ARCHIVIO ISTITUZIONALE
DELLA RICERCA

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Glass artefacts conservation: finding materials and methods for glass vessels' reconstruction

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:
Betti, E., Ferucci, S., Bernardi, E., Chiavari, C., Vandini, M. (2024). Glass artefacts conservation: finding materials and methods for glass vessels' reconstruction. THE EUROPEAN PHYSICAL JOURNAL PLUS, 139, 1-16 [10.1140/epjp/s13360-023-04776-7].

Availability:
This version is available at: https://hdl.handle.net/11585/953058 since: 2024-01-31

Published:
DOI: http://doi.org/10.1140/epjp/s13360-023-04776-7

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (https://cris.unibo.it/).
When citing, please refer to the published version.

(Article begins on next page)

15 October 2026

This is the final peer-reviewed accepted manuscript of:

Elena Betti, Silvia Ferucci, Elena Bernardi, Cristina Chiavari, Mariangela Vandini "Glass artefacts conservation: finding materials and methods for glass vessels' reconstruction" The European Physical Journal Plus 139 (2024) 20

The final published version is available online at: https://doi.org/10.1140/epjp/s13360-023-04776-7

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (https://cris.unibo.it/)

When citing, please refer to the published version.

Glass artefacts conservation: finding materials and methods for glass vessels' reconstruction

Elena Betti[1,a], **Silvia Ferucci**[1,2], **Elena Bernardi**[3], **Cristina Chiavari**[2], **Mariangela Vandini**[2]

[1] Kriterion s.n.c., Castenaso, Bologna, Italy
[2] Department of Cultural Heritage, Alma Mater Studiorum – University of Bologna, Bologna, Italy
[3] Department of Industrial Chemistry, Alma Mater Studiorum – University of Bologna, Bologna, Italy
[a] e-mail: e.betti@kriterion.it (corresponding author)

ABSTRACT

This paper will address art glass conservation, focusing on the search for the best products and methods to be employed in glass vessels' reconstruction, including case studies.

In 2000, an archaeological site was found in Padua (Northern Italy) where the Santa Chiara in Cella Nova Monastery once stood (1325-1797), and thousands of Renaissance artefacts came to light. Thanks to a collaboration between the Soprintendenza Archeologia, Belle Arti e Paesaggio per l'Area Metropolitana di Venezia e le Province di Belluno, Padova e Treviso and the University of Bologna, a huge conservative project started. The conservative intervention on the precious glass vessels became the starting point of a research on the best products to be employed in their reconstruction.

More than for other materials, an analytical approach is necessary while dealing with glass: commonly employed techniques need to be adapted to suit features of every object, and new ones must be examined. Furthermore, testing and comparing well known products to most recent ones or to ones developed for other purposes is essential.

In this study, an acrylic resin and four epoxy resins were tested, the latter both pure and added with three different colouring agents. Accelerated ageing tests were run to find out the products most resistant to discolouration through time. The results were compared with practical application's tests to select the best combination of products and techniques. Finally, the intervention on two glass vessels, coming from Santa Chiara Monastery, is presented briefly.

1. INTRODUCTION

Glass conservation can be considered a niche field. In particular, due to the peculiarity of this material, conservation products to be employed should have specific properties: In addition to the chemical stability and durability, they should be transparent and have a similar refractive index to the glass. Moreover, they should be workable, pourable and have a straightforward application method [1].
When first polymers were developed, they were studied for different purposes; nowadays this field has noticeably improved, and some products specifically developed to be used on glass are available [2, 3]. However, it is necessary to continue the research, also including products originally made for different fields.
The conservative intervention over some Renaissance glass vessels gave us the opportunity to investigate products and techniques for their reconstruction.
They were archaeological glass artefacts, coming from an underground building discovered where the Santa Chiara in Cella Nova Monastery in Padua once stood. This hexagonal structure was used firstly as an icehouse and then as a midden. Because of this, lots of objects were found inside, including precious Venetian glass artefacts, whose production can be dated between 1450 and 1530 [4]. As soon as they came to light, it was clear that an urgent conservation treatment was needed to guarantee their survival. Soprintendenza[1] conservators managed to carry out a first aid intervention on site, to make them safe. From that moment, different conservation campaigns were held to display a selection of objects in various expositions.[2] In 2019, the Soprintendenza[3] and University of Bologna collaborated on the conservative project of the rest of glass finds. This project aimed to reconstruct as many objects as possible from the thousand fragments coming from Santa Chiara archaeological site, to make them available for further studies. During XV and XVI centuries, Venetian glass production was at its peak, and there was a vast variety of techniques and materials employed [5]. Among the fragments coming from the hexagonal structure, brightly coloured glasses were found too, as well as calcedonio and lattimo ones. Furthermore, some of them were richly decorated with gold leaf and enamels (Fig. 1). As all of them were incomplete and had several losses, compromising their legibility and stability, we planned gap-filling realization. To this purpose, we took into consideration different resins that could be employed in their reconstruction, and dyestuff to colour the compensations accordingly to the original glass hue, to be tested in ageing conditions reproducing the indoor environments where they were likely be conserved.
The ageing behaviour of resins used in glass conservation (acrylics, epoxies, polyesters) had been previously studied [6, 7, 8, 9]. However, few investigations were made about mixing them with colouring agents and on the effects of additives on discolouration [10].
Thus, we decided to run experimental application trials but also ageing tests on different resins and dyestuffs, aimed at finding the best combination of products for indoor conserved glass artefacts.

[1] Then Soprintendenza per i Beni Archeologici del Veneto, now Soprintendenza Archeologia, Belle Arti e Paesaggio per l'Area Metropolitana di Venezia e le Province di Belluno, Padova e Treviso
[2] *Restituzioni*, Palazzo Leoni Montanari, Vicenza (Italy), 2002
Restituzioni, Gallerie d'Italia, Milano (Italy), 2016
Le memorie ritrovate, Noventa di Piave, Venice (Italy) 2011, and Este, Padua (Italy), 2012,
Èmailler le verre à la Renaissance, Musèe National de la Renaissance Château d'Ècouen, Paris (France), 2021-2022
[3] Soprintendenza Archeologia, Belle Arti e Paesaggio per l'Area Metropolitana di Venezia e le Province di Belluno, Padova e Treviso

Fig. 1 *Searching connections between the coloured and decorated glass fragments coming from Santa Chiara in Cella Nova site.*

2. EXPERIMENTAL

2.1 *Products tested*

In glass conservation epoxy and acrylic resins are commonly used. As for the latter, Paraloids®[4] are the most versatile ones. They are thermoplastic products, with good adhesive and consolidant properties. They are usually diluted in solvents like acetone, toluene, xylene, ethyl acetate or diacetone alcohol. As the solvent evaporates, a transparent film forms. Due to a low crosslinking tendency, they remain soluble through time, making them highly reversible [2].
Epoxy resins are usually two-components products, they are transparent and can have very low viscosity, that make them easily pourable. However, they contain strong polar functional groups, as epoxy (made by two Carbon's atoms and one Oxygen's atom disposed in a ring structure), hydroxyl or amine ones, that form a complex reticulum, which keeps crosslinking, getting stronger and stronger [2]. Therefore, these products are hardly reversible and can create tensions when directly applied on fragile glass artefacts. Their use as adhesive should be avoided, when possible, as for thick, opaque, or highly degraded glass fragments, and limited to very transparent and thin [11]. However, their features make them the best choice for casting gap-fills.
For our study, we decided to test:

- Paraloid B-72 acrylic resin, (binary copolymers of methyl acrylate/ethyl methacrylate), which is the softest Paraloid formulation and the most used on glass artefacts [12, 13].
- Araldite 2020 epoxy resin (containing bisphenol A ed epichlorohydrin), currently one of the most employed products on ancient glass.
- Epo-Tek 301-2 epoxy resin (bisphenol A diglycidyl ether), usually used on porcelain objects, but sometimes also for glass artefacts.
- Hxtal Nyl-1 epoxy resin (cyclohexanol,4,4'-(1-methylethylidene)bis- polymer with 2-(chlormethyl)oxirane), hardener: poli(oxi)(methyl-1,2-ethanedil), alfa-hydro-omega-(2-

[4] Also known as Acryloids® (USA)

amminomehyletoxi)-ether 2-etil-2-(hydroximethyl)-1,3-propanediol), also very diffused, specifically studied for use on glass [14].

- Plexi Fluid 2.0 epoxy resin (with reactive diluents, hardener: aliphatic ammine); this product was developed for artistic and model-making hobbies, but the Istituto Centrale del Restauro (ICR, Rome) tested it as a gap-filling material with good results [15].

Paraloid B-72 was only tested clear, as it had to be used as adhesive and consolidant, while epoxy resins were also added with colouring agents.

The colouring agents tested were:

- Microlith® T, in Red BR-T, Yellow 2040T and Blue 7080T; they are industrial powder micro-pigments produced by BASF Group, they are tested to be suitable with different resins but the only study in the conservation field dates to the ’90s [16].
- Orasol® KREMER, in Pink 478, Gelb 4 GN (yellow), Blau 855 (blue); they are powder dyes, the most employed colouring agents as they are recommended by Hxtal Nyl-1 producers.
- Vitrail® Lefranc & Bourgeois, in Purple, Yellow and Blue; they are translucent liquid colours, usually employed to paint on glass or plastics. They contain acetone, aromatic hydrocarbons, cyclohexanone, solvent naphtha and white spirit. They were introduced in the conservation field from the ICR, Rome [17].

The different combinations taken into account are summarized in Table 1:

Table 1 *Abbreviations used to identify each sample, some of them were multiples.*

	0 CLEAR	1 RED MICROLITH T	2 YELLOW MICROLITH T	3 BLUE MICROLITH T	4 RED ORASOL	5 YELLOW ORASOL	6 BLUE ORASOL	7 RED VITRAIL	8 YELLOW VITRAIL	9 BLUE VITRAIL
A ARALDITE 2020	A0	A1	A2	A3	A4	A5	A6	A7	A8	A9
E EPO-TEK 301-2	E0	E1	E2	E3	E4	E5	E6	E7	E8	E9
H HXTAL NYL-1	H0	H1	H2	H3	H4	H5	H6	H7	H8	H9
P PLEXI FLUID 2.0	P0	P1	P2	P3	P4	P5	P6	P7	P8	P9
D PARALOID B-72	D0									

2.2 *Samples preparation*

Samples were prepared by pouring the epoxy resins, mixed with the hardener, into silicone moulds. Vitrail was added directly to the resins, while for powders a small amount of highly pigmented resin was prepared. The mixture obtained was then added to the clear resin prior to mixing it with the hardener. Samples for outdoor exposure were circular, with a 2 cm diameter, while samples to be aged in the climate chamber were rectangular (2 cm x 4 cm). Both were 0.5 cm ca thick.

Paraloid B-72 could not be poured as it is a solid product. The pearls were dissolved in acetone (30% w/v), then ethanol was added (1:5 ratio). The solution was poured in a large silicone mould, that was

then closed into boxes and placed in a PET bag. This was necessary to slow down the solvent evaporation and prevent bubbles developing. The sheet was extracted and cut after 14 days (2 cm x 4 cm) [13]. One of each sample was made both for outdoor and chamber ageing tests, but for the latter some replicas were made of the clear resins (3 of the epoxies and 2 of the Paraloid B-72). Paraloid B-72 was only tested in the climate chamber.
While preparing the samples, we were able to elaborate some preliminary practical observations on the behaviour of the resins. Resins showed different curing times, the longest time was taken by Hxtal Nyl-1. Considering the workability, Araldite 2020, Hxtal Nyl-1 and Plexi Fluid 2.0 were more easily mixed and poured, while Epo-Tek 301-2 needed to be heated before. In fact, at room temperature the latter tended to crystallize, as shown by the presence of white crystals in the samples is formed during the curing time. Concerning dyestuffs, Microlith T and Vitrail gave excellent aesthetical outcomes, but difficulties occurred with Orasol dyes: Clumps formed, and colour showed visible variation when the hardener was added (Fig. 2). This phenomenon was more noticeable with blue and yellow ones. Orasols' instability is well known and reported in the literature [18]; however, being the most employed colouring agents, they have been included as reference in the experimentation.
The obtained samples were submitted to ageing tests.

Fig. 2 *Images show Epo-Tek 301-2 with blue Orasol before and after the hardener was added.*

2.3 *Ageing tests*

Accelerated ageing tests aimed at verifying the good durability of Paraloid B-72, finding the most resistant epoxy resin to discolouration through time, and the best combination of epoxy resins and colouring agents. Two parallel ageing tests were conducted: An accelerated ageing inside a climate chamber, to simulate critical indoor conditions, and an outdoor field exposure. The outdoor exposure can be considered as accelerating the samples' degradation, because environmental variations are more intense than in an indoor space, where glass vessels will be displayed.
For the climate chamber test, a CLIMACELL 111 with a Black Light Blue lamp was used. As there are no standards concerning the parameters when testing these products, we took into account different aspects. Recent climate studies inside European Museums were analysed and compared, to better understand the average climate parameters of indoor displayed artefacts (Tab. 2). We also considered the ASTM guidelines concerning plastics ageing, in particular D4329-13 Standard Practice for Fluorescent Ultraviolet (UV) Lamp Apparatus Exposure of Plastics, and the Italian DL 112/98, which suggests a UV radiance <1.2 µW/cm for average sensibility materials, and <0.05 µW/cm^2 for highly sensible ones. Finally, we compared these data to the UNI 10829/1999 standard, which states that for a correct conservation of Cultural Heritage degraded glasses temperature (T)

must stay between 20 and 24°C, temperature variation (ΔT) must not exceed 1.5°C and relative humidity (RH) must be 40-45% ca.

Table 2 *All environmental studies taken into account are here summarized, results of the climate change analysis are also reported.*

REFERENCE	MUSEUM	T Max (°C)	RH Max (%)	T Min (°C)	RH Min (%)	T Average (°C)	RH Average (%)
[19] H. L. Shellen, 2010	Our Lord in the Attic Museum, Amsterdam[5]	18,7	66	13,3	50	(16)	(58%)
	Rijksmuseum, Amsterdam[5]	23	54	20	50	(21,5)	(52)
	Haunting Lodge, St. Hubert[5]	25	60	15	40	(20)	(50)
[20] F. Sciurpi et al. 2017	Corridoio Vasariano, B[6]	32,5	80	8	33	(20)	(56,5)
	Corridoio Vasariano, C[6]	29	66	11	41	(20)	(53,5)
[21] R.P. Kramer et al., 2016	Hermitage Museum, Amsterdam - class A[5]	23,5	60	21	40	(22)	(50)
	Hermitage Museum, Amsterdam - class AA[5]	24	56	20	44	(22)	(50)
[22] D. Camuffo et al., 2000	Correr Museum, (summer)[7]	29	57	25	51	(27)	(50)
	Sainsbury Centre for Visual Arts, (summer)[8]	26	67	19	40	(22,5)	(53,5)
[23] A. Troi et al., 2011	Bode Museum – room 129 (with climate control)[9]	24	55	19	40	(21,5)	(47,5)
[24] P. Uring et al., 2019	Cluny Museum[10]	30	80	14	25	(22)	(52,5)
	Villa Kèrylos[10]	32	72	11	20	(21,5)	(46)
[25] J. Ferdyn-Grygierek, et al., 2019	Museum A	33	76	14	22	(23,5)	(49)
	Museum B	28	80	15	10	(21,5)	(45)
	Museum C	31	76	16	12	(23,5)	(44)
[26] K. Gysels, et al., 2003	Royal Museum of Fine Arts – Ruben's room (winter)[11]	21	65	19,5	42	(20)	(53,5)
[27] D. Camuffo, et al., 2001	Uffizi – Pollaiolo's room (winter)[6]	20	90	11	40	(15,5)	(65)
	Uffizi – Pollaiolo's room (summer)[6]	27,5	70	25	55	(26,5)	(62,5)
[28] G. Sturaro, et al., 2003	Kunsthistorisches Museum, (exibition)[12]	24	64	19	52	(21,5)	(58)

This research emphasised differences between guidelines' theory and everyday reality. Thus, for the accelerated ageing the following programme has been set up: A 12h cycle divided into 4 steps (Tab. 3), so alternating critical daily conditions in term of T, RH and UVA irradiation, selected by taking into account the different hours of the day, the changing of the seasons and the irregular flow of visitors in exposition rooms. Samples were arranged on a grate. To evaluate the effect of the UVA

[5] Netherlands
[6] Florence, Italy
[7] Venice, Italy
[8] Norwich, UK
[9] Berlin, Germany
[10] France
[11] Antwerp, Belgium
[12] Vien, Austria

radiation, half of each sample was covered by a thin foil of aluminium, not in contact with the surface (Fig. 3). The ageing cycle was repeated 28 times.
The circular samples described in section 2.2 were cut into two pieces, to make a side-by-side comparison. Half of them were exposed on a rooftop (at a height of 6m) in the city of Cesena (Northern Italy), from 22 November 2020 to 11 May 2021 for a total of 171 days (Fig. 4).

Table 3 *Reporting the parameters of each step.*

STEP	DURATION (h)	TEMPERATURE (°C)	RELATIVE HUMIDITY (%)	UVA IRRADIANCE (mW/cm^2)
1	1	20	40	0
2	7	35	20	1
3	1	20	40	1
4	3	5	80	0

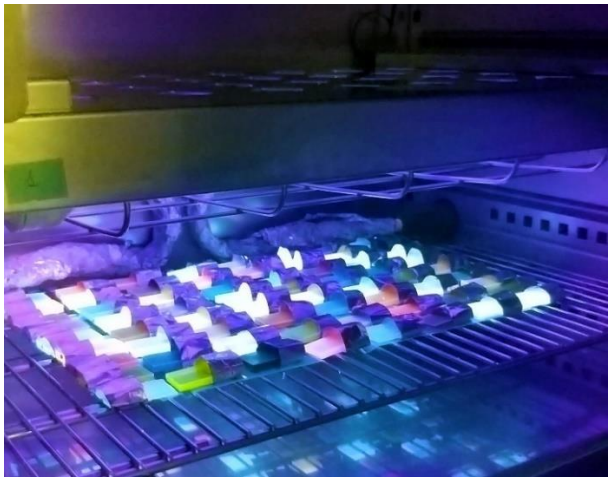

Fig. 3 *Samples during the ageing inside the climate chamber*

Fig. 4 *Samples during the outdoor ageing period*

2.4 *Colour change analysis: results discussion*

After the exposure, some samples showed visible variations (Figs. 5, 6); however, to obtain objective and comparable data, they were analysed with a spectrophotometer CM-2600d Konica Minolta with horizontal alignment, D 65 illuminator, d/8° illuminator/observer geometry, specular component excluded (SCE). This instrument provides quantifiable data about the colour change as reflectance spectrum and colorimetric coordinates in the CIE(Lab) colour space. In this colour space, the chromatic differences can be expressed as ΔE value.

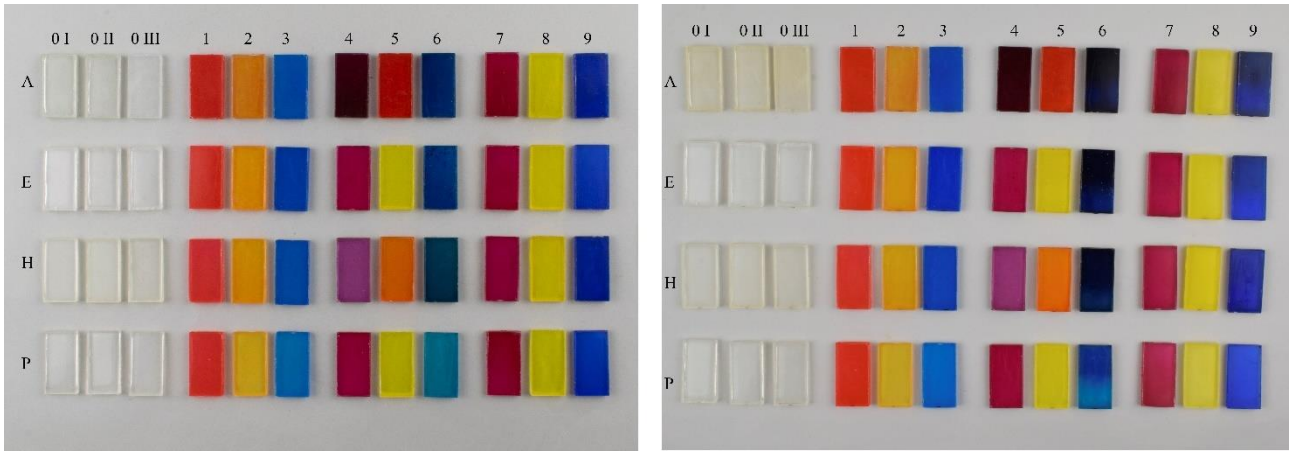

Fig. 5 *Samples aged in the climate chamber, before and after the ageing. Differences can be seen also between the UV radiation exposed half (the upper one) and the covered half (the lower one).*

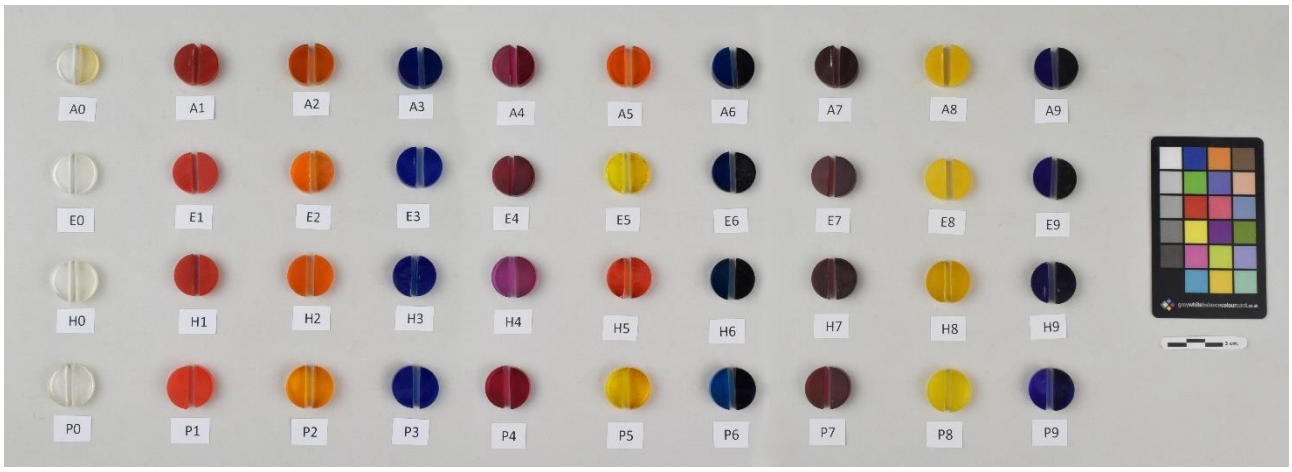

Fig. 6 *Samples aged outdoor, on the left the non-exposed half, on the right the aged one. Colour differences can be seen.*

ΔE had been calculated using the formula: $\mathbf{\Delta E^*ab = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}}$

L values express lightness, *a* expresses the red/green component, and *b* expresses the blue/yellow component.

Each specimen has been analysed before and after the accelerated ageing processes.

Two Paraloid B-72 independent samples and three clear independent samples of each epoxy resin were analysed, to verify their colour variability. Average values of colour coordinates and related standard deviation reported in (Tables 4, 5) show good sample homogeneity within each class of resin both before and after ageing.

Table 4 *Average L, a and b values for each sample set before climate chamber ageing.*

AVERAGE COLOUR COORDINATES before ageing			
	L	**a**	**b**
A0	61 ± 3	-0.1 ± 0.1	6 ± 1
E0	66 ± 3	1.00 ± 0.05	6.2 ± 0.2
H0	67 ± 3	0.3 ± 0.2	8 ± 1
P0	70 ± 1	0.9 ± 0.1	6.1 ± 0.4
D0	76 ± 7	0.5 ± 0.2	5 ± 1

Table 5 *Average L, a and b values for each sample set after climate chamber ageing, both exposed to UV radiation and not.*

AVERAGE COLOUR COORDINATES after ageing						
	NO UV			UV		
	L	**a**	**b**	**L**	**a**	**b**
A0	61 ± 3	0.10 ± 0.16	9.0 ± 1.2	60.0 ± 2.2	0.5 ± 0.2	10.4 ± 0.6
E0	67.0 ± 1.7	0.93 ± 0.04	6.8 ± 0.1	68.0 ± 2.5	0.88 ± 0.06	6.53 ± 0.34
H0	68.3 ± 0.81	0.40 ± 0.06	8.1 ± 0.8	68.0 ± 3.1	0.5 ± 0.1	8.0 ± 0.8
P0	70.0 ± 1.4	0.81 ± 0.07	6.5 ± 0.5	70.2 ± 0.6	0.74 ± 0.02	7.2 ± 0.5
D0	74.0 ± 0.4	0.63 ± 0.02	5.1 ± 0.3	75.4 ± 0.6	0.56 ± 0.08	4.8 ± 0.1

Usually, measured changes in ΔE less than 3 are considered as zero within experimental error, acceptable from 3 to 5, and unacceptable when more than 6 [29]. However, these standards are based on different fields of application. We revised them, as in our case more tolerance was allowed, especially considering that no methods are currently available to inhibit completely resins discolouration, and research must focus on finding the most resistant option [1].
To identify acceptability limits we compared ΔE values to visual observations of the samples, finding that, for our purpose, $\Delta E<5$ could be considered optimum as no difference was noticeable to the naked eye, and values up to 10 are acceptable.
The following tables summarize the results obtained for outdoor-exposed samples' ΔE (Tab. 6), and climate chamber exposed samples' ΔE (Tab. 7).

Table 6 *Summarising colour change measurement results for outdoor exposed samples.*

OUTDOOR		MICROLITH			ORASOL			VITRAIL		
RESIN	0 (pure)	1 (red)	2 (yellow)	3 (blue)	4 (red)	5 (yellow)	6 (blue)	7 (red)	8 (yellow)	9 (blue)
A (Araldite 2020)										
E (Epo-Tek 301-2)										
H (Hxtal Nyl-1)										
P (Plexi Fluid 2.0)										

LEGEND	
	$0 \leq \Delta E \leq 5$
	$6 \leq \Delta E \leq 10$
	$\Delta E \geq 11$

Table 7 *Summarising colour change measurement results for chamber exposed samples. The upper half of each box shows UV-exposed portion values, while the lower half shows results for the covered portions.*

CHAMBER			MICROLITH			ORASOL			VITRAIL		
RESIN		0 (pure)	1 (red)	2 (yellow)	3 (blue)	4 (red)	5 (yellow)	6 (blue)	7 (red)	8 (yellow)	9 (blue)
A (Araldite 2020)	UV										
	/										
E (Epo-Tek 301-2)	UV										
	/										
H (Hxtal Nyl-1)	UV										
	/										
P (Plexi Fluid 2.0)	UV										
	/										
D (Paraloid B-72)	UV										
	/										

LEGEND	
	$0 \leq \Delta E \leq 5$
	$6 \leq \Delta E \leq 10$
	$\Delta E \geq 11$

These tables, studied in parallel with the reflectance spectra, permitted us to easily compare the different products' combination. Significant changes, in fact, could be seen in peaks too. Images 7 and 8 show the difference between Epo-Tek 301-2 + blue Orasol (E6) climate chamber spectrum, where the reflectance spectrum has changed after the ageing with a significant decrease in the blue region, more noticeable where the UV component is considered, and Hxtal Nyl-1 + blue Microlith T climate chamber one (H3), where the reflectance spectra are perfectly overlayed, both considering and excluding the UV radiation component.

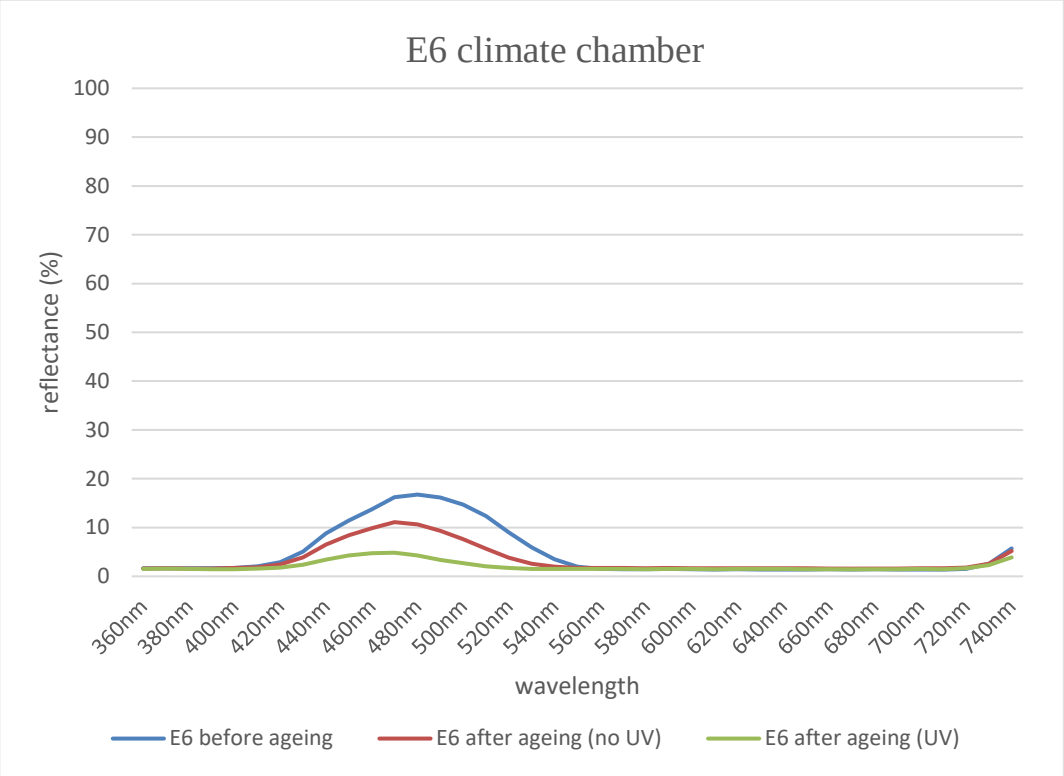

Fig. 7 *Sample E6 climate chamber (Epo-Tek 301-2 + blue Orasol) reflectance spectrum. Differences can be noticed between the spectra before and after the ageing process.*

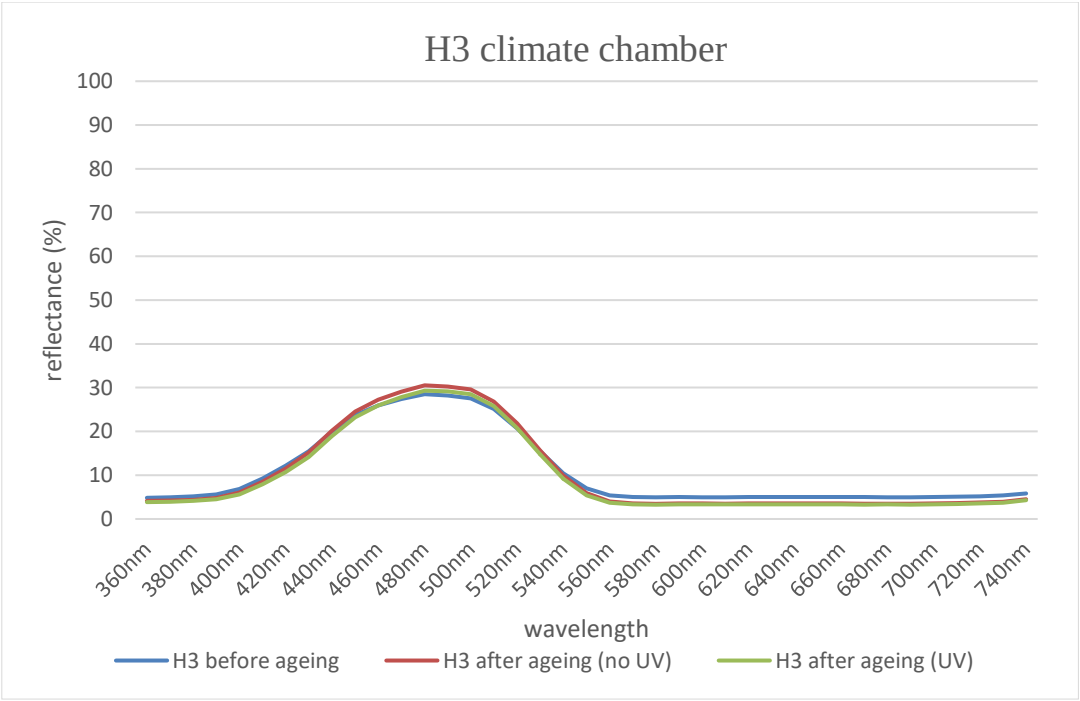

Fig. 8 *Sample H3 climate chamber (Hxtal Nyl-1 + blue Microlith) reflectance spectrum. Lines are perfectly overlayed.*

Orasol dyes were the most unstable colouring agents, especially the blue one. Significant changes were visible to the naked eye, both after chamber and outdoor exposure. Our results agree with other studies carried out on these dyes, proving the hardener addition can significantly vary their hue, making it difficult to match the original colour of an artefact, and they cannot guarantee enough stability with ageing [10, 30]. This, in addition to problems occurred during the samples' preparation (see section 2.2), lead us to exclude their use. Vitrail proved to be more stable to temperature variations, but poorly light-fast. Climate chamber samples exposed to UV radiation visibly changed, as well as outdoor ones, as shown before (Tables 6, 7).

As colouring agents, Microlith T seemed the best performing ones, showing unacceptable results only when combining the yellow one with Epo-Tek 301-2 and Plexi Fluid 2.0 and exposing outdoors. This general better performance can be expected because Microlith T are pigments in the form of micronized particles, while Orasol and Vitrail are dyes. However, these results demonstrate that a crucial role in their light-fastness is also played by the resin system, being Hxtal Nyl-1 the best performing in combination with Microlith T.

Concerning epoxy resins, all of them gave acceptable responses to the tests, except for the Araldite 2020 outdoor-exposed sample, which was visibly changed. Epo-Tek 301-2 was also excluded, due to its tendency to crystallisation at low temperatures. In outdoor-exposed sample, we also noticed that the surface had become extremely rough. Both Hxtal Nyl-1 and Plexi Fluid 2.0 were easily mixable and pourable, samples had no imperfections, and showed good ageing properties in clear samples.

Our choice was then guided by the observation of the coloured samples' behaviour and fell on Hxtal Nyl-1, the only resin having, as discussed before, good or acceptable results for each of the Microlith T-pigmented samples in every ageing conditions. This choice is also supported by previous publications testing Hxtal Nyl-1 ageing behaviour compared to other resins [7, 9].

Finally, Paraloid B-72 confirmed its good resistance to discolouration [6, 31].

Its employment as gap-filling material was excluded as many bubbles formed while preparing the samples. Moreover, the process required too long and to shape the foil heating the resin could have been necessary. Finally, some studies stated that thick Paraloid B-72 films could deform when stored in hot environments (30-35°C) [32].

Some overall conclusions can be made. Most of the products tested proved to be more sensitive to UV or natural light exposure, testifying that light is the main cause of their deteriorating processes. Coloured outdoor-exposed samples showed in some cases less discolouration than pure resins (see Figs. 9 and 10), maybe as some colouring agents could act as UV absorbers.

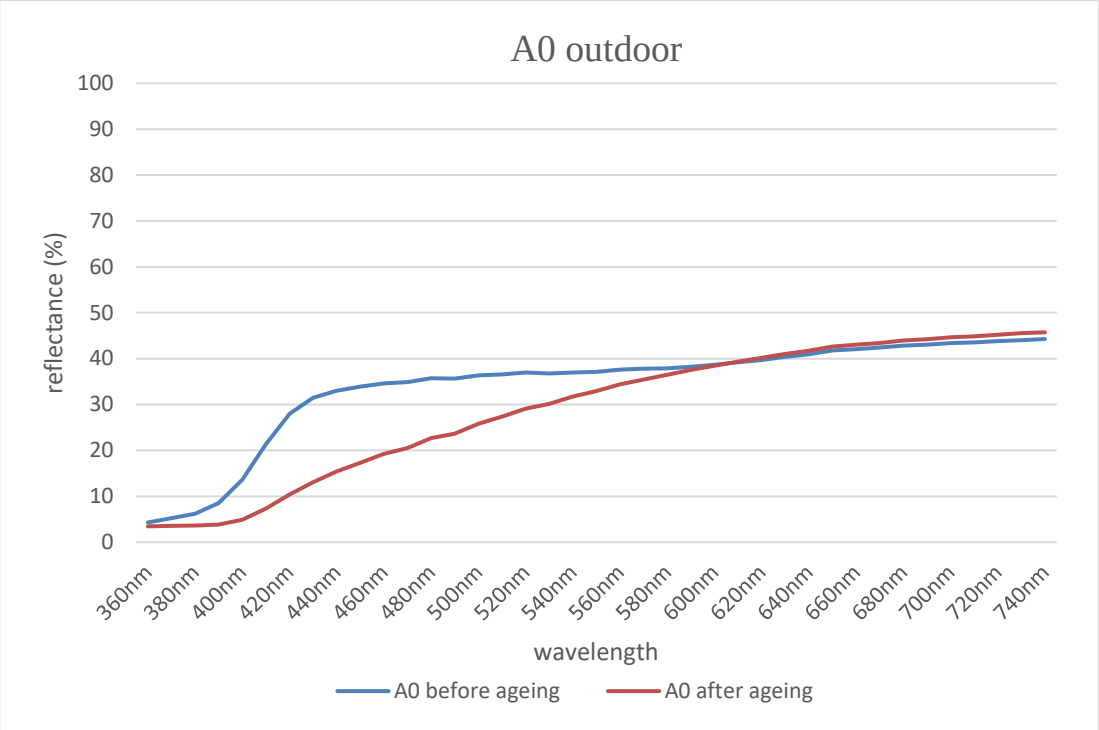

Fig. 9 *Sample A0 outdoor (Araldite 2020, clear) reflectance spectrum. After ageing the spectrum significantly changed.*

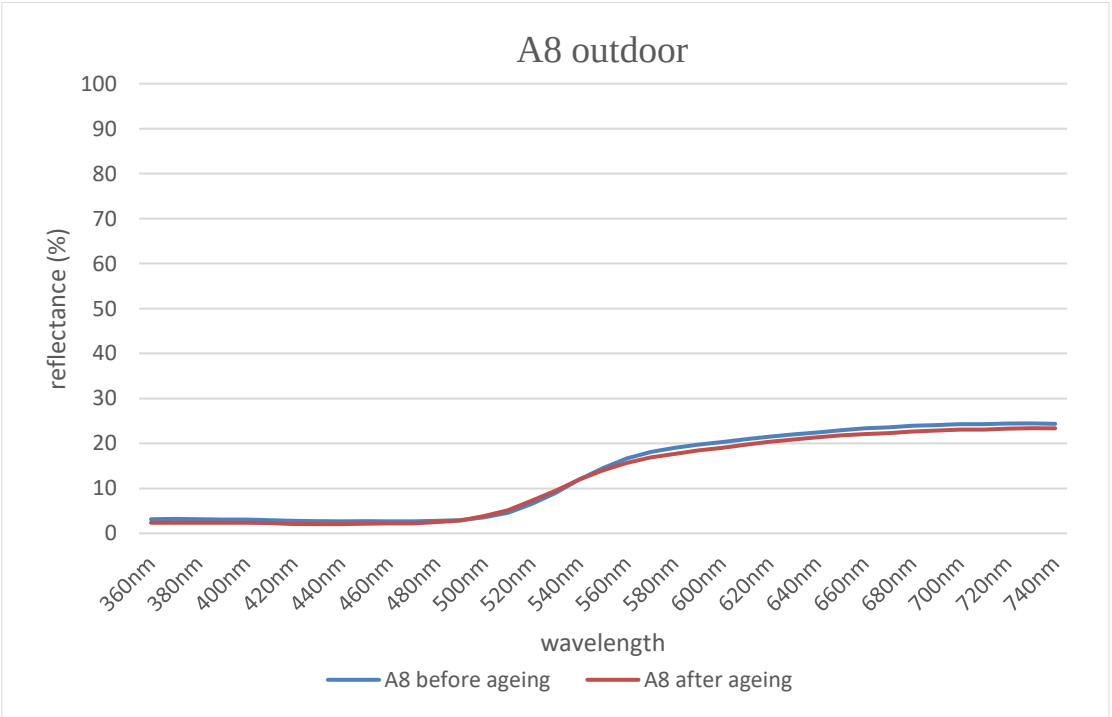

Fig. 10 *Sample A8 outdoor (Araldite 2020 + yellow Vitrail) reflectance spectrum. No significant differences occurred after the ageing.*

2.5 CONSOLIDANTS

Glass surface consolidation treatment should be avoided when not strictly necessary, as its reversibility cannot be guaranteed. Even highly soluble products can be very difficult to remove from severely degraded surfaces. However, in dealing with archaeological glass vessels, the use of consolidants should be considered [12]. During burial, due to the water in the ground, iridescent layers can form. This results in a fragile surface [33]. Moreover, glass objects coming from the hexagonal structure were gilt and enamelled, and most of them exhibited flaking decoration layers.

As stated before, the identification of the best performing product is essential in glass conservation, thus, we decided to compare the commonly used resin Paraloid B-72 to an innovative product: Siox-5-RE20C.[13] It is a ready-to-use alcohol-based formulation, containing nano-structural silica gel, that creates an amorphous silica layer. This material can be considered more chemically compatible with glass; moreover, it is also compatible with acrylic resins applied *in situ* by Soprintendenza[14].

Both products were primarily applied on modern glass fragments, giving good results in aesthetical terms. Then, we tried them on a selection of 50 fragments from the Santa Chiara site, that had no connection with others. Half of them were treated with Siox-5-RE20C, by applying it with a soft brush, being careful not to reapply it on already coated areas. Paraloid B-72 in acetone (7.5% w/v) was also applied with a brush.

Results were observed under a stereomicroscope. Siox-5-RE20C-coated fragments showed non-homogeneous/uneven results: Some of them had considerably improved, with the iridescence layers re-adhered to the surface and transparency regained, the others' condition, however, worsened, showing cracks and uplifts of the degraded layers (Fig. 11).

Paraloid B-72 showed good results: uplifted layers reattached to the surface and transparency slightly improved (Fig. 12).

Sol-gel products do not have good adhesive properties [12], this could be the reason behind the unpredictable outcomes of Siox-5-RE20C's coatings on detaching layers. Thus, we decided to use Paraloid B-72 in acetone.

[13] https://www.siltea.eu/prodotto-siox-5-re20c/

[14] Primal AC-33 in demineralized water and/or Paraloid B-72 in acetone, ad different percentages.

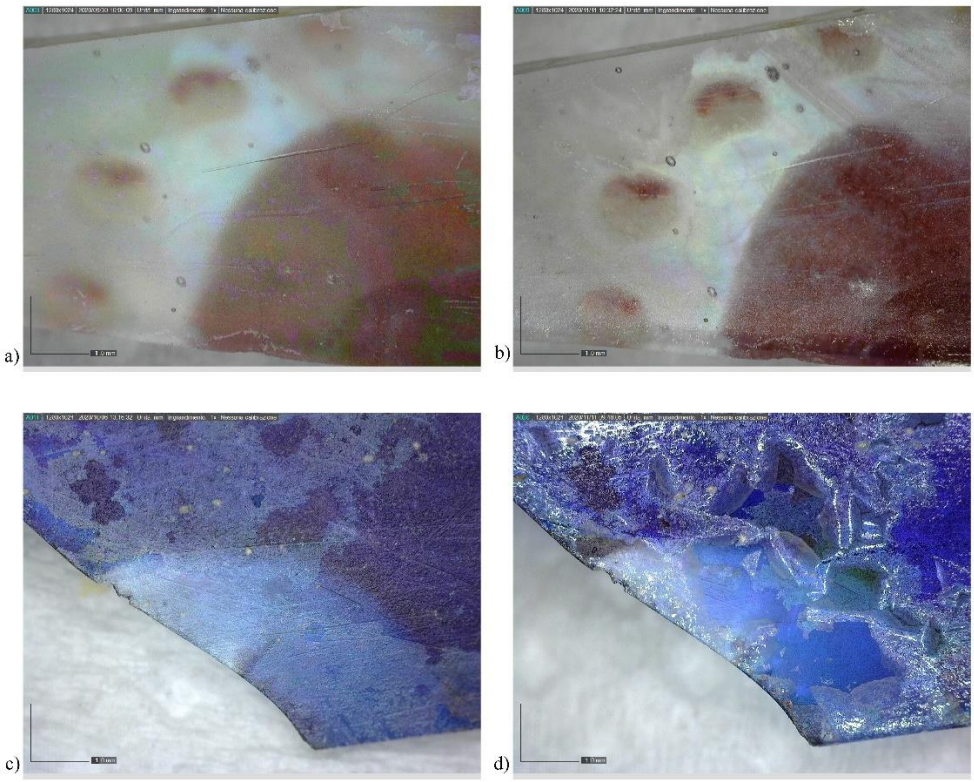

Fig. 11 *a) Enamelled glass fragment before the Siox5-RE20C application; b) the same fragment after the consolidation. Transparency is improved; c) blue glass fragment before the Siox5-RE20C application; d) the same fragment after the consolidation. Iridescent layers cracked and uplifted.*

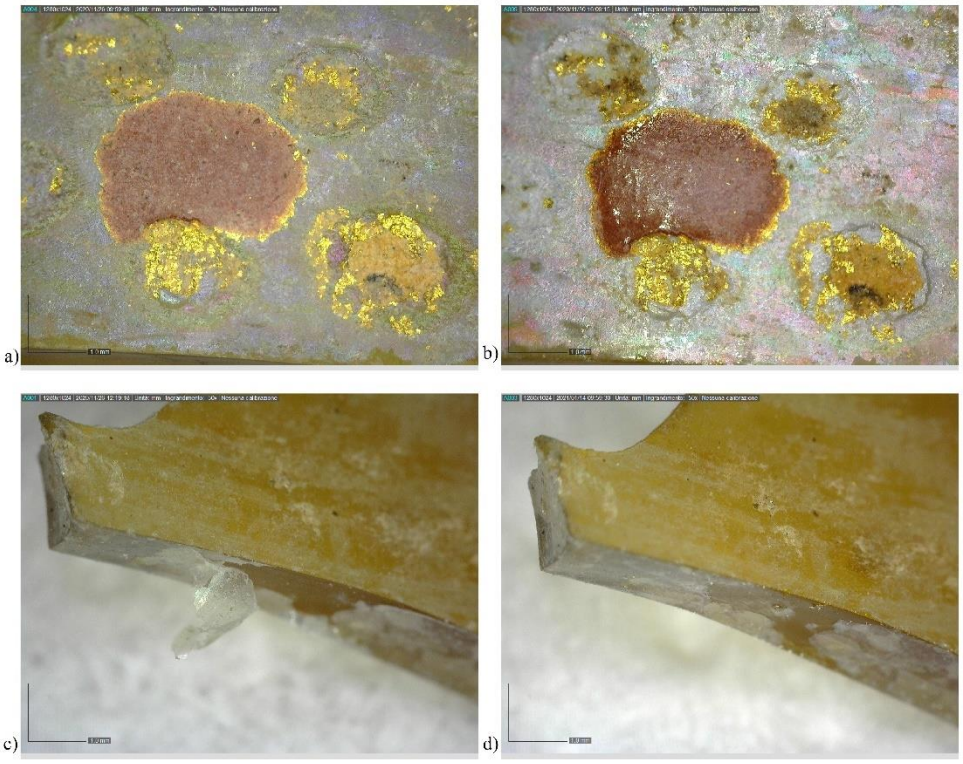

Fig. 12 *a) Enamelled and gilded glass fragment before Paraloid B-72 application b) the same fragment after the consolidation. Transparency and colour vibrancy slightly improved; c) glass fragment with uplifted layers before the Paraloid B-72 application; d) the same fragment after the consolidation. Uplifted layers reattached to the surface.*

3. CONSERVATIVE INTERVENTION

In this section, two case studies will be presented, showing how the selected products were used. The importance of carefully choosing the best techniques to be employed, according to every glass object's conservative state, will also be discussed.

3.1 *Case study 1: amber-coloured beaker*

The first artefact is a gilt and enamelled, amber-coloured beaker.
The beaker was in 16 fragments, but only 8 were connected together. The foot was entirely preserved, while the walls and the rim were incomplete. Despite the consolidation treatment made in situ by the Soprintendenza, using Primal AC33 (in water, 20% w/w), the surface was in a bad conservative state. The thick iridescent layers were uplifted, as well as most of the gold leaf. Some enamel dots were missing, while others were degraded to the point that their original colour was not recognisable anymore. As the object had been already cleaned and the surface was fragile, the first step was the application of Paraloid B-72 in acetone (7.5% w/v) as a consolidant. A soft brush was used, gently patting it on the uplifted layer, to make them re-adhere.
The fragments were then glued, using Paraloid B-72 in acetone (70% w/w), as the fragments were thick and opacified and the bubbles due to the solvent evaporation would not have been noticeable.
The presence of extended losses made the reconstruction unstable. As a minimal intervention is advisable, we made a digital drawing, to better understand which areas needed to be filled. Two main gaps compromised the beaker's stability (Fig. 13).

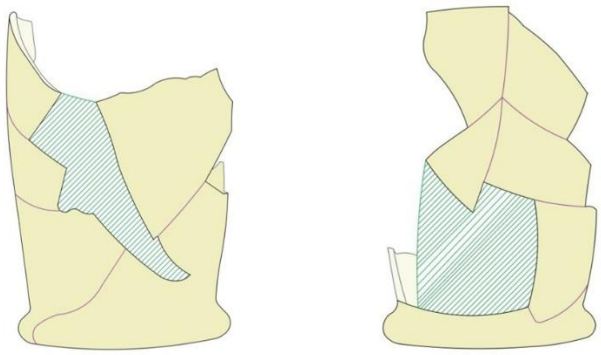

Fig. 13 *Digital drawing: projected gap-fills are coloured with a green-line pattern.*

When filling glass artefacts, direct and indirect methods can be employed.
The first ones consist in pouring a resin directly on the object, into moulds that can be realized with different materials. If the moulds are precise, direct castings need less finishing work, but letting the resin cure on the glass surface can create tensions due to the resin strength, as epoxies are the most used for this operation. Moreover, it makes the operation less reversible [34, 35].
Indirect loss compensations involve the realization of the fills separately from the object. Different methods can be employed, but the most common one is the making of a positive of the missing area from where a mould can be made to pour the resin. Another common method is the use of pre-cured resin sheets, that can be cut and shaped to fit the loss. Once the fill is obtained, it can be glued as the

other glass fragments. These methods are easily reversible if a soluble adhesive is used and would be preferred [36, 37].

Fig. 14 *The images show some phases of the fills realization.*

The regular thickness of the beaker's walls and the bad conservative state of its surface led us to choose the sheets method. The application of moulds directly on the degraded glass should have been dangerous, and even modelling a detached positive would have required continuous handling of the object. Hxtal Nyl-1 epoxy resin was added with Microlith T micro-pigment, till the desired hue was obtained. We decided to make it slightly lighter than the original one, to make our intervention more recognisable. The coloured resin was then mixed with the hardener and cast into a silicone rubber rectangular mould. Thickness was measured using a calliper.

Usually, resin sheets are removed from the mould when completely cured and shaped by heating them [38]. To avoid this operation, which could accelerate the ageing processes, we decided to remove our sheet when not completely cured. The sheet needed to be soft enough to be cut and shaped, but not too much, to prevent impressing fingerprints. The long curing time of Hxtal Nyl-1 was perfectly suitable for this purpose. The sheet was then cut, using scissors and a scalpel, the edges were finished using fine sandpaper and glued in the right position while still soft, using Paraloid B-72 adhesive (Fig. 14).

At this point, the fills perfectly fit into the gaps, however, as they were extended, they disturbed the legibility of the beaker's decoration. Thus, we decided to paint some dots, using Maimeri Polycolor® acrylics, reproducing the scale motif.

The lower band was not reproduced, as the original colour of the enamel was not intelligible (Fig. 15).

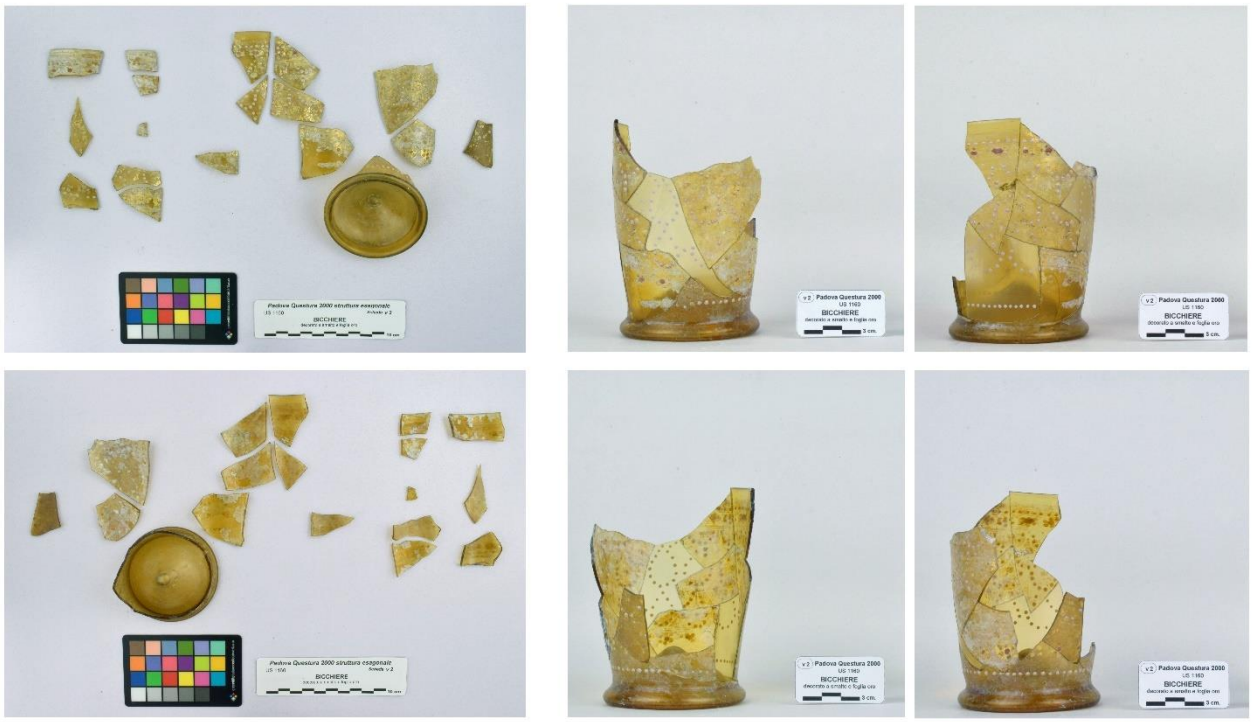

Fig. 15 *The amber-coloured glass before (on the left) and after the conservative intervention (on the right)*

3.2 *Case study 2: emerald-green bowl*

The second case study presented is a footed and ribbed emerald-green bowl.
It was in 65 pieces, most of them in connection. Most of the foot was missing, as well as some portions of the walls and part of the rim. The surface was slightly iridescent but there were no uplifted layers, for this reason consolidation treatments were not applied either during the first-aid intervention, or in our laboratory. The dust deposition was removed using cotton buds, wet in a solution of demineralised water, ethanol and acetone (1:1:1 ratio). Before gluing the fragments, we pre-assembled them using 3M Premium 3030 tape, to better understand the correct order to reassemble them. This operation is helpful when dealing with a multitude of fragments. It was immediately clear that a huge loss compromised the bowl's reconstruction stability, and a fill was needed.
Paraloid B-72 in acetone (70% w/w) was used as adhesive. The floating portions were assembled in a second step, just before the fill's realization, as the connecting areas were too small compared to these portions' width and weight and they would have surely collapsed.

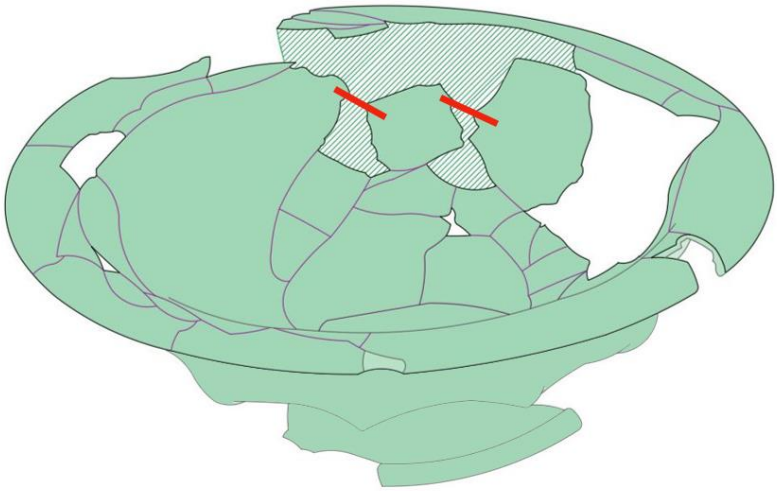

Fig. 16 *Digital drawing: projected gap-fills are coloured with a green-line pattern. Red lines indicate limits of each fill made separately.*

A digital drawing was used again to plan the fill's realization (Fig. 16). The bowl's loss had a complex shape and was variable in thickness; moreover, the presence of two narrowings made it impossible to realize it in one piece. We decided to divide the upper part from the lower ones.
As for the method to be employed, shaping a resin sheet into this loss would have been difficult and would not be aesthetically pleasing. Thus, for the upper part, we opted for a different indirect method, modelling a positive using Milliput® White, a workable but strong epoxy putty, commonly employed in porcelain conservation. Usually, plaster is used instead but it is brittle, and, in this case, it would have broken. We created an open mould, impressing a dental wax sheet to a better-preserved area, and then we placed it where the gap was. Along the glass edges a release agent was applied, to help the Milliput positive's extraction, and then the putty was applied. When completely cured, we detached the floating rim's portion using acetone, simultaneously removing the product in excess from the edges using a scalpel. The Milliput portion was finished separately, with the help of spatulas, and different sandpapers, but its shape was constantly verified by placing it in the gap.
Once the right shape was obtained, the surface was sprayed with Maimeri Polycolor Film transparent varnish, to give it a glass-like finish. To create moulds, the most employed products are pourable silicone rubbers; however, they have a long curing time and are prone to bubbles formation. Dental silicone rubbers are used to create moulds for direct castings; as they cure in a short time, they are ideal to be applied on vertical surfaces such as vessel walls [39]. We decided to try their application also for indirect castings. We glued metal wires to the Milliput positive, which would have been the canals for pouring resin and for air-escaping. We applied a thin layer of a less viscous silicone rubber, covering all the Milliput positive, and then another layer of a more viscous, less precise one, to reinforce the mould. To prevent any deformation, a plaster base was created, fitting the curved part of the mould. The Milliput positive was then removed through a lateral cut and the mould was sealed using the softer silicone rubber. Then the metal wires were removed, and two straws were glued and sealed, to enlarge the canals on the outer. The canals' collocation had been previously studied, to guarantee the complete fill of the mould and prevent bubbles.
As for the beaker, we added Microlith T micro-pigments to Hxtal Nyl-1, making samples to verify that the colour matched the bowl one, and then the resin was poured into the mould (Fig. 17).

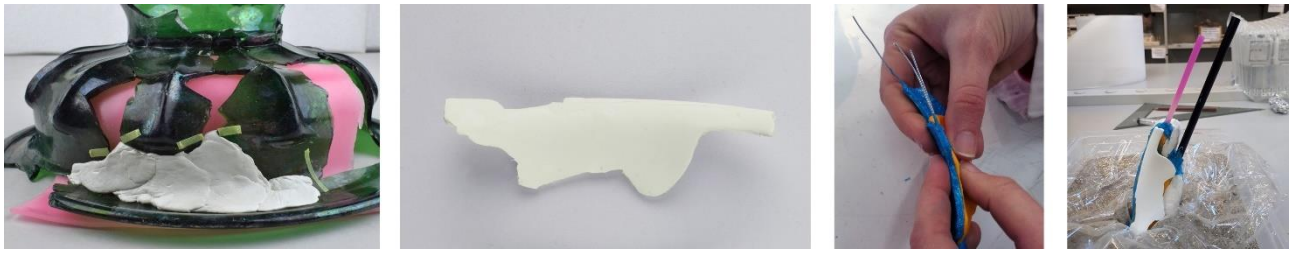

Fig. 17 *The images show some phases of the indirect fills' realization.*

During the finishing of the Milliput positive, the lower floating fragments detached several times, making it clear that a different solution must be adopted to compensate those losses. We decided to cast them directly. The rim fragments were glued, as well as the Milliput positive, which kept them in the right position. All along the edges Paraloid B-72 in acetone (10% w/v) was applied as primer, to make the epoxy resin more reversible. On Milliput positive edges a layer of microcrystalline wax was applied as well, as release agent.

Fig. 18 *The images show some phases of the direct castings.*

Two-part moulds were made by applying the two silicone rubbers mentioned above right on the glass surface where the walls were conserved. Then, we cut them and positioned them on the losses, using Kulzer® adhesive, which is specific for use with silicone rubbers. Dealing with direct castings, the project is particularly relevant, as finishing should be limited to the bare minimum. The canals placement must be correct, and the inclination of the object is equally crucial to avoid any flaws. Usually, canals should be put on the corners, and the loss edges should not be horizontal, as some air would be trapped inside. To help us to correctly orient the bowl, we draw indicators directly on the mould. Two straws were glued on each mould, where holes had been previously made, as canals, and sealed with the softest silicone rubber. Then, the coloured resin was poured (Fig. 18).
Once cured, the Milliput positive was removed and substituted with the Hxtal Nyl-1 one.
Joints' lines were not evident, and the three parts in which the fill was divided fitted nicely.
As for the foot, a support was preferred over the loss compensation, as this solution would have helped distributing the weight of the bowl on a larger and more solid area. We decided to use Balsite®, a lightweight epoxy putty. We created a dental wax open mould and gently push the putty inside till the foot was completely full. Once cured, we finished it with sandpapers, and we coloured it with acrylics.

Fig. 19 *The bowl before and after the conservative intervention. In the second image, the gap-fills and the foot support can be seen.*

CONCLUSIONS

Dealing with the conservation of some coloured glass vessels from the Santa Chiara in Cella Nova archaeological site (Italy) highlighted the importance of a good understanding of ageing behaviour of coloured resins. This is necessary to project an intervention that would be durable and postpone, as long as possible, the need of a new intervention on fragile glass artefacts.
Results obtained during accelerated ageing tests showed that Hxtal Nyl-1 has good discolouration resistance and demonstrated that Microlith T micro-pigments, not only have a better light-fastness but also a good aesthetical appearance. Therefore, they could be considered as a valid substitute to Orasol (which are still the most employed dyes despite the clear evidence of their inadequacy). Paraloid B-72 resistance was also demonstrated.
These products were employed in the reconstruction of the vessels coming from the hexagonal structure, but choosing the best method to use them was equally important.

AKNOWLEDGMENTS

Authors want to thank the Soprintendenza ABAP per l'Area Metropolitana di Venezia e le Province di Belluno, Padova e Treviso, especially the Conservator Sara Emanuele, for the opportunity to work on the conservation of the precious Santa Chiara in Cella Nova glass artefacts.
We also thank the Department of Cultural Heritage and the Department of Industrial Chemistry of the University of Bologna for the possibility of carrying out this research.
Finally, we would like to thank Doctor Cristina Tonini, for her precious help.

DATA AVAILABILITY STATEMENT

Access to all data mentioned in this paper can be requested from the corresponding author.

REFERENCES

1 J. L. DOWN, *Review of CCI Research On Epoxy Resin Adhesives For Glass Conservation* (Studies in Conservation 46, 2001), pp. 39-46

2 M. MATTEINI, R. MAZZEO, A. MOLES, *Chemistry for Restoration. Painting and Restoration Materials* (Nardini Editore, Firenze, 2017)

3 S. DAVISON, *Conservation and Restoration of Glass* (Butterworth-Heinemann 2nd Ed., an imprint of Elsevier Science Ltd, Oxford, 2003)

4 ed. by F. COZZA, *Le memorie ritrovate del monastero di Santa Chiara di Cella Nova a Padova* (Nuova Grafotecnica Casalserugo (PD), 2011), pp. 9-11

5 R. BAROVIER MENTASTI, *La vetraria veneziana*, in *Storia di Venezia* (Enciclopedia Italiana Treccani, 1995), pp. 871-872

6 J. DOWN, L. MACDONALD, A. MAUREEN et al. *Adhesive Testing at the Canadian Conservation Institute--an Evaluation of Selected Poly(vinyl acetate) and Acrylic Adhesives* (Studies in Conservation 41, 1996), pp. 19-44

7 I. COUTINHO, F. M. B. FERNANDES, A. M. RAMOS, A. LIMA, *Studies on Degradation Of Epoxy Resins Used for Conservation of Glass* in *Holding it all together: Ancient and Modern Approaches to Joining, Repair and Consolidation* (London: Archetype PuLettieri 2008), pp. 127-133

8 N. H. TENNENT, S. P. KOOB, *An Assessment of Polymers Used in Conservation Treatments at The Corning Museum of Glass*, in H. ROEMICH (edited by) *Glass and Ceramics Conservation* (International Council of Museums, 2010)

9 I. D. SIDERIDOU, E. C. VOUVOUDI, G. D. PAPADOPOULOS, *Epoxy Polymer Hxtal NYL-1TM Used in Restoration and Conservation: Irradiation with Short and Long Wavelengths and Study of Photo-Oxidation by FT- IR Spectroscopy*, vol. 18, (Journal of Cultural Heritage, 2016), pp. 279-289

10 M. I. CELORICO, J. L. FERREIRA, I. COUTINHO, *The color effect of Orasol dyes in epoxy resins Hxtal NYL-1 and Araldite 2020 for glass and ceramics conservation*, in *Short paper of the 6th YOCOCU Conference – Dialogues in Cultural Heritage – Matera*, ed. By A. Macchia, N. Masina, M. F. La Russa, F. Prestileo (eds.), (YOCOCU & CNR-IBAM, 2018), pp. 155-158

11 S. P. KOOB, *Tips and tricks with epoxy and other casting and molding materials*, in *Object's speciality Group Postprints*, vol. 10, ed. By V. GREENE, D, HARVEY, P. GRIFFIN (The American Institute for Conservation of Historic and Artistic Works, Washington DC, 2004), pp. 158-172

12 S. CHAPMAN, D. MASON, *Literature Review: The Use of Paraloid B-72 as a Surface Consolidant for Stained Glass*, vol. 42, no. 2, Objects Issue (Journal of the American Institute for Conservation, 2003), pp. 381-392

13 S. P. KOOB, S. BENRUBI, N. A. R. VAN GIFFEN, N. Hanna, *An Old Material, a New Technique: Casting Paraloid B-72 for Filling Losses in Glass* in *Adhesives and Consolidants for Conservation: Research and Application* (CCI Symposium, Ottawa, Canada, 2011)

14 E. AGNINI, A. M. LEGA, *Il restauro della Porcellana*, in *Quaderni di restauro della ceramica*, vol. 3, ed. By A. M. LEGA (Museo Internazionale delle Ceramiche in Faenza, Faenza, 1999), pp. 27-28

15 Webinar "*Studio tecnologico, degrado e restauro dei vetri policromi: tre vetri della necropoli altomedioevale di Castel Trosino (AP)*" (YOCOCU, Museo delle Civiltà MuCiv, Istituto Centrale del Restauro ICR, Italian AIHV Comitee, 2019) https://www.youtube.com/watch?v=f4HM2u9pWXA&t=9169s

16 C. ECKMANN, *Ein schnellhärtender Silikonkautschuk auf Vinylpolysiloxan-Basis als Manschettenmaterial bei Ergänzungen von Gläsern* (Arbeitsblätter, 1995)

17 R. BOLLATI, E. HUBER, M. E. PRUNAS, *Il Restauro della vetrata della cappella della Maddalena*, no. 20-21 (Bollettino ICR, 2010), pp. 46-63

18 S. KOOB, *Conservation and Care of Glass Objects* (Archetype Pubblications Ltd., London, 2006)

19 H. L. SHELLEN, *A sound indoor climate for a museum in a monumental building,* in *Thermal Performance of the Exterior Envelopes of Whole Buildings - 11th International Conference* (Clearwater, Florida, 2010)

20 F. SCIURPI, C. CARLETTI, G. CELLAI, V. MURATORE, A. ORSI, L. PIERANGIOLI, G. RUSSO, E. D. SCHMIDT, *Environmental Monitoring and Building Simulation Application to Vasari Corridor: Preliminary Results,* vol. 133 (Energy Procedia, 2017), pp. 219-230.https://doi.org/10.1016/j.egypro.2017.09.393

21 R.P. KRAMER, H.L. SCHELLEN, A.W.M. VAN SCHIJNDEL, *Impact of ASHRAE's museum climate classes on energy consumption and indoor climate fluctuations: full-scale measurements in museum Hermitage Amsterdam* (2016), https://doi.org/10.1016/j.enbuild.2016.08.016

22 D. CAMUFFO, R. VAN GRIEKEN, H. J. BUSSE, G. STURARO, A. VALENTINO, A. BERNARDI, N. BLADES, D. SHOOTER, K. GYSELS, F. DEUTSCH, M. WIESER, O. KIM, U. ULRYCH, *Environmental monitoring in four European museums* (2000), https://doi.org/10.1016/S1352-2310(01)00088-7

23 A. TROI, P. BALDRACCHI, M. PAMPLONA, M. KRÜGER, C, AIBÉO, S. BACHMAIER, B. BUCZYNSKI, S. SIMON, J. CHAPUIS, *Museum Environment: Monitoring Fully and Partially Conditioned Rooms Within Smoohs Project* (Cultural Heritage Preservation - EWCHP, NILU, Kjeller, 2011), pp. 62-69

24 P. URING, A. CHABAS, S. ALFARO, M. DERBEZ, *Assessment of Indoor Air Quality for a Better Preventive Conservation of some French museums and Monuments* (2019), https://doi.org/10.1007/s11356-020-10257-6

25 J. FERDYN-GRYGIEREK, J. KACZMARCZYK, M. BLASZCZOK, P. LUBINA, P. KOPER, A. BULI´NSKA. *Hygrothermal Risk in Museum Buildings Located in Moderate Climate* (2019). https://doi.org/10.3390/en13020344

26 K. GYSELS, F. DELALIEUX, F. DEUTSCH, R. VAN GRIEKEN, D. CAMUFFO, A. BERNARDI, G. STURARO, H. J. BUSSE, M. WIESER, *Indoor environment and conservation in the Royal Museum of Fine Arts, Antwerp, Belgium* (2003). https://doi.org/10.1016/j.culher.2004.02.002

27 D. CAMUFFO, A. BERNARDI, G. STURARO, A. VALENTINO, *The Microclimate Inside the Pollaiolo and Botticelli Rooms in the Uffizi Gallery, Florence* (2001). https://doi.org/10.1016/S1296-2074(02)01171-8

28 G. STURARO, D. CAMUFFO, P. BRIMBLECOMBE, R. VAN GRIEKEN, H. J. BUSSE, A. BERNARDI, A.VALENTINO, N. BLADES, K. GYSELS, F. DEUTSCH, M. WIESER, S. BUCZOLITS, *Multidisciplinary Environmental Monitoring at the Kunsthistorisches Museum, Vienna* (2003), https://doi.org/10.1081/TMA-120020262

29 J. Y. HARDEBERG, *Acquisition and Reproduction of Color Images: Colorimetric and Multispectral approaches* (Universal Publishers, Parkland), 2001

30 N. H. TENNENT J. H. TOWNSEND, *The Photofading of Dyestuffs in Epoxy, Polyester And Acrylic Resins* (Glasgow Museums and Art Galleries, 1984)

31 O. CHIANTORE, M. LAZZARI *Photo-Oxidative Stability of Paraloid Acrylic Protective Polymers* (2000). https://doi.org/10.1016/S0032-3861(00)00327-X

32 A. VINÇOTTE, E. BEAUVOIT, N. BOYARD, E. GUILMINOT, *Effect of Solvent on Paraloid B72 and B44 Acrylic Resins Used as Adhesives in Conservation* (2019) https://doi.org/10.1186/s40494-019-0283-9

33 A. VAN GIFFEN, *Weathered archaeological glass*, in *All About Glass* (Corning Museum of Glass, 2014) https://www.cmog.org/article/weathered-archaeological-glass

34 S. FERUCCI, C. CAMERLO, *L'uso dei siliconi dentistici nella integrazione delle lacune dei reperti vitrei*, in *XII Congresso Nazionale IGIIC – Lo Stato dell'Arte – Accademia di Belle Arti di Brera –* (Milan, 2014)

35 S. DAVISON, *Reversible fills for transparent and translucent materials*, Journal of the American, vol. 37, no. 1 (Institute for Conservation, 1998), pp. 35-47 https://doi.org/10.2307/3179910

36 S. FERUCCI, *Conservazione e Restauro del Vetro* (VETRO E CERAMICA - Altare - IV Scuola Nazionale di Chimica per i Beni Culturali, Italy, 2002)

37 S. P. KOOB, *New techniques for the repair and restoration of ancient glass*, in *Tradition and innovation. Advances in conservation, Contributions to the Melbourne Congress* ed. By A. ROY, P. SMITH (2000) pp. 92-95 https://doi.org/10.1179/sic.2000.45.Supplement-1.92

38 L. HOGAN, *An Improved Method of Making Supportive Resin Fills for Glass*, no. 50 (Conservation News, 1993), pp. 29-30

39 H. BLANPAIN, D. DRIESMANS, S. BENRUBI, *Silicone as a moulding material for loss compensation: how to choose the right one?,* in *ICOM Conference: Recent Advances in Glass, Stained-Glass, and Ceramics Conservation*, *Amsterdam* (ICC committee per la conservation, Paris France 2013), pp. 319-321