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A radioactive shamanic apron with glass disease

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Summary A shamanic apron produced in Siberia in the nineteenth century was selected as an integral part of a new display at the British Museum. The apron, made from reindeer hide, is heavily adorned with free-moving amulets, metal rings and tassels threaded with colourful beads. A visual assessment identified glass disease – crizzling, cracking and fragmentation – occurring only on the pale yellow beads. Analysis using energy dispersive X-ray spectrometry in a scanning electron microscope confirmed that an unstable glass composition was the cause.

To enable the public to see this striking object that is unique within the British Museum collection before the beads fragment beyond repair, it was approved for temporary display and conserved. Even with an ideal, tightly controlled environment, the beads with advanced glass disease will continue to deteriorate at an indeterminable rate. An interventive approach was taken to provide temporary cohesion for the beads in the form of localized consolidation and detached elements were reintroduced to restore the appearance of the apron.

Analysis also indicated the presence of uranium, added as the glass colourant. Using a Geiger counter it was established that the pale yellow beads were emitting ionizing radiation. This result, combined with ultraviolet-induced fluorescence imaging, confirmed that only the pale yellow beads contained uranium.

This was first time uranium glass had been discovered in a composite object at the British Museum and as such it was necessary to identify protocols for its handling, storage and display. Fortunately the levels emitted were low enough that the radioactive nature of the apron will not preclude its future display or careful handling. The apron will continue to be monitored regularly, but its conservation and display ensures that access to this beautiful and unique object is maximized before the pale yellow beads, which are intrinsic to the object, are inevitably lost beyond repair.

INTRODUCTION

"All the equipment worn and used by a shaman was considered to be charged with psychic power, as if radioactive, and so was very dangerous to those not trained to work with it" [1].

In 2009 assessment and analysis showed that a shamanic apron produced in Siberia in the nineteenth century contained elements that were both radioactive and spontaneously deteriorating, Figure 1. The apron had been collected by Henry Seebohm (1832–1895) and purchased by the British Museum in 1913. The apron is unique within the collection and had been selected for display as part of the regular rotation of objects in the Wellcome Trust Gallery at the British Museum. The shamanic elements provide an excellent illustration of one way in which the Dolgan people of Siberia sought to protect their community from illness and other harmful events. The plan was to display the apron with a range of objects from diverse regions of the world that focus on the maintenance of health and wellbeing.

THE APRON

The apron is constructed from two separate pieces of oil-tanned reindeer hide. Stitched onto the upper and lower areas are densely couched strands of small, differently coloured glass beads, Figure 1. Nine freely moving copper alloy rings are suspended from the lower beaded section on pairs of hide thongs. Two additional rings are suspended from a copper alloy chain. Ten hide tassels hang in pairs, some of which support an ivory amulet and a beaded purse. Both the thongs and tassels are threaded with combinations of larger coloured glass beads measuring approximately 7–10 mm in diameter. A heart-shaped copper alloy amulet also hangs from a separate long hide thong.

FIGURE 1. The shamanic apron (British Museum As1913,1114.58) from Siberia after conservation treatment. Size 91 × 43cm

This item of shamanic paraphernalia was produced in the regions of subarctic tundra in north central Russian Siberia that are now known as the Dolgan-Nenets Autonomous Region and the Sakha Republic. Dolgan people were nomadic reindeer herders, hunters and fishermen until they were forcibly settled during the Soviet era. Their shamanic skills and understanding played an important part in their ability to survive in this harsh environment. Certain men or women called *Oiun* or *shamans* relied on items such as this ornate apron during their ecstatic encounters, as they contacted and negotiated with the parallel spirit world to protect their community from illness and harmful events or to ensure successful hunts [2]. The densely worked beaded patterns, copper alloy rings and amulets on this apron are all shamanic and during the *Oiun's* performance their sound and movement was important for their efficacy. Both shamans (male or female) and pregnant women were especially in need of protection from malignant forces. As complex decorative design was thought to provide extra protection, this abundantly decorated apron may well have been worn by either shamans or pregnant women [3]. The complexity of this garment takes it beyond the everyday male/female dichotomy in dress, just as the powerful abilities of shamans took them beyond the same duality and into the spirit world.

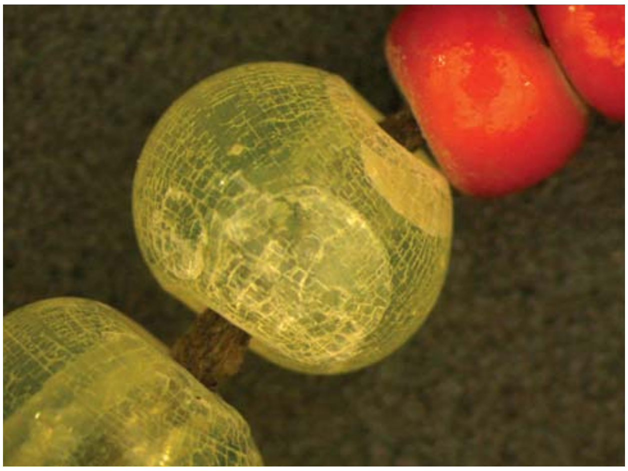

FIGURE 2. One of the pale yellow beads displaying crizzling and spalling. Field of view 15 × 11 mm

CONSERVATION ASSESSMENT

Overall, the hide appeared stable and the densely couched beaded areas were secure, with the beads in these areas showing no signs of deterioration. The amulets and the beaded purse were also in good condition and required no treatment. The copper alloy rings showed minimal signs of corrosion at points of contact with the leather thongs and tassels, but again these were considered to be stable and not to require treatment. Most damage had occurred to the lower part of the apron where two of the nine hide thongs from which the copper alloy rings hang had split. One beaded tassel was completely detached from the apron and three others had no ornament or knot at their ends. As a result, four beads had become detached and additional beads were vulnerable to loss. Even to the naked eye, it was clear that all but two of the 69 pale yellow glass beads were deteriorating. These formed approximately 40% of the larger beads found on the thongs and tassels. Initially it was thought that this damage might be physical, caused by impact with, or abrasion by, the heavy ornamental metal rings. After further examination under magnification, two factors indicated that the deterioration was the result of the phenomenon commonly referred to as 'glass disease'; first, damage was limited to beads of one particular colour (pale yellow) and second, visible signs of all the various stages of glass disease were present on these beads [4, 5]. This included the presence of small white crystals on the surface of most pale yellow beads and a fine network of uniform cracks or 'crizzling' crossing the surface of 55 of the 69 beads. This crizzling appeared to be more prevalent around the bead holes. A total of 32 beads had areas of spalling, or advanced crizzling, where cracks had extended further into the glass structure, Figure 2. Many had areas that had already spalled and the fragments lost. Vertical cracks extending through the glass were present on 37 beads and four beads had become detached due to complete fragmentation. This visual assessment was recorded on a condition plan (Figure 3), which was also used to record conservation treatment details. Such patterns of deterioration often stem from a problem with the original glass recipe, which causes subsequent structural instability. Unfortunately, because this is an intrinsic manufacturing fault, glass disease cannot be halted or reversed and it is only through tight control of the environment in which the glass is stored or displayed that there is the potential to stabilize the rate of deterioration. With no previous conservation record available, it was impossible to ascertain when the pale yellow beads began to deteriorate or at what rate it has since been occurring.

FIGURE 3. A plan indicating the stages of deterioration of the pale yellow beads and the locations of interventive treatments

TABLE 1. Non-normalized results of SEM-EDX analyses of a yellow bead, expressed as weight percentages

Sample	F*	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	FeO	As_2O_5*	PbO	U*	Total
Bulk glass	*c.* 3	20.2	bdl	0.6	61.2	bdl	0.7	1.1	5.8	6.4	0.1	bdl	bdl	*c.*1	bdl	*c.* 0.4	100.5
Deteriorated glass	*c.* 5	2.2	bdl	0.6	70.1	0.1	0.7	1.4	2.4	7.1	0.2	bdl	0.1	*c.*1	bdl	*c.* 0.6	91.5

Notes
bdl denotes below detection limit
* denotes that due to a lack of suitable glass standards for comparison, the values for these elements/oxides should be viewed as semi-quantitative

COMPOSITIONAL ANALYSIS

Glass recipe

In order to investigate the exact cause of the instability of the pale yellow glass, quantitative chemical analysis was carried out using a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDX: see experimental appendix). A *c.*3 mm^3 fragment of a detached pale yellow bead was used for this purpose as its original position was impossible to locate. This fragment was mounted in epoxy resin, polished with diamond paste to a 1 μm finish, coated with carbon and analysed.

The analytical results for the bulk glass and the deteriorated surface region are presented in Table 1. These show that the glass beads have a rather unusual composition. Three important factors were noted which confirmed that the severe deterioration seen on these beads was primarily due to their composition.

First, the beads contains around 20% sodium oxide (Na_2O), which is at the higher end of the range for stable soda–lime–silica glasses as determined experimentally by Brill [6]. However, these beads also contain approximately 5% potassium oxide (K_2O), leading to a total alkali content of *c.*25%, which has a detrimental effect on the durability of the glass. Alkali fluxes are added to lower the melting point of the glass and to improve its working properties, but the hygroscopic nature of this essential component means that, even in glass with a stable composition, prolonged contact with water causes leaching of the alkali metals ions from the surface region of the glass. The reaction is more likely to occur if the glass has an elevated alkali content and if the environment around the glass has a high relative humidity (RH). As the alkali leaches from the surface region, the chemical structure changes leading to the signs of deterioration visible on these beads. Evidence that this process is occurring can be seen by comparing the very different levels of Na_2O and K_2O in the bulk and deteriorated regions of the glass, Table 1. The greater deterioration noted around the bead holes suggests that changes in chemical structure were more pronounced where the hide thong made contact with the bead. A build-up of moisture at this contact point may have exacerbated the problem [7].

Second, this glass contains some lime (CaO), very low levels of alumina (Al_2O_3) and no detectable magnesia (MgO). In stable glasses the positively charged ions associated with these components – Ca^{2+}, Al^{3+} and Mg^{2+} – modify and strengthen the structure by offsetting the reduction in durability caused by the high alkali content [4, 5]. The low levels of stabilizers in these beads indicate that there is insufficient compensation for the high levels of alkali.

Finally, fluorine (F) was also found in both the bulk and deteriorated glass. Because oxygen (O^{2-}) and fluorine (F^-) ions have similar ionic radii, when fluorine is present it can replace oxygen in the glass structure, leading to further instability and deterioration [8, 9]. It is this quality that also allows fluorides to act as fluxing agents in glass manufacture, in a manner similar to the alkalis discussed above. When added in larger quantities (above *c.*2–4 %, depending on overall composition) fluorine can also act as an opacifying agent [8]. The transparency of the pale yellow beads in this study shows that the levels added were too low to produce opacity and it was therefore probably added as a flux.

Colourant

SEM-EDX analysis was conducted primarily to understand the mechanism of deterioration for the pale yellow beads. However, uranium, which had presumably been added to the glass melt as a colourant, was identified at a level of 0.5%, Table 1. Uranium has been intentionally used as a glass colourant since the late eighteenth century [10], but only a limited number of chemical analyses of uranium glasses from varying production areas have been reported to date, e.g. [11]. As such it is not currently possible to link the composition of the apron's beads to a particular production area or time period.

Although uranium does not affect the stability of the glass and is not associated with the glass disease, its presence is a potential health hazard even at these low levels. Uranium generally produces a green or yellow glass when used alone but other colours, including opaque white or brown, can result when it is combined with other metal oxides. The possibility that some of the other beads might contain uranium was therefore investigated. Glass containing uranium often fluoresces when illuminated with ultraviolet (UV) light. When the apron was examined under these conditions, only the pale yellow beads were found to produce visible fluorescence, Figure 4. All the beads were further surveyed using a Geiger counter (Rotem RAM

FIGURE 4. Detail of two tassels: (a) in visible light; and (b) under ultraviolet illumination showing the fluorescence emitted by the uranium-containing pale yellow beads

GENE-1 dose rate and contamination meter) to detect and measure any ionizing radiation being released. Only the pale yellow beads gave a reading above background levels –13 counts per second (cps) above background levels – confirming that no other beads were emitting radiation.

HANDLING, STORAGE AND DISPLAY IMPLICATIONS

Radioactivity

Research carried out by Strahan [12] and Lopez [13] concluded that uranium glass on display in a museum environment poses a minimal health risk for both museum workers and visitors due to low levels of ionizing radiation and limited contact time. In 2006, three pieces of uranium glass from the British Museum collection were analysed [14] and assessed by the Health Protection Agency [15]. All three pieces were designated safe to handle for short periods of time using disposable gloves. On average these pieces contained three times the percentage of uranium found in the bead sample from the apron. Although the level of ionizing radiation emitted by the beads was measured as only just above background levels, the health risks associated with such radiation are cumulative and it is necessary to take some simple precautions regarding the handling and storage of this and similar objects [16]. To ensure exposure levels are kept as low as possible, handling should be infrequent and brief, and disposable gloves should always be worn.

It is recommended that sources of ionizing radiation should not be stored together as this will increase the total dose rate in the area increasing the health risk [16]. The apron is currently the only item in the Museum's textile store identified as containing uranium, but if more are identified, the location will be reviewed. It has also been suggested that thermoluminescence dates of objects such as ceramics can be affected through storage in close proximity to sources of ionizing radiation [12]. While recognized as a concern, the absence of ceramics in both the textile store and in the proposed display case means that this is currently not an issue. As required by legislation [16], all Museum curatorial and conservation records for the apron and the labels on its storage packaging now indicate the presence of uranium; they also indicate the level of risk and the recommendations for handling.

Displaying individual objects that have low uranium contents, such as the apron, poses minimal risks to the public as the dose rate is negligible unless the object is in physical contact with the visitor [14]. In this instance the apron was to be exhibited within a display case, further reducing the likelihood of exposure to radiation.

Unstable glass (glass disease)

Whether on display or in storage the main environmental factor that will affect the rate at which the pale yellow beads deteriorate is RH. For such highly susceptible glass with a history of deterioration, current British Museum guidelines recommend a RH set point between 38 and 42% and daily fluctuations of ±3% RH [17]. In addition, airflow within this controlled environment is recommended to prevent the build-up of moisture near the hygroscopic surface of the glass. For glass exhibiting early stages of glass disease these control measures can virtually arrest the progression of deterioration [18]. Sadly, the majority of the beads on the apron already show advanced stages of glass disease suggesting that such an environment could only slow deterioration. It is therefore only a matter of time before the beads fragment beyond repair.

Objects such as this apron, which contain both deteriorating glass and organic components, present a complex situation due to potentially conflicting environmental requirements. For many organic materials it is often desirable to provide a RH higher than the *c*.40% that might help to prolong the life of the beads in this apron [17]. Fortunately, stable oil-tanned hides are quite forgiving and should not suffer damage at this lower RH [19]. In theory this would allow the entire object to be stored under conditions most favourable for prolonging the life of the glass beads. However the very narrow range of RH recommended for deteriorated glass is rarely achievable in practice. Environmental monitoring data from the store in which the apron was kept showed an annual mean RH of 40% with daily fluctuations of no more than ±5%, suggesting that the deterioration rate could be controlled to some extent in storage. For exhibition, however, the apron was to be displayed in a case alongside other objects, the majority of which had rather different environmental requirements. The proposed display case in the Wellcome Trust Gallery is currently controlled between 40 and 60% RH with daily fluctuations ranging between ±5% and ±17%. This suggests that the rate of deterioration while on display would be greater than that in long-term storage.

BALANCING ACCESS AND DETERIORATION

While it was clear that deterioration of the glass beads was likely to proceed more rapidly under display conditions than in store, the apron would form an integral part of the exhibition for which there was no suitable alternative object in the collection. The dilemma faced here is not unfamiliar to conservators, as similar decisions are routinely made concerning the display of very light-sensitive objects. In the latter case, the rate of deterioration can be reduced almost to zero by dark storage rather than display, whereas for the apron the rate of deterioration will probably only be reduced slightly in storage, as the pale yellow beads are inherently unstable.

After careful consideration it was decided that rather than slightly extend the life of the beads through closed storage, it would be better to place this unique and striking object temporarily on display before integral parts of it deteriorate beyond repair. The decision was taken that the apron should be displayed for three years, which is the standard British Museum time on exhibition for a range of environmentally sensitive materials that are rotated to prolong their life. While the apron is on display the condition of the beads will be monitored frequently by visual inspection. If any significant changes are noted the decision to display the apron can be reassessed along with options for future conservation treatments. A consequence of the decision to display the apron was an increase in the amount of interventive conservation treatment thought necessary. This included considering options for providing temporary stability to the pale yellow beads.

CONSERVATION TREATMENT

To restore the appearance of the apron it was decided that the detached tassel and the four fragmented beads would be reintroduced. Those beads that exhibited the final stages of glass disease were also treated in an attempt to extend their life. The option of removing deteriorated beads for storage in optimum conditions and replacement with suitable substitutes was considered, but deconstructing the apron in this way would have been highly interventive and was not considered justified at this time. Two of the authors, who specialize in the conservation of organic artefacts (NR) and glass (RS), developed a treatment proposal that took into account the individual and combined requirements of the composite elements. Initially, a fine layer of surface dust was removed from the hide and the stable areas of beadwork using gentle vacuum suction and a soft sable brush.

It is currently recommended that glass showing the symptoms of the early stages of glass disease should be washed using deionized water to reduce its surface pH [4]. However, this was not carried out as the deterioration on many of the beads was so severe that it was feared that water would remain in the cracks and exacerbate future deterioration. In addition, any aqueous treatment has the potential to cause undesirable staining of the hide. Instead, crystals were removed from the surface with a dry sable brush, isolating one bead at a time with acid-free tissue paper.

In the past, methods that coat the surface of the glass have been used to inhibit the progress of glass disease but, as these techniques have now been shown to be unsuccessful [20], they were also discounted. In the 1990s the use of organosilanes was investigated as a consolidant for deteriorating glass and it was reported to increase the lifetime of glass by a factor of around 10 [21], but more recent concerns about the health risks associated with the use of silanes have restricted their use. Recent trials carried out at the Corning Museum of Glass using Paraloid B72 (ethyl methacrylate copolymer) to provide cohesion, followed by storage in a tightly controlled environment, have proved successful [18]. Paraloid B72 is used widely as a consolidant for glass as it has excellent long-term stability, refractive properties similar to most soda–lime–silica glasses and is permeable to moisture, which prevents a build-up of water at the glass surface. As temporary cohesion was desirable for the pale yellow beads displaying advanced stages of deterioration, this material was chosen as the consolidant.

As it was necessary to carry out consolidation *in situ*, small strips of silicone release paper were inserted through the bead holes to protect the organic components. Trials on a bead on the detached tassel indicated that a 2% solution of Paraloid B72 in acetone could be drawn into advanced areas of deterioration by capillary action and provide the desired adhesion. All the beads with advanced crizzling and cracks were locally consolidated using a micropipette to apply the solution. Once it was judged (visually) that the area was adequately consolidated, a small wooden stick was used to remove excess Paraloid B72 from the surface. The four fragmented beads were reassembled *in situ* with a 40% solution of Paraloid B72 in acetone. The positions of these beads were deduced from the pattern of beads on the other tassels, Figure 3. To prevent beads slipping off the unsecured tassels, narrow, twisted lengths of *tengujo* long-fibred mulberry paper (11 $g.m^{-2}$) were wrapped around the end of each tassel, just beneath the last bead [22, 23], Figure 5a. The paper had previously been toned with Liquitex acrylic paints and coated with a 20% solution of Lascaux 360 HV adhesive (a thermoplastic acrylic polymer dispersion based on methyl methacrylate and butylacrylate) dissolved in deionized water. To secure the paper twists in place the adhesive was reactivated with industrial methylated spirit vapour.

The four complete beads that had become unthreaded were placed back onto the detached tassel. This tassel and the two split thongs were then extended and reattached using narrow, flat strips of the same toned and adhesive-coated mulberry paper. The paper was coiled around the loose ends, secured in position by solvent reactivation, as above, and then tightly twisted along its length by rolling it between the fingers. The paper twist extensions were fed through the existing holes and secured with a loose knot against the back of the apron, Figure 5b. The long-fibred mulberry paper provides strength and flexibility and allows the reintroduced tassel to hang freely, as originally intended, while the adhesive and paper twists used in this treatment blend in well with the original materials and are easily removable [22].

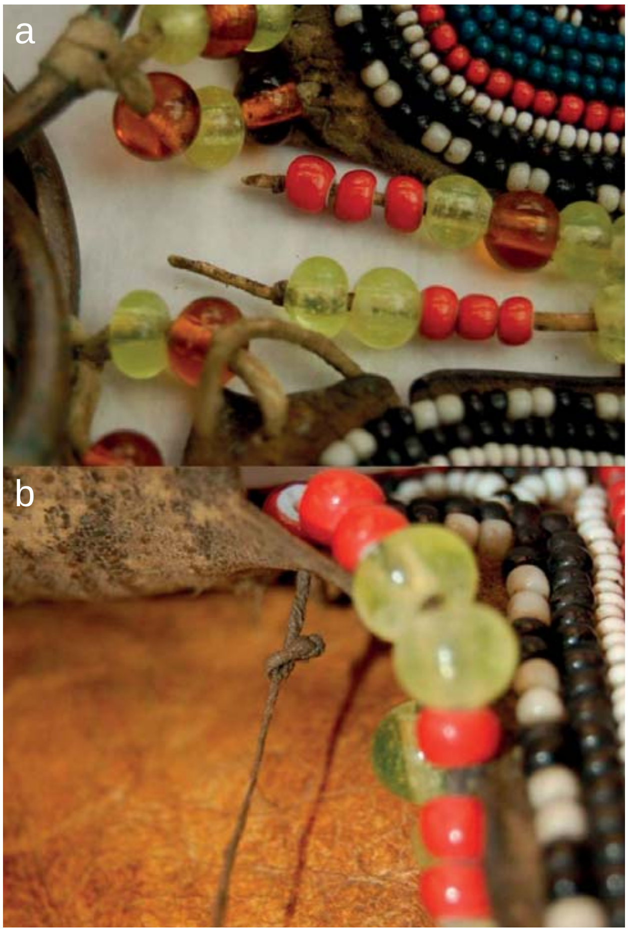

FIGURE 5. Details of (a) mulberry paper used to secure beads onto the tassels; and (b) mulberry paper extensions used to reintroduce a detached tassel

CONCLUSIONS

While this apron was being worn as a garment to protect against illness, unknown to the wearer, the hide would also have provided protection from the low levels of radiation emitted by the pale yellow glass beads. In many cultures, shamanic objects are considered dangerous to the untrained, but fortunately the level of danger from ionizing radiation created by this apron is minimal. Although the presence of uranium influences future handling and storage recommendations, the levels of ionizing radiation do not preclude its display. Objects made from uranium glass are not unusual in museum collections, but this is the first instance in which it has been identified in a composite object at the British Museum and it was necessary to develop appropriate recommendations for its handling and display.

More serious for the longevity of the object, inspection and analysis highlighted the severe deterioration of the pale yellow beads as a result of glass disease and identified the inherent compositional reasons behind this degradation. While a tightly controlled environment might slow deterioration, the life of the beads is limited and the decision was therefore made to place this remarkable apron on display. It can then be appreciated by the public as a striking example of Dolgan culture, within the context of other objects that speak of the health and wellbeing of communities, before the pale yellow beads cease to exist.

The treatment of the apron provided an excellent opportunity for conservators, scientists and curators to collaborate in tackling the complex issues and decisions that arose from the goal of placing it on public display. Choices about the display and treatment were made in the knowledge that, as creating a tightly controlled environment for this object is not possible and consolidation alone can provide only a short-term benefit, the beads will continue to deteriorate whether in storage or on view. Finally, the condition of the apron – and the beads in particular – will be monitored regularly to inform future decisions about conservation and display.

EXPERIMENTAL APPENDIX

Analysis was carried out using a Hitachi S3700 VP-SEM under the following operating conditions: high vacuum mode, 20 kV, 0–10 keV spectral range, 2.30 nA probe current, a 150 seconds counting time and calibrated using pure elements, mineral and oxide standards. A Corning A glass standard was analysed to verify that this calibration was producing accurate results. Detection limits were calculated using a spectrum synthesis programme on the Oxford Instruments INCA Analyser software. This analytical method resulted in detection limits for most metal oxides of around 0.1–0.2%.

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MATERIALS AND SUPPLIERS

- Paraloid B72: Conservation Resources (UK) Ltd., Unit 2 Ashville Way, Cowley, Oxford OX4 6TU, UK, www.conservationresources.com
- Liquitex acrylic paint: L. Cornelissen & Son, 105 Great Russell Street, London, WC1B 3RY, UK, www.cornelissen.com
- *Tengujo* mulberry paper: Shepherds Bookbinders Ltd (formerly Faulkiner Fine Papers), 76 Southampton Row, London WC1B 4AR, UK.
- Lascaux Acrylic Adhesive 360 HV: AP Fitzpatrick, 142 Cambridge Heath Road, London E1 5QJ, UK.

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