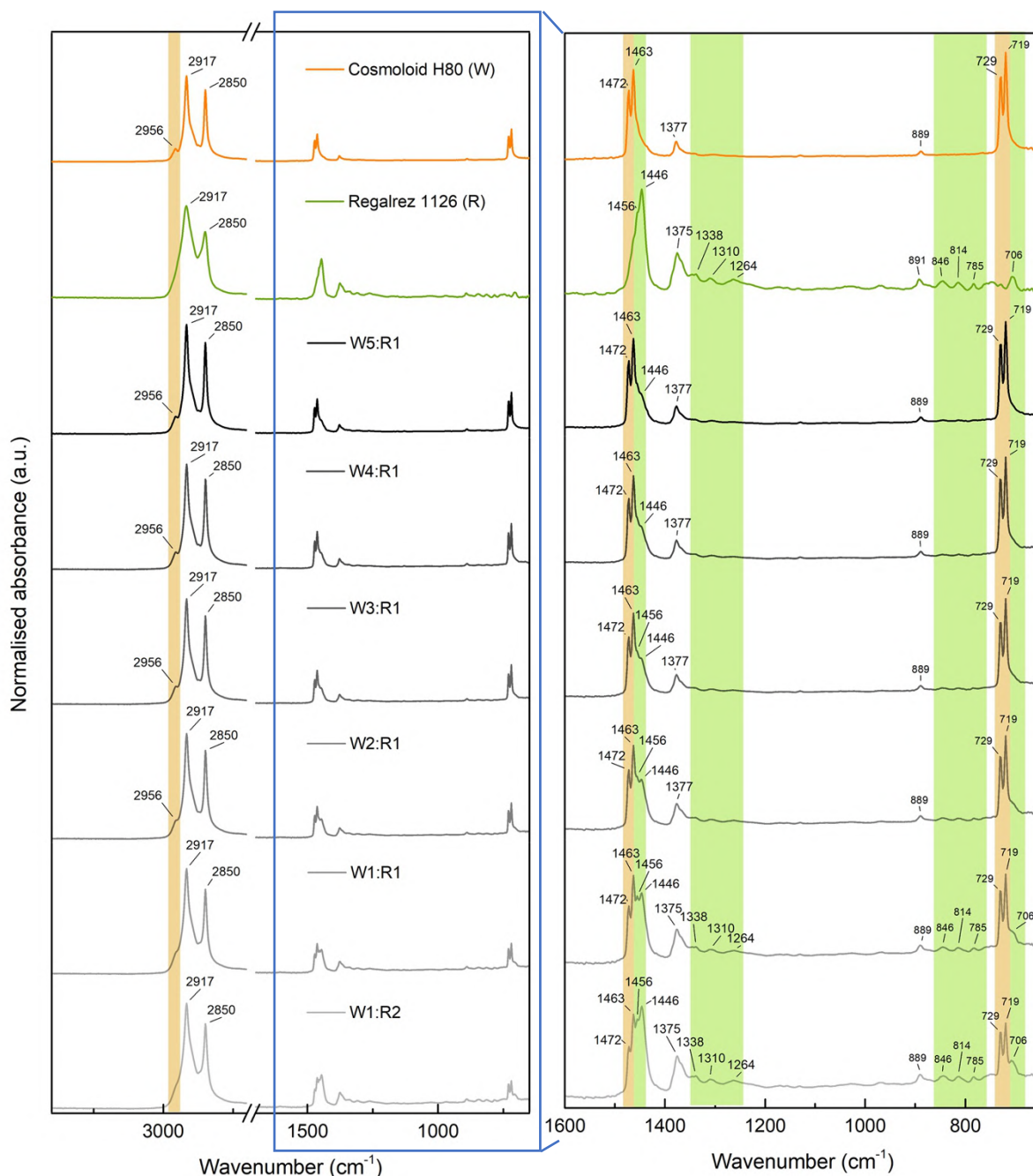


Figure 12. Spectra of six wax-resin formulations of different ratios and of Cosmoloid H80 and Regalrez[®] 1126. In yellow are the markers for Cosmoloid H80 and in green for Regalrez[®] 1126. W = Cosmoloid H80; R = Regalrez[®] 1126

The main markers for the differences in the Cosmoloid H80:Regalrez[®] 1126 ratios were found to be:

- Band at $\sim 2956 \text{ cm}^{-1}$ which is much more defined in the mixtures containing a higher amount of Cosmoloid H80 wax and almost disappears in the mixture with 1 part of Cosmoloid H80 to 1 part of Regalrez[®] 1126 resin. This band, attributed to the asymmetric stretching CH_3 groups (Maia, et al., 2013, p. 76) is

present in the ATR-FTIR reference spectrum of Cosmoloid H80 and not in the one of Regalrez[®] 1126;

- Band at **~1447 cm⁻¹** becomes more defined and intense as the amount of resin increases. This is one of the main bands present in the ATR-FTIR spectrum of Regalrez[®] 1126 and is attributed to the asymmetric bending vibrations of CH₃ groups (Derrick, et al., 1999, p. 94);
- Low intensity bands between **1263 and 1339 cm⁻¹** and between **845 and 782 cm⁻¹**, are present in the spectrum of Regalrez[®] 1126 (no attribution has been found). These bands are not visible in the spectrum of the sample with the highest amount of wax, and only begin to show when the amount of resin increases;
- Bands at **~729 and 719 cm⁻¹** become lower in intensity with a decrease in the amount of wax present. These bands can be found in the reference spectrum for Cosmoloid H80 and have been attributed to the rocking vibrations of aliphatic hydrocarbons (Baglioni, et al., 2018, p. 4).

4.2.2. Gamblin-WR

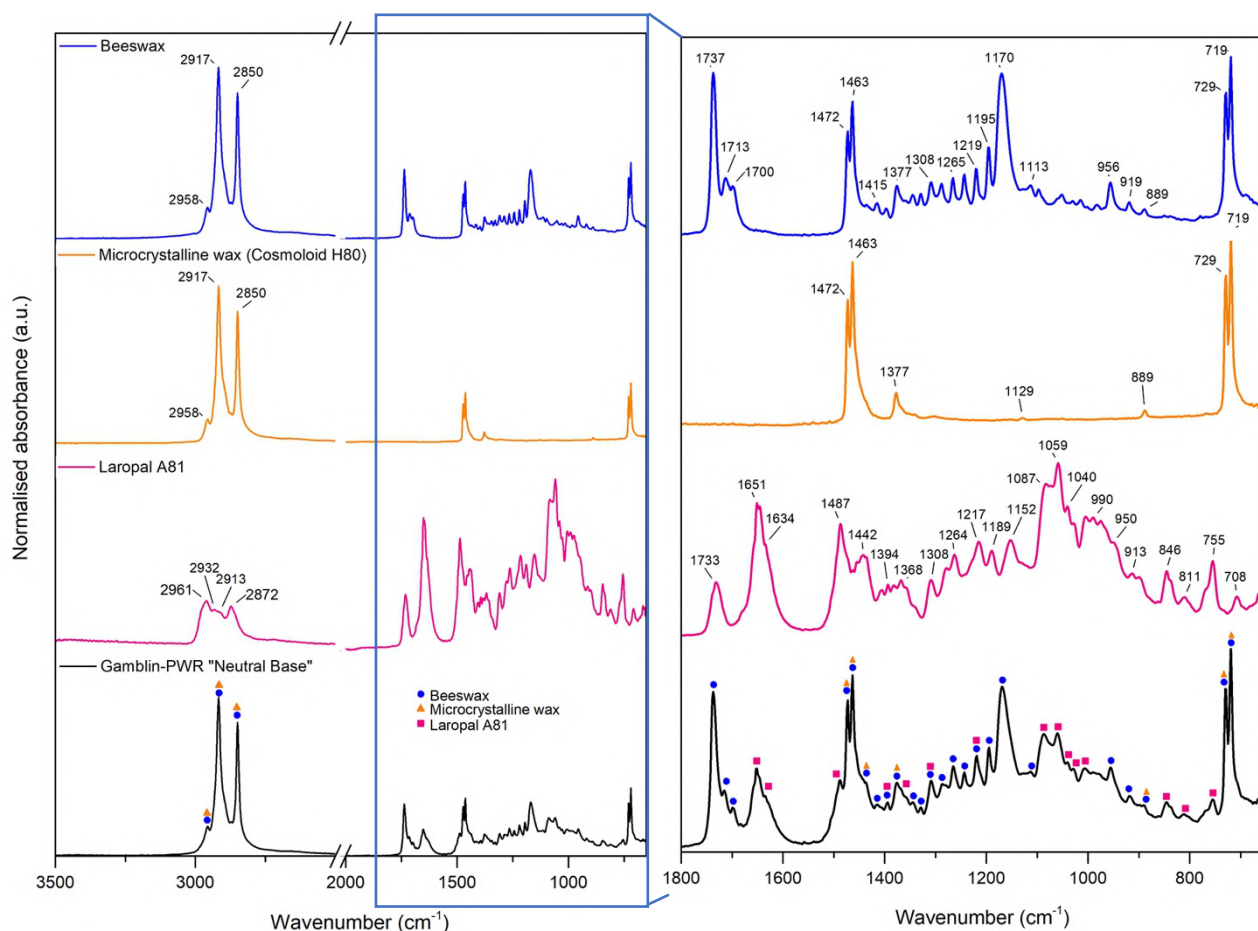


Figure 13. Spectra of the Gamblin-PWR "Neutral Base" formulation and of its components (Beeswax, a microcrystalline wax and Laropal® A81)

The spectrum of the Gamblin-PWR stick labelled "Neutral Base" clearly is a combination of the spectra of the three components reported to be present by Gamblin Conservation Colors (Gamblin Conservation Colors, n.d.): beeswax, a microcrystalline wax and Laropal® A81. Even though Cosmoloid H80 is not the microcrystalline wax present in the Gamblin formulations, the band correspondence between the reference wax and the Gamblin-PWR sample was notorious, possibly due to the similarity in composition of microcrystalline waxes, independent of the brand used.

5. Environmental chamber trials and radiant heat exposure

The stability of the selected formulations to different environmental conditions was also investigated. Five different environmental trials were conducted in an environmental chamber at the Civil Engineering Department of the NOVA School of Science and Technology (Equipment, Appendix I).

Test samples were made from a selection of NOVA-PWR formulations (see Appendix V) and four Gamblin-PWR formulations.

5.1. Environmental conditions

One of the main goals in exposing test samples to fluctuating environmental conditions was to determine if replacing beeswax entirely with microcrystalline wax (Cosmoloid H80) would improve the stability of the final product, especially when it came to the development of surface exudates (e.g., bloom with beeswax) and softening in high temperatures. For this reason, it was important to consider the conditions used by other authors in their studies of beeswax samples (according to Čížová et al. 2018, there are no standards for the accelerated ageing of beeswax).

Isa von Lenthe's research on the stability of beeswax in beeswax-chalk-pigment infill materials was ideal for establishing the necessary parameters since the environmental conditions and results are clearly reported in her master's thesis (von Lenthe, 2019, p. 36). Von Lenthe subjected samples of beeswax and beeswax-Cosmoloid H80 to three different trials with different environmental conditions: the first trial lasted for one week and consisted of temperature fluctuations between 20°C and 26°C, in one-hour intervals, while the relative humidity remained stable at $\pm 55\%$; in the second trial, for 2 weeks, temperature fluctuated more widely from 10°C to 40°C also in 1-hour intervals (RH remained stable at $\pm 55\%$). In the third trial, (2 weeks) the relative humidity fluctuated between 40 and 60%, while the temperature remained at $\pm 23^\circ\text{C}$ ¹⁶.

Following results reported by von Lenthe (2019), and the experience from **Trial 1** below, it was decided to set the Environmental Chamber conditions as follows: fluctuating relative humidity (10-90%) with stable temperature (25°C); fluctuating

¹⁶ All the trials were done in four different intervals of one hour each (e.g., in trial 1, one hour at 20°C, then one hour increase to 26°C, then one hour at 26°C and finally one hour decreased to 20°C, repeat).

temperature (10-40°C) with stable RH (55%) and high temperatures of 50°C and 60°C, and uncontrolled RH.

In addition, it was considered important to test the effect of radiant heat using a tungsten lamp to simulate the heat effect from sunlight striking a painting in comparison with the heating conditions in the environmental chamber.

5.1.1. Environmental chamber trials (1-5)

In **Trial 1**, the samples were subjected to simultaneous fluctuations in relative humidity and temperature. Twelve different ratios of Cosmoloid H80 to Regalrez[®] 1126 were tested, and one containing 100% of Cosmoloid H80 was also included. In addition, two different ratios of Cosmoloid H80:Regalrez[®] 1126 (1:1 and 2:1, parts by weight) were chosen and mixed with different amounts of Champagne chalk, titanium white, chrome oxide green and burnt umber.

Trial 1 was interrupted because the samples (placed upright to ensure good air circulation (figure 14a) became soft and fell over, resting on top of one another (figure 14b). Nevertheless, some results proved very useful, as samples containing more than 2 parts of Cosmoloid H80 to 1 part of Regalrez[®] 1126 (by weight) could be eliminated: all had become too soft and had developed blisters on their surfaces, as will be detailed further.

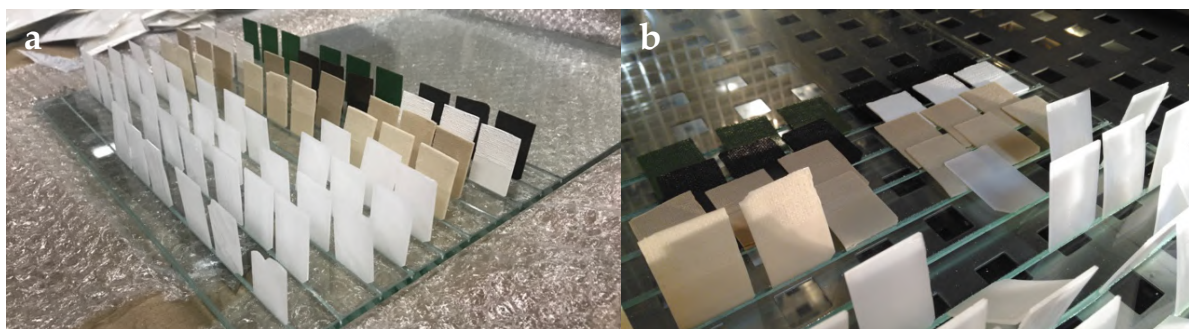


Figure 14. Rectangular samples with imprinted canvas texture placed in an upright position before entering the environmental chamber for trial 1 (a) and after ~100 hours of trial (b)

Following this, further trials were conducted where only one variable was fluctuating and the other remained stable. Limiting the variables in this way allowed a better evaluation of the effect of either relative humidity or temperature on the development of bloom, the softening or embrittlement of the material, and for molecular changes that could be visible with ATR-FTIR.

The primary purpose of **Trial 2** was to understand if samples containing Cosmoloid H80 and Regalrez[®] 1126 would develop bloom when subjected to fluctuating cycles of relative humidity, with values as low as 10% and as high as 90% (temperature

remained constant at 25°C). Both NOVA-PWR and Gamblin-PWR were tested to evaluate the role of beeswax and its replacement by Cosmoloid® H80.

In addition to the impact of relative humidity on the development of bloom, temperature was also reported to play a crucial role (Bartl, et al., 2013, p. 292; Coggshall & Morse, 1984 in von Lenthe, 2019, p. 19). Therefore, **Trial 3** was carried out to determine whether bloom could be associated with fluctuating temperatures. Trial 3 also aimed to study the effect temperature might have on softening (with higher temperatures) or shrinkage (with lower temperatures). Softening was to be assessed mainly by observing the shape of the circular protrusion in the rectangular samples and the lines carved into the filled losses in the model paintings. Shrinkage was not expected to be visible on the rectangular samples alone and was assessed using the test samples applied to the model paintings.

Since no visible changes related to higher temperatures were detectable in Trial 3, the decision was to test the samples further with two specific temperatures, rather than fluctuations. **Trial 4** consisted of increasing the temperature from room temperature to 50°C in one hour, maintaining that temperature for one hour, and then decreasing it to room temperature for one hour. The same was done in **Trial 5**, with the difference that the maximum temperature was 60°C.



Figure 15. Model painting, rectangular samples and circular samples inside the environmental chamber. For trials 2-5, the samples were placed on a glass plate partially covered with a Reemay® 2004 acid-free polyester tissue¹⁷. The Reemay® was not completely attached to the glass, allowing for air to circulate under the samples.

¹⁷ The Reemay® tissue was chosen for its capability of retaining its physical properties when wet and with humidity fluctuations (Safe Plastics and Fabrics for Exhibit and Storage, 2010, p. 5), for being referred to as having only a 0.5 moisture pickup and for not being affected by temperatures up to 177°C (Conservation Support Systems, n.d.)

5.1.2. Radiant heat exposure (trial 6)

Trial 6 consisted of irradiating the samples with light from an incandescent light bulb which produces heat, to simulate the effect of direct sunlight. An incandescent light bulb from Philips, with a luminous power of 670 lumen, a radiant flux of 60W, and voltage of 230 volts, was used. Each sample was placed approximately 3 cm from the light bulb. An infrared thermometer was used to constantly measure the temperature of the sample, while pictures of the sample were being taken at every 2.5°C increase. Each sample was irradiated for approximately 40 minutes, until the measured temperature reached 70°C.

Table 9. Summary of the environmental conditions for each trial, together with the type and number of samples included in each of them

Trial	Relative humidity	Temperature	Time	Samples
1	Fluctuating between 10% and 90%	Fluctuating between 10°C and 60°C	Planned: 600h Actual time: ~100h	72 rectangular samples of 24 different NOVA-PWR formulations, both pigmented and unpigmented, with imprinted canvas texture on one half of the sample
2	Fluctuating between 10% and 90%	Constant at 25°C	600h	120 rectangular samples with one glossy and one matte side and a protuberance in the centre, which included 6 samples of each 18 NOVA-PWR formulation and 3 samples of each 4 Gamblin-PWR formulation; 44 circular samples for hardness measurements, which included 2 samples of each 18 NOVA-PWR formulation and 2 samples of each 4 Gamblin-PWR formulation; 1 model painting, losses filled with NOVA-PWR and Gamblin-PWR formulations.
3	Constant at 55%	Fluctuating between 10°C and 40°C	600h	Same as trial 2.
4	Not controlled	Rising from room temperature (~21°C) to 50°C for 1 hour, staying at 50°C for 1 hour and lowering to room temperature 1 hour	3 hours	66 rectangular samples with one glossy and one matte side and a protuberance in the centre, which included 3 samples of each 18 NOVA-PWR formulation and 3 samples of each 4 Gamblin-PWR formulation. 22 circular samples for hardness measurements, which included 1 sample of each 18 NOVA-PWR formulation and 1 sample of each 4 Gamblin-PWR formulation.
5	Not controlled	Rising from room temperature (~21°C) to 60°C for 1 hour, staying at 60°C for 1 hour and lowering to room temperature 1 hour	3 hours	Same as trial 4.

6	Not controlled	Coming from a tungsten light bulb and measured with an infrared thermometer. The measured temperatures went from 30°C to 75°C.	Each sample was irradiated with light coming from an incandescent light bulb for approximately 40-45 minutes, until the temperature of 70°C was reached.	12 rectangular samples with one glossy and one matte side and a protuberance in the centre. The formulations tested were: unpigmented NOVA-PWR in the ratios of 1:1, 1.5:1 and 2:1 (wax:resin); NOVA PWR 1.5:1 (wax:resin) containing chalk, Titanium white, Chrome oxide green and Burnt Umber; Gamblin-PWR labelled "Neutral base", "Titanium white", "Chrome oxide green" and "Burnt Umber"
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5.2. Results and discussion

The following five parameters were evaluated in all trials using the environmental chamber and radiant heat:

- a. Development of bloom;**
- b. Loss of surface features;**
- c. Surface changes and deformation;**
- d. Embrittlement and/or cracking;**
- e. Changes in hardness;**
- f. Molecular changes evident with ATR-FTIR.**

All parameters were evaluated both on the NOVA-PWR samples (containing Cosmoloid H80, Regalrez® 1126 and a selection of three pigments and one filler) and the Gamblin-PWR samples. The images presented in each section below are selected examples for a specific parameter. Images of all samples, before, during and after each trial, taken either with macro-photography or digital microscopy, can be provided as supplementary digital material, upon request.

a. Development of bloom

Bloom was not detected in the NOVA-PWR samples, as expected, and was found in the samples made from the Gamblin-PWR sticks. However, an important finding was that bloom was only detected on the rectangular Gamblin-PWR samples without substrates and not on the infills of the same formulations where applied to losses in the three model paintings. It is likely that the development of bloom on the Gamblin-PWR samples could be related to the application method and the more matte finish of the infills, as opposed to the glossy side of the samples, which is where bloom was visible in the vast majority of the cases. Therefore, in this section, when referring to bloom on the Gamblin-PWR, only the rectangular samples are referred to.

Bloom was more easily detected on the Gamblin-PWR samples containing burnt umber pigment likely because they were dark, creating a higher contrast with the bloom and making it stand out. However, bloom also developed in all the other Gamblin pigmented and unpigmented samples (figure 16).

Results also showed that both fluctuations in relative humidity and in temperature promote bloom in the Gamblin-PWR formulations. In addition, it was observed that the control samples of Gamblin-PWR started developing bloom after two weeks of being stored in ambient conditions¹⁸.

¹⁸ Samples were stored in small plastic bags, inside of which a pH neutral cardboard was placed with the goal to both prevent the samples from breaking and to absorb some of the moisture in the air. The small plastic bags, which were left slightly open so as not to create a micro-climate inside, were, in turn, stored inside cardboard boxes and kept in ambient conditions. A data-logger placed inside one of the cardboard boxes measured temperatures from 14.5 to 26 °C and relative humidity from 49.5 to 57.5% between November 2020 and August 2021.

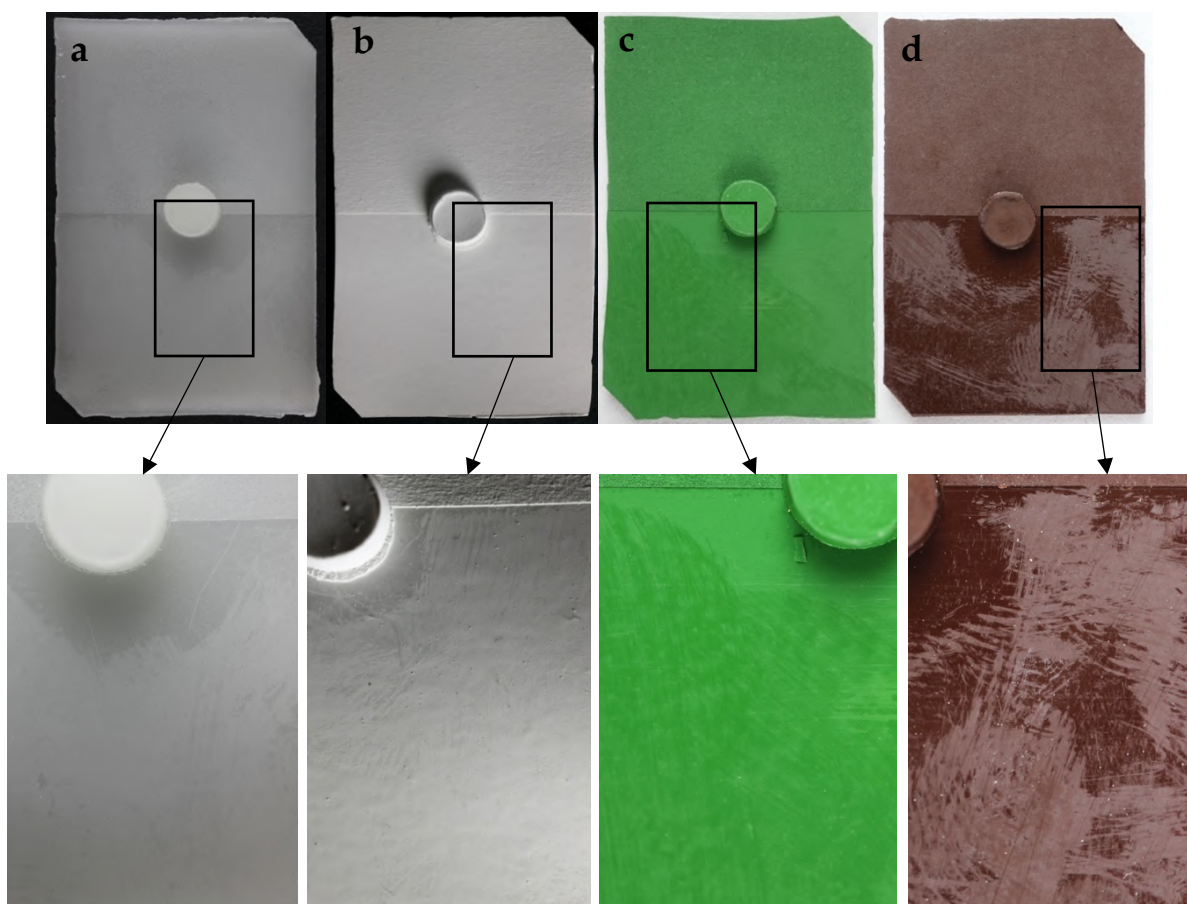


Figure 16. Top row: Gamblin-PWR samples, from sticks labelled “Neutral Base” (a), “Titanium White” (b), “Chrome Oxide Green” (c) and “Burnt Umber” (d), showing bloom; Bottom row: detail of areas of bloom

When comparing results from the different trials, Gamblin-PWR samples that were subjected to relative humidity fluctuations (figure 17a-b) developed a less intense blooming effect with a different appearance than those subjected to temperature fluctuations (figure 17c-d) during the same amount of time. Fluctuating relative humidity resulted in clearly distinct whitish areas and lines, while fluctuating temperature resulted in an overall cloudy appearance. The difference in intensity and morphology of the bloom layer is clearly visible in the images taken with a digital microscope with raking light (figure 17).

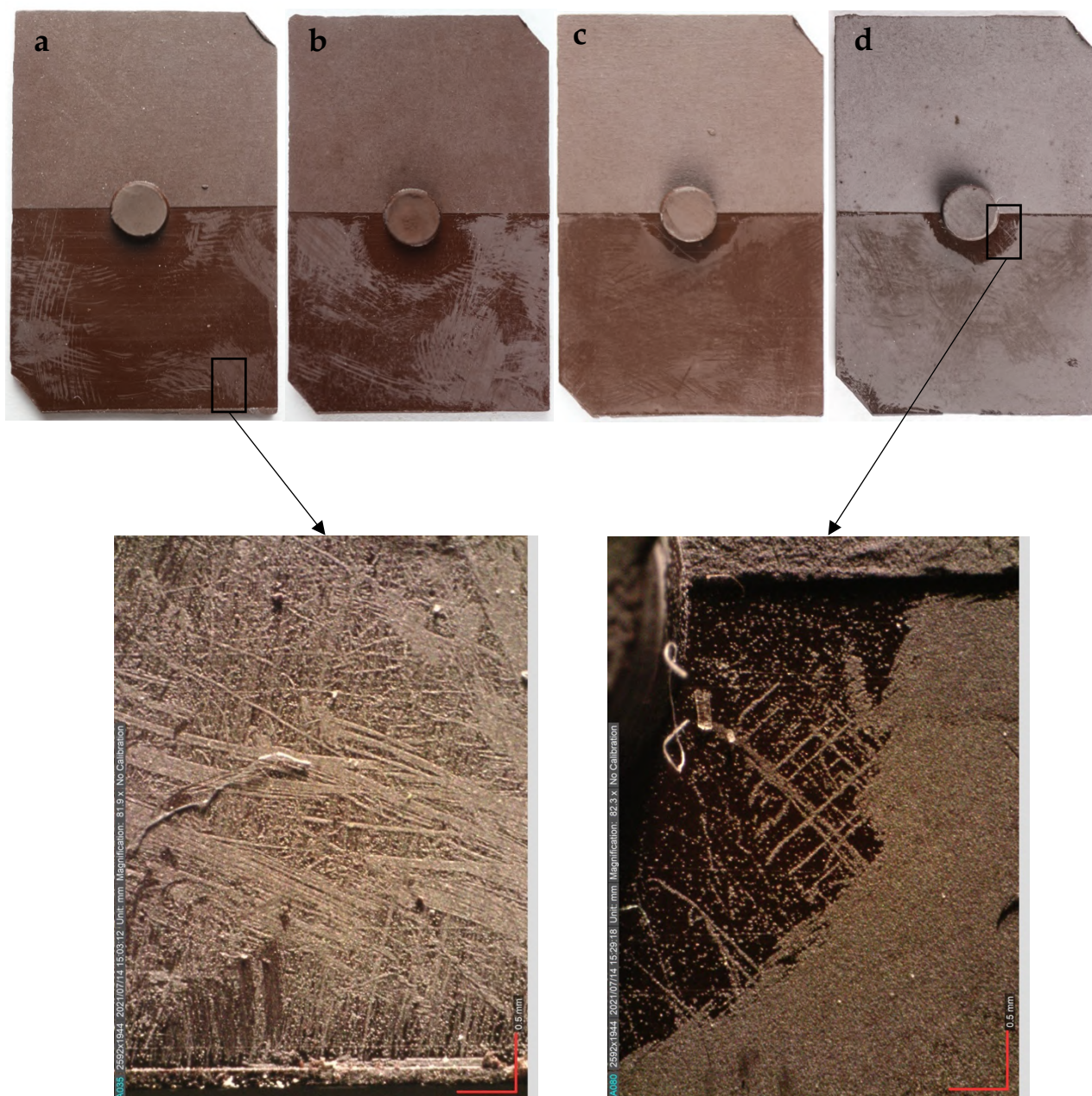


Figure 17. Gamblin-PWR samples from sticks labelled “Burnt Umber” after the fluctuating RH trial (a and b); and after the fluctuating temperature trial (c and d). Detail images of the bloom layer below taken with a Dino-light digital microscope.

Despite the extreme thinness of the bloom layer, it was possible to scrape a small portion of it from one of the samples of Gamblin-PWR labelled “Burnt Umber” which had been subjected to fluctuating RH. This was analysed using ATR-FTIR.

The resulting spectrum (figure 18) shows a strong similarity to the reference spectrum for beeswax; a strong indication that bloom results (or partially results) from the migration of beeswax components to the surface. These results are in accordance with previous studies, which found bloom to be mainly composed of linear

unsaturated hydrocarbons that naturally occur in beeswax (Bartl et al., 2013, p. 292; Bartl et al., 2015, p. 509). These results are a very good indication that, since beeswax is not used in the NOVA-PWR, bloom is not expected to develop in the formulations presented in this study.

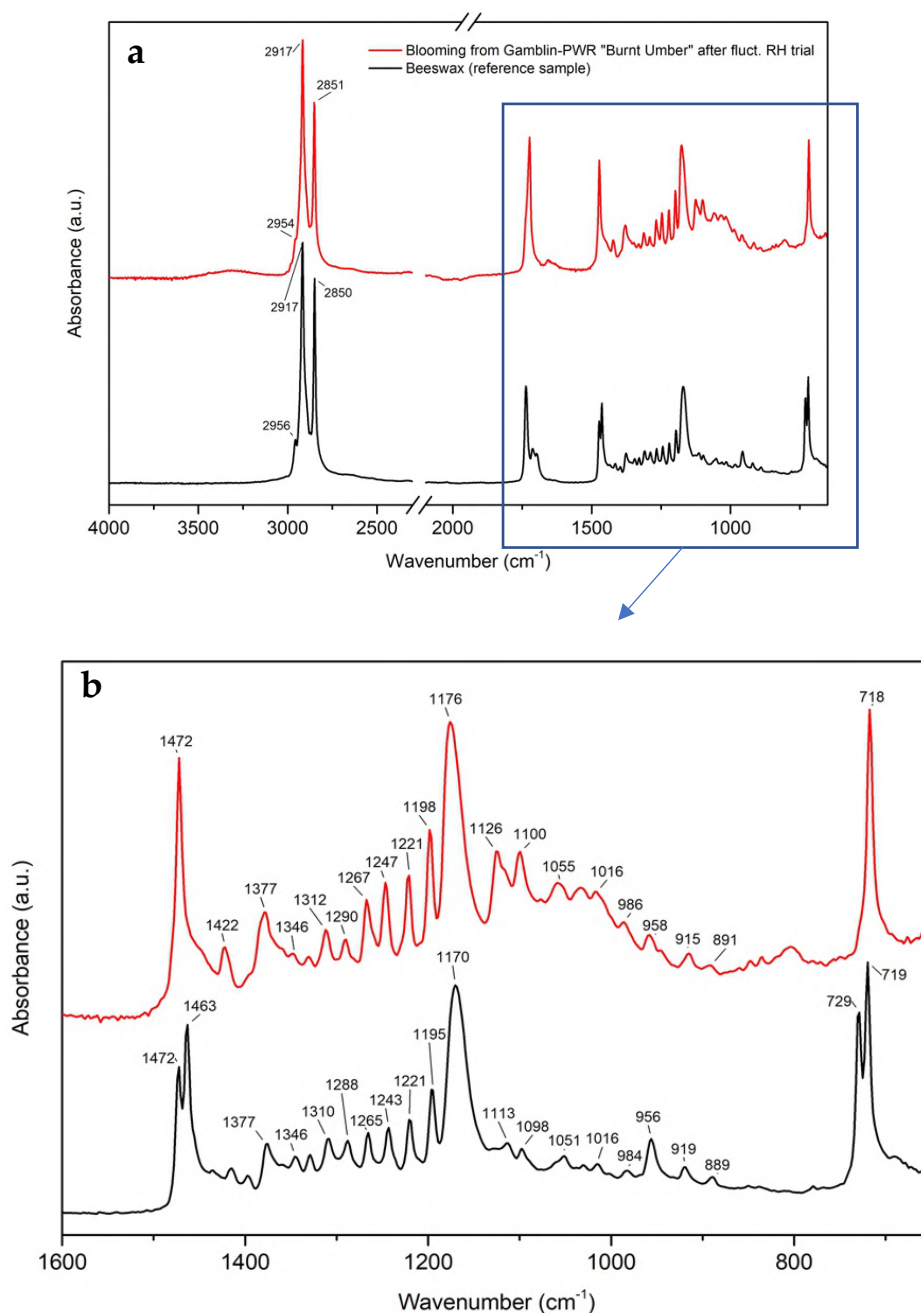


Figure 18. Spectra of the bloom layer taken from Gamblin-PWR labelled "Burnt Umber" sample (red) and beeswax (black), in the 4000-650 cm⁻¹ region (a) and detailed in the 1600-650cm⁻¹ region (b)

b. Loss of surface features

Loss of surface features was evaluated primarily after the trials involving high temperatures. It was assessed by close observation of the canvas texture on samples from **Trial 1** and of the circular protrusion on the samples from **Trials 3 to 5**. In addition, the carved lines in the infilled holes in the model painting that had been subjected to fluctuating temperature were also closely observed to assess any changes in their shape. Since samples in **Trial 1** were not viable after some collapsed onto others (figure 14b) the results are not presented here. However, where test samples were not in contact with others in Trial 1 their canvas textured surfaces remained clear and sharp.

The most significant result was that none of the samples (both NOVA-PWR and Gamblin-PWR) subjected to fluctuating temperature up to 40°C (**Trial 3**), exposed to temperatures of 50°C or 60°C for one hour (**Trials 4 and 5**) or even exposed to radiant heat (**Trial 6**) showed any visible changes in the circular protrusions, which maintained their shape in all cases. In the specific case of the samples applied to losses in the model painting used in **Trial 3**, the carved lines did not change in sharpness nor depth (figure 19). These results are a very good indication that, even if the PWR soften to a certain extent (at least with temperatures up to 70°) they tend to keep the shape that has been given to them. This is apparently true for cases in which the shape of the PWR fill is given with a silicone mould (e.g., reproducing a specific texture), when it is carved on the fill (e.g., with a scalpel) or when it is sculpted creating three-dimensional features.

As will be seen, while no changes were visible in the circular protrusions, some of the samples which were subjected to high temperatures with radiant heat (specifically 60°C and 70°C) deformed. Images of the circular protrusions before and after being subjected to these temperatures (Trials 5 and 6) are presented in tables 10 and 11.

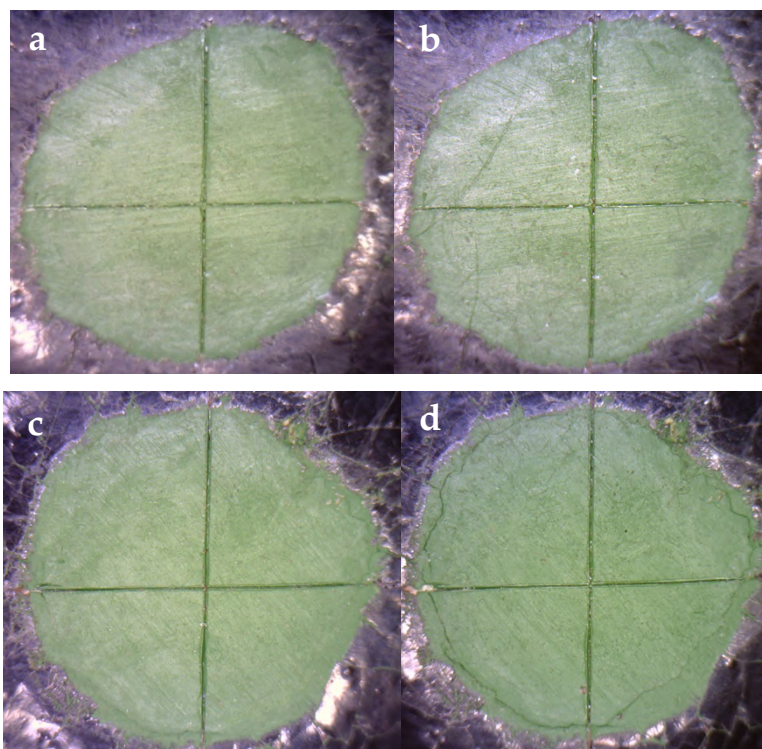
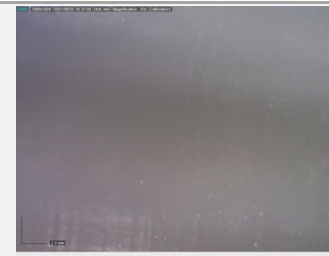
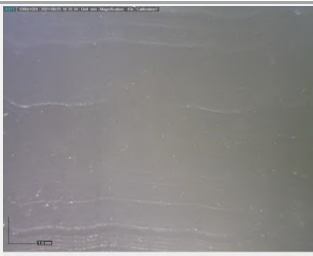
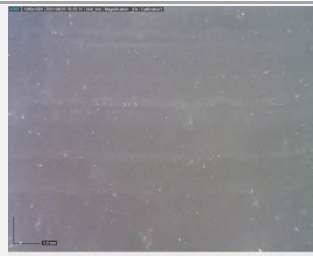
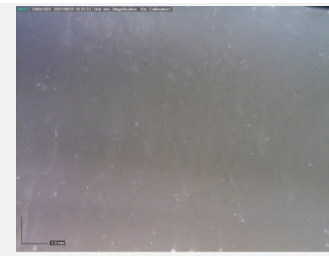
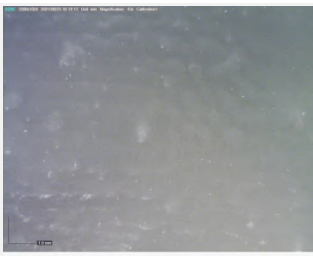
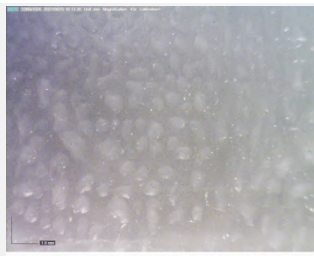
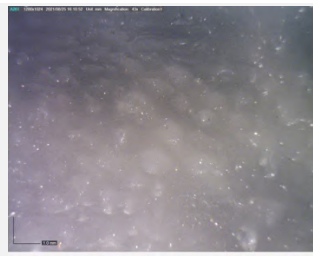
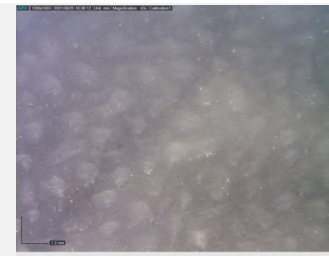
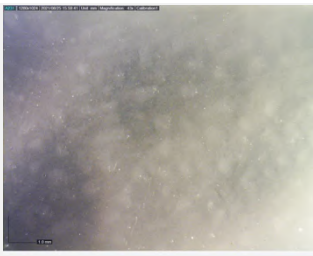
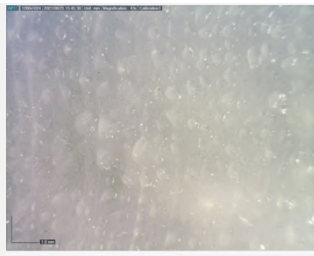
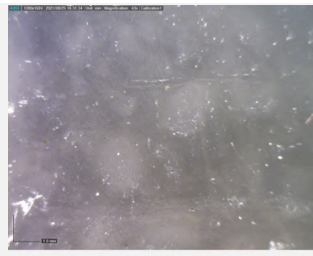


Figure 19. Filled losses scored with horizontal and vertical lines, on model painting with NOVA-PWR (1.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126, with chrome oxide green pigment) before (a) and after (b) 600h of fluctuating T; Filled losses on model painting with Gamblin-PWR (labelled “Chrome Oxide Green”) before (c) and after (d) 600h of fluctuating T

c. Surface changes and deformation

Results from **Trial 1** (maximum temperature 60°C) greatly influenced the choice of Cosmoloid H80:Regalrez® 1126 ratios for subsequent trials. Samples from Trial 1 containing a higher amount of Cosmoloid H80 wax (from 2 parts of Cosmoloid H80 to 1 part of Regalrez® 1126 ratio upwards) developed surface **blisters** (table 10). The intensity of the blisters correlated to the amount of wax in the mixture (the higher the amount of wax, the wider the blisters and the more intense the overall effect).

Table 10. Surface of unpigmented NOVA-WR infills in different Cosmoloid H80:Regalrez® 1126 ratios

1 part of Cosmoloid H80 to 2 parts of Regalrez® 1126	1 part of Cosmoloid H80 to 1.5 parts of Regalrez® 1126	1 part of Cosmoloid H80 to 1 part of Regalrez® 1126	1.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126
			
2 parts of Cosmoloid H80 to 1 part of Regalrez® 1126	2.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126	3 parts of Cosmoloid H80 to 1 part of Regalrez® 1126	3.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126
			
5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126	4.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126	5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126	Cosmoloid H80 100%
			

The fact that this effect was only observable in samples with a higher amount of wax is a good indication that blistering is closely related to the wax (which has a lower melting temperature than the resin). Blisters were also clearly visible in the pigmented samples made with the ratio of 2:1 (Cosmoloid H80:Regalrez® 1126, by weight). All pigmented samples, regardless of the different amounts of pigment in the mixtures (or the fact that some contained Champagne chalk as well), developed this effect in a similar way to a similar extent (figure 20). The exception was the samples containing only Champagne chalk where the effect was much less pronounced and with a different morphology (figure 21).

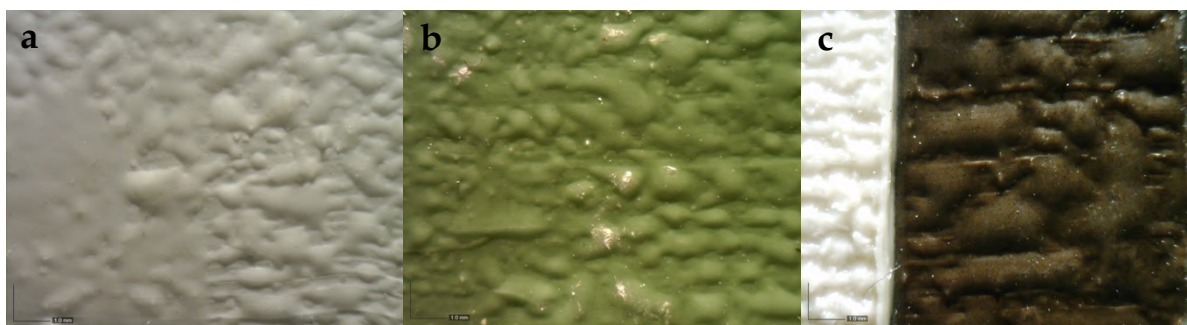


Figure 20. Detail of the blisters that developed in the samples made from the mixture with 2 parts of Cosmoloid H80 to 1 part of Regalrez[®] (by weight) with titanium white (left), chrome oxide green (centre) and burnt umber (right)

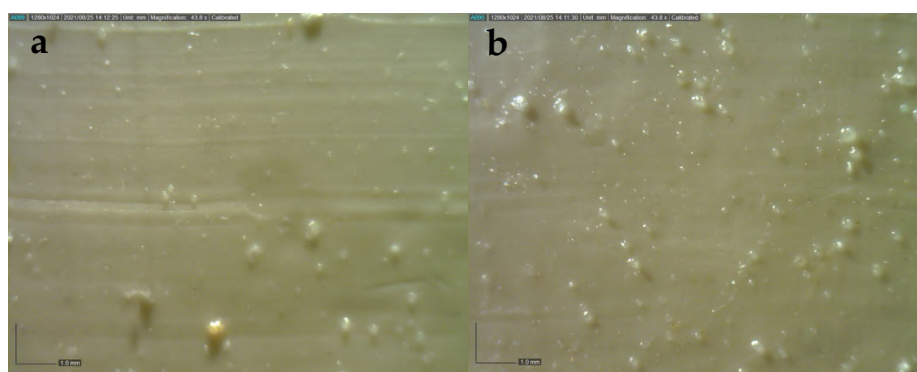


Figure 21. Detail of the blisters that developed in the samples made from the mixture with 2 parts of Cosmoloid H80 to 1 part of Regalrez[®] (by weight) with Champagne chalk

The blister-effect from Trial 1 was not observed in samples exposed to fluctuating temperatures between 10 and 40°C (**Trial 3**) nor in those exposed to 50°C (**Trial 4**). It was, however, evident (although in a lower extent and with a slightly different appearance), in two out of three unpigmented NOVA-PWR in the 2:1 ratio (Cosmoloid H80:Regalrez[®] 1126, by weight) exposed to 60°C in **Trial 5**. This is a very good indication that this effect is unlikely to occur with temperatures lower than 60°C, at least in formulations of Cosmoloid H80 and Regalrez[®] 1126 in the ratios of 1:1 and 1.5:1 (parts by weight).

Finally, most of the samples exposed to radiant heat developed blisters at temperatures between 65-70°C. An exception was found in the NOVA-PWR samples containing Champagne chalk and titanium white: they did not develop any visible surface change during the entire trial, although having softened (felt by touch). The Gamblin-PWR sample labelled “Burnt Umber” started developing blisters at 60°C. These burst open around 65°C and left holes in the surface (figure 22).

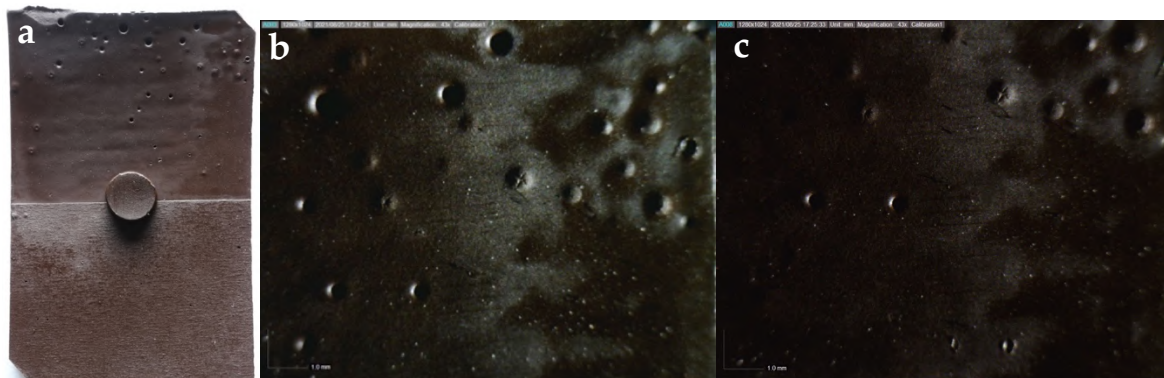


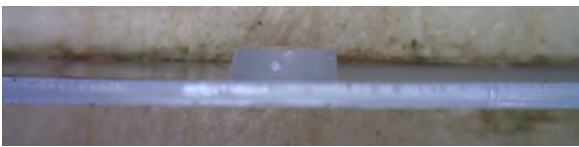
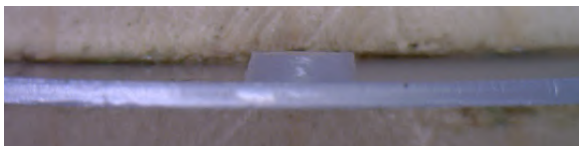
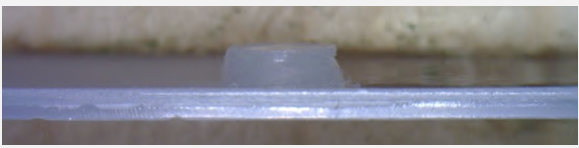
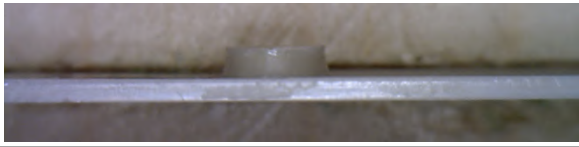
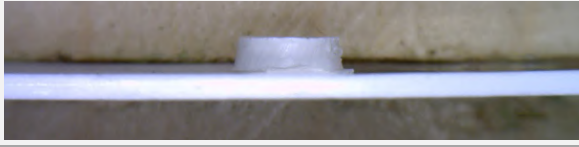
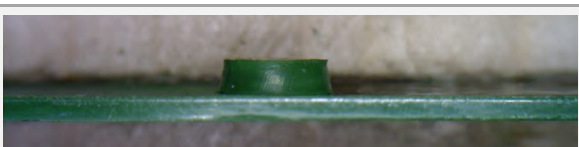
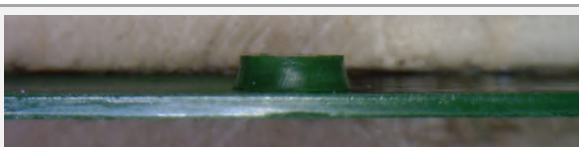
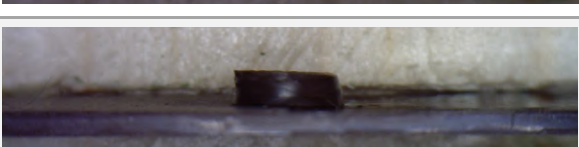
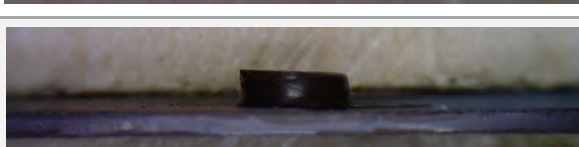
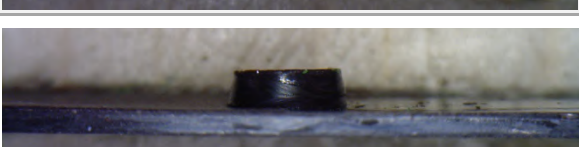
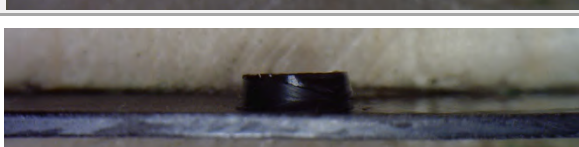
Figure 22. Gamblin-PWR sample labelled “Burnt Umber” after being subjected to the radiant heat trial (a), with details of the blisters taken with a digital microscope (b-c)

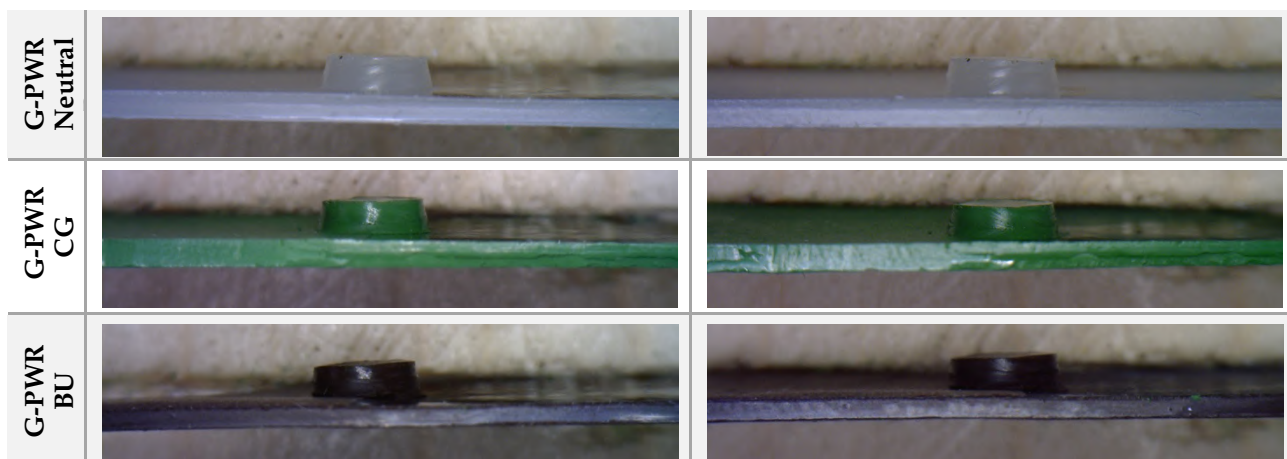
Deformation was clearly visible both in the samples exposed to 60°C (**Trial 5**) and to those exposed to radiant heat up to 70°C (**Trial 6**), (tables 11 and 12, respectively). In both cases, while the circular protrusions very clearly kept their shape in all cases, deformation occurred in the shape of the overall rectangular samples: they started to curve slightly when observed from the side. The samples exposed to radiant heat, most likely because higher temperatures were reached, and possibly due to the heat being received only from the top surface (leaving a cooler underside), deformed to a greater extent when compared to those exposed to 60°C in the environmental chamber.

In the case of samples from **Trial 5** (60°C), most of the unpigmented NOVA-PWR rectangular samples showed some slight but visible deformation. On the contrary, all the samples containing pigments or filler maintained their shape. The Gamblin-PWR formulations also did not develop any kind of deformation, although the presence of beeswax, with a lower T_g than that of the microcrystalline wax, would have been expected to exhibit visible deformation.

The images below were taken with a digital microscope, with each sample placed on a wooden stand with an opening as wide as the thickness of the samples, thus allowing the samples to remain upright without falling. The digital microscope was positioned above and set to focus on the circular protrusion.

Table 11. NOVA-PWR and Gamblin-PWR samples before and after being exposed to 60°C for 1h in the environmental chamber (see Appendix V for recipes of the samples)

	Before exposure to 60°C for 1 hour	After exposure to 60°C for 1 hour
W1:R1		
W1.5:R1		
W2:R1		
W1.5:R1 + CC		
W1.5:R1 + TW		
W1.5:R1 + CC + TW		
W1.5:R1 + CG		
W1.5:R1 + CC + TW		
W1.5:R1 + BU		
W1.5:R1 + CC + BU		

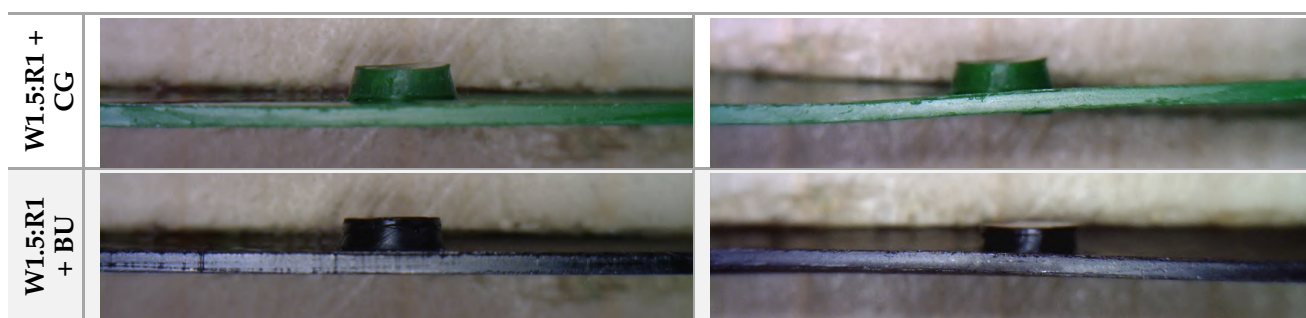


W = Cosmoloid H80; R = Regalrez® 1126; CC = Champagne chalk; TW = titanium white; CG = chrome oxide green; BU = burnt umber; G-PWR = Gamblin Pigmented Wax/Resin

Where exposed to radiant heat, samples from both NOVA-PWR and Gamblin-PWR which contained pigments and filler deformed the most. However, in all cases the circular protrusions maintained their shape, making it clear that the structure softens to a certain extent, but does not melt. It is important to note that the radiant heat trial has a higher margin of error since it was conducted manually. Although the intention was to minimize variants (e.g., by always placing the light bulb at the same distance to the sample), the fact that each sample was individually irradiated opened the possibility for small changes in the set-up that could have influenced the results. The table below contains the photographs of the samples, after they have been exposed to radiant heat and reached a temperature of 70°C.

Table 12. NOVA-PWR samples before and after being exposed to radiant heat (see Appendix V for recipes of the samples)

	Before exposure to radiant heat	After exposure to radiant heat
W1.5:R1		
W1.5:R1 + CC		
W1.5:R1 + TW		



W = Cosmoloid H80; R = Regalrez® 1126; CC = Champagne chalk; TW = titanium white; CG = chrome oxide green; BU = burnt umber

d. Embrittlement, shrinkage and cracking

PWR samples in losses on the model painting subjected in the environmental chamber to fluctuating RH (**Trial 2**) and fluctuating T (lowest temperature 10°C (**Trial 3**)), were assessed for physical changes such as embrittlement and cracking. Note that the images chosen are examples of the observations made – images of all the samples before, during and after each of the trials can be given as supplementary digital material, on request.

After 300 hours in each trial, cracking was already visible in both the NOVA-PWR and Gamblin-PWR samples. In most cases, cracking did not develop further between 300 hours and 600 hours. It is important to note that the model paintings themselves were already severely cracked before losses were created and filled for this study.

Test infills subjected to fluctuating relative humidity (**Trial 2**) (figure 23 and 25) presented less severe cracks and in a much lower number of samples (42 out of 63 presented cracks) than the infills in Trial 3. Cracking was more severe in the samples subjected to fluctuating T (**Trial 3**) (figure 24 and 26) and occurred in 60 out of 63 samples after 600h.

The most significant finding was related to the differences in cracking between the NOVA-PWR and the Gamblin-PWR samples, visible in both trials: while the NOVA-PWR are apparently cracking across in line with the model painting's existing cracks, the Gamblin-PWR seem to be cracking just inside the interface with the model painting. The first case suggests embrittlement of the material and, although cracking in line with the surrounding cracks is sometimes looked for and simulated to make the infills less detectable, this requires further research. The latter case may suggest shrinkage of the Gamblin-PWR. These results imply that the Gamblin-PWR may be tougher and less prone to cracking than the NOVA-PWR, even though the cracking visible in the NOVA-PWR may not be problematic if they do not develop further.

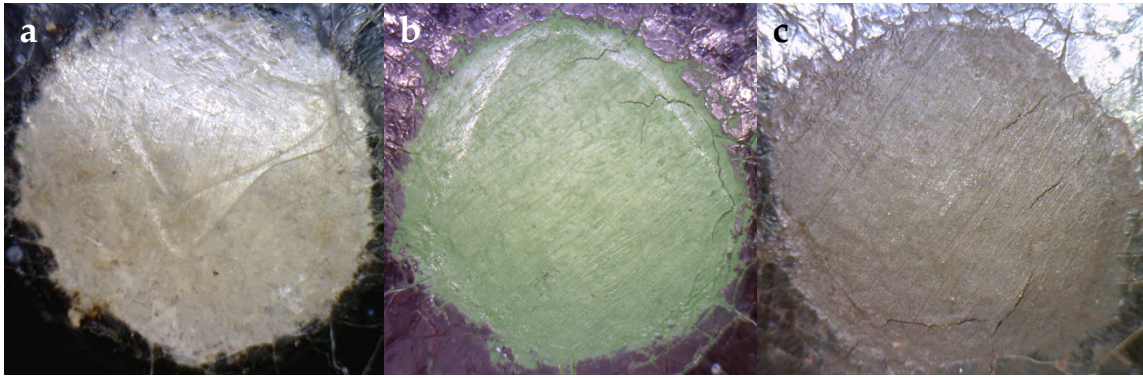


Figure 23. Filled losses with NOVA-PWR (1 part of Cosmoloid H80 to 1 part of Regalrez® 1126, by weight) after 600h of fluctuating RH; a) unpigmented; b) with chrome oxide green; c) with burnt umber

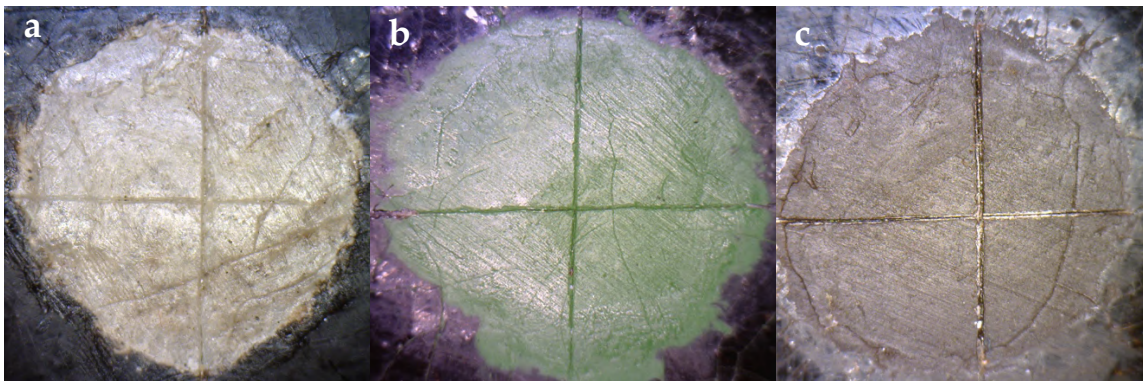


Figure 24. Filled losses with NOVA-PWR (1 part of Cosmoloid H80 to 1 part of Regalrez® 1126, by weight) after 600h of fluctuating T; a) unpigmented; b) with chrome oxide green; c) with burnt umber; Note: the horizontal and vertical lines were carved with a scalpel

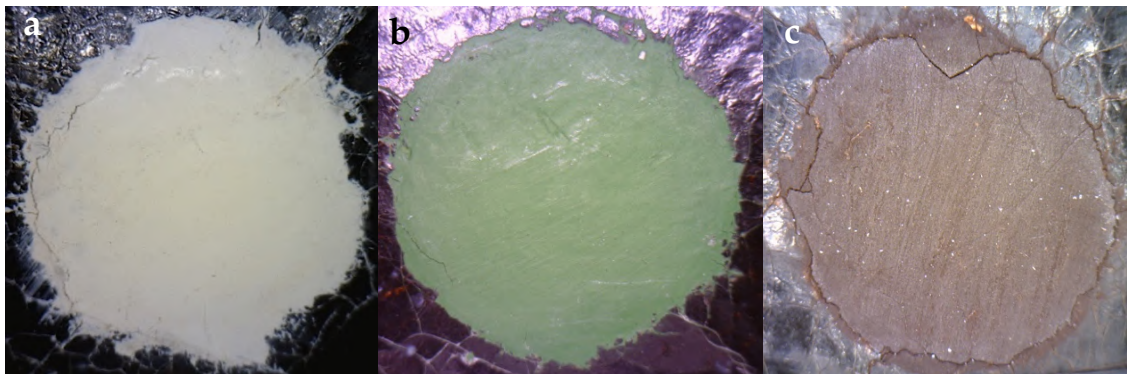


Figure 25. Filled losses with Gamblin-PWR after 600h of fluctuating RH, from sticks labelled "Titanium White" (a), "Chrome Oxide Green" (b) and "Burnt Umber" (c)

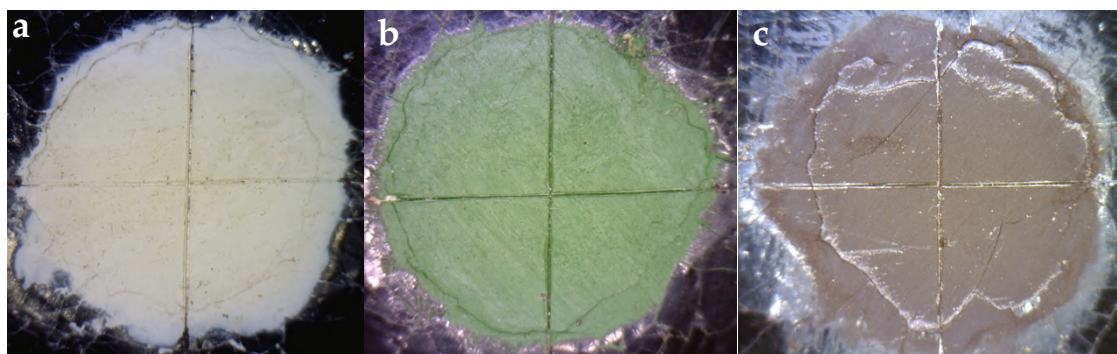


Figure 26. Filled losses with Gamblin-PWR after 600h of fluctuating T, from sticks labelled "Titanium White" (a), "Chrome Oxide Green" (b) and "Burnt Umber" (c). Note: the horizontal and vertical lines were carved with a scalpel

When comparing the NOVA unpigmented wax-resin samples, those presenting a higher degree of cracking correspond to those containing the highest ratio of Regalrez[®] 1126 to Cosmoloid H80 (in this case, it was the ratio 1:1, Cosmoloid H80:Regalrez[®] 1126, parts by weight). This is an expected result since the resin is more rigid and more prone to cracking than the wax. Figures 27b and 27c, of samples with higher amount of wax (1:5:1 and 2:1, Cosmoloid H80:Regalrez[®] 1126, parts by weight, respectively), do not show any visible cracking.

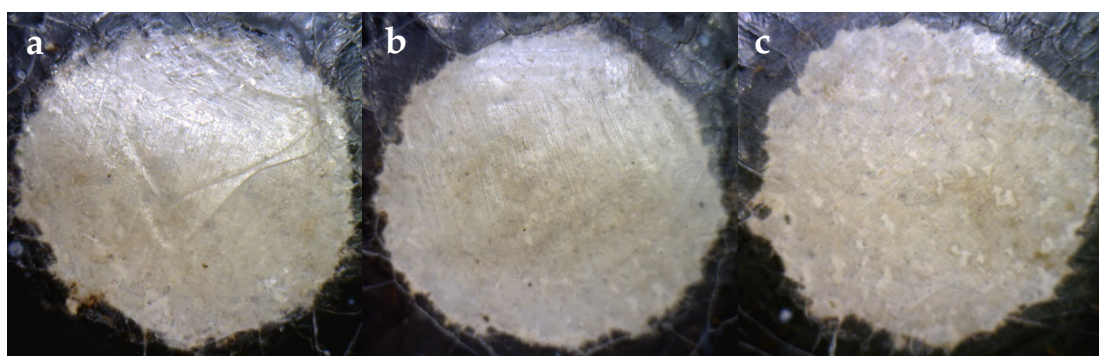


Figure 27. Filled losses with unpigmented NOVA-WR in the ratios of 1:1 (a), 1.5:1 (b) and 2:1 (c) (Cosmoloid H80: Regalrez[®] 1126, parts by weight), after 600h of fluctuating RH

In terms of the influence of pigments/ fillers, in general, the samples without cracks or with less intense cracking contained Champagne chalk, either alone or mixed with one of the pigments. This was especially true for the samples subjected to fluctuating relative humidity, and was not as evident in samples subjected to fluctuating temperature.

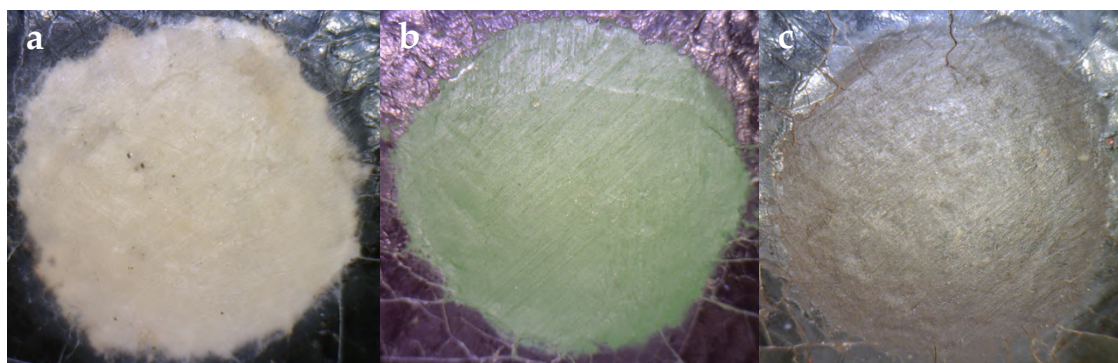


Figure 28. Filled losses with NOVA-PWR, with Champagne chalk (a), Champagne chalk and chrome oxide green (b), and with Champagne chalk and burnt umber (c)

When comparing the different pigments in the various formulations (both NOVA-PWR and Gamblin-PWR), burnt umber developed the highest degree of cracking, followed by chrome oxide green and, finally, titanium white.

d. Changes in hardness

Hardness was measured after each environmental trial and compared with the control samples. Three measurements were done in order to calculate their average and standard deviation. The results (table 13) correspond to the difference between the hardness measured after each trial and the hardness measured in the control samples. Negative values correspond to a decrease in hardness and positive values to an increase in hardness. As noted, the hardness values presented can only be used for comparison between the different formulations and between the control samples and those exposed in the environmental chamber. Because the standard deviation was higher or very close to the calculated variation in hardness, these results were generally inconclusive. However, there were some trends evident:

- A slight increase in hardness was measured in the majority of the samples subjected to fluctuating relative humidity (10-90%) and fluctuating temperature (10-40° C);
- A slight loss in hardness was measured in samples exposed to temperatures of 50 and 60°C, although the difference was very small or very close to the calculated standard deviation;
- In general, samples containing pigments/filler presented lower differences in hardness after exposure in the environmental chambers than those containing only Cosmoloid H80 and Regalrez® 1126;
- The highest differences in hardness were measured in samples exposed to 60°C.

Table 13. Differences in hardness measured in NOVA-PWR samples and one Gamblin-PWR sample, with a Shore D durometer, after environmental trials 2-5 (see Appendix V for recipes of the samples)

Sample	Δ after fluctuating RH trial	Δ after fluctuating temperature trial	Δ after exposure to 50°C	Δ after exposure to 60°C
Gamblin "Neutral Base"*	1.5 ± 0.8	1.0 ± 1.0	-1.5 ± 1.1	-3.0 ± 0.8
W1:R1	2.5 ± 1.1	1.5 ± 0.7	-1.5 ± 0.8	-3.5 ± 1.3
W1.5:R1	2.0 ± 1.0	2.5 ± 1.1	-1.0 ± 0.8	-1.5 ± 1.5
W2:R1	1.0 ± 0.9	3.0 ± 0.8	-1.0 ± 0.8	-2.0 ± 0.6
W1:R1 + CC	-0.5 ± 1.2	-0.5 ± 0.7	-0.5 ± 0.9	-1.5 ± 0.9
W1.5:R1 + CC	1.0 ± 0.5	1.0 ± 1.0	-1.0 ± 0.9	-3.5 ± 0.9
W2:R1 + CC	1.0 ± 1.1	1.5 ± 1.4	0.5 ± 1.3	-3.5 ± 1.2
W1:R1 + TW	1.0 ± 0.4	0.0 ± 0.6	-2.0 ± 1.0	-3.0 ± 0.7
W1.5:R1 + TW	0.5 ± 0.7	0.5 ± 0.7	-1.5 ± 0.9	-2.5 ± 0.9
W2:R1 + TW	1.0 ± 0.6	1.5 ± 0.6	0.0 ± 0.5	-3.0 ± 0.6
W1:R1 + CG	-1.0 ± 1.3	1.5 ± 1.6	-1.5 ± 1.6	-2.5 ± 1.6
W1.5:R1 + CG	0.0 ± 0.8	-1.0 ± 0.7	-0.5 ± 0.8	-2.0 ± 0.6
W2:R1 + CG	0.0 ± 0.7	-0.5 ± 0.6	-2.0 ± 0.6	0.5 ± 0.7
W1:R1 + BU	-1.0 ± 1.1	-1.0 ± 0.7	-1.0 ± 1.0	-3.5 ± 1.0
W1.5:R1 + BU	-0.5 ± 0.7	-0.5 ± 1.1	-1.0 ± 0.7	-2.5 ± 0.9
W2:R1 + BU	0.0 ± 1.0	0.5 ± 0.8	-2.0 ± 0.9	-4.0 ± 0.7
W1.5:R1 + TW + CC	0.0 ± 0.9	-1.0 ± 0.6	-1.5 ± 0.7	-2.0 ± 0.9
W1.5:R1 + CG + CC	0.5 ± 0.8	1.5 ± 1.3	0.5 ± 0.8	-1.0 ± 1.1
W1.5:R1 + BU + CC	1.0 ± 0.6	1.0 ± 0.6	-2.0 ± 0.6	-3.5 ± 0.8

W = Cosmoloid H80 (wax); R = Regalrez® 1126 (resin); CC = Champagne chalk; TW = titanium white; CG = chrome oxide green; BU = burnt umber

*Due to the lack of available materials, it was only possible to conduct hardness measurements on the "Neutral Base" formulation from Gamblin Conservation Colors

e. Molecular changes evident with ATR-FTIR

A set of NOVA-PWR and Gamblin-PWR samples were analysed using ATR-FTIR to determine whether fluctuating relative humidity and temperature, or extreme temperature induced detectable molecular changes. The set included samples subjected to relative humidity fluctuations (10-90%), samples subjected to moderate temperature fluctuations (10-40°C) and samples that were heated up to 60°C in the environmental chamber environment (with uncontrolled RH). Control samples (stored in ambient conditions¹⁹) were included.

Results show that none of the NOVA-PWR samples subjected to environmental trials showed clear differences in the ATR-FTIR spectra when compared to the control samples. Even though some minor differences in the relative intensity of the bands were visible, these were not detected in all replicates submitted to the trial, therefore, they cannot be considered. This was true for samples with wax-resin only and those with the three pigments and filler, either alone or in combination. No new bands were formed, and no bands disappeared or shifted. The spectrum of the samples in the ratio 1.5:1 (Cosmoloid H80:Regalrez® 1126, parts by weight) is given below as an example of the results (figure 29).

¹⁹ Conditions in footnote 18 (page 49).

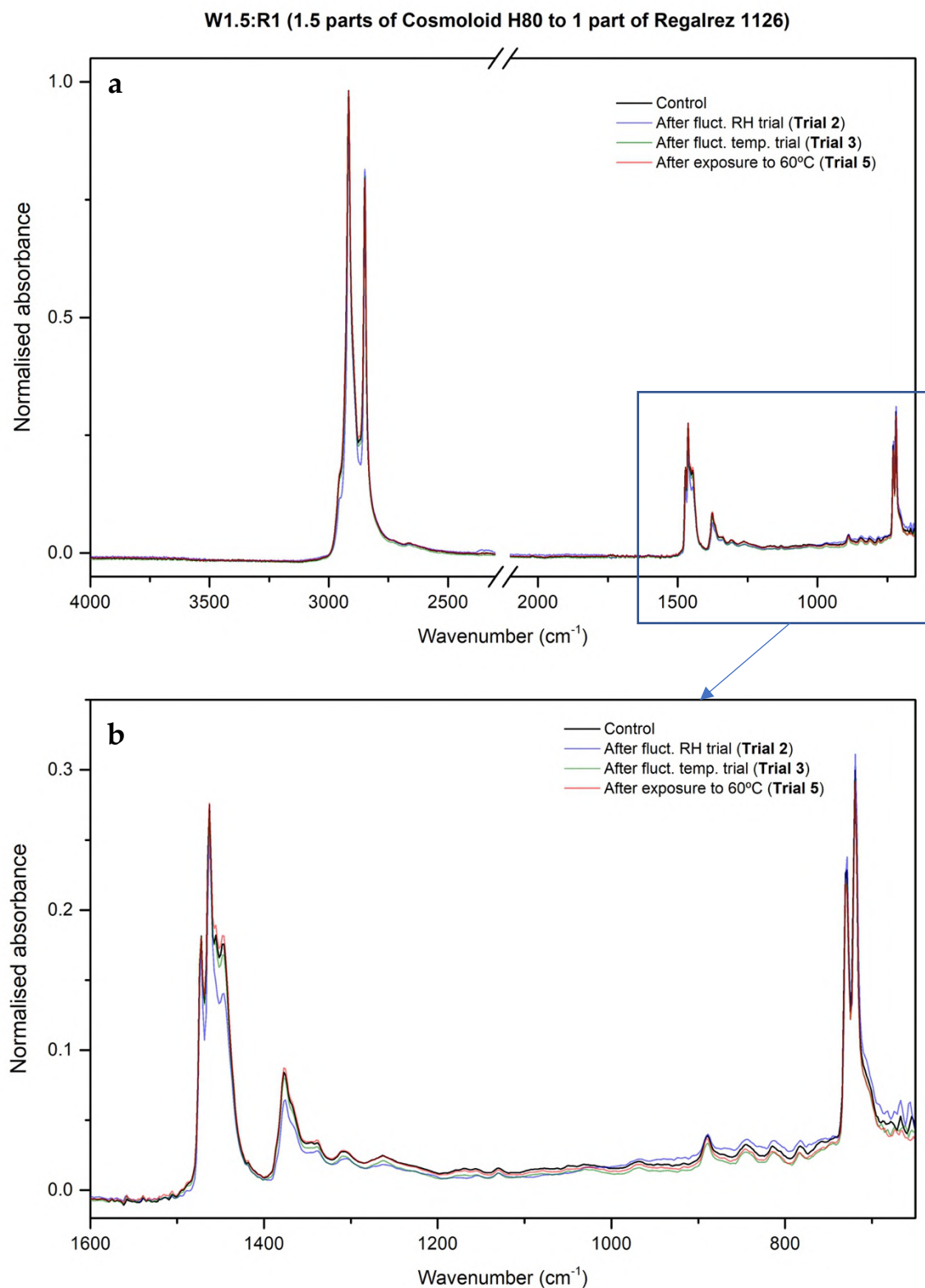


Figure 29. a) Overlapped ATR-FTIR spectra of the NOVA-PWR in the ratio of 1.5:1 (Cosmoloid H80:Regalrez[®] 1126, parts by weight) control sample and the samples of the same formulation after being subjected to trials 2, 3 and 5. Region between 2100 and 2350 cm^{-1} removed for not showing any relevant information; b) Detail of spectra above in the 1600-650 cm^{-1} region.

The ATR-FTIR spectra of the Gamblin-PWR samples subjected to the environmental trials did, however, show some significant changes when compared to their respective control samples. The variations were, in general, the same for both pigmented and unpigmented samples, and were mostly visible in the region of 1600-650 cm^{-1} . These were:

- The bands at 1472 and 1463 cm^{-1} change in intensity, i.e., in the control sample, the band at 1472 cm^{-1} is lower in intensity than the band at 1463 cm^{-1} , while in all the samples subjected to environmental trials, the band at 1472 cm^{-1} is much higher in intensity than the one at 1463 cm^{-1} . These bands were visible in the reference spectra of beeswax and microcrystalline wax and were attributed to the CH_2 scissor deformation vibrations;
- A new band appears at 1126 cm^{-1} . This band – for which no attribution has been found – is not visible in any of the spectra from the control samples but is present in all the spectra of the samples that went through environmental trials. The new band is clearly visible in figure 30(c).

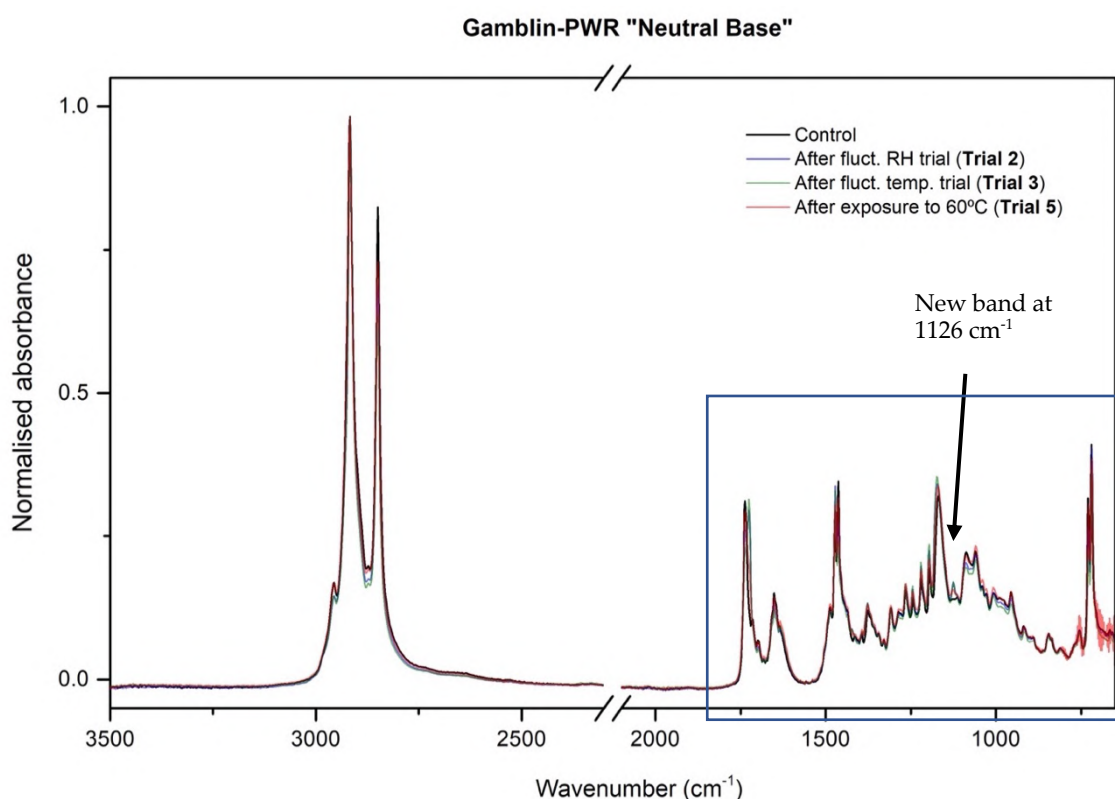


Figure 30. Overlapped ATR-FTIR spectra of the Gamblin-PWR “Neutral Base” control sample and the samples of the same formulation after being subjected to trials 2, 3 and 5. Region between 2100 and 2350 cm^{-1} removed for not showing any relevant information. Detail of the 1600-650 cm^{-1} region in the image below.

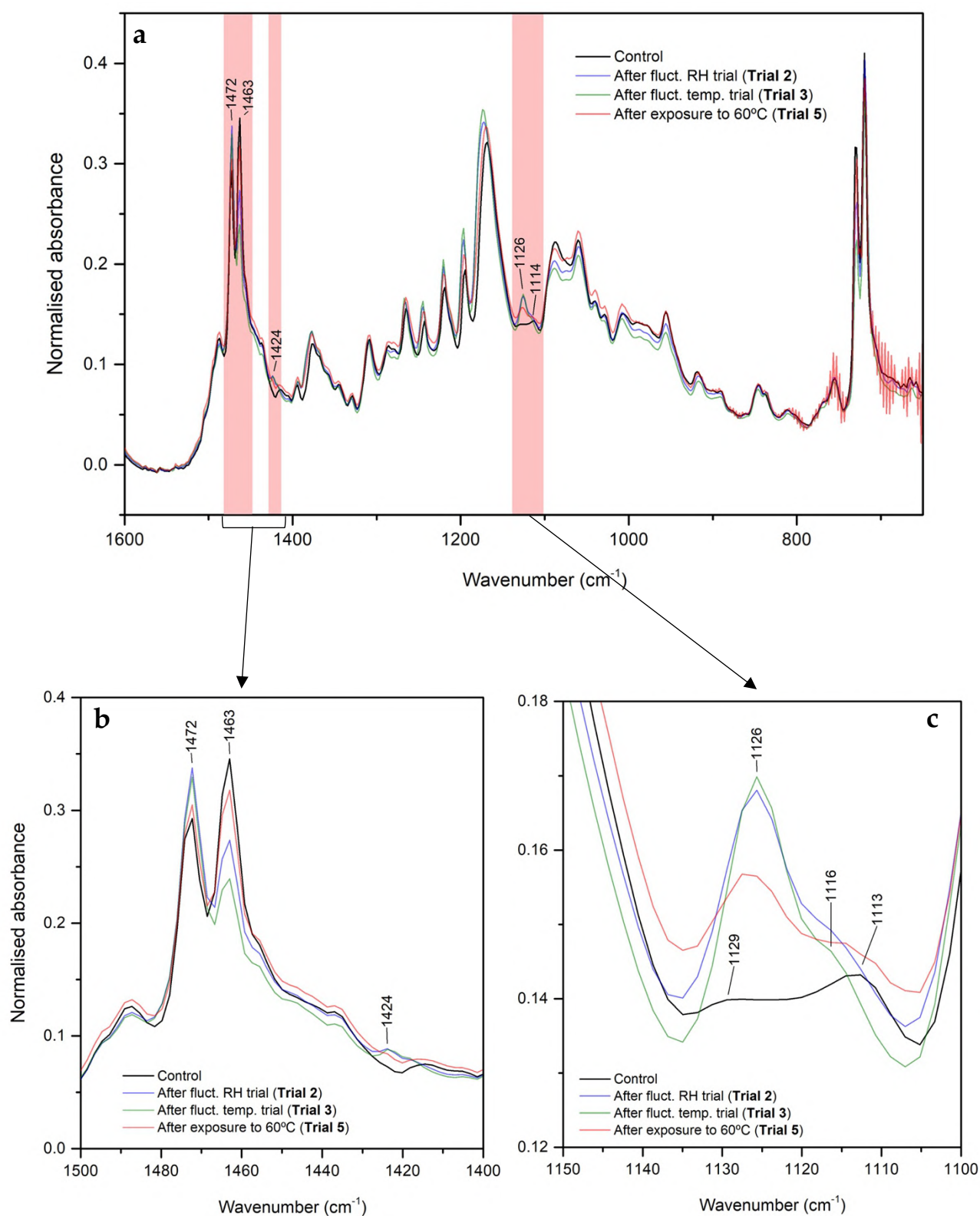


Figure 31. Overlapped ATR-FTIR spectra of the Gamblin-PWR “Neutral Base” control sample and the samples of the same formulation after being subjected to trials 2, 3 and 5, in the region between 1600-650 cm^{-1} (a), 1500-1400 cm^{-1} (b) and 1150-1100 cm^{-1} (c)

6. Compatibility of the NOVA-PWR formulations with a selection of varnishes and inpainting media, with notes on the removability of the PWR

The last parameter studied was the compatibility of the NOVA-PWR to a selection of varnishes and inpainting media. This was done considering the possibility of the PWR mixtures serving three purposes:

- 1) Allow an accurate and quick colour match which does not change on application. This is possible because pigmented wax-resin mixtures do not change from warm to cool temperature states, whereas generally it's harder to get an exact colour match with the other inpainting materials. Moreover, it is also possible to place a piece of room temperature PWR directly on top of the paint surface to see how well it matches. Pre-matched coloured PWRs may or may not require a varnish layer on top depending on whether the painting is varnished. (Note that PWRs can be polished with a soft cloth to achieve a high gloss, or touched with solvent to render them matte);
- 2) Allow minor surface adjustments to colour-matched PWRs using glazes (for old or distressed surface effects or for slight changes in hue). In this case, it would be necessary to use inpainting media, perhaps more diluted and with or without a protective coating layer underneath;
- 3) Following a more traditional method of reintegrating losses, PWR are also meant to allow areas to be infilled solely with a base colour and inpainted afterwards. In this case, wax-resin mixtures could be applied together with an inert filler, such as chalk, or a pigment, such as titanium white, or even a mixture of both, depending on the required base colour. An isolation layer would be applied on top of the infill to protect it in case the subsequent inpainting layer needed to be removed (requiring solvents that could attack the infill). Inpainting would be carried out on top of the isolation layer. In specific cases, an isolation layer may not be necessary or even recommended (e.g., if the inpainting media were only compatible with varnishes whose solvents would attack the infill) and inpainting would have to be done directly on top on the infill.

To determine compatibility, five NOVA-PWR formulations, all prepared in a 1.5:1 ratio (Cosmoloid H80:Regalrez® 1126, parts by weight), one unpigmented and the others containing Champagne chalk, titanium white, chrome oxide green and burnt

umber, were applied on a prepared canvas and given a texture to evaluate any changes or dissolution of the material by the action of solvents in the varnishes to be clearly visible.

The formulations were, afterwards, brush²⁰ coated with six synthetic resin varnishes (see Table 14) in different areas (leaving one area unvarnished). Six different inpainting media were, then, applied on top on the varnish layers (and the unvarnished areas) and, afterwards, removed with two different solvents. Removing the inpainting media with solvents was done to establish whether the varnish isolation layers were sufficient to protect the PWR infill from being attacked by the solvents.

Of the six inpainting media tested (see Table 14), only Gamblin Conservation Colours – the ones expected to have the best results – were applied in three different colours: Indian yellow and burnt umber (commonly used as glazes for old/disturbed surface effects); and ultramarine blue, to create a slight contrast to the colour of the infills. Two different dilutions were employed: taken directly from the jar and diluted with ethanol to create glaze effects. The other inpainting media were applied mixed with ultramarine blue and in one dilution. The various inpainting media were applied on top of three Paraloid B-72 varnishes and on the unvarnished area. Table 14 summarises the results for the varnishes and the inpainting media.

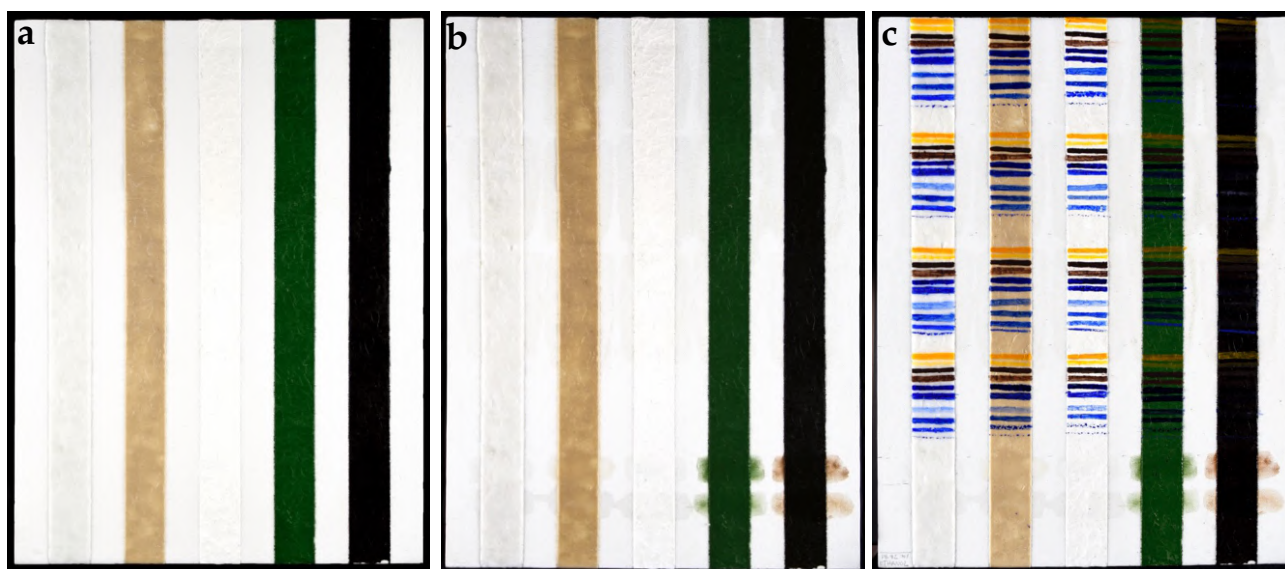


Figure 32. a) Strips of NOVA-PWR fillers applied on a prepared canvas; b) the same strips of NOVA-PWR after varnishes had been applied on top; c) the same strips of NOVA-PWR after varnishes and inpainting media had been applied

²⁰ Although the results might be more positive for some varnishes if they had been sprayed, the decision to brush-apply the varnishes was based on the principle that good results with a brush application are more likely to signify good results in a spray application than the opposite.

Table 14. Results from the application of varnishes and inpainting media on top of the PWR infills

Varnishes	Varnish alone	Inpainting media applied on top of the varnish layer				
		Gamblin Conservation Colors in Laropal® A81	Kremer retouching chips in Paraloid B72 (solvent: ethanol 96%)	Kremer retouching colours in Shellac (solvent: ethanol 96%)	Golden acrylics (solvent: distilled water)	Kremer watercolours in Gum Arabic (solvent: distilled water)
PB72 10% in 1-methoxy-2-propanol (10g in 100ml)	✓	✓	✓	✓	✓	✗
PB72 5% in 1-methoxy-2-propanol (5g in 100ml)	✓	✓	✓	✓	✓	✗
PB72 2.5% in 1-methoxy-2-propanol (2.5g in 100ml)	✓	✓	✓	✓	✓	✗
PB72 10% in ethanol (10g in 100ml)	✓	✓	✓	✓	✓	✗
Laropal® A81 20% in Shellsol® A and Shellsol® D40 (20g in 40ml of Shellsol A + 60ml of Shellsol D40)	✗	-	-	-	-	-
Regalrez® 1094 25% in Shellsol® T (25g in 100ml)	✗	-	-	-	-	-
No varnish	n.a.	✓	✓	+/-	✗	✗

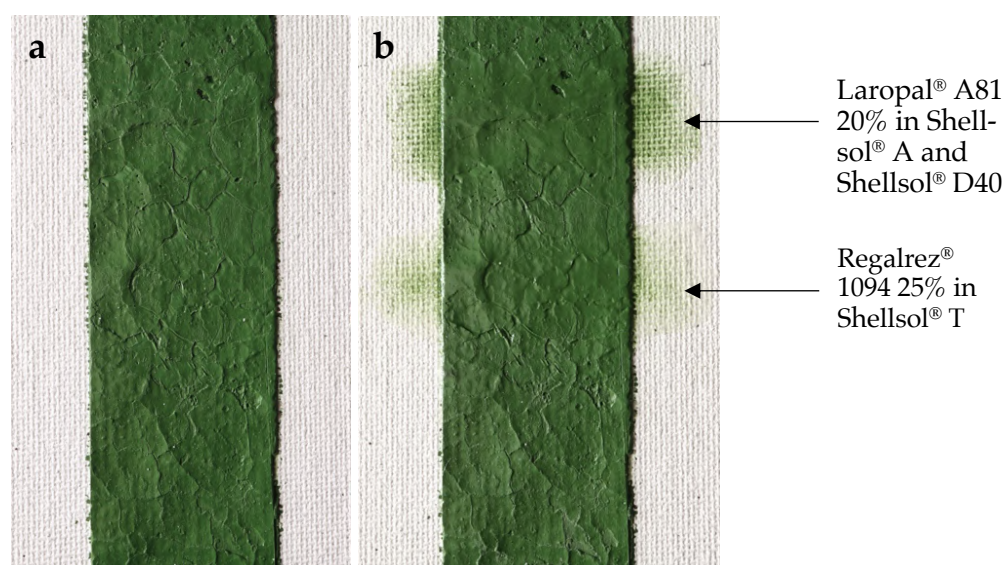


Figure 33. Area of the infill made with NOVA-PWR with chrome oxide green before (a) and after (b) the application of Laropal® A81 20% in Shellsol® A and Shellsol® D40 and Regalrez® 1094 25% in Shellsol® T

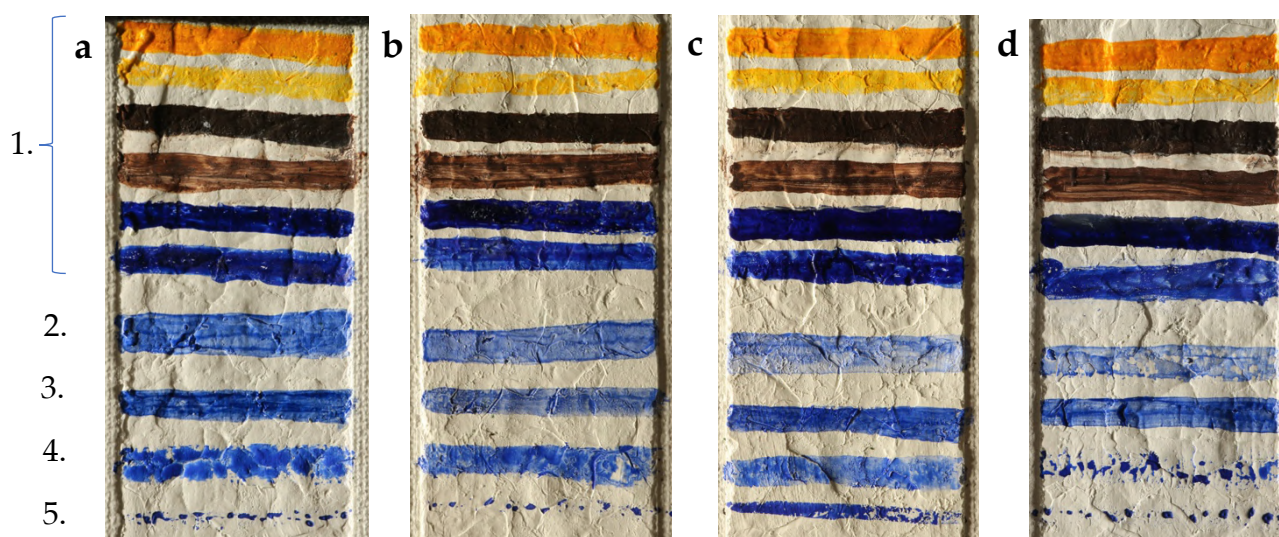


Figure 34. In-painting media applied on NOVA-PWR with titanium white, varnished with Paraloid B72 10% (a), 5% (b) and 2.5% (c) in 1-methoxy-2-propanol, and unvarnished (d). 1. – Gamblin Conservation Colours in Laropal® A81; 2. – Kremer in Paraloid B72; 3. – Kremer in Shellac; 4. - Golden acrylics; 5. – Kremer watercolours in gum arabic

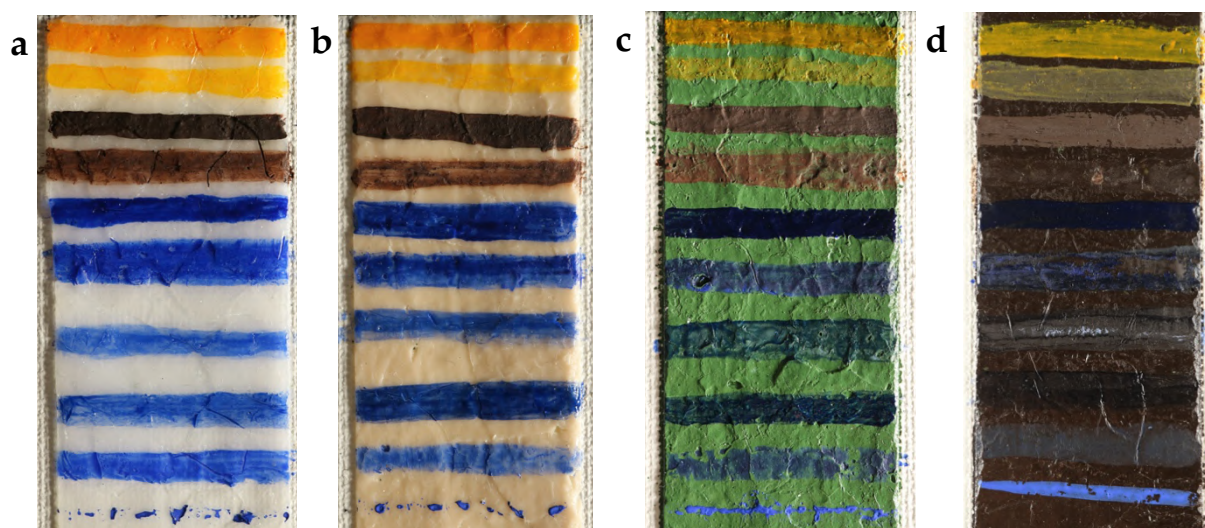


Figure 35. In-painting media applied on NOVA-PWR unpigmented (a), with Champagne chalk (b), chrome oxide green (c) and burnt umber (d). In all cases the in-painting media was applied on top of a varnish layer of Paraloid B72 10% in 1-methoxy-2-propanol

To evaluate the protective function of each isolating varnish all in-painting media were removed using both ethanol and white spirit (~17% aromatics). The cotton swabs used for removal were observed for evidence of colour or binder pick-up. Since the in-painting media had only been applied on top of three Paraloid B-72 varnishes in 1-methoxy-2-propanol, only those were considered for this assessment and compared with the non-varnished area. The results for PWR infills containing chrome oxide green are given here since green pigment was not used for in-painting making it easier to detect any green on the cotton swabs from the underlying infill.

Table 15. Results from removability of inpainting materials with solvents in cotton swabs

Varnish layer	Ethanol 96%	White spirit (~17% aromatics)
PB72 10% in 1-methoxy-2-propanol	1	3
PB72 5% in 1-methoxy-2-propanol	2	5
PB72 2.5% in 1-methoxy-2-propanol	2	8
No varnish	3	10

1 – No visible PWR pickup; 10 – Cotton swab completely green

The results were close to what was expected: 96% ethanol had almost no effect on the PWR infill, even where no varnish layer had been applied, while white spirit, which is known to dissolve mixtures of wax and resin, did promote the dissolution of the infill, even with a protective varnish layer. When comparing the three varnish layers, the one with the highest percentage of resin (10%) was the most effective in protecting the PWR underneath from both solvents. The varnish with the lowest percentage of resin (2.5%), still proved to be rather effective in protecting the PWR infill from 96% ethanol, but offered almost no protection from white spirits (~17% aromatics).

In conclusion, the best results were obtained with Paraloid B-72 in 1-methoxy-2-propanol, with the proportion of 10% Paraloid B-72 being the most effective in protecting the infill layer. Of the inpainting media tested, Gamblin Conservation Colors with Laropal® A81 and Kremer Retouching Chips in Paraloid B-72 showed the most promising results and were compatible both with the varnish layers and with the unvarnished PWR infill.

Based on these results, varnishing PWR infills with an isolation layer of a Paraloid B-72 in 1-methoxy-2-propanol (between 5 and 10%) and inpainting on top with either Gamblin Conservation Colors with Laropal® A81 or Kremer Retouching Chips in Paraloid B-72 produced positive results. Both inpainting media can also be applied directly onto the infill without disturbing the surface texture. It is important to note, however, that 1-methoxy-2-propanol, for its “high-moderate” swelling action on oil paint (Phenix et. al., 2021, p. 572) should only be used in a local isolation layer over the fills and not as solvent for varnishing oil paintings.

Notes on the removability of the PWR:

The removability of the PWR formulations was not tested in depth in this research, however positive results were experienced when removing excess PWR both

mechanically and with mild aliphatic solvents (in this case, white spirits) during their use in the case studies (Appendix VIII). The ease of removability has been covered by Vega, who tested the removability of the WRs infills both mechanically (using a wooden stick) and with solvents (Shellsol[®] D and white spirit) two weeks after application (Vega, 2016, p. 28). According to Vega, “most of the material can be gently removed with the sharp edge of a bamboo stick without causing damage to the paint surface”. Following mechanical removal, Vega suggests “cleaning with white spirit or one of the Shellsols[®] (e.g., Shellsol[®] D)” (Vega, 2016, p. 33).

Conclusions and future work

Pigmented wax-resin formulations containing **Cosmoloid H80 (wax) and Regalrez® 1126 (resin) (NOVA-PWR), in a ratio of 1.5:1** (wax:resin, parts by weight), and mixed with pigments and/or fillers, have shown very promising results in terms of workability and stability to different environmental conditions. They promise to be good alternatives to other infilling materials and methods already in use by paintings conservators, and offer an alternative to Gamblin Pigmented Wax/Resins, for example for paintings on metal substrates. They are of particular value for infilling paintings which will not be inpainted or varnished²¹ (e.g. glossy infills) where bloom would be a problem.

This study shows that the best binder ratio in NOVA-PWR is that of 1.5:1 (Cosmoloid H80:Regalrez® 1126, parts by weight) and that it should be maintained for successful fills across a wide range of RH and temperature. Also demonstrated is that the amount of filler and pigment added can be significantly adjusted to meet the desired visual properties (e.g., in terms of opacity) and physical properties (such as hardness and flexibility) of the infill. See Appendix V for the recipes of the most successful formulations (highlighted in green).

Significant findings regarding the development of bloom were made. The most important was a confirmation that NOVA-PWR formulations do not develop bloom in the same environmental conditions in which Gamblin-PWR clearly develop the

²¹ Although this was not studied in detail in this dissertation, von Lenthe's results indicated that bloom was visible on unvarnished pigmented beeswax samples but not visible in the same samples when varnished or coated with inpainting materials and subjected to same environmental trials.

phenomenon. Gamblin-PWR develop bloom in both fluctuating relative humidity (10-90%) with constant temperature (25°C), and fluctuating temperature (10-40°C) with constant relative humidity (55%), although the resulting appearance differed and was more intense with fluctuating temperature.

While bloom was mainly visible on the glossy side of Gamblin-PWR rectangular samples, it was not visible on Gamblin-PWR applied to losses in the model painting. In the latter case, these infills had a more matte appearance due to having been levelled with solvent. This difference is a very good indication of the role that the level of gloss of the PWR surface plays in making bloom more or less visible. ATR-FTIR analysis of the bloom layer from a Gamblin-PWR “Burnt Umber” sample subjected to the fluctuating RH trial showed a strong similarity with the beeswax reference sample, confirming previous studies suggesting that bloom is a migration to the surface of components present in beeswax.

In terms of stability to high temperatures, NOVA-PWR in the ratio of 1.5 parts of Cosmoloid H80 to 1 part Regalrez® 1126 (by weight) was able to withstand temperatures up to 70°C without losing carved texture or three-dimensional surface features (e.g., recreations of brushstrokes). This does not mean that the material itself will not soften, but rather that it will keep its given shape if it cools down again without being disturbed (e.g., by touching). This wax:resin ratio did not develop blisters on the surface when subjected to temperatures between 60 and 70°C (as observed in samples with higher amounts of wax).

Embrittlement and cracking are problems that need further attention. However, as detailed in Appendix IV, the model paintings used for this project were prepared in 2011 not using oil paint, but rather a coating made of Dammar resin dissolved in distilled turpentine and dry pigments. This meant that the paintings were exceptionally hard and brittle, possibly leading to unrealistic results and greatly influencing the cracking lines in the NOVA-PWR samples. Repeating this experience, using model paintings made, for example, with oil paint, could lead to more realistic results in terms of cracking and embrittlement of the PWR formulations.

The differences in the visual appearance of cracking between the NOVA-PWR and Gamblin-PWR also require further research. Results suggest that Gamblin-PWR are tougher and more resistant to cracking than the NOVA-PWR, although the former are more prone to cracking near the paint/infill edges suggesting possible shrinkage. To mitigate embrittlement/cracking, one option could be to replace the Regalrez® 1126

resin with a resin of lower T_g ²² (considering, however, that lowering the overall T_g of the mixture may cause it to be softer at room temperature and more prone to attract dirt). Another option, although much less favoured, would be to add a plasticiser that is compatible with both the wax and the resin. KratonTM G rubbers are commonly used together with Regalrez[®] resins to improve their plasticity, but require investigation in terms of their compatibility with the wax-resin combination. Moreover, they are dissolved in solvents and not with heat, leading to the necessity of adding solvents to the mixture. Adding chalk to the PWR mixtures seemed to have improved the behaviour of the infills in terms of cracking, although this effect also requires further testing.

While hardness measurements were not conclusive, results suggest that an increase in hardness may be related to fluctuating relative humidity and temperature (possibly to lower temperatures) and that a decrease in hardness may result from exposure to higher temperatures.

On a molecular level, no visible differences in the ATR-FTIR spectra of the NOVA-PWR samples were detected before and after the environmental trials. A new band was, however, detected on the spectra of the Gamblin-PWR after exposure. No attribution was found for the new band at 1126 cm^{-1} , but further research on this could lead to valuable results, both for the manufacturer and the conservators using these materials. The changes in the ATR-FTIR spectra for the Gamblin-PWR samples were not sufficient to conclude that they result from a deterioration process. They may, for example, be related to physical changes and the movement of components within the samples which cause different bands to become more visible or intense. A more sensitive technique, such as micro-FTIR or Gas Chromatography Mass Spectrometry (CG-MS), could provide more precise results that are not visible with ATR-FTIR.

Moreover, NOVA-PWR were found to be compatible with Paraloid B-72 isolation varnishes applied with 1-methoxy-2-propanol, and with widely available inpainting media. A successful reintegration using the NOVA-PWR infill in the ratio of 1.5 parts of Cosmoloid H80 to 1 part of Regalrez[®] 1126 (by weight), mixed with pigments and/or fillers, can be achieved with an isolation layer of Paraloid B-72 10 or 5% in 1-methoxy-2-propanol, followed by inpainting with Gamblin Conservation Colors (in Laropal[®] A81) and finished with another local coating layer of Paraloid B-72. For a

²² One possibility – that requires testing – could be to go back to Regalrez[®] 1094 resin, used by Vega (2016) in his research. Regalrez[®] 1094 resin has a T_g of 40°C (Kremer Pigmente, n.d. (b)), as opposed to the T_g of 67°C (Kremer Pigmente, n.d.), of Regalrez[®] 1126.

final coating layer to be applied overall on an oil painting (and not locally on the infill), it is highly recommended to replace the 1-methoxy-2-propanol solvent because of its medium-high swelling effect on oil paint, as explained above. Other solvents could be considered if the final varnish layer is sprayed instead of brushed on the surface, lowering the likability of it affecting the wax-resin fill (especially if it has received inpainting and/or local varnishing on top). Other options, as discussed above, are possible.

Finally, the practical work presented in the Appendix VIII demonstrated the versatility of the NOVA-PWR formulations, which proved to be useful both in infilling a 17th century oil painting, and in reintegrating a modern abstract acrylic painting. In the first case, the NOVA-PWR were used not only to infill several losses, of different dimensions and shapes, but were also applied on a large insert, in which texture was imprinted using a silicone mould. Various application methods were tested and confirmed, as well as removability techniques and ways to manipulate the surface (e.g., carving texture with a scalpel or a dental probe). The second case study was especially useful in validating the great advantage of the NOVA-PWR of infilling and reintegrating a loss in one single step, by adding pigments (or mixtures of pigments) to the Cosmoloid H80-Regalrez® 1126 binder. Missing areas of impasto were easily recreated by sculpting the NOVA-PWR with a spatula and mild heat. Also confirmed was the possibility of rendering the surface of the PWR infill glossier, by simply rubbing the surface with a spatula; or more matte, by placing a sheet of non-silicone coated baking paper (intended for cooking) over the infill and slightly scraping on top with a spatula, or by gently touching the surface of the infill with a cotton swab dipped in white spirits.

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Appendices

Appendix I – Equipment, materials and suppliers

1) Equipment description:

- o **Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR):** The spectra were obtained by an Agilent Handheld 4300 spectrophotometer equipped with a wire-wound source, a ZnSe beam splitter, a Michelson interferometer, and a thermoelectrically cooled DTGS detector. Spectra were acquired with a diamond ATR module, 128 scans and 4 cm⁻¹ resolution, between 4000-650 cm⁻¹. The spectra were analysed in the Omnic 8 software but edited and normalised (to [0, 1]) in Origin Pro 2016;
- o **Digital microscopy:**
 - Digital microscopy photographs of the bloom layer of the Gamblin-PWR samples were acquired with a Dino-Lite Edge Optical Microscope AM7915MZTL. The photographs were acquired with and without the polarization filter and the magnification used varied from 50x to 85x. The DinoCapture 20.0 programme was used to visualize, capture and process the images.
 - All the other digital microscopy photographs were taken with a Dino-Lite Digital Microscope PRO AD413 series. The magnification used varied from 20x to 50x. The DinoCapture 20.0 programme was used to visualize, capture and process the images.
- o **Digital photography:**
 - Studio photographs with normal light were taken with a Nikon D500 digital camera, with a 18-200mm f3.5-5.6G ED AF-S DX VR Zoom-Nikon lens
- o **Macro-photography:**
 - Macro photographs of the samples were taken with a Canon EOS M10 digital camera, with a Canon Macro Lens EF-M 28 mm 1:3.5 IS STM

2) Other equipment:

- o Byko opacity charts, BYK-Gardner GmbH, Lausitzer Str. 8, D-82538, Prufkarte 2854
- o Environmental chamber Aralab FITOCLIMA 300 EC20
- o Cosori® coffee mug warmer. <https://www.amazon.com/COSORI-Induction-Warmer-Beverage-Temperature/> (consulted June 2021)
- o Data Logger: EL-USB-2 Temperature & Humidity Data Logger with USB, Lascar Electronics
- o Digital precision balance standard, Ohaus
- o Digital Shore D durometer hardness tester, with a sharp cone point SR0.1mm, 30° included angle, range 0~100HD, resolution 0,5HD. Model nr.: 0226064
- o Digital thermometer, Habor
- o Hot plate magnetic stirrer, 34532, Snijders
- o Hydraulic Dry Mounting and Laminating Heat Press on Stand, Ademco, Model 2226
- o Rekoma High Intensity Daylight Lamps, article nr. 5521010. <https://deffner-johann.de/en/rekoma-high-intensity-daylight-lamp-black.html> (consulted June 2021)
- o Saga Baking Paper, from Sligro. <https://www.sligro.nl/p.32405.html/saga-kook-bakpapier-38-cm-rol-50-meter.html> (consulted June 2021)
- o Tacking Spatula Iron Thermocontrolled, Restaurar & Conservar
- o Whipmix Wax CarvingPencil: Wax carving pencil, commercialised by Gamblin, America. <https://www.gamblincolors.com/conservation-colors/> (consulted June 2021)

Table I. 1. Materials used in the research and their suppliers and date of purchase

Material	Supplier	Date of purchase
1-methoxy-2-propanol ≥99.5%	Sigma-Aldrich www.sigmaaldrich.com	FCT-PNT stock
96% ethanol		FCT-PNT stock
Arbocel® BC 200	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	SRAL stock
Beeswax, bleached		Purchased 2021
Champagne chalk (#58000)		SRAL stock and purchased 2020
IGI Wax Cosmoloid H80 microcrystal-line wax	The International Group, Inc. https://igiwax.com/	FCT-PNT stock a
Evacon R Conservation adhesive	Conservation By Design, Ltd. https://www.cxdinternational.com/	SRAL stock
Gamblin Conservation Colors “Ultramarine Blue”, “Burnt Umber” and “Indian Yellow”	Gamblin Conservation Colours www.gamblincolors.com	FCT-PNT stock and purchased 2021
Gamblin Pigmented Wax/ Resin “Neutral Base”, “Burnt Umber”, “Chrome Oxide Green” and “Titanium White”		FCT-PNT stock and purchased 2020
GEPE Diapositive frames, 34 x 23 x 1 mm GP2 004	Kamera Express https://www.kamera-express.nl/	Purchased 2019
Golden Acrylics “Ultramarine blue”	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	Purchased 2021
Kaolin (#58250)	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	SRAL stock
Kremer® retouching chips in Paraloid B 72 “Ultramarine blue”		Purchased 2021
Kremer® retouching colours in Shellac “Ultramarine blue”		
Kremer® watercolours in Gum Arabic “Ultramarine blue”		
Klucel® G		SRAL stock
Laropal® A81	PEL Preservation Equipment www.preservationequipment.com/	FCT-PNT stock
Melinex® 100μ		SRAL stock
Parafil RT 20 non-woven polyester fabric	Deffner & Johann GmbH https://deffner-johann.de/en/	SRAL stock
Paraloid™ B-72	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT stock
Pigments: Alizarin, Burnt Umber, Terra di Sienna, Titanium White and Yellow Ochre		SRAL stock
Pigments: Cobalt blue and Madder Lake	H. Schmincke & Co. GmbH & Co. KG www.schmincke.de/en.html	SRAL stock
Plextol® D360 and B500	CTS www.ctseurope.com/gb/	SRAL stock
Portafill® A40	Laboratory Jan de Poorter www.ankerpoort.com	SRAL stock
Reemay® fabric	Restaurar e Conservar, Lda. www.restaurarconservar.com	Purchased 2020
Regalrez® 1094	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT stock
Regalrez® 1126	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT stock, SRAL stock and purchased 2020
Shellsol® A	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT stock
Shellsol® D40		FCT-PNT stock
Shellsol® T		FCT-PNT stock
Silicone coated Melinex® sheet	PEL Preservation Equipment www.preservationequipment.com/	SRAL stock
Silicone Condensation 20 (Medium Hard)	Silicones and More www.siliconesandmore.com	SRAL stock
Silicone mould Aquasil Ultra+	Dentsply Sirona www.dentsplysirona.com/en-ca/shop	SRAL stock
White spirit EC-No. 919-446-0	Valente e Ribeiro, Lda. www.valenteribeiro.com	Purchased 2020

Appendix II – Further information Cosmoloid H80 and Regalrez® 1126

Cosmoloid H80 microcrystalline wax

Cosmoloid is a brand name for a series of microcrystalline wax formulations, supplied by companies such as Kremer Pigmente GmbH & Co. KG, Talas, C.T.S and Zeus, and manufactured by Astor (now The International Group, Inc.). Cosmoloid waxes have been used in conservation for several purposes, including the lining of paintings and the coating of metal surfaces [1-3], stone [4] and as a material for “sealing small cracks, pinholes or leaks” in musical instruments [5]. It has been added to varnishes to lower gloss and saturation by conservators [6, p. 651]. The use of a microcrystalline wax instead of a natural wax in varnishes is related to the concern that “the natural wax will separate out, imbibe dust, make the varnish sticky, or become cloudy” [6, p. 643].

Microcrystalline waxes are chemically modified waxes obtained from the distillation of petroleum fractions, which are produced from the processing of crude oil. Presently, they are widely used as substitutes for beeswax as well as for new applications [7, p. 25]. Microcrystalline waxes are, according to Pillon [8, p. 65], composed of 0-15 wt% of n-paraffins, 15-30 wt% of iso-paraffins (branched), and 65-75 wt% of naphthenes, with 30-60 carbon atoms and an average molecular weight of 500-800. Depending on the ratio of compounds present, their melting point can range from 60° to 90°C. Other authors refer that their melting range can be between 70 and 100°C, having the highest melting range among waxes obtained from crude oil [9, p. 21].

In the literature, different information on the production of the microcrystalline wax Cosmoloid H80 was found, Von Lenthe [9, p. 20] quotes Jeberien (2003) who reports that “Cosmoloid H80 is a microcrystalline, highly cross-linked wax produced during the polymerization of ethylene”, while McIntyre [10, p. 25] mentions that Cosmoloid H80 is “a petroleum-based, microcrystalline wax, with saturated branched and cyclic aliphatic hydrocarbon chains”, with a melting range of 74-80°C and a flash point of 260°C.

In 1996, Sommermeyer refers to the edition of “Materials in Conservation” published in 1990 in which Horie recommends Cosmoloid as being an inert material with a suitable degree of hardness [9, p. 21]. In the most recent edition of the book there is, however, no explicit reference to Cosmoloid H80. In terms of ageing behavior, Cosmoloid H80, being a highly cross-linked synthetic wax with a very fine crystal structure, has no functional groups on which oxidation processes can take place. It is, therefore, considered to be highly stable against chemical degradation [9, p. 21].

Regalrez® 1126 hydrogenated hydrocarbon resin

Regalrez® 1126 is a synthetic low molecular weight (LMW) hydrogenated hydrocarbon resin that, side by side with Regalrez® 1094, has been widely used in conservation. Even though Regalrez® 1094 is more commonly used, especially as a picture varnish [11], Regalrez® 1126 was chosen for its higher molecular weight, higher glass transition temperature (T_g) and higher softening point (values given in Table 3). In the particular case of being used in a formulation to be used for infilling, having a higher softening point could mean that a recreation of an impasto or a texture reproduction are more likely to maintain their shape and sharpness when exposed to higher temperatures. The higher T_g of Regalrez® 1126 also means that the resin is less “tacky” at room temperature, being less likely to attract dirt. Even if a higher T_g could lead to a more brittle material, the combination with wax (in wax-resin formulations), which

has been used as a plasticizer to Regalrez® resins [12, p. 365], is expected outcome this problem.

The Regalrez® series (which includes at least seven different hydrocarbons [14, p. 1]) was introduced by Hercules Inc. in 1983 [13, p. 69], and is currently produced by Eastman Chemical Co. The use of Regalrez® products in the conservation field started in the 1990s, after René de la Rie and Christopher McGlinchy published on their application as varnishes for paintings [11].

LWW resins, which have a weight-average molecular weight in the range 800–6500 [15, p. 134], have been described as “a class of highly amorphous materials (...) with high refractive index” [16, pp. 563-564], low viscosity [17, p. 51] and a higher glass transition temperature than natural resins [11, p. 70]. They are also known to dissolve in “far less polar solvents than are necessary for natural, ketone, and methacrylate resins” [14, p. 127].

The hydrogenated hydrocarbon resins from the Regalrez® series are produced by the polymerization of pure monomer hydrocarbon feedstocks (styrene and methyl styrene monomers) and the subsequent hydrogenation of the benzene rings to form saturated aliphatic compounds [18, 19, p. 187].

Castelli et al. [20, p. 146] note that the hydrocarbon, cyclic and saturated nature of these resins, together with their very low polarity and absence of heteroatomic functional groups, make them very stable in the usual conditions in which cultural objects are found (in terms of RH, temperature and lighting of storage and exhibition environments). After being intensively studied in their ageing behavior and stability [19, p. 187], Regalrez® resins were considered to be among the LMW resins with greater photochemical stability [11, p. 172], “considerably more stable than the LMW resins used by paintings conservators, such as natural and ketone resins”, while having the highest UV stability for their category of hydrocarbon resin [14, p. 2]. They have been reported to resist cross-linking and to show no increase in polarity [6] under accelerated conditions.

Appendix III – Properties of pigments and fillers used in the research

Pigment/inert filler (C.I.)	Chemical formula	Opacity	Refractive index	Thermal stability (°C)	Density (g/cm ³)
Titanium white (PW 6.77891)	TiO ₂ [21]	Opaque [21]	2.72 [22, p. 308]	300 [22, p. 310]	3.4 – 4.3 [23]
Chrome oxide green (PG 17.77288)	Cr ₂ O ₃ [24]	Opaque [24]	2.5 [22, p. 273]	1000 [25; 22, p. 278]	5.2 [26]
Burnt umber (PBr 8.77727)	Fe ₂ O ₃ + Al ₂ O ₃ + Mn ₂ O ₃ + SiO ₄ + CaCO ₃ [27]	Semi-transparent [28]	2.2 – 2.3 [29]	300 [27]	4.2 [27]
Champgne chalk (PW 18.77220)	CaCO ₃ [30]	Low [30]	Low [31, p. 206]; 1.486/1.658 [31, p. 208]	>600 [32]	2.3 – 2.8 [33]
Kaolin (PW 19.77004)	Al ₂ Si ₂ O ₅ (OH ₄) [34]	Not found	1.558; 1.565; 1.564 [35]	Not found	2.6 [36]
Portafill® A40	Al(OH) ₃ [37]	Not found	1.57 [37]	~200 [37]	2.4 [37]

Note: References in Appendix IX

Appendix IV – Preparation of PWR samples for environmental chamber trials and testing

1) Rectangles with applied canvas texture (34 x 23 x 1 mm)

These samples were made by pouring the PWR mixtures, while in a liquid form, into the inside of a diapositive frame, placed on top of a silicone coated Melinex sheet. A spatula or a razor blade were used to level the PWR to the surface of the frame (figure IV.1). To apply texture on part of the sample, a silicone mould from Aquasil Ultra+ Smart Wetting Impression Material was used. The silicone mould was poured on top of a piece of canvas with a relatively open weave and pressed with a glass plate (figure IV.2a). For an easier application of the texture, the mould was cut to a rectangular shape that would fit exactly half of the sample. After the mould had been placed covering half of the sample, a heating spatula, set to a temperature of approximately 90°C, was used to iron the surface of the mould, softening top surface of the sample allowing for it to receive and retain the texture (figure IV.2b-c).

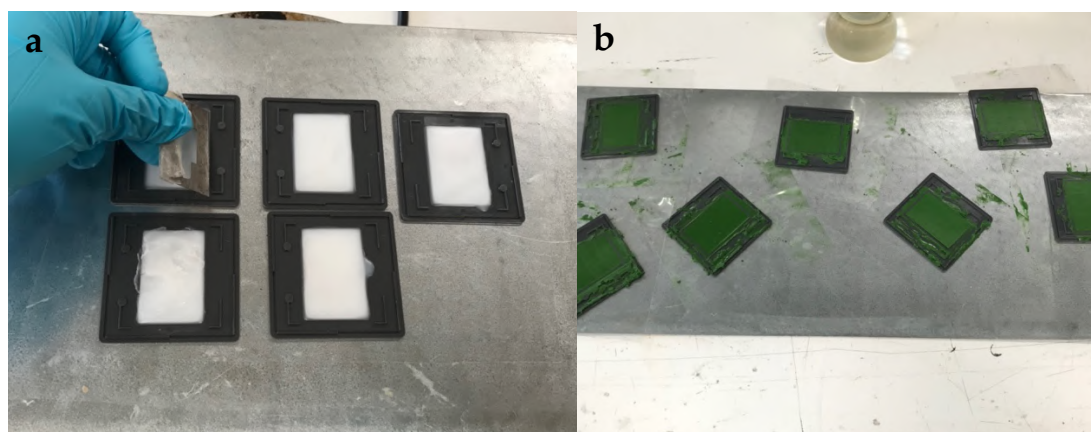


Figure IV. 1. Unpigmented NOVA-WR (a) and with chrome oxide green (b) poured into diapositive frames

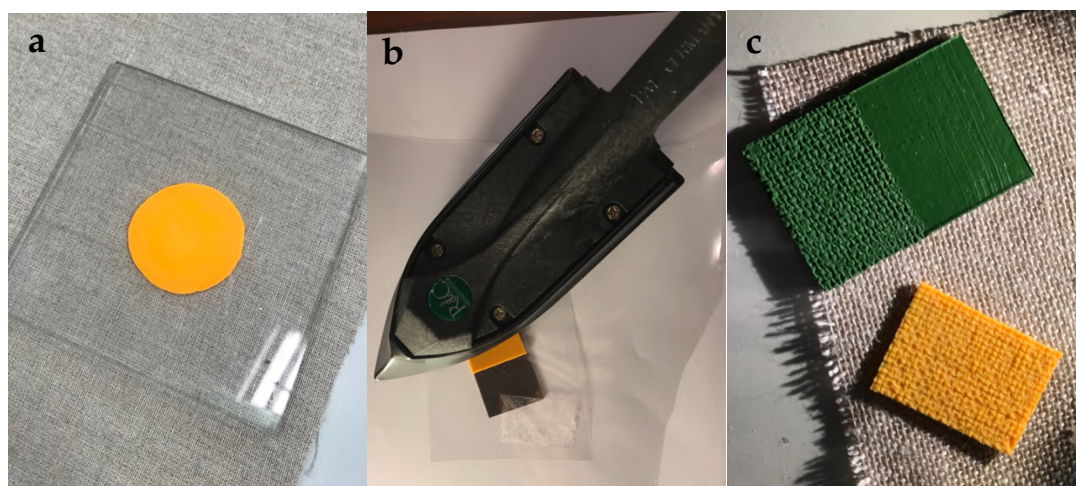


Figure IV. 2. Texture imprinting with silicone mould

2) Rectangles with circular protuberance (34 x 23 x 1 mm)

These samples were made with the same diapositive frames as above, with a small circular protuberance in the centre to allow for assessment of softening of the material due to exposure to higher temperatures. They were also made with a matte side and a glossy side, because different results were expected on both sides (e.g., bloom was expected to appear on the glossy side of the samples and not on the matte side). This was accomplished by pouring the wax-resin mixture on top of a sheet of baking paper, where a long piece of silicone coated Melinex[®], with the width of half of the diapositive frames, had been adhered to. From previous experience with the material, it was known that it imprints any texture to a very small detail on its surface. This meant that, if poured onto a roughly texturized surface, such as the one on the baking paper, the texture would be imprinted on the sample and its surface would become matte, because light would be scattered with the texture. The opposite would happen if the mixture was poured into a very smooth surface, such as the one on the Melinex[®] sheet: the surface of the sample would also become very smooth and light would be reflected instead of scattered, giving it a very glossy appearance. To adhere the Melinex[®], keeping the silicone coated side upwards to prevent the PWR mixture from sticking into it, a piece of transparent tape was adhered onto the non-silicone coated side and another piece of tape was placed across the first one, with the glueing side down for it to stick onto the table (and not on the baking paper because it has non sticking properties). To have the Melinex[®] sheet laying flat on top of the baking paper, it was slightly stretched while being adhered onto the table. To prevent the baking paper from moving, small weights were used. The diapositive frames were, then, placed in a way that, when the material was poured on the inside, half of it would be poured on top of the silicone coated Melinex[®] sheet and the other half on top of the baking paper. A diagram of the preparation of these samples is presented below.

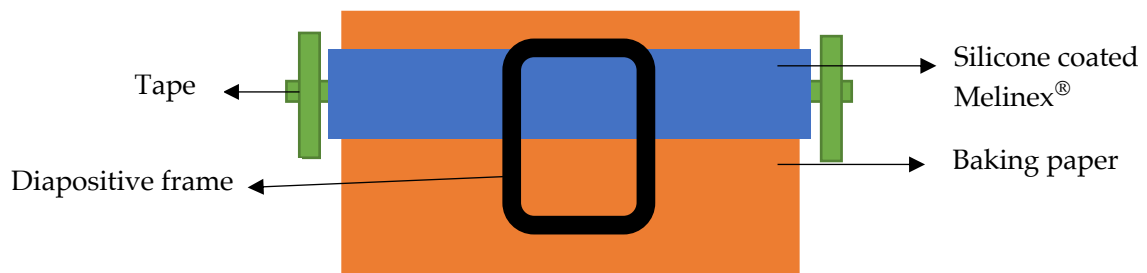


Figure IV. 4. Diagram of the preparation of the samples

After the PWR mixture was poured, the sample was allowed to harden for a few minutes and was then removed from the frame and placed with the glossy/matte sides upwards. Making the circular protuberance went as follows: a piece of silicone mould, with an approximate thickness of 0.2 cm, was chosen and a hole was cut in the centre of it using a hole puncture utensil with a 0.5 cm diameter. The punctured silicone mould was then placed on top of the rectangle, roughly in its centre where the glossy and matte side met, and the same mixture used to make the rectangle was poured inside the hole. A spatula was then used to remove the excess from the top.

3) NOVA-PWR formulations with three different fillers applied on pieces (8 cm x 6 cm) of a linen canvas sized with Plextol B500

These samples were made according to the method used for the insert made for Case study 1: *Saint Norbert of Xanten*, explained in Appendix VIII, for which a hot press was used. The only difference was that, in this case, the PWR were applied on a piece of canvas sized by brush with Plextol B500 and did not receive any texture.

4) NOVA-PWR and Gamblin-PWR applied on three model paintings.

The model paintings used for this research had been made in 2011 for Dina Reis' master's thesis project, by the student herself and Professor Dr. Leslie Carlyle. The paintings consisted of a "medium weight linen fabric" [38, p. 79] sized with "rabbit skin glue (RSG) *Zecchi*® 7% in distilled water (weight/volume)" [38, p. 80], with a 2-layered "chalk-based gesso with a 7% RSG binder" [38, p. 81] ground and a 2-layered surface coating made of "31% wt/vol Dammar resin (FCT-UNL supplies) dissolved in distilled turpentine (Winsor and Newton™) and coloured with (...) a mixture of dry pigments (...): Raw Umber *Cornelissen*® (30g), Alizarin Crimson *Cornelissen* (2g), Blue pigment (unidentified, FCT-UNL stock) (3.5g), Black pigment (unidentified, FCT-UNL stock) (3g)" [38, p. 82]. "The same varnish without the pigments (un-coloured) was used as the final coating" [38, p. 36]. Different back protections were attached to the three model paintings, which were then installed in a room in Palácio Nacional da Pena, on a wall "showing signs of extensive mould growth" with "evidence of high levels of moisture" [38, p. 37]. The three paintings used for the present research had, since 2011, been stored in the Historically Accurate Reconstructions Technical (HART) laboratory at the NOVA School of Science and Technology. Because different back protection options offered different degrees of protection (to RH, temperature, dust, etc.) to the paintings, they were not in the same condition. It was especially clear that one of the paintings showed a much more severe cracking problem than the other two. In order to make the condition of the paintings more uniform, the three paintings were placed in the environmental chamber where they were subjected to two cycles of fluctuating RH.

Creating the losses on the model paintings was done with a hole puncher with a diameter of 1 cm. The hole puncher was placed on the area where the loss was intended and pressed and rotated against the painting, underneath which a wooden board had been placed. A scalpel was then used to remove the rest of the varnish and preparation layers. In order to apply the PWR in the losses, each formulation was melted on a small hot plate (in this case a Cosori coffee mug warmer) and transferred to the loss with a spatula. The Whipmix wax carving pencil was used to soften and smooth the surface of infill. A cork bottle stopper, sanded to have a smooth horizontal surface, was dipped in white spirits (~17% aromatics) and used to level the infill to meet the surface of the painting exactly.

Appendix V – Recipes of NOVA-PWR formulations used in the research, what they were tested for and which environmental trials they were subjected to

The different NOVA-PWR formulations made are described in the table V.1 below. The weight in grams of each component corresponds to the amount needed to make approximately 5 rectangular samples of each formulation. The table includes which properties were tested for each formulation and to which environmental trials each formulation was subjected to.

Successful formulations in workability and stability are highlighted in **green**; successful formulations in workability, but not tested for stability (or only subjected to Trial 1), are highlighted in **blue**.

Table V. 1. NOVA-PWR formulations used in the research, what they were tested for and which environmental trials they were subjected to

	Formulations			Tested for (*)	Environmental trials (**)
	Cosmoloid H80 (parts by weight)	Regalrez 1126 (parts by weight)	Filler/Pigment (parts by weight)		
Unpigmented	1 part (3.3g)	2 parts (6.7g)		W, H	1
	1 part (4g)	1.5 parts (6g)		W, H	1
	1 part (5g)	1 part (5g)		W, H	1 – 6
	1.5 parts (6g)	1 part (4g)		W, H	1 – 6
	2 parts (6.7g)	1 part (3.3g)		W, H	1 – 6
	2.5 parts (7.1g)	1 part (2.9g)		W, H	1
	3 parts (7.5g)	1 part (2.5g)		W, H	1
	3.5 parts (7.8g)	1 part (2.2g)		W, H	1
	4 parts (8g)	1 part (2g)		W, H	1
	4.5 parts (8.2g)	1 part (1.8g)		W, H	1
	5 parts (8.3g)	1 part (1.7g)		W, H	1
With fillers	1 part (5g)	1 part (5g)	1 part <u>Champagne chalk</u> (5g)	W, H	1 – 5
	1.5 parts (6g)	1 part (4g)	1.25 parts <u>Champagne chalk</u> (5g)	W, H, O, F	2 - 6
	1.5 parts (6g)	1 part (4g)	2.5 parts <u>Champagne chalk</u> (10g)	W, H, O, F	1
	1.5 parts (6g)	1 part (4g)	5 parts <u>Champagne chalk</u> (20g)	W, H, O, F	1
	2 parts (6.7g)	1 part (3.3g)	1.5 parts <u>Champagne chalk</u> (5g)	W, H, F	1 - 5
	2 parts (6.7g)	1 part (3.3g)	3 parts <u>Champagne chalk</u> (10g)	W, H, F	1
	2 parts (6.7g)	1 part (3.3g)	6 parts <u>Champagne chalk</u> (20g)	W, H, F	1
	1.5 parts (6g)	1 part (4g)	1.25 parts <u>kaolin</u> (5g)	W, H, O, F	-
	1.5 parts (6g)	1 part (4g)	2.5 parts <u>kaolin</u> (10g)	W, H, O, F	-
	1.5 parts (6g)	1 part (4g)	5 parts <u>kaolin</u> (20g)	W, H, O, F	-
	2 parts (6.7g)	1 part (3.3g)	1.5 parts <u>kaolin</u> (5g)	W, H, F	-
	2 parts (6.7g)	1 part (3.3g)	3 parts <u>kaolin</u> (10g)	W, H, F	-
	2 parts (6.7g)	1 part (3.3g)	6 parts <u>kaolin</u> (20g)	W, H, F	-

With pigments	1.5 parts (6g)	1 part (4g)	1.25 parts <u>aluminium hydroxide</u> (5g)	W, H, O, F	-
	1.5 parts (6g)	1 part (4g)	2.5 parts <u>aluminium hydroxide</u> (10g)	W, H, O, F	-
	1.5 parts (6g)	1 part (4g)	5 parts <u>aluminium hydroxide</u> (20g)	W, H, O, F	-
	2 parts (6.7g)	1 part (3.3g)	1.5 parts <u>aluminium hydroxide</u> (5g)	W, H, F	-
	2 parts (6.7g)	1 part (3.3g)	3 parts <u>aluminium hydroxide</u> (10g)	W, H, F	-
	2 parts (6.7g)	1 part (3.3g)	6 parts <u>aluminium hydroxide</u> (20g)	W, H, F	-
	1 part (5g)	1 part (5g)	1 part <u>titanium white</u> (5g)	W, H, O	1 - 5
	1.5 parts (6g)	1 part (4g)	0.3 parts <u>titanium white</u> (1.25g)	W, O	-
	1.5 parts (6g)	1 part (4g)	0.6 parts <u>titanium white</u> (2.5g)	W, O	-
	1.5 parts (6g)	1 part (4g)	1.25 parts <u>titanium white</u> (5g)	W, H, O	2 - 6
	1.5 parts (6g)	1 part (4g)	2.5 parts <u>titanium white</u> (10g)	W, O	-
	2 parts (6.7g)	1 part (3.3g)	1.5 parts <u>titanium white</u> (5g)	W, H, O	1 - 5
	1 part (5g)	1 part (5g)	1 part <u>chrome oxide green</u> (5g)	W, H, O	1 - 5
	1.5 parts (6g)	1 part (4g)	0.3 parts <u>chrome oxide green</u> (1.25g)	W, O	-
	1.5 parts (6g)	1 part (4g)	0.6 parts <u>chrome oxide green</u> (2.5g)	W, O	-
	1.5 parts (6g)	1 part (4g)	1.25 parts <u>chrome oxide green</u> (5g)	W, H, O	2 - 6
	1.5 parts (6g)	1 part (4g)	2.5 parts <u>chrome oxide green</u> (10g)	W, O	-
	2 parts (6.7 g)	1 part (3.3g)	1.5 parts <u>chrome oxide green</u> (5g)	W, H, O	1 - 5
	1 part (5g)	1 part (5g)	1 part <u>titanium white</u> (5g)	W, H, O	1 - 5
	1 part (5g)	1 part (5g)	0.6 parts <u>burnt umber</u> (3g)	W, H, O	1 - 5
	1.5 parts (6g)	1 part (4g)	0.3 parts <u>burnt umber</u> (1.25g)	W, O	-
	1.5 parts (6g)	1 part (4g)	0.6 parts <u>burnt umber</u> (2.5g)	W, O	-
	1.5 parts (6g)	1 part (4g)	0.75 parts <u>burnt umber</u> (3g)	W, H, O	2 - 5
	1.5 parts (6g)	1 part (4g)	2.5 parts <u>burnt umber</u> (10g)	W, O	-
With filler + pigment	1.5 parts (6g)	1 part (4g)	0.625 parts <u>Champagne chalk</u> (2.5g) + 0.625 parts <u>titanium white</u> (2.5g)	W, H, O	2 - 5
	1.5 parts (6g)	1 part (4g)	0.625 parts <u>Champagne chalk</u> (2.5g) + 0.625 parts <u>chrome oxide green</u> (2.5g)	W, H, O	2 - 5
	1.5 parts (6g)	1 part (4g)	0.625 parts <u>Champagne chalk</u> (2.5g) + 0.625 parts <u>burnt umber</u> (2.5g)	W, H, O	1 - 5

(*) W: workability; H: hardness; O: opacity; F: flexibility

(**) **Trial 1:** fluctuating RH (10-90%) and fluctuating T (20-60°C) (this trial was interrupted); **Trial 2:** fluctuating RH (10-90%) with constant T (25°C); **Trial 3:** Fluctuating T (10-40°C) with constant RH (55%); **Trial 4:** exposure to a T of 50°C, with uncontrolled RH; **Trial 5:** exposure to a T of 60°C, with uncontrolled RH; **Trial 6:** exposure to radiant heat (T up to 70°C)

Appendix VI – Main bands found in the ATR-FTIR spectra of unpigmented NOVA-PWR and Gamblin-PWR formulations

1. Unpigmented NOVA-PWR containing solely Cosmoloid H80 and Regalrez® 1126

Band wavenumber (cm ⁻¹)	Component(s) ²³ (cm ⁻¹)		Attribution	Reference(s)
	Cosmoloid H80	Regalrez® 1126		
2956	2956	-	CH ₃ asymmetric stretching (2957cm ⁻¹)	[39, p. 76]
2917	2917	2917	Aliphatic hydrocarbons asymmetric stretching (2915 cm ⁻¹)	[40, p. 4]
2850	2850	2850	Aliphatic hydrocarbons symmetric stretching (2848 cm ⁻¹)	[40, p. 4]
1472	1472	-	Aliphatic hydrocarbons in-plane vibrations (1471 cm ⁻¹)	[40, p. 4]
1463	1463	-	Aliphatic hydrocarbons in-plane vibrations (1464 cm ⁻¹)	[40, p. 4]
1456	-	1456	CH ₃ asymmetric bending	[41, p. 11]
1446	-	1446	CH ₃ asymmetric bending	[42, pp. 94-96]
1375	1377	1375	Aliphatic hydrocarbons in-plane vibrations (1375 cm ⁻¹)	[40, p. 4]
1338	-	1338	Not found	-
1310	-	1310	Not found	-
1264	-	1264	Not found	-
889	889	891	Not found	-
846	-	846	Not found	-
814	-	814	Not found	-
785	-	785	Not found	-
729	729	-	Aliphatic hydrocarbons rocking vibrations (720 cm ⁻¹)	[40, p. 4]
719	719	-	Aliphatic hydrocarbons rocking vibrations (720 cm ⁻¹)	[40, p. 4]
706	-	706	Not found	-

2. Sample from Gamblin-PWR labelled “Neutral Base”

Band wavenumber (cm ⁻¹)	Component(s) ²⁴ (cm ⁻¹)			Attribution	Reference(s)
	Beeswax	Microcrystalline wax	Laropal A81		
2958	2956	2958	2961 (?)	CH ₃ asymmetric stretching (2957cm ⁻¹)	[39, p. 76]
2917	2917	2917	2913 (?)	CH ₂ asymmetric stretching (2921 cm ⁻¹)	[39, p. 76]
2850	2850	2850	-	CH ₂ symmetric stretching (2852 cm ⁻¹)	[39, p. 76]
1737	1737	-	-	C=O (of carboxylic groups involved in an ester linkage) stretching vibrations (1738 cm ⁻¹)	[39, p. 76]
1715	1713	-	-	C=O (of carboxylic groups of free carboxylic acids) stretching vibrations (1714 cm ⁻¹)	[39, p. 76]
1700	1700	-	-	Not found	-

²³ From comparison with the reference spectra of Cosmoloid H80 and Regalrez® 1126.

²⁴ From comparison with the spectra of reference samples of beeswax, Cosmoloid H80 and Laropal® A81.

1651	-	-	1651	Tertiary amide carbonyl absorption (1653 cm ⁻¹)	[43, p. 10]
1634	-	-	1634	Not found	-
1487	-	-	1487	Methylene CH ₂ vibrations (1489 cm ⁻¹)	[43, p. 10]
1472	1472	1472	-	CH ₂ , CH ₃ deformations (1473-1446 cm ⁻¹)	[41, p. 480]
1463	1463	1463	-	CH ₂ scissor deformation (1464 cm ⁻¹)	[39, p. 76]
1437	1435	1437	-	Not found	-
1415	1415	-	-	Not found	-
1394	1395	-	1394	NO ₂ symmetric stretch (1395-1380 cm ⁻¹)	[41, p. 481]
1377	1377	1377	-	CH ₂ deformation vibrations	[44, p. 115]
1368	-	-	1368	CH ₃ asymmetric stretching of a group	[43, p. 10]
1357	-	-	1357	Not found	-
1346	1346	-	-	CH deformation (1350-1330 cm ⁻¹)	[41, p. 481]
1329	1329	-	-	CH deformation	[41, p. 481]
1308	1308	-	1308	C-N in amide groups stretching vibrations (1311 cm ⁻¹)	[43, p. 10]
1286	1288	-	-	CH ₂ twist and rock (1310-1175 cm ⁻¹)	[41, p. 481]
1265	1265		-	CH in-plane deformation (1270-1251 cm ⁻¹)	[41, p. 481]
1243	1243	-	-	Not found	-
1219	1219	-	1217	Geminal methyl groups in C(CH ₃) ₂ deformation (1218 cm ⁻¹)	[43, p. 10]
1195	1195	-	-	Not found	-
1169	1170	-	-	C=O stretching vibrations of and C-H bending vibrations (1172 cm ⁻¹)	[39, p. 76]
1087	-	-	1087	Not found	-
1060	-	-	1059	Not found	-
1040	-	-	1040	Not found	-
1029	-	-	1029	Not found	-
1006	-	-	1005	Not found	-
956	956	-	-	Not found	-
919	919	-	-	Not found	-
890	889	889	-	CC skeletal stretch (905-837 cm ⁻¹)	[41, p. 482]
846	-	-	846	CC skeletal stretch (905-837 cm ⁻¹)	[41, p. 482]
839	839	-	839	CC skeletal stretch (905-837 cm ⁻¹)	[41, p. 482]
810		-	811	Not found	-
768	-	-	768	Not found	-
755	-	-	755	Not found	-
729	729	729	-	CH ₂ rocking vibrations (722 cm ⁻¹)	[45, p 13]
719	719	719	-	CH ₂ rocking vibrations (722 cm ⁻¹)	[39, p. 76]
708	-	-	708	Not found	-
665	-	-	665	Not found	-
659	-	-	660	Not found	-

Appendix VII – Specific RH and T values used for trials 1-3 in the environmental chamber

Trial 1: Fluctuating RH (10-90%) and fluctuating T (20-60°C)

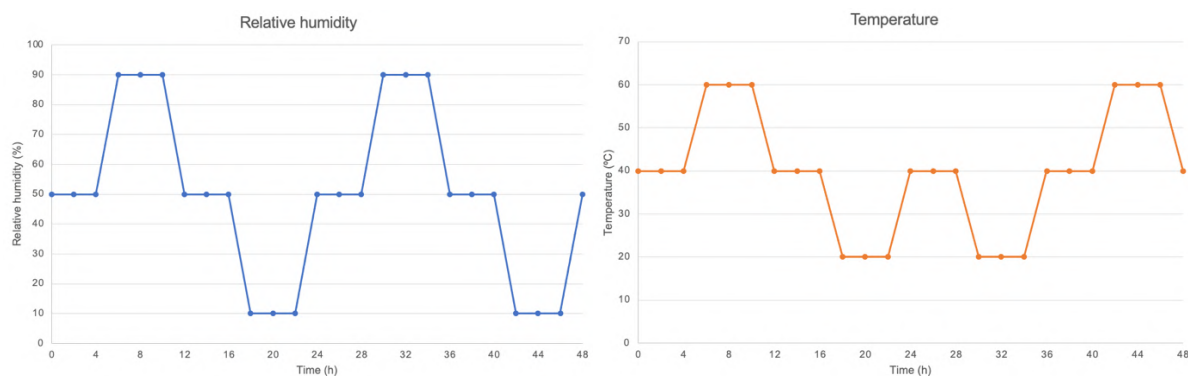


Figure VII. 1. RH and T fluctuations used in Trial 1

Trial 2: Fluctuating RH (10-90%) with constant T (25°C)

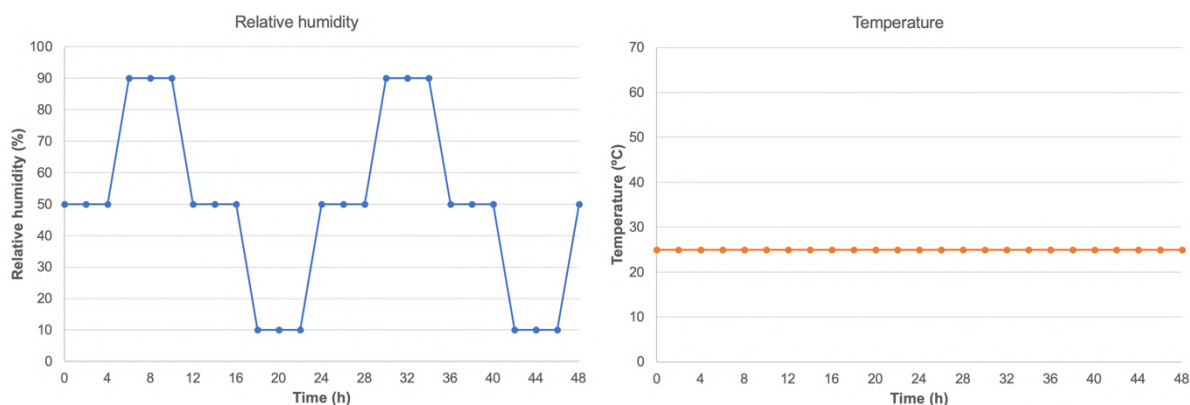


Figure VII. 2. RH fluctuations used in Trial 2 (left) with constant T (right)

Trial 3: Fluctuating T (10-40°C) with constant RH (55%)

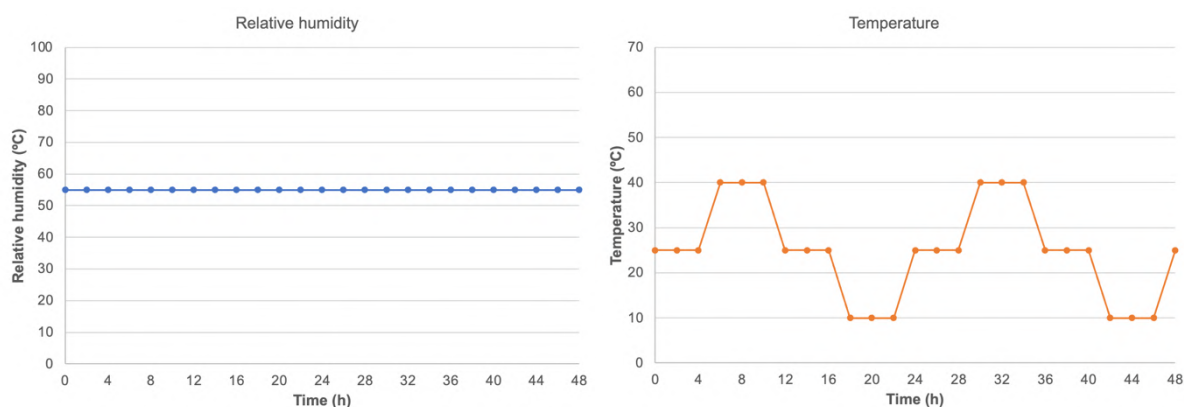


Figure VII. 3. T fluctuations used in Trial 2 (right) with constant RH (left)

Appendix VIII – Practical application of the NOVA-PWR on two case studies from SRAL

1. Introduction

Two canvas paintings were studied, analysed and treated by the author during a 9-month internship at the Stichting Restauratie Atelier Limburg (SRAL) based in Maastricht, the Netherlands.

Although very different both in their materiality and their age, the subject depicted and the pathologies present, the paintings had a common problem that made them ideal candidates for testing pigmented wax-resin infills: both presented several paint and ground losses that needed to be infilled, textured, and retouched. The fact that they were different in their materiality – one being a four-century-old painting made with oil on a linen canvas and the other one having been made less than twenty years ago using acrylic paint on a commercially prepared cotton canvas – proved very useful for testing the versatility of the PWR infill formulations. In addition, the type and size of the losses present enabled the author to test different application techniques and to prove the suitability when used solely as an infill that works as a base for retouching, and as a material that does the infill and reintegration of a loss in one single step. The usefulness of the material for its ability to receive texture, as well as the possibility of making it look more matte or glossy depending on how the surface is worked, was also tested and verified.

2. Case study 1: Saint Norbert of Xanten (unknown artist, ca. 17th century)

The first case study consists of an oil painting on linen canvas, probably dating from the 17th century or later, whose dimensions²⁵ are of 99 x 78,5 cm, that currently belongs to the SRAL's collection of deaccessioned works of art. Before being donated to SRAL, for educational purposes, the painting belonged to the Collection of the Bishop of Limburg (Bisschoppelijke Collectie).

The painting presented severe structural and aesthetic problems associated with physical damage, water damage and exposure to high humidity. The most significant damage was the large triangular-shaped loss in the centre of the canvas and the rectangular-shaped one adjacent to it. These losses constituted points of high fragility from which other problems might easily develop, especially with handling. The canvas was extremely stiff but also brittle and fragile, and two long horizontal tears had already occurred, apart from several smaller tears associated with the triangular-shaped loss – see mapping in Figure VIII.1.

The main challenge was, therefore, to find a way to fill the triangular-shaped and rectangular-shaped losses, which, given its size and the fact that a large portion of canvas had been lost, had to be done with inserts. The infilling material had to be able to receive texture, ideally from a mould to more accurately replicate the cracking pattern present in the rest of the painting. A PWR infill, for its ability to soften with high temperatures and very accurately receive texture from moulds applied with heat, was, therefore, considered an ideal candidate. The rest of the losses, due to their much smaller size and the fact that most of them still contained canvas underneath²⁶, did not

²⁵ Excluding the frame and including tacking margins.

²⁶ Losses without the canvas substrate had been previously filled with a mixture of cellulose “fluff”, methylcellulose (Methocel™ A4M 4%) and an emulsion of vinyl-acetate ethylene (Evacon™ R).

require inserts, and could simply be infilled with PWR mixtures. The fact that this was a deaccessioned work, enabled the author to test wax-resin mixtures with different fillers, as well as wax-BEVA mixtures used at SRAL, in order to assess their workability and suitability in this case. A map of the losses and the materials with which they were infilled is given below.

Due to the high fragility of the canvas, lining the painting was considered a crucial step in its treatment. The canvas replacement (insert) had to be secured from the back and an interleaf was to be applied between the insert and the lining canvas. This step was to be done after infilling. Determining whether the infills would be kept in place and maintain their applied texture after lining – in this case, mist-lining²⁷ – was also one of the purposes of testing the PWR infills in this painting.

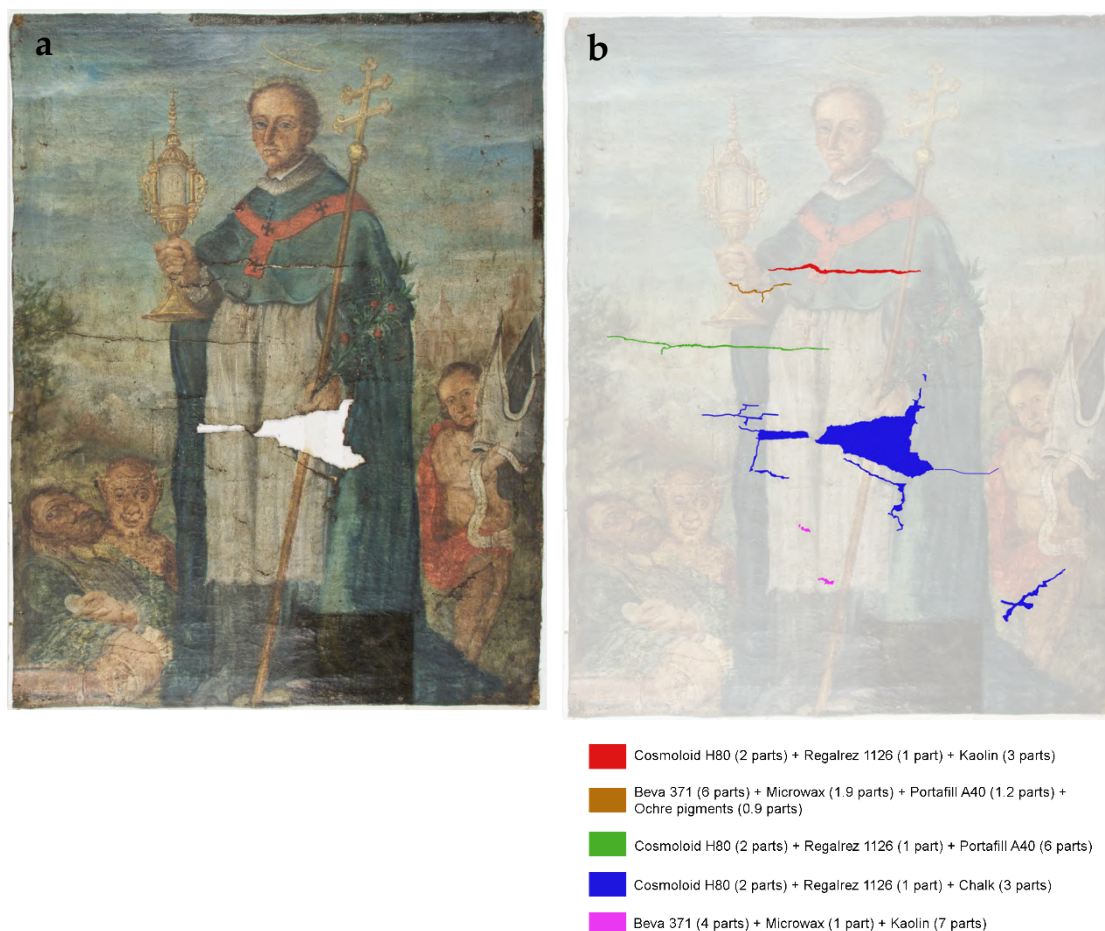


Figure VIII. 2. Saint Norbert of Xanten before the treatment conducted by the author of this dissertation (a); map of the main losses present in the painting with the materials used for infilling (b)

2.1. Canvas inserts

2.1.1.1. Choice of materials

The inserts consisted of pieces of linen canvas (figure VIII.2), with a density close to that of the original canvas, pre-sized with sturgeon glue. A filling material was to

²⁷ Mist-lining is a lining technique developed at SRAL by Jos van Och. It is a cold lining system using a mixture of acrylic dispersions. The lining is performed by “means of solvent activation under low pressure using a low-pressure envelope” [46, p. 12]. The adhesive used was composed of 60% of Plextol® K360 and 40% of Plextol® D512. Ethanol was the solvent used for reactivation of the adhesive.

be applied on top of this canvas. It was to be made of a NOVA-WR mixture (with Cosmoloid H80 wax and Regalrez® 1126 resin) with an inert filler (Champagne chalk, kaolin or Portafill® A40). To decide both on the Cosmoloid H80:Regalrez® 1126:filler ratio and on the actual filler to use, a set of samples was made and tested for their ability to bend without breaking (see Part II).

The mixtures with the best results contained Champagne chalk as the filler, in a ratio of 50% of wax-resin binder to 50% of filler. The ratio of Cosmoloid H80:Regalrez® 1126 chosen for the inserts was **1.75:1** (parts by weight), an intermediate value between the two previously tested (2:1 and 1.5:1). The production of the NOVA-WR mixture with Champagne chalk for infilling was done as described in Part II of the thesis (Section 2.2).



Figure VIII. 3. Triangular-shaped loss and smaller rectangular loss (a); pieces of linen canvas used as inserts for both losses prior to being cut to the exact size of the losses (b)

2.1.1.2. Applying the filling material on the pieces of linen canvas

In order to apply the previously made NOVA-WR with Champagne chalk on the canvases for the inserts in a uniform layer with the exact thickness of the original, a heat press (figure VIII.3a) was used. The first step consisted of measuring the thickness of the original painting (canvas + ground and paint layers) and of the canvas to be used for the insert, using a calliper. Since both canvases had a very similar thickness, the filling material to be applied on the insert would have to be slightly thinner than the original ground and paint layers, to anticipate the thickness of retouching to be done at a later stage.

It was decided to apply a layer of 0.8 mm of the NOVA-WR with Champagne chalk on the two pieces of canvas inserts. To achieve that thickness within the heat press, pieces of thin metal plate were piled up and pressed together to reach a total thickness of 2 mm. The total thickness needed was to accommodate the following layers: canvas for the insert + the desired thickness for the filling material + the thickness of two silicone coated Melinex® sheets + the thickness of one baking paper sheet. These layers were placed inside the heat press, to prevent it from moving when pressure and heat were being applied.

The two silicone coated Melinex® sheets were used, both under and above the canvas with the NOVA-WR with Champagne chalk filling, to protect the plates of the heat press from being contaminated with the filling mixture. The baking paper sheet, placed directly on top of the filling material and under the silicone coated Melinex®, was used to ensure a matte surface on the filling material, which would have been glossy if it was in direct contact with the Melinex® sheet while being pressed.

With pieces of metal plate on one side of the heat press and the canvas with chips of the NOVA-WR mixture with Champagne chalk, the baking paper and the Melinex® sheets on the other side, the heat press was set to a temperature of, approximately, 80°C, and pressure was applied by turning the wheel of top of the heat press. As expected, it was only possible to apply pressure until the height of the pieces of metal plate. The result for both inserts was a uniform layer of filling material, with a thickness of 0.8 mm.

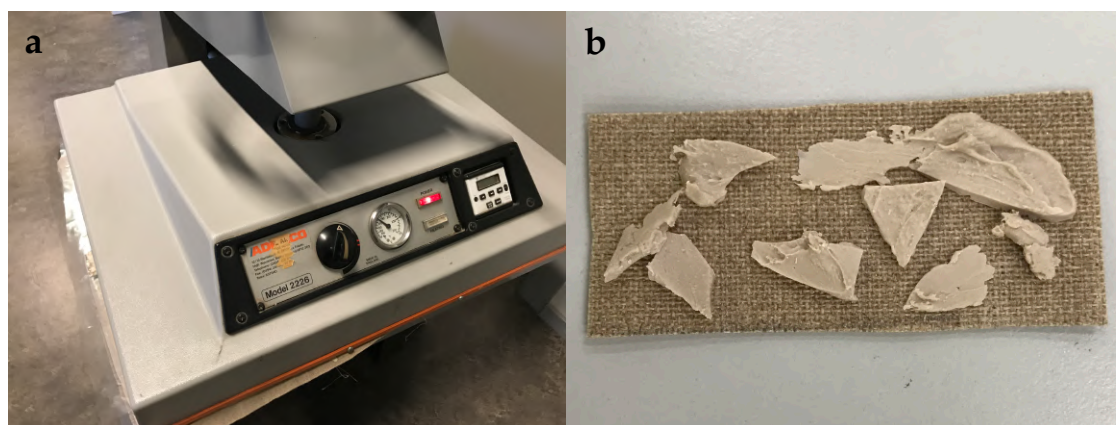


Figure VIII. 4. Heat press (a); insert with hardened chips of the infill before going to the heat press (b)

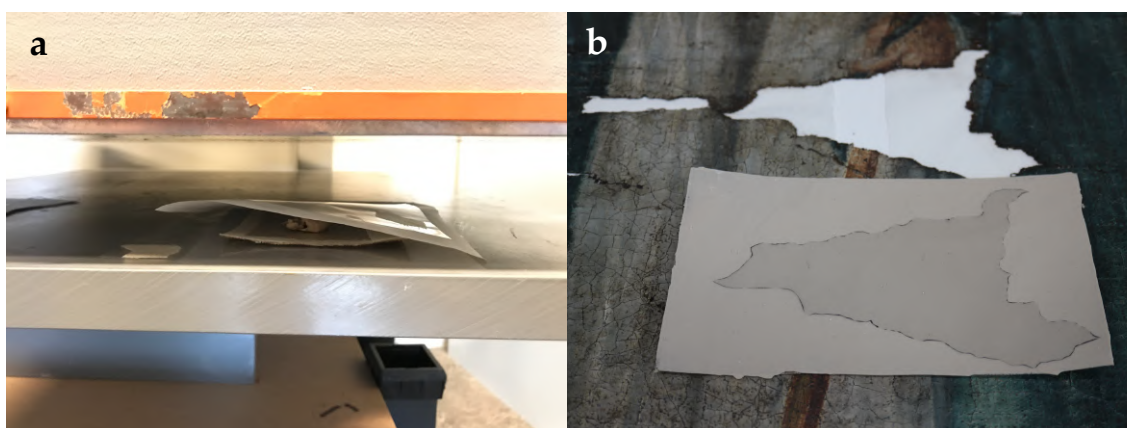


Figure VIII. 5. Materials inside the heat press (a); insert for the triangular shaped loss after being in the heat press (b)

2.1.1.3. Texturing the infilling material on the inserts using a silicone mould

Once the NOVA-WR filling mixture with Champagne chalk had been applied to the two pieces of canvas, the next step was to apply texture to their surfaces. Texturing the applied fills is a crucial part in loss reintegration for it will – if properly and accurately done – allow the reintegration to blend in with the original, becoming almost invisible to the eye of the viewer.

For this important step, and as recommended by several authors [47, pp. 149–56; 48, pp. 597, 600–603; 49, pp. 159–162], the decision was to use a silicone mould to replicate the existing texture from a chosen area of the painting. The use of a silicone mould allows for a very accurate reproduction of the texture of the painting.

The preparation and application of the silicone mould followed the steps given by Folkes and Reddington [49, pp. 159–162]. As recommended by the authors, the painting was at a state where it had already been cleaned but the intermediate coat of varnish prior to retouching had not yet been applied. The area of the paint surface selected for the texture was not adjacent to the loss but below it and included the same

colours – therefore, the same cracking pattern – as the ones that would have been in the area that was lost.

Before making the silicone mould, a thin coat of Regalrez[®] 1094 10% varnish (80g of resin in 200ml of white spirit, 400ml of iso-octane and 200 ml of Shellsol[®] D40) was brushed over the selected area of the painting to protect it from “direct contact with the silicone” [49, p. 159]. The silicone mould – Silicone C 20²⁸ by Silicones and More – was prepared according to the instructions given by the manufacturer, by mixing 100g of component A with 2g of component B (hardener) in a glass beaker. The mixture was left aside for approximately one hour to let the “bubbles in the mixture rise to the surface before brushing out the solution over the designated area on the painting” [49, p. 160]. The silicone solution was then brushed over the painting, creating a layer of approximately 2 cm. A sheet of Melinex[®] 100 μ was placed on top. The use of the Melinex[®] sheet was recommended by Folkes and Reddington, because it “facilitates the mould’s removal from the painting and provides a resistant-free surface during the process of ironing” [49, p. 160]. The silicone mould was left to cure for approximately 24 hours, after which it was removed from the painting with the help of a spatula and a small cylinder. The cylinder was used to roll the mould with the Melinex[®] sheet, which proved to be very helpful when detaching them from the painting (figure VIII.5a) . After the mould was detached, the layer of Regalrez[®] 1094 varnish applied prior to the brushing of the mould, was removed with isooctane applied with cotton swabs.

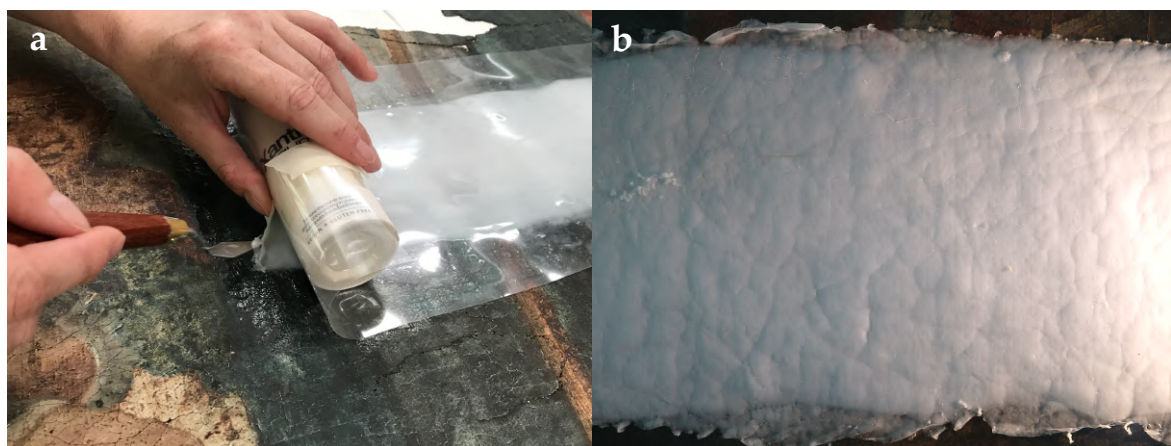


Figure VIII. 7. Silicone mould after being brushed onto the surface of the painting (a); Silicone mould after being removed from the surface of the painting, with the cracking texture of the painting (b)

To imprint the texture on the inserts, the mould was placed and aligned on top of them. Since the surface of the painting that was used to reproduce the texture had a few imperfections that stood out, care was taken when placing the mould to avoid having those imperfections transferred to the filling.

A heat spatula, set to a temperature of approximately 90°C, was then used to iron over the surface of the mould. The top surface of the filling became somewhat molten transferring the texture to the filling. Folkes and Reddington [49, p. 161] warn not to use temperatures that are too high since that would “leave a slightly wavy and uneven surface as the wax begins to flow” and also note that temperatures not high enough would not transfer the impression.

²⁸ According to the manufacturer, “the silicone C(ondensation) 20 - A+B is a 2-component (poly-condensation) casting silicone which is used in room temperature cures. The silicones are well liquid, provide a lot of detail and have a very high tensile strength” [50].

The texture was transferred to the inserts before they were cut to their final shape, because this meant that it would be possible choose which part of the imprinted texture to include. To cut the inserts to the shape corresponding as closely as possible to the shape of the losses, an outline of each loss was first drawn on Melinex[®] sheets using a permanent marker pen, then the Melinex[®] sheet was cut out and placed over the filling material. Using a scalpel, the filling material was cut out along the outline. To aid the cutting process, a soft, malleable surface was placed under the insert. In this case, a thin lead plate was used for that purpose (figure VIII.6a).

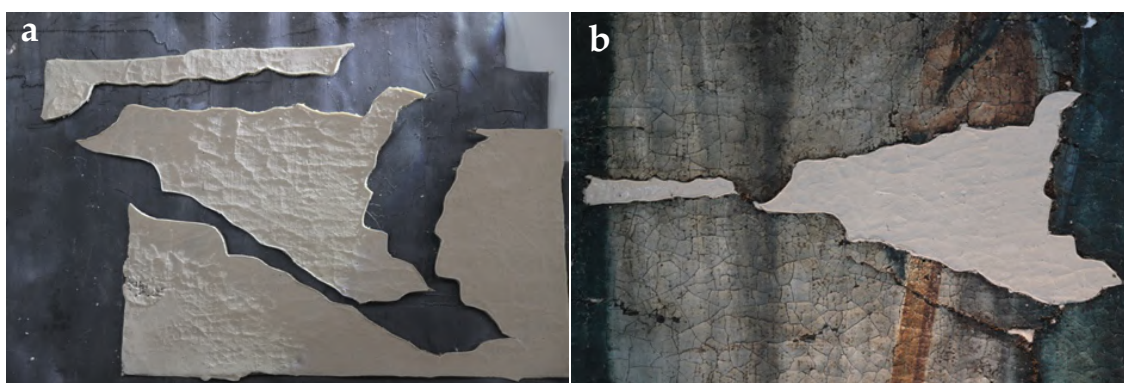


Figure VIII. 8. Insert with applied after (a) being cut to shape of the loss; Insert placed on the loss (b)

The attachment of the inserts within the losses in the painting was done from the reverse. BEVA[®] 371 film was the adhesive chosen for its ease of application and strength. BEVA[®] 371 film was melted directly onto the space between the inserts and the original canvas, using a hot needle (figure VIII.7a) set to a temperature of approximately, 65 to 70° C. Where there was a visible gap between the inserts and the canvas, linen *fluff* (made from scraping linen threads with a scalpel) was added to the adhesive, to make it “bulkier”.

To ensure that the inserts would stay in place over time, an interleaf of Parafil RT 20, a non-woven polyester fabric, covered with Plextol[®] D360 was attached from the reverse (figure VIII.7b). The adhesive of the interleaf was reactivated with heat, using a heated spatula, already having in mind that, when mist-lining with the same adhesive, the one present in the interleaf would be reactivated again and would more strongly adhere to the canvas. In addition, the lining canvas would help secure both the interleaf and the inserts.

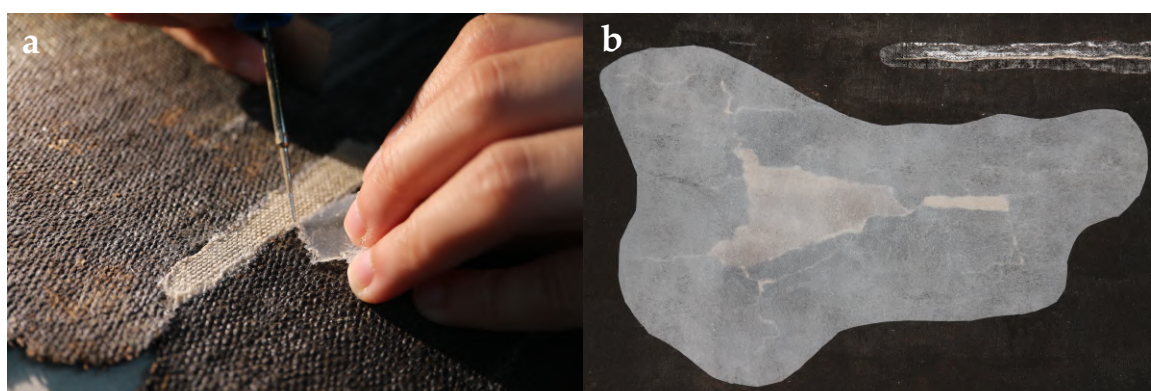


Figure VIII. 10. Attachment of the insert with BEVA[®] 371 film using a hot needle (a); interleaf of a non-woven fabric placed on top of the inserts and horizontal losses around them (b)

With the inserts successfully secured from the reverse, the painting was turned face-up to allow for smoothening and flattening of the edges of the inserts. This step was done using a spatula that was regularly heated on a small hot plate to soften the filling material, making it easier to work with (figure VIII.8).

Where a gap was visible between the insert and the canvas (already filled with linen fluff and BEVA® 371 from the reverse), small amounts of the same NOVA-WR filling mixture (with Champagne chalk) were melted directly into the gap using a wax carving pencil or hot needle. The goal of this step was to make the inserts perfectly match the height of the original canvas and fill all the gaps between the inserts and the original canvas, creating continuity from one to the other. Raking light, from different angles and directions, was used during the entire process and to evaluate the final result.

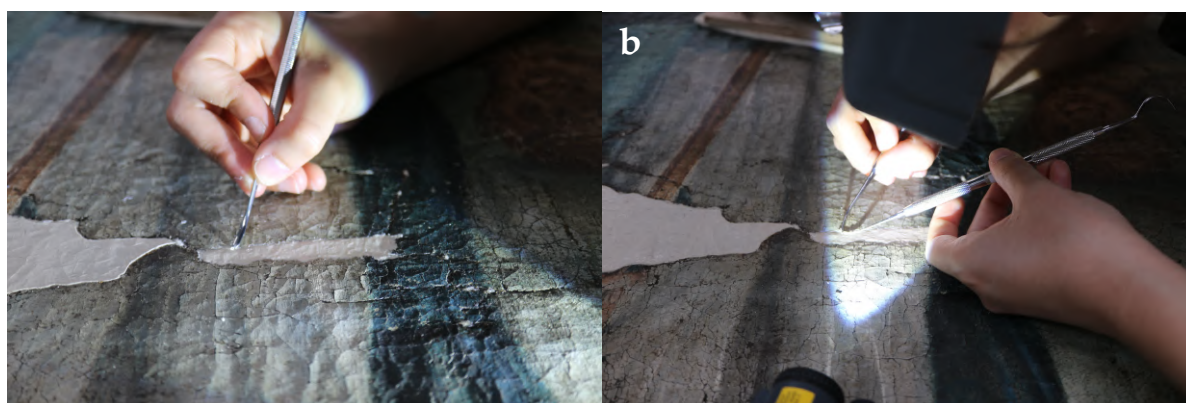


Figure VIII. 11. Levelling of the insert using a spatula and raking light (a and b)

2.1.2. Infilling

In addition to the large triangular and rectangular-shaped losses, other losses, mainly horizontal tears, required filling. These had been mended previously either with linen pulp or BEVA® 371. For these fills, the goal was to evaluate the suitability, workability, ability to receive texture and visual appearance of three NOVA-WR mixtures (1.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126, by weight) containing Champagne chalk, kaolin and Portafill® A40 (in a ratio of 2 parts of wax-resin binder to 1 part of inert filler, by weight).

In addition to the NOVA-WR mixtures, two mixtures containing BEVA® 371 and a microcrystalline wax (Microwax, n° 62620 from Kremer Pigmente) and pigments which are used at SRAL, were applied on the painting for comparison. A map of the different filling mixtures used in each tear can be found below.

The application process was similar for all the mixtures. Some steps were done in two or more different ways, independently of the filling material being applied.

1. The **NOVA-WR mixtures with the three different fillers were prepared** according to the procedure described in **Section 2.2** of the dissertation– the only difference was in the type of inert filler added to the wax-resin binder. These mixtures were then left to harden.
2. The hardened **NOVA-WR mixtures with the different fillers were melted and applied to the tear area**. This step was done in two different ways:
 - a. By placing the desired amount of the hardened NOVA-WR mixture with each filler on a sheet of aluminium on top of a small hot plate set to a

temperature of approximately 70°C, until it was slightly molten allowing it to be taken and applied roughly to the tear area with a metal spatula (figure VIII.9). The working time was quite short (approx. 10 seconds before the mixture completely hardens again), which meant that this step had to be done quickly. Any excess filling material could be kept on the aluminium sheet²⁹ for future use;

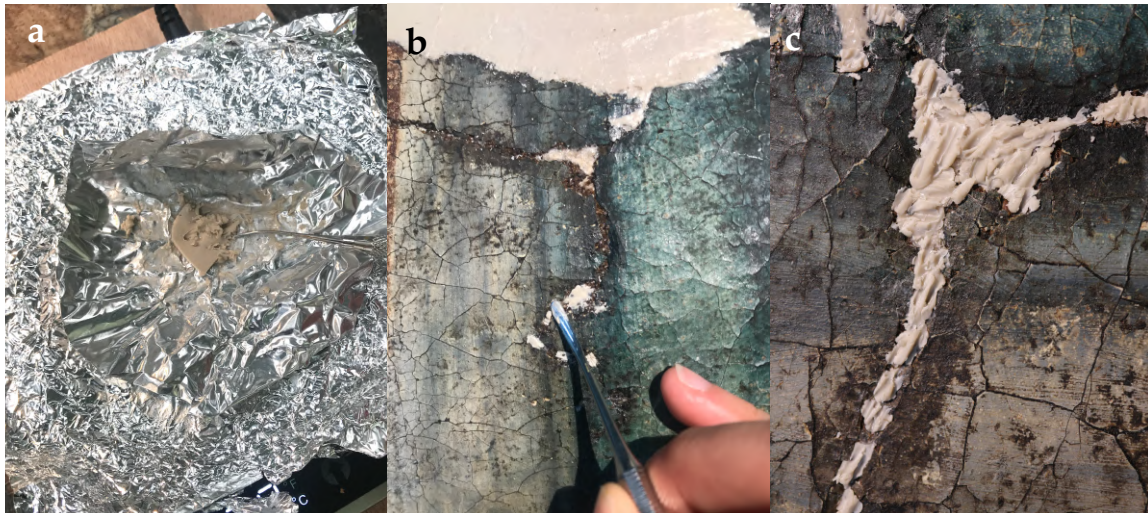


Figure VIII. 12. NOVA-WR mixture with Champagne chalk being melted on the small hot plate (a) and applied to the loss area with a spatula (b); Roughly applied mixture on the loss area (c)

- b. By melting the hardened NOVA-WR mixture with each filler directly into the area of loss using a wax carving pencil or a small hot spatula. For this method, it was easier to use thin films of the filler which were placed on the area and melted, little by little, with the tip of the wax-carving pencil or hot spatula;

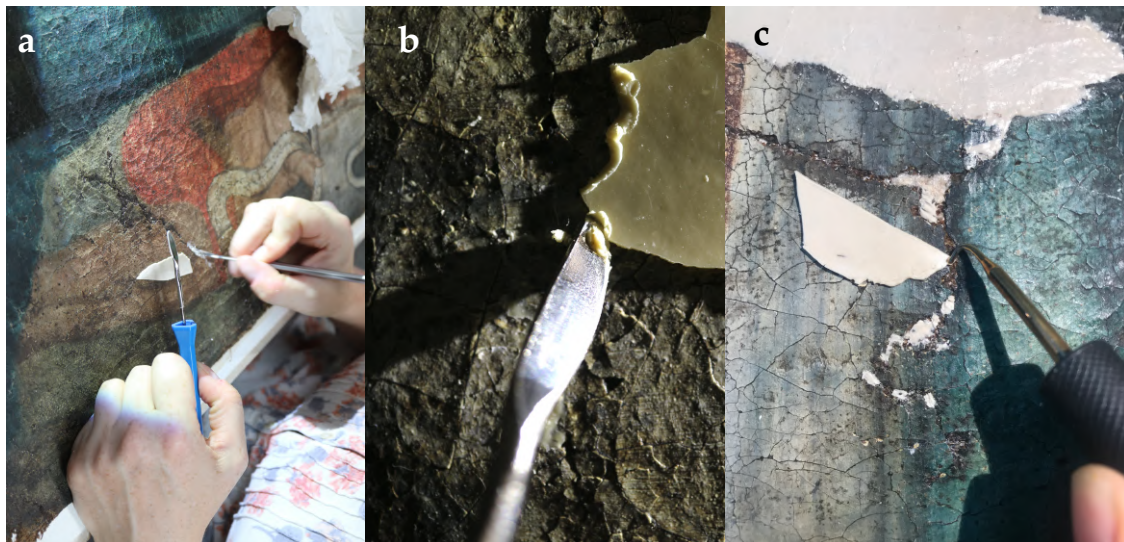


Figure VIII. 13. Hardened NOVA-WR mixture with Champagne chalk being applied to the loss area with a small hot spatula (a and b) and a wax carving pencil (c)

²⁹ The aluminium sheet was cut from aluminium drip catchers meant to be placed under electric elements in domestic stoves. Normal aluminium foil for kitchen/laboratory use is not thick enough.

3. After the mixture had hardened in the tear area, it was **smoothed and levelled**. Smoothing can be carried out in at least three different ways:
 - a. With a spatula that is warmed up on the hot plate. It is very important to warm up the spatula because it will soften the filling mixture, making it easier to smoothen just by slightly rubbing the surface. A hot spatula or wax carving pencil proved not to be useful for this step because they keep softening the filler, making it move inside, and sometimes transfer outside the loss area. Heating a normal spatula is much more useful because it does start by softening the filler but, as soon as it cools down, it just rubs the surface where needed;
 - b. With a small cotton swab dipped in white spirit that is carefully rubbed on the surface;
 - c. With a “old wine cork cut at an angle and sanded so that the face is smooth”. The end is dipped in white spirit and “rotated in a circular motion to remove surplus filler” [49, p. 160-161].
4. Both application methods mentioned in step 2, when done carefully, do not tend to leave residues that smear onto the surrounding paint. However, if that happens, it is possible to **clean the residues using a cotton swab dipped in white spirit**. To illustrate this option, one of the tears was filled with less precision, leaving extensive residue on the surrounding paint. All residue was easily removed without damaging the paint underneath and the filler in the tear was smoothened at the same time.

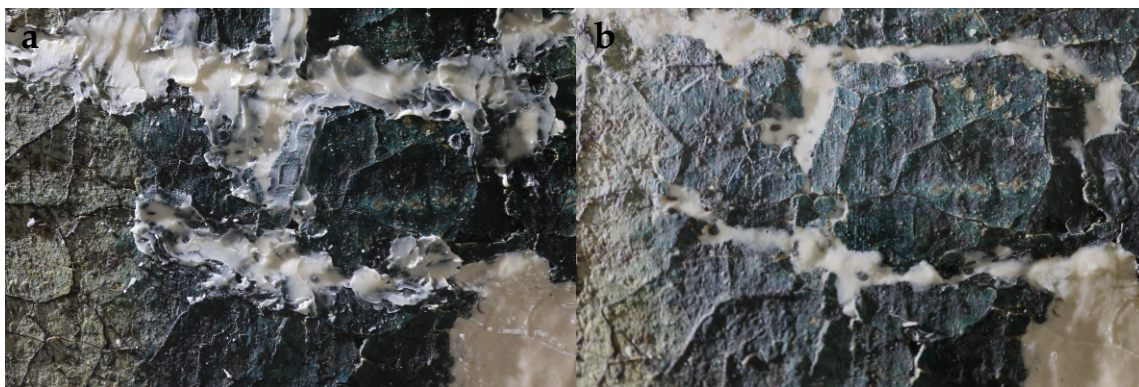


Figure VIII. 14. Filled area with residues on the surrounding paint before (a) and after (b) being removed with white spirit

5. After the surface of the infilling material is smooth and levelled, it was crucial to **replicate the surrounding texture** on it, using silicone moulds or simply carving with a scalpel. For these smaller fills, a scalpel was used to carve the continuation of crack lines, connecting the existing ones from the area above and below the tear. The use of raking light from different angles is very important when replicating texture, for it will enhance greatly the existing texture on the painting.

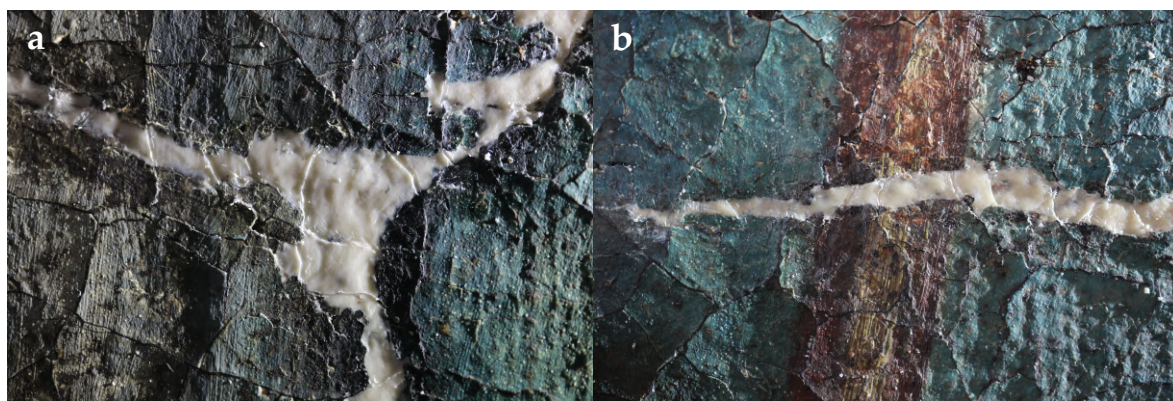


Figure VIII. 15. Two infilled loss areas with a NOVA-WR mixture with Champagne chalk after texture had been carved on them

All the Cosmoloid H80-Regalrez[®] 1126 (NOVA-WR) mixtures with fillers tested proved to be useful for filling tears, giving satisfactory results. It was possible to melt and apply all of them easily and to carve the texture using a scalpel. The main differences were related to the final colour of the filling, with a light beige tone with Champagne chalk (figure VIII.12, above), a dark yellowish beige with kaolin (figure VIII.13a) and a much whiter and lighter tone in the case of Portafill[®] A40 (figure VIII.13b). Application was slightly easier with the filler with chalk and more difficult with Portafill[®] A40.

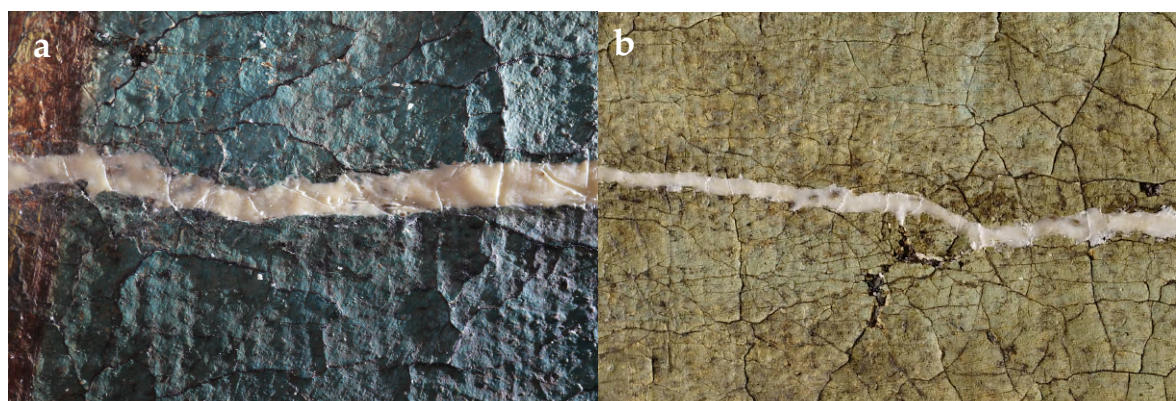


Figure VIII. 16. Losses filled with NOVA-WR mixtures with kaolin (a) and Portafill[®] A40 (b)

2.2.2. Results after mist-lining

After mist-lining, no changes were observed in any of the infills, including the inserts. The solvents used during mist-lining did not affect the NOVA-WR mixtures with any of the fillers. The results were evaluated by photographing the painting with normal and raking light and with Reflectance Transformation Imaging (RTI). The images below were taken after the painting had been mist-lined and re-stretched onto its original strainer. The next step of the treatment would have been to apply an isolation varnish over the NOVA-WR infill and reintegrate on top.



Figure VIII. 18. *Saint Nobert of Xantan* after infilling and mist-lining

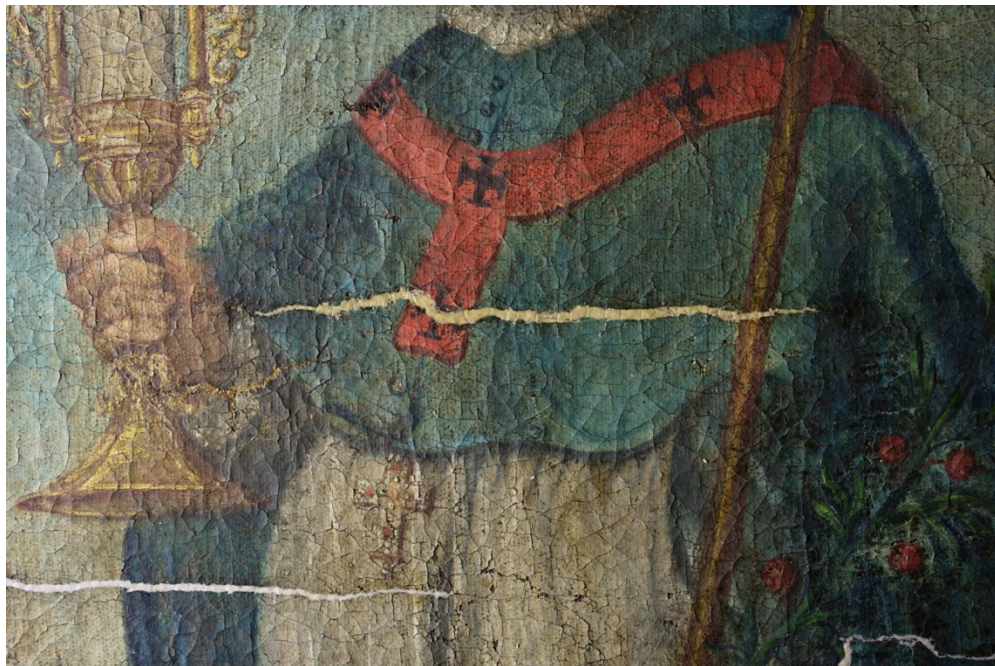


Figure VIII. 21. Losses filled with NOVA-WR mixtures with kaolin (loss above) and Portafill® A40 (loss below)



Figure VIII. 22. Inserts with NOVA-WR mixture with Champagne chalk



Figure VIII. 23. Loss filled with NOVA-WR mixture with Champagne chalk

Case study 2: *Untitled*, JOZ (?), 2002, 70 x 50 cm

The second case study was an abstract acrylic painting on a commercially prepared canvas, signed “JOZ ‘02”. The painting also belongs to the SRAL’s collection of deaccessioned works, after being part of the collection of a private owner.

The most significant problem that the painting presented was related to the fact that it had been cut off from the stretcher along the edges, most likely with a sharp blade. The painting was, therefore, separated in two different parts – the “inside”,

which contained most of the painted surface but was not attached to the stretcher; and the “outside”, which included the stretcher, tacking margins (with staples), and the small remaining edge of the painted surface. Except for this major problem, the painting was overall in a good condition, apparently stable. Neither the paint nor the canvas were damaged or destabilised in areas other than where it had been cut.

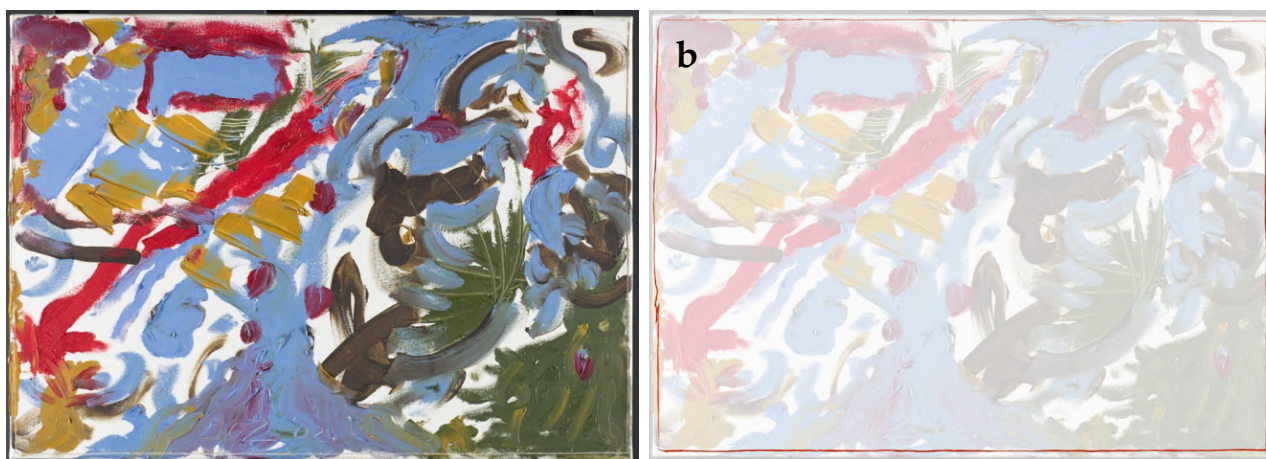


Figure VIII. 26. *Untitled*, JOZ, 2002 (a); Map of damages with gap area in red (b)

Unlike case study 1, this painting had already been mist-lined³⁰ before the treatment conducted by the author took place. Due to the fact that both parts of the canvas had been separated for a long time, the “inside” canvas shrank, not matching completely with the “outside”. This proved to be a problem during and after mist-lining, for a gap between both parts remained visible along the entire painting (see figure VIII.18b). The first step in filling the gap consisted of applying a mixture of Arbocel® BC 200, with Portafill® A40, Klucel® G 4% in water (4g in 100ml) and Evacon R. The resulting paste had a consistency similar to that of the canvas and was applied to the height of the canvas (excluding paint layers) (figure VIII.19).

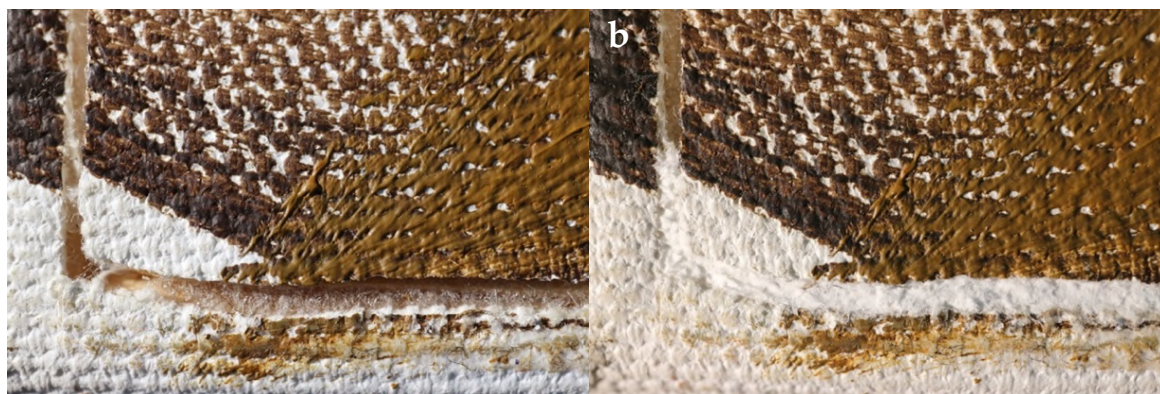


Figure VIII. 28. Gap between both parts of the painting before (a) and after (b) being filled with the Arbocel® BC 200, with Portafill® A40, Klucel® G 4% in water (4g in 100ml) and Evacon R mixture

³⁰ During the Mist-Lining Workshop, part of the Getty Foundation’s Conserving Canvas Initiative, that took place at SRAL between March and July 2019

To reintegrate on top of the Arbocel® BC 200 mixture, PWR formulations (in this case, NOVA-PWR) were ideal candidates for three main reasons: 1) they could infill the missing area and re-create three-dimensional features (e.g. brushstrokes) where needed; 2) this could all be done while adding pigments to the formulations that would match the surrounding paint area in colour, not requiring any further retouching; 3) if necessary to further blend the reintegration with the surrounding painting, texture could be applied using a silicone mould or carved using a scalpel.

3.1. Reintegrating with NOVA-PWR (with Cosmoloid H80, Regalrez® 1126 and pigments)

Due to the variety of colours present in the painting and that would be required to reintegrate the missing areas, the decision was to mix the pigments with the binder during the reintegration process and not before (e.g., using pre-made sticks). This allowed for more than one pigment to be mixed with the binder at the same time to match the surrounding colour more accurately and for small adjustments to be made for specific areas. For this purpose, the **NOVA-WR binder (1.5 parts of Cosmoloid H80 to 1 part of Regalrez® 1126, by weight)** was previously prepared and left to harden. Pigments for the reintegration were selected according to the colours present in the area surrounding the gap. The following were assembled: a small hot plate (a coffee mug warmer from Cosori®), metal spatulas and dental probes of different shapes and sizes, optivisors and appropriate lighting for retouching.

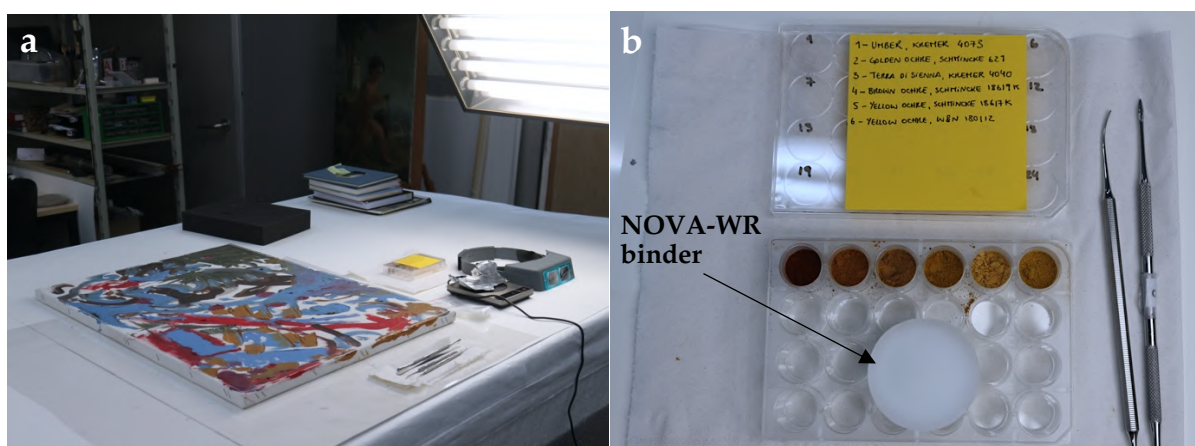


Figure VIII. 29. Set-up and equipment used during reintegration (a); hardened NOVA wax-resin binder (with Cosmoloid H80 and Regalrez® 1126 in the ratio of 1.5:1, parts by weight) and powder pigments to mixed with the binder (b)

The Reintegration of the losses was done in several steps:

1. **Melting the NOVA-WR binder** (figure VIII.21a) – the binder was melted in a piece of thick aluminium with the hot plate set to a temperature of approximately 75°C. The temperature could be increased as necessary and was used in a range between 75 and 85°C.
2. **Adding the pigments to the NOVA-WR binder** (figure VIII.21b-c). This step must be done while the binder is at a molten state, meaning that it is also done on the hot plate. In some cases, more than one pigment was added to the binder to match the colours in the painting.

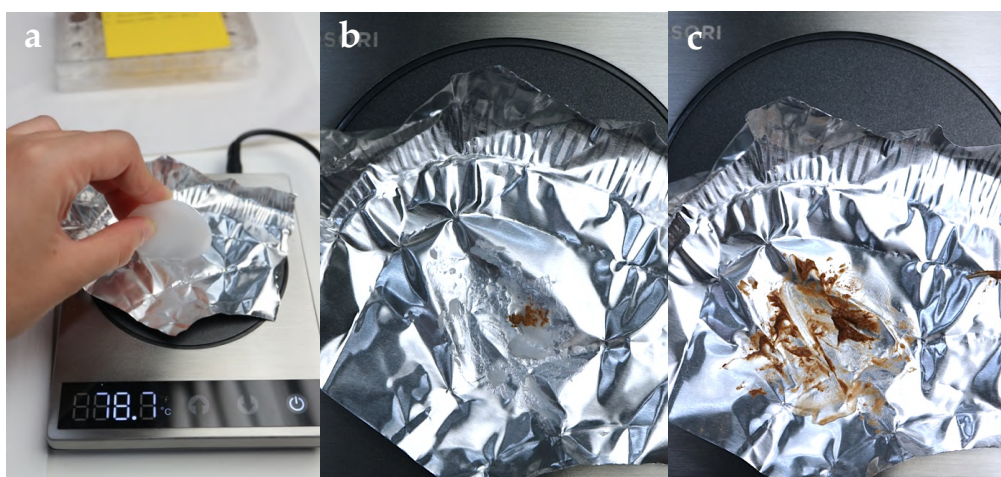


Figure VIII. 30. NOVA-WR binder being melted (a); pigment added to (b) and mixed (c) with the binder

To ensure that the pigmented wax-resin matched the surrounding paint, it was previously applied on a commercially prepared canvas and placed near the gap for visual evaluation (figure VIII.22). This could have also been done by taking a small piece of hardened NOVA-PWR and placing it in the gap area.

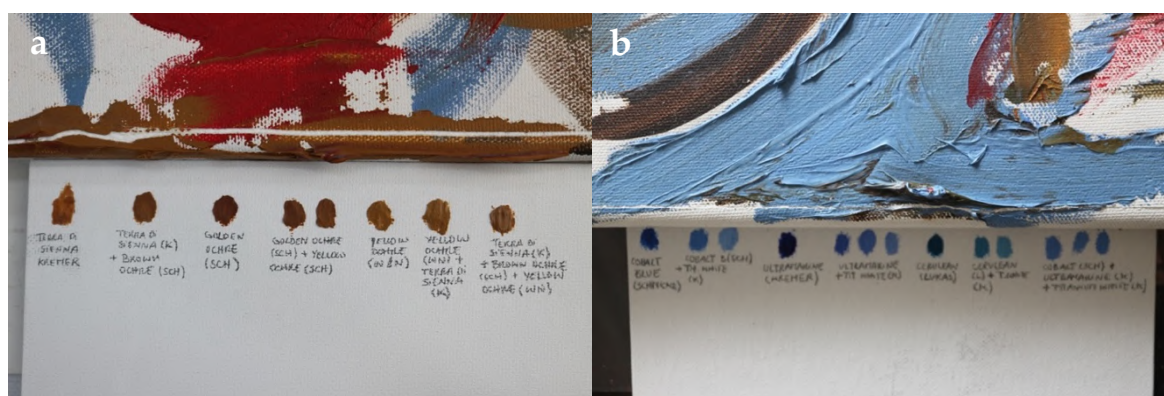


Figure VIII. 31. Colour tests made before choosing the pigment/pigment mixtures to use in each infill

3. **Applying the NOVA-PWRs** (1.5 parts of Cosmoloid H80, 1 part of Regalrez® 1126, by weight, and different pigments) **into the area of loss**. This step was done with a small spatula or dental tool to take the mixture from the hot plate and apply it into the loss. Application in layers was possible, because the mixture underneath hardens quickly (approximately 7 seconds) and stays in place when a new layer is applied. This makes it easy to build up part of a brushstroke or areas of impasto. The small spatula or dental tool can be heated on the hot plate or using a hot air gun, so that it softens the mixture when touching it, allowing for readjustments and/or corrections of the fill. A wax carving pencil can also be very useful for this purpose. A set temperature of, approximately, 75-78°C is suitable for melting the NOVA-PWR fill, while a temperature between 55 and 60°C will soften the material, allowing for its sculpting and shaping, crucial to make it match the surrounding paint.

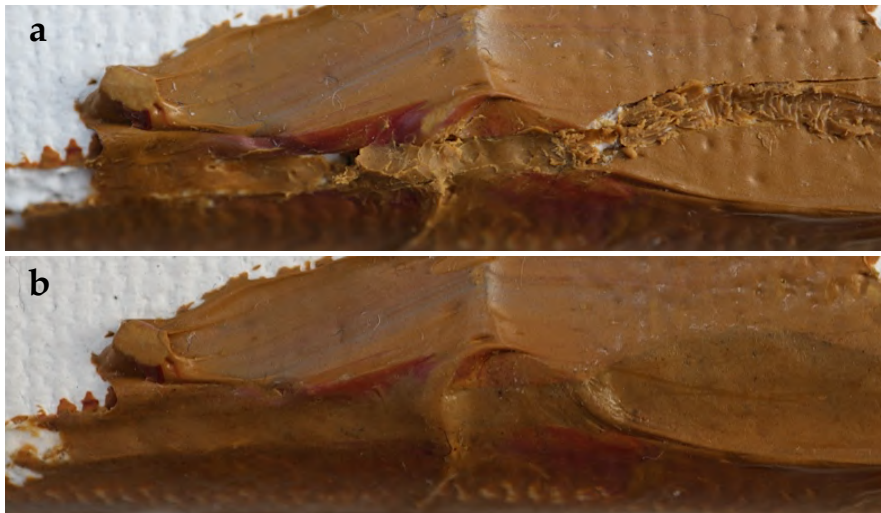


Figure VIII. 32. Gap area during (a) and after (b) infilling with a NOVA-PWR with yellow ochre (Kremer Pigmente) and terra di Sienna (Schmincke)

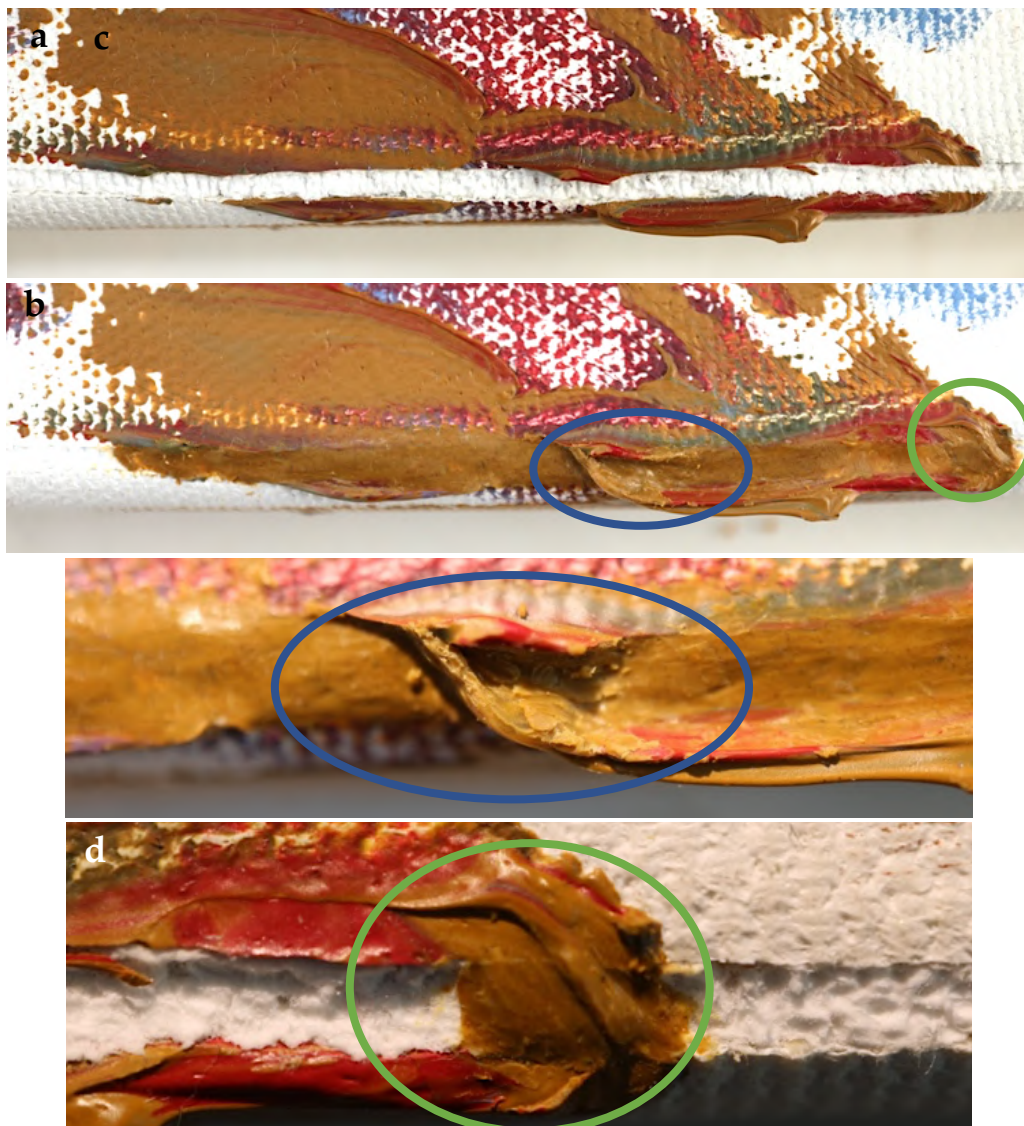


Figure VIII. 33. Gap area before (a) and after (b) infilling with NOVA-PWR with yellow ochre (Kremer Pigmente) and terra di Sienna (Schmincke); details of two brushstroke recreations in that area (c and d)

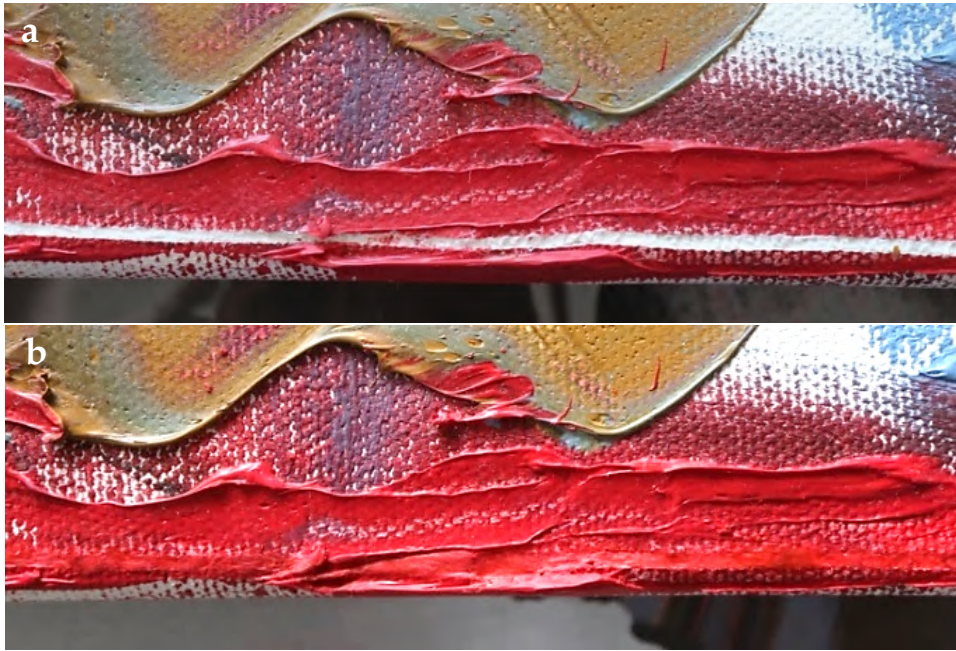


Figure VIII. 34. Gap area before (a) and after (b) infilling with NOVA-PWR with alizarin (Kremer Pigmente) and madder lake (Schmincke)

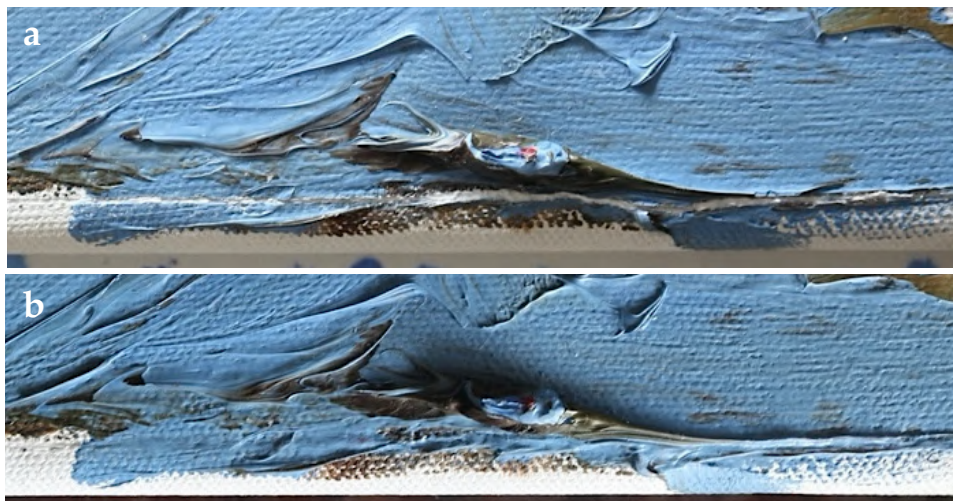


Figure VIII. 36. Gap area before (top) and after (top bottom) infilling with NOVA-PWR with cobalt blue (Schmincke) and titanium white (Kremer Pigmente)

4. **Creating a matte surface on the infill** was necessary since during application and sculpting of the infill it was also being polished and becoming glossier; not matching the surround paint. In this case, to make the infill matt was a piece of non-silicone coated baking paper (intended for cooking) was placed over the infill, and it was slightly scraped on top with a spatula (figure VIII.27).



Figure VIII. 37. Process of mattifying the NOVA-PWR infill with a sheet of baking paper and a spatula

This simple process is enough for the infill to retain the texture of the baking paper, turning into a surface that is no longer glossy. This effect can also be achieved by carefully touching the glossy surface with a cotton swab moistened with white spirit.

5. The last step, which was done only in the areas where required, consisted of **imprinting the texture of the canvas on the NOVA-PWR infill**. A silicone mould was made from the canvas on the back of the painting (with a layer of a Regalrez® 1094 varnish applied beforehand for protection). After curing, the mould was placed on the infilled area and small hot spatula was used to apply heat on top of it. Texture was imprinted on the PWR infill making it blend with the rest of the painting.



Figure VIII. 39. Green infilled area (NOVA-PWR with chrome oxide green) during (a) and after (b) imprinting texture with a silicone mould (differences in colour between both pictures are due to differences in lighting)

Appendix IX - References in the Appendices

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