Thermocasting of PARALOID B-72: Solvent-Free Production of Acrylic Flat-Glass Restoration Casts

ABSTRACT

Although praised as one of the most versatile and chemically stable adhesives and consolidants in conservation, PARALOID B-72 used as a solvent-based casting resin is less widespread. This paper presents the preliminary results of a new method, in which pure PARALOID B-72 is heated in silicone moulds in order reconstruct lost flat-glass fragments.

Making use of the polymer's low glass-transition temperature of 40 °C, pure, undissolved PARALOID B-72 can be melted in a silicone rubber mould using a hot air oven at 180 °C. The result is a clear, bubble-free cast that can be made to any thickness within one day and without significant shrinkage. Preliminary testing of the photostability of thermocast PARALOID B-72 suggests no adverse effects due to exposure to high temperatures. This paper outlines practical aspects of satisfactory melting and colouring of PARALOID B-72 in silicone moulds.

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INTRODUCTION

When compensating losses in glass, the use of clear synthetic resins as filling materials has many advantages. The nature of some resins currently used in conservation, including epoxies, acylates, and polyesters, is such that very realistic imitations of glass can be produced through direct or separate mould casting (Koob 2003; Davison 1998). Nevertheless, many of these casting resins are chemically unstable and an initially clear and colourless resin infill can develop a disfiguring shade of yellow in a relatively short time (Tennent 1979; Down 1984; Down 1986; Down 2001). Replacing degraded infills is certainly not without risk for the object (Koob 2006), and can present health and safety issues for conservators, considering the toxicity of solvents often required to dismantle old restorations (Caen, De Vis, and Tennent 2009). Despite these disadvantages, unstable resins continue to be used in conservation studios (Tennent and Koob 2010; Jackson 1989).

PARALOID B-72, an ethyl methacrylate methyl acrylate copolymer produced by Röhm and Haas, meets contemporary conservation standards of reversibility, low toxicity, and long-term chemical stability (Horie 1982; Ciabach 1983). Because of these desirable properties, a method was developed at the Corning Museum of Glass to use solvent-cast PARALOID B-72 as a stable and versatile filling material for glass (Koob et al. 2011; Van Giffen, Koob, and O'Hern 2013). To prevent

Figure 1. *Siliconen Culinair platinum-cured, addition silicone rubber mould filled with ground PARALOID B-72*

the formation of the bubbles for which solvent-cast PARALOID B-72 is notorious, a controlled solvent evaporation procedure must be strictly followed. Depending on the solvents used and on the thickness and size of the film, the setting time ranges from a couple of days to up to a week.

This paper introduces an alternative approach to casting PARALOID B-72. Instead of solvents, heat is used to liquefy pure, undissolved resin pellets in a silicone rubber mould to produce a PARALOID B-72 'thermocast'. Heat-formed PARALOID B-72 does not shrink and sets fully while cooling down, therefore, a thermocast can be placed into a lacuna immediately. The method will be presented here in the context of indoor stained-glass conservation but can also be adapted to the conservation of other types of glassy materials.

THERMOCASTING PARALOID B-72

Heating PARALOID B-72

When heated incrementally, a thermoplastic polymer like PARALOID B-72 passes from a glassy state, to a rubbery state (the glass transition temperature, Tg), to a state in which it acts like a flowing liquid. Despite the resin's relatively low glass transition temperature of approximately 40 °C (Schilling 1989), solid pellets of PARALOID B-72 will melt into a clear resin film only at temperatures above 150 °C. At this temperature, the viscosity of the resin still prevents air, trapped between the resin pellets, from escaping. Exposure to temperatures over 200 °C makes the resin very fluid, but has been shown to induce yellowing and the formation of gas bubbles in the resin. Heating at 180 °C has been found to be favourable: at this temperature, PARALOID B-72 has the viscosity of honey and will take the form of any substrate or mould onto which it is melted. Cooling down, PARALOID B-72 returns to its solid, glassy state, forming a clear resin film without noticeable shrinkage.

In order to facilitate more efficient melting of the resin, finely ground PARALOID B-72 was used instead of the usual cylindrical pellets. Air pockets enclosed in the resin during the heating process appear to escape better when a small resin particle size is used. To obtain these small resin particles,

Figure 2. *Finished uncoloured PARALOID B-72 thermocast before adhering into a lacuna at the corner of a piece of sheet glass*

PARALOID B-72 pellets were milled in a food processor and passed through a 500 µm sieve.

For the initial testing of heating PARALOID B-72, a household electric heat radiation oven set to 180 °C was used. This oven had top and bottom heating elements and no air circulation function. As supplied by Röhm and Haas, PARALOID B-72 contains a small amount of toluene, which is present in the free volume of the polymer network (less than 1.0 percent w/v). When heated above its Tg, a thermoplastic resin will gradually release any retained solvent. As a safety precaution, the oven was used in a fume cupboard to remove any vapours that may be released.[i] While inside the polymer network, solvents have a plasticizing effect. As heating to 180 °C removes these solvents from the polymer network, a denser and, consequently, more brittle film is formed upon cooling.[ii] An additional quality of heated PARALOID B-72 is that it has a hydrophobic surface, and thermocasts seem far less sensitive to moisture as compared to solvent-based casts (Farmakalidis et al. 2016).

Thermocasting in silicone rubber

The heat involved in thermocasting PARALOID B-72 necessitates casting separately from the object. Nevertheless, separate casting of resin in a silicone rubber mould has the advantage of minimising handling of fragile glass objects and is therefore often used in glass conservation (Hogan 1993; Koob 2006; Davison 1998). To make a separate resin cast, a silicone mould is first made for the missing glass fragment. This silicone negative is filled with a thin layer, less than 2 mm, of finely ground PARALOID B-72 and is placed in a pre-heated oven at 180 °C (Figure 1). It takes approximately half an hour for a layer of PARALOID B-72 to flow into a clear film, at which point another layer can be added on top. Building up in thin layers is important as it allows trapped air to be released from the viscous resin. A 3-5 mm thick cast can be built up in less than two hours at 180 °C (Figure 2). Starting with a preheated silicone mould appears to make the process more efficient.

After the silicone mould has been completely filled with PARALOID B-72, the cast can be finished by

Figure 3. *Glass sample holder with (from left to right) thermocast PARALOID B-72 and HXTAL NYL-1, Araldite 2020, and Fynebond epoxy resins before (above) and after (below) 600 hours in a Xenotest chamber*

pressing an additional pre-heated flat sheet of silicone rubber onto the mould and placing it back in the oven for another 15 minutes. This creates, in fact, a double-sided mould that gives both sides of the cast a glass-like surface.

For this study, several different brands and types of silicone rubber were tested for their suitability for thermocasting PARALOID B-72 at 180 °C. Silicone rubbers that cure with a condensation reaction release volatile and uncured components, such as alcohols, acetic acid, and amines, into the melted resin. This seemed to be leading to the formation of additional gas bubbles and a yellow discolouration in the cast. This is believed to be a different mechanism than the thermal decomposition of the resin discussed above, since neither yellowing nor excessive bubble formation was observed when PARALOID B-72 was melted onto an inert glass substrate at 180 °C. Also, strongly pigmented silicone rubbers were found to transfer pigments into the transparent resin.

Silicone rubbers that cure with an addition reaction should, in theory, form no by-products that can contaminate a cast (Anonymous 2016; Horie 2010). Nevertheless, before using a silicone rubber mould, a post-cure treatment is advised by most manufacturers, in which a fresh mould is heated at 140 °C for 2 hours and, afterwards, thoroughly cleaned with soap in order to remove any remaining contaminants. Good results were achieved using Siliconen Culinair silicone rubber, a food-grade, heat-resistant to 280 °C, addition-curing white silicone rubber. Consequently, all moulds used for this study were made with this material.

Light-aging of thermocast PARALOID B-72

In the field of conservation science, the long-term chemical stability of PARALOID B-72 has been extensively studied, and the resin has been proven to remain soluble and not significantly discolour after exposure to high amounts of ultraviolet-

(UV) radiation or elevated temperatures of 100-150 °C. These characteristics have led to the adoption of PARALOID B-72 by conservators worldwide (Feller 1984; Chiantore and Lazzari 2001; Melo et al 1999; Farmakalidis et al. 2016; Lazzari and Chiantore 2000). Even though PARALOID B-72 thermocasts can be successfully produced without initial yellowing, concern remained as to whether the elevated temperatures required to melt PARALOID B-72 would negatively affect the long-term stability of the resin.

To assess the photostability of thermocast PARALOID B-72 that has been exposed to temperatures of 180 °C for one hour, a sample of the material was artificially light aged.

Four circular resin samples, each 3 mm in thickness and 25 mm in diameter, were cast in a modern float glass sample holder (Figure 3). As would be the case for an in-situ resin infill, each resin sample is open to the atmosphere on both sides. The PARALOID B-72 sample was directly cast in the glass sample holder on a Siliconen Culinair substrate at 180 °C for one hour, which is usually enough time to fully melt a 2-3 mm thick film. For comparison, the remaining three sample slots were filled with epoxy resins HXTAL NYL-1, Araldite 2020, and Fynebond, cast on the same type of silicone rubber substrate.

An Atlas Xenotest Alpha High Energy weathering instrument with a xenon arc lamp was used for light aging. Daylight behind window glass was simulated through the addition of a 320 nm filter, resulting in an illumination of 105,000 lux. In the Xenotest chamber, the relative humidity and temperature were kept constant at 40 percent and 50 °C, respectively.

The resin samples were placed in the chamber for 600 hours, which is comparable to 150 years at museum conditions at 200 lux. Figure 3 clearly shows that light-aging induced significant yellowing of both Fynebond and Araldite 2020. HXTAL NYL-1 has yellowed very slightly, while PARALOID B-72 showed no noticeable yellowing after 600 hours of light-aging. These results suggest that the heating of PARALOID B-72 to 180 °C does not compromise the photostability of the resin, as assessed by visual inspection.

COLOURING THERMOCAST PARALOID B-72

Dyes and pigments

Glass in museum collections is rarely water white and perfectly clear as unintended contaminants in the raw ingredients colour historic glass, lending a characteristic green, blue, or straw hue. Colouring solvent-based PARALOID B-72 is usually done by mixing dry pigments or dyes into the dissolved resin. Pigments have an opacifying effect, whereas dyes impart colour while maintaining the transparency of the resin (Koob et al. 2011).

The process of colouring thermocast PARALOID B-72 differs from colouring solvent-cast PARALOID B-72. This is because the thermocasting process, as described above, does not start with a fluid resin in which pigments or dyes can be dissolved. To use dyes or pigments when thermocasting PARALOID B-72, the resin must first be made sufficiently fluid to mix in the colourant of choice. This can be done by heating the resin in a receptacle on a hot plate while monitoring the temperature of the resin. This should always be done using vapour extraction.

Promising results have been achieved using Ciba ORASOL dyes. According to the manufacturer, most ORASOL dyes start decomposing well above 200 °C. However, there are exceptions like Ciba ORASOL Blue BL, which starts decomposing at 165 °C (Anonymous 2001). When placed in the oven at 180 °C, this dye quickly fades to a dark grey. Following the technical data sheets of Ciba ORASOL dyes, a selection of high temperature resistant dyes can be made that remain colour-fast during the thermocasting process.

Heat-fused surface colour

An alternative method of giving colour to the resin was explored, using a single-sided surface film of Golden High Flow Acrylic paint, achieving an effect much like flashed or *plaqué* glass. An advantage of applying a surface colour layer is that the eventual colour is not influenced by the thickness of the resin cast, as is the case when casting fully coloured resin. Nevertheless, a painted or sprayed-on surface colour will, to some extent, always keep the appearance of an added paint layer and may not satisfactorily imitate bulk coloured glass. This problem is overcome by heat-fusing a colour film onto the thermocast. Applied

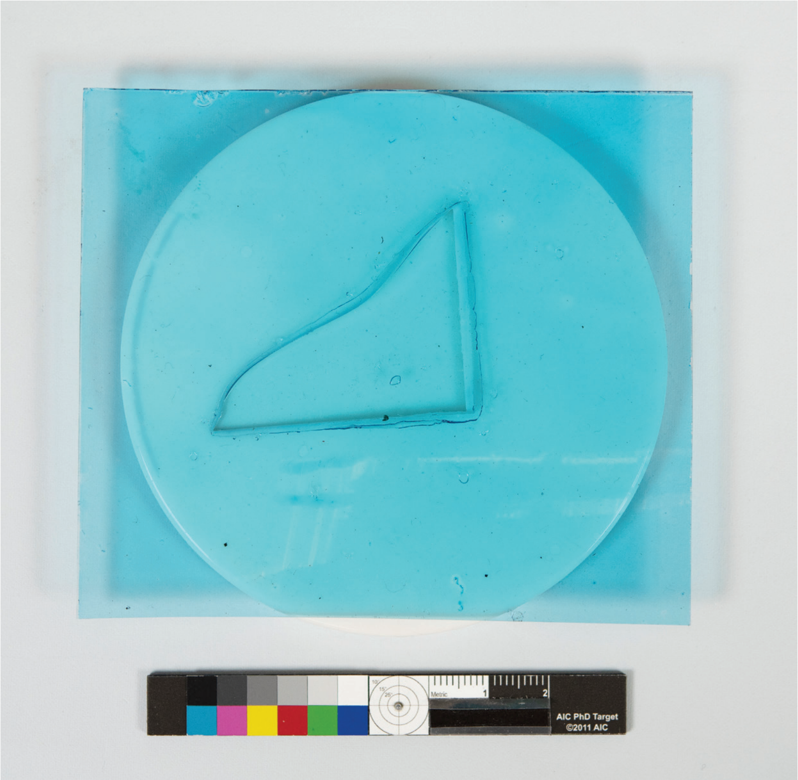

Figure 4. *Blue colour film of Golden High Flow Acrylic paint heat-fused from a sheet of glass onto thermocast PARALOID B-72*

in this way, brush strokes or the typical texture of spray-painting will disappear.

To create such a colour film, Golden High Flow Acrylic paint is sprayed in thin layers onto a glass-like, heat-proof substrate (glazed tile or a sheet of glass), which is then heat-fused onto a PARALOID B-72 thermocast by pressing the paint film onto the hot resin and placing the package back in the oven for 30 minutes (Figure 4).

After cooling to room temperature, the thermocast is released from the substrate by freezing; the differences in coefficients of thermal expansion eventually separate the resin from the sheet glass. Most casts separate within a few hours. To avoid thermal shock, a basin of water can be used as a temperature buffer. When successfully released, the paint film will now be fused to the PARALOID B-72 thermocast. Surface-coloured thermocasts made in this way have a pristine glassy surface and are practically indistinguishable from PARALOID B-72 thermocasts that have been coloured all the way through.

The applicability of thermocast PARALOID B-72 with heat-fused colour is demonstrated on a 16th-century Southern Netherlandish stained-glass panel depicting Christ carrying the cross up the Calvary mountain (Figure 5). Dimensional manipulation of PARALOID B-72 to match the undulations in the original glass was achieved by slightly softening the cast with a hot air gun.

Additional examples of coloured thermocasts are shown in Figure 6. The orange and red casts are fully coloured using Ciba ORASOL dyes, Red 395 and Yellow 2RLN. On close inspection, some poorly dissolved dye particles can be seen in the orange cast. The light blue thermocast is coloured with a single-sided heat-fused film of Golden High Flow Acrylic paint, Transparent Phthalo Blue green shade. The transparent thermocast is included in the picture as a reference.

For both colouring procedures, the effects of heat on the long-term stability of the colour have yet to be investigated. Additionally, thermocasts coloured using the heat-fusing method can sometimes end up slightly bigger than the original

Figure 5. *Stained-glass panel representing a scene from the Via Calvari with reconstructed PARALOID B-72 top right corner, before adhering. ca. 1525-1550 CE, H 23 cm × W 18 cm. Collection of J.M.A. Caen, CA 120*

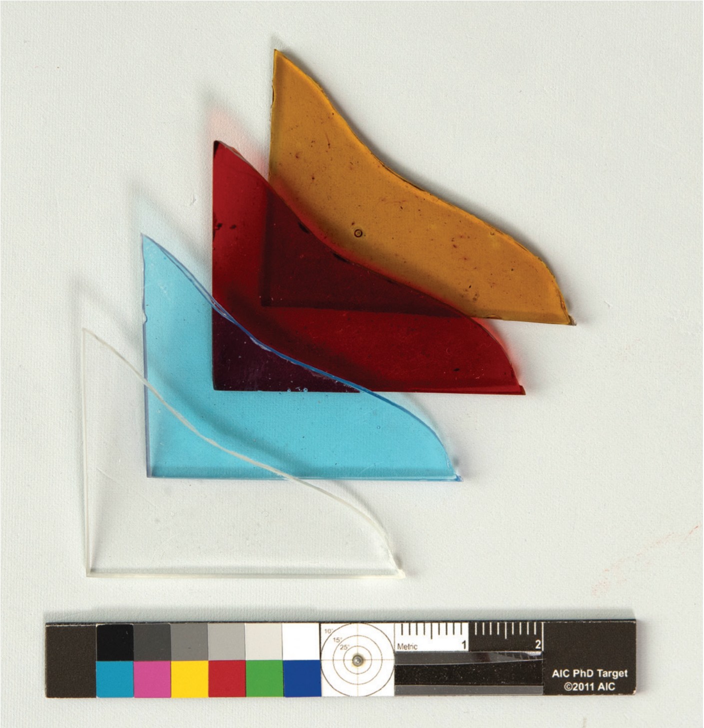

Figure 6. *Coloured PARALOID B-72: orange and red thermocasts coloured with Ciba ORASOL dyes, and blue thermocast coloured with a heat-fused film of Golden High Flow Acrylic*

mould, likely due to large differences in thermal expansion coefficients among the silicone rubber, PARALOID B-72 resin, and glass substrate onto which the paint film is applied. However, the thermal expansion coefficient of silicone rubber can be reduced, and it is expected that further research will help refine this alternative method of surface colouring.

LIMITATIONS AND FURTHER RESEARCH

Silicone rubber mould material

Although the initial results of thermocasting in silicone rubber have been promising, the interaction between silicone rubber and PARALOID B-72 is not yet fully understood. How and why in some cases excessive bubble formation and yellowing of the resin was observed demands further research. In this article, thermocasting in silicone rubber moulds has been limited to flat open moulds, and the use of closed and curved moulds has been left unaddressed. Experimentation in this direction continues.

Mechanical properties

PARALOID B-72 was initially produced by Röhm and Haas as an ink medium and was never intended to be used as an adhesive or filling material. The mechanical characteristics of the polymer make it suitable for use as a thin film or coating, at best. When fully set, regardless of it being solvent-cast or thermocast, PARALOID B-72 is a very brittle polymer. That being said, it can be argued that, in many conservation applications, a resin restoration cast does not have to fulfil a truly structural role, and that the mechanical properties of PARALOID B-72 are of lesser importance. Nevertheless, solvent-cast PARALOID B-72 retains a certain flexibility for quite a long time. This can certainly be an advantage when a complex resin infill needs to be inserted in a lacuna.

Solvent vapour release

As a precaution, all tests for this study were performed in an extraction cabinet. Research has to be undertaken into the nature and possible risks of solvents and other vapours that may be released when heating PARALOID B-72. Adopting this technique requires some additional investments in the technical setup of the conservation studio, such as extraction, a hot plate, ideally adjustable, and a laboratory oven.

CONCLUSION

This research explored the viability of thermocasting PARALOID B-72 in silicone rubber moulds. Using heat instead of solvents, convincing imitations of glass and glassy materials can be produced out of PARALOID B-72 in a very short time. Artificial aging of thermocast PARALOID B-72 suggests that exposure to temperatures up to 180 °C does not negatively impact the aging characteristics of the resin.

Through this ongoing research into thermocasting of PARALOID B-72, it is hoped to offer an alternative to the established technique of solvent-cast PARALOID-B-72. Using the thermocasting method, thick casts can be produced solvent-free without shrinkage and the formation of concave edges, making this technique especially suitable for larger and thicker casts.

Even though good results have been achieved, this pilot study calls for further research into the standardization of the various steps and parameters related to PARALOID B-72 thermocasting. Issues to be considered are the sensitivity, i.e. bubble formation and yellowing, of PARALOID B-72 to certain silicone rubbers. The need for further research also applies to the process of colouring the resin: the possibilities and limitations when using heat to fuse a single-sided colour film onto a thermocast, but also the interaction between heated polymers and dyes, and how this affects the aging characteristics of both materials.

NOTES

[i] The effects the small quantities of retained solvents released when heating PARALOID B-72 may have on an electric oven have not been assessed.

[ii] Röhm and Haas reports heating PARALOID B-72 up to 150 °C, during which the ‘final properties’ (Tukon hardness 12,1) of the resin are simulated, without mentioning any undesirable side effects.

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SELECTED MATERIALS

Siliconen Culinair®: Platinum cured (Addition) white silicone rubber, manufactured and ordered at Silicones and More Hofdwarsweg 20, 6161 DD Geleen, Nederland https://www.siliconesandmore.com/nl/