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A Great Lakes pouch: black-dyed skin with porcupine quillwork

Pippa Cruickshank, Vincent Daniels and Jonathan King

Summary A late eighteenth-century North American pouch (1937,0617.1) represents an important type of a black-dyed skin bag decorated with porcupine quillwork. The pouch was made by women of the Ojibwa or Ottawa people and was probably used in medicine ceremonies. It came to the British Museum in the mid-twentieth century and when first examined in detail in the 1970s had already deteriorated. The skin has degraded due to the presence of a black dye, although an early watercolour painting of the bag discovered in the 1990s illustrates how the bag once looked. Black dyes containing both iron and tannin are well known to increase the rate of deterioration of many organic substances and the pouch was found to contain 1.63% iron. Experiments with a series of brain-tanned skin samples stained with various iron-tannin solutions and artificially aged showed that the presence of iron accelerated the deterioration of the skin.

A conservation treatment carried out in the 1970s, which included consolidation with soluble nylon and backing with nylon net adhered with an early thermoplastic adhesive, was no longer succeeding in keeping the bag intact, and further conservation was carried out to protect the 75% of the bag that survives. As the pouch is of a rare type it was decided to infill the missing areas to make it more suitable for display. The use of adhesives was kept to a minimum and solvent-reactivated adhesives were chosen in preference to those reactivated by heat. No further chemical stabilization was attempted in this treatment.

INTRODUCTION

In the Northeastern Woodlands of North America, buckskin for bags and clothing was sometimes dyed dark brown or black to provide a strong colour contrast with the dyed porcupine quillwork or dyed moose hair with which it was often decorated. The native use of flattened dyed porcupine quillwork for appliqué is unique to North America. The pouch from the Great Lakes (1937,0617.1: Figure 1) that is the subject of this contribution is made of black-dyed semi-tanned skin decorated with native religious imagery in dyed porcupine quillwork and dates to the period 1755–1780. Although it is one of a small group that are known to have survived, much of the front flap and parts of the main bag have completely disintegrated.

Black-dyed objects are common to most civilizations. Although black or dark-coloured dyes can be made by combining several dyes, for example blue and red, the majority of natural blacks are made from tannins (plant polyphenols) and a source of iron. The ingredients for dyeing are commonly available: tannins are present in a wide variety of plants, barks, leaves and fruits of trees or shrubs, which possess high contents of easily extractable tannins, while black, anaerobic, iron-rich muds occur naturally and have been much used for dyeing. It is likely that black dyeing techniques were developed after it was observed – in disparate communities – that tannin-rich vegetation became dyed black when accidentally immersed in certain muds. In addition, a black coloration can also be produced by the reaction of iron corrosion products with tannins, for example when iron nails that have been hammered into oak, or through vegetable-tanned leather, corrode.

These black iron/tannin dyes are widely found in artefacts, for example in inks such as iron gall ink on manuscripts and in black dyes used on textiles made of silk, wool, cotton or other plant fibres. In each case the black dye can accelerate the rate of deterioration of the object, causing the material to become brittle and weak with little tensile strength; this leads to easy tearing or shattering and, in the case of skin, to the surface becoming very friable and powdery. On skin this deterioration is sometimes called 'black rot' a term analogous to 'red rot', a phenomenon in which undyed, tanned leather becomes weak and powdery while becoming redder. The principal mechanism of deterioration in both red and black rots is oxidation of the leather.

FIGURE 1. The pouch after completion of the recent conservation treatment

In North America, materials including skins and porcupine quills were dyed by soaking and boiling in water mixed with plant substances and an iron-containing clay [1]. In the Great Lakes area the bark of a walnut tree often provided the tannin for the brown-black dye used for the skins [1]. If the dyeing was carried out in a copper or iron pot, metal ions leached from the vessel might have affected the colour, as these could also act as a mordant to help fix the dye [2].

FORMATION AND DECAY OF IRON/TANNIN BLACK DYES

The tannins used to form black dyes are complex polyphenols that can be classed either as hydrolyzable tannins (those tannins that are susceptible to decomposition of an ester bond in acidic solutions), which generally produce a black/blue coloration, or condensed tannins (polymeric tannins less susceptible to acid hydrolysis), which give a blue, green or brown stain in the presence of iron; for more details see [3; pp. 691–701]. Many natural sources of tannin contain a mixture of the two types. When extracted from these sources, the tannins are colourless or have a pale tint, only forming an intense dark colour when complexed with iron or another metal.

The iron used in dyeing or staining derives either from a soluble iron source such as the sulphate or acetate salts (or an iron-containing mud or clay), or from a solid iron source such as iron dust from sharpening iron or steel tools, or corroded iron (rust). In some cases, as mentioned above, a proportion of the iron may derive from a metal vessel in which dyeing is conducted, particularly if this is corroded.

There are different methods for the creation of these black dyes, either in dye baths or directly on the surface of an object. If a dye bath is used, the black dye can be formed in the dye vat before the object is exposed to the colorant or by adding the iron and tannin components sequentially. Many natural dyes need a two-stage process in which a metal-containing mordant is applied first, followed by an organic material, but in black dyeing of skin it is not so critical which of the dye components is applied first as both have a strong affinity for the proteinaceous substrate. For example, since tannins have the characteristic property of being able to tan – or colour – animal skins, vegetable-tanned skins can then be stained black by deliberate or accidental contact with iron.

There are two principal mechanisms for the decay – oxidation and hydrolysis. It is known that iron is a catalyst for the oxidation of a number of substrates, for example in the 'black rot' described above. Although the iron in the dye is probably inert while it is bound in the initial dye complex, when this deteriorates free iron is released that is chemically active; free iron may also be present due to an excess of iron in the dyeing process. In addition, other metal ions, such as those of copper (which is often a contaminant in iron sulphate used in dyeing), can act as oxidation catalysts. Hydrolysis of proteins reduces the length of the molecular chains in the collagen fibres by breaking some of the chemical bonds that join the constituent amino acids together. Excessive acidity (or indeed alkalinity) increases the rate of hydrolysis. The physical manifestation of both these degradation mechanisms is a reduction of tensile strength and extensibility in the fibres.

PREVIOUS WORK ON BLACK-DYED SKINS

The few published conservation treatments on similar black-dyed skin artefacts were consulted prior to developing the strategy for the recent treatment of the pouch. Investigations on black-dyed native North American skin and wool material were carried out at the Canadian Conservation Institute (CCI) in the 1980s [4]. Elemental analysis of the skin of a badly degraded black moccasin included in this study was carried out using X-ray emission spectroscopy and showed the presence of sulphur and iron. The degree of degradation was assessed by measuring the leather shrinkage temperature (T_s) and by examining the skin by polarizing light microscopy (PLM). Under the microscope, the collagen fibres of which skin is composed can be seen to shrink suddenly at a particular temperature during heating in water; the temperature at which shrinkage occurs (T_s) is used as an indicator of degradation, as the T_s decreases as the skin degrades [5]. New skin and semi-tanned leather fibres shrink over the range 62–68°C in water. The fibres in the moccasin sample did not shrink, indicating a T_s below ambient temperature and, hence, an advanced degree of degradation. Under crossed polars, the fibres of undegraded leather appear white due to birefringence, while the fibres from the moccasin showed no birefringence as they had degraded and lost their crystalline structure [4, 5].

Also in the 1980s, Fenn investigated adhesives and consolidants for skins, including very brittle black skins affected by 'black rot'. While advising that the use of consolidants should be restricted as much as possible, Pliantex (an ethyl acrylate resin), dissolved in slow-evaporating solvents, was suggested as a possible consolidant for degraded skins [6]. Chapman suspected that the stiff and friable condition of some black-dyed moccasins was due to a metal salt used in the dyeing process [7]. The black dye had not penetrated the skin completely and the surface of the skin was acidic, with a pH of 4. Attempts to consolidate and improve the flexibility with sorbitol, glycerine and Bavon ASAK 520S were unsuccessful [7]. The use of such humectants or water-based consolidants would not be recommended today as water can increase the rate of acid-catalyzed hydrolysis.

More recently, a velvet cape trimmed with black-dyed fur/skin was studied and conserved at CCI [8]. This large circular cape, measuring about two metres across, possibly originated from Ireland and dates to the last quarter of the nineteenth or first quarter of the twentieth century. The black fur/skin had little tensile strength, the pH was 3.8 ± 0.1 and the T_s of the fibres varied from room temperature to 60°C [9]. The black dye was not positively identified, but it was suggested that it might be a synthetic oxidation dye [10], and that copper and iron identified on the fur were likely to be from dye mordants used to fix the dye to the material.

One of the authors (PC) assisted in the conservation of the black-dyed fur/skin trim of this cape during an internship at CCI in 1996 [11]. Although the hair was still firmly attached to the skin, the skin itself had broken into numerous pieces. The hair was probably in better condition than the skin because it is composed of keratin as opposed to collagen. Although the surface on the flesh side of the skin was powdering, it had been decided not to consolidate it due to concerns over the stiffening that could result. Despite some concerns about applying heat to the weak and degraded skin, a heat-reactivated adhesive had been chosen to adhere an open-weave polyester lining, as it fulfilled most of the desired criteria. In particular, Beva® 371 was felt to be the most suitable adhesive to provide the necessary strength and flexibility to enable the cape to be displayed as worn while maintaining the drape of the garment [8]. Beva® 371 is now commonly used for skin repairs, as it provides a nap bond without the adhesive penetrating the skin [12].

Experiments with dyed leather samples

In 1998 several samples of traditionally dyed, brain-tanned leathers were obtained from Brent Boyd (a craftsman, artist and researcher from Williamsburg, Ontario who was trying to replicate traditional Native American techniques) and subjected to accelerated ageing; the methods of production for these samples have already been described [13]. The leather samples in this group were undyed skin and skin that had been surface-treated with solutions or suspensions containing: iron; hemlock (the bark of the Eastern hemlock *Tsuga canadensis*); iron with hemlock; iron with hemlock and black walnut; iron with hemlock and sumac.

Each sample was cut in two so that a replicate sample was available. The surface pH of a portion of each of the treated skins was measured using a surface pH electrode and then artificially aged at 70°C for 28 days in a glass desiccator humidified to approximately 75% relative humidity using a glycerol/water mixture [14]. As the samples were only surface dyed, the strength of the dyed skin was assessed qualitatively by rubbing a cotton swab over the surface to see whether any black material was removed.

No sample showed significant loss of material or dye transfer to the swab before ageing, but all the treated skins except that dyed with hemlock alone were markedly more affected by rubbing after ageing, with the pale background showing through in the rubbed areas. The colour of some samples had become browner and the cotton swabs rubbed off small particles from the degraded fibres that could be seen under the microscope when the swabs were examined. Any change in pH in the aged samples was negligible (–0.1 to 0.2), except for skin treated with a combination of iron, hemlock and sumac, which decreased in pH from 5.6 to 4.7. Although the changes in pH are small, the increased vulnerability of the surface in these experiments suggests that iron-containing black dyes increase the rate of deterioration of brain-tanned skins.

THE BRITISH MUSEUM GREAT LAKES POUCH

History and cultural context

The British Museum pouch (1937,0617.1) was acquired in the 1930s as a donation from Harry Beasley of the private Cranmore Museum [15]. Purchased at an unidentified auction sale in the rooms of Stevens, Covent Garden, it was at the time of acquisition undocumented. Dale Idiens, of the Royal Scottish Museum commented on the significance of the pouch during a visit to the British Museum 40 years later, during the late 1970s and, as a result, the pouch was conserved for display. In the early 1990s Michael Graham-Stewart located one of perhaps 50 albums of watercolour drawings by Sarah Stone showing objects in the Leverian Museum in London in the 1780s [16]. One of the 40 watercolours depicts the pouch at near life size (Figure 2), and this identification assisted in making the case for the ultimately successful purchase of the album by the British Museum. At the moment little can be said of the pouch's history between about 1786, when Stone sketched it, and 1937 when it came to the British Museum.

Stylistically the pouch falls into a group of black-dyed bags associated with the American Revolution or War of Independence (1775–1783), many of which are decorated with Thunderbirds and Underwater Panthers, that is to say mythic creatures of the Upper and Lower Worlds. Three similar examples from the collection of General Frederick Haldimand, governor of British territory from 1778 to 1784, in the Musée d'Yverdon, Switzerland, are in good condition and are well documented: another is in the Canadian Museum of Civilization [17]. No original ethnic attributions are provided, but Feest is satisfied that the pouch in Canada is Ojibwa [17]. That these pouches are likely to be Ojibwa is confirmed by the contemporary portrait of Sir John Caldwell, who served in the King's Regiment in North America from 1776 to 1780. Caldwell is depicted in an original oil portrait, still in the possession of Caldwell's family, wearing the hybrid costume of a military Ojibwa (including a pouch) during a council meeting at the Shawnee village of Wakatomica (now Dresden, Ohio) on 17 January 1780 [18].

FIGURE 2. Watercolour painting (British Museum Am2006,Drg.53) of the pouch by Sarah Stone *c.*1785

The Ojibwa missionary Reverend Peter Jones, also known as Kahkewaquonaby, 'sacred feathers' or 'sacred waving feathers', was depicted in early images with two similar pouches of this type, one with a Thunderbird. When he was photographed in 1845 by Hill and Adamson the costume and pouches were by then archaic [19, 20]. The practical use of the pouches is uncertain, but they may have contained personal items, or materials for ritual use such as tobacco; both Caldwell and Jones are carrying pipe-tomahawks in their portraits. Elaborate costumes of this type were perhaps first created as part of the diplomatic efforts associated with Sir William Johnson, of Johnson Hall, Johnstown in the Mohawk Valley, New York, who was Superintendent of Indian Affairs for the Crown from 1755 to 1774. While these costumes may have been designed for diplomacy, it is likely that the symbolism incorporated in the individual elements, especially the quilled decoration of religious articles, would have been extremely ambiguous in meaning. The Thunderbirds probably had different meanings to the women who made the objects, to the Ojibwa men who are likely to have gifted the pouches to Europeans, and to the men who wore the costumes as a means of communicating across ethnic divisions, both European and Native North American.

Originally living around the northern and western Great Lakes in what is now Ontario, the Ojibwa became prominent in northern Minnesota and Wisconsin after European contact in the seventeenth century. They are the pre-eminent Algonquian-speaking hunters and trappers around the western and northern Great Lakes, known by themselves today as Anishnaabe, and in the United States as Chippewa. Long involved in the Canadian fur trade, with the French as their main allies, the defeat of France in the French and Indian (or Seven Years) War of 1753–1763 would have brought about major changes in every aspect of Ojibwa life. The creation of black-dyed pouches, with a Thunderbird (*animikii* in Fond du Lac dialect) depicted, may have come out of a period of rapid change, affecting Ojibwa religion both in the Grand Medicine Lodge or Midewiwin and Ojibwa shamanism [21]. For the Ojibwa, Thunderbirds used lightning bolts to kill underwater spirits, were associated with the creation and the protection of birds and provided associational names adopted at puberty (the source of Peter Jones' name, which perhaps lies behind his dressing with a Thunderbird pouch for photography) [22]. The Beasley pouch considered here is unusual in that the two Thunderbirds are depicted with lightning.

FIGURE 3. The pouch (British Museum 1937,0617.1) prior to conservation treatment in the 1970s

FIGURE 4. The pouch prior to recent conservation treatment

The 1970s conservation treatment of the pouch

The pouch was in an advanced state of deterioration by the 1970s when it was first conserved; this is evident from the conservation record and photographs taken at the time, Figure 3. The front flap had become detached and only its outer skin rim remained. Some of the lengths of coiled white porcupine quillwork had survived where the skin beneath had not, so they were left unattached. Parts of the main bag were also missing, including the upper left corner of the bag (as viewed), the top edge and much of the right side of the reverse (as viewed). The carrying strap, made of wool decorated with glass beads, was only tenuously attached to the bag at one side.

Comparing the pouch with Sarah Stone's illustration gives a good idea of the original appearance of the bag, although it is evident that there has been some artistic licence in recording the detail [16]. The watercolour in Figure 2 shows some of the features that are now missing from the bag. Most noticeably, the central portion of the front flap was once decorated with a strip of brightly coloured red, yellow and black zigzag quillwork in a geometric design. In addition, the majority of the tassels, composed of metal cones and red-dyed hair, hanging down at the lower edge of the pouch are missing; just two of the 19 illustrated are now present.

The pouch was conserved in the 1970s so that it could be exhibited at the Museum of Mankind in 1982 in an exhibition entitled *Thunderbird and Lightning* [20]. The friable skin was consolidated with a 5% solution of soluble nylon, a chemical modification of nylon 66 that is soluble in hot methanol or ethanol (usually with some added water) and which forms a gel on cooling. This was a standard treatment at the time [23]. Nylon net coated with an early thermoplastic adhesive, Vinamul 6515, was used as the backing to support and infill missing areas and to form the seams at the sides of the bag.

This conservation treatment was re-evaluated in 2006 as the repairs were no longer helping to keep the bag intact. The adhesive was failing and the front flap had become detached from the main part of the bag, Figure 4. There were quite a number of separate small skin fragments secured to the net on the upper left corner of the bag (as viewed), Figure 5. Some of the white stitched quillwork and skin fragments on the front flap had become detached from the nylon net and the net had developed some very unsightly holes

FIGURE 5. The fragmentary state of the top left corner of the bag prior to the recent conservation treatment

where it had been used to infill the missing central area of the front flap. The remains of the glossy adhesive could be seen in the mesh of the net and, because the adhesive had become slightly tacky, the exposed net had attracted much powder from the degraded skin. The skin appeared stiffer than in the photographs taken prior to the 1970s treatment, which may have been caused by cross-linking of the soluble nylon. Sease pointed out the shortcomings of soluble nylon and it has not been regarded as a useful conservation material for some time [24].

Analysis and investigation of the black-dyed skin

A useful first step in examining the degradation mechanism is the confirmation of the presence of iron in the degraded artefact. The pouch was analysed by X-ray fluorescence analysis (XRF), which can detect elements with an atomic number greater than about 13 (aluminium). Iron was detected, although as no specific calibration had been carried out it was not possible to determine the quantity of iron present. The XRF spectrum (Figure 6) of an area of the bag shows that in addition to iron the only other element detected was a trace amount of copper.

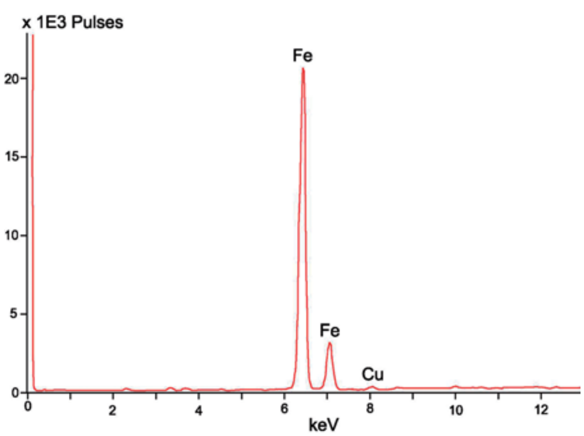

FIGURE 6. X-ray fluorescence spectrum of the skin of the black-dyed pouch

Quantitative analysis of the amount of iron in the leather was performed colorimetrically by extracting the iron into solution using hot 10% hydrochloric acid and then measuring the strength of the red colour formed by adding ammonium thioglycolate [25]. The iron content was found to be 1.63%, which is similar to the 2.0% found by Dignard and Gordon in a piece of badly deteriorated black-dyed fur that also contained 0.6% copper [8]. Microscopic examination of the leather showed that the weak fibres had shattered into small fragments. The sample exhibited no birefringence and the fibres did not shrink on warming, suggesting a lack of crystallinity, a low T_s and a much deteriorated state.

It appears that the quillwork is less affected by the black dyes than the skin. Assuming that the black quillwork of this bag was dyed in a similar manner to the skin, this might be due to differences in susceptibility of the keratin proteins in the quill compared to the collagen proteins in the skin.

Recent conservation treatment of the pouch

The front flap was treated first as it was only attached to the remaining bag at one side, enabling it to be moved aside to facilitate the work. The old nylon net was very gradually removed by gentle hand pressure and the application of a minimal amount of acetone with a fine sable paintbrush as necessary. The skin was so impregnated with consolidant that further consolidation was ruled out and it was decided to keep the use of adhesives to a minimum. Water-reactivated adhesives were avoided as they might stain the skin and because iron-catalyzed deterioration is accelerated by humidity [26]. Solvent-reactivated adhesives were chosen in preference to heat-reactivated adhesives of the type used in the previous treatment of this pouch, and in the treatment of the degraded black-dyed fur trimmed velvet cape at CCI that has already been discussed. It was considered preferable to avoid the use of heat on such degraded skin and the pressure of using a heated spatula might have caused damage to the stiff and inflexible pouch.

The weakest areas around the rim of the flap, composed of many separate pieces, were first strengthened and held in place with small patches of a fine mulberry paper coloured with acrylic paints diluted in distilled water. These were adhered to the reverse using a 20% solution of Klucel G in industrial methylated spirit (IMS), which was chosen as it dried very quickly and was therefore unlikely to stain the skin. To provide the necessary support for the flap it was decided to use an encasing method, in which the skin is encased between two layers of fabric. There is a greater range of nylon nets available today than in the 1970s, including some finer, softer and sheerer fabrics suitable to be used as overlays. Although a sheer polyester fabric was considered because of its long-term stability, it was judged to be visually unacceptable as an overlay. Nylon net was, therefore, selected and once dyed to a suitable colour was barely noticeable except on close viewing. Nylon net was, however, ruled out for the lining as using two layers of net directly on top of each other can lead to a disturbing moiré effect. In addition, it was felt that a material providing greater support would be desirable. Non-woven polyesters were first investigated, but discounted as it was decided that a woven fabric was required to hold the sewing stitches of the repair adequately. A fine-woven cotton fabric was finally chosen as it was easy to dye to an appropriate colour with Solophenyl® azo dyes. The nylon net and some monofilament silk thread were dyed dark brown with Lanaset® direct dyes.

The flap of the pouch was sandwiched between the dyed cotton backing (Figure 7) and the dyed nylon net overlay, encasing the fragments by stitching around their edges and the remaining sections of the flap using the dyed silk thread. Slits were cut in the net at the position of the tassels so that the net could be folded back to the reverse of the cotton backing and secured to it with the silk thread.

The main bag of the pouch was then treated, Figure 8. The old net was first removed from the bag in areas where it came away easily but was left in place where it was felt that, due to the friable nature of the skin, its removal would be damaging. The small loose pieces of skin on the front and back were carefully removed after recording their position for future replacement. The vulnerable edges of the brittle skin were strengthened with mulberry paper using the method described above.

Large sections of the skin of the main bag had survived intact, which made the encasing technique used for the flap inappropriate, as it would have necessitated completely covering the entire front of the bag including the quillwork decoration with an overlay of net. Dyed cotton fabric was again used as the lining fabric but, as it was not possible to stitch through the skin, it was here secured to the paper-strengthened edges around the missing areas with a minimal amount of adhesive.

Various adhesive films were made by brushing adhesive onto polythene sheeting and letting it dry. By removing the polythene backing, a free film of adhesive was obtained. Paraloid® F10 was chosen as the most suitable of the adhesives tested as it adhered well to both the cotton fabric and the paper-backed skin. This adhesive was reactivated by introducing white spirits through a Gore-Tex® membrane. Working on one side of the bag at a time, the adhesive film was cut into small squares that were placed between the cotton lining and the paper-backed skin at intervals around the missing areas at points where, away from the extreme edges, the skin was stronger. White spirits were applied to a small piece of blotting paper and the adhesive reactivated locally through the membrane for five minutes while applying slight finger pressure, which was maintained as it dried.

For the overlay an adhesive was chosen that was soluble in a solvent that would not affect the Paraloid® F10 adhesive used to secure the lining. Lascaux 498 HV adhesive was selected as it has been used successfully as a solvent reactivated adhesive on both textile and skin artefacts [27]. It is often mixed with Lascaux 360 HV, but in this case 498 HV was used alone as 360 HV can remain slightly tacky and its greater flexibility was not essential for this treatment. Some

FIGURE 7. The flap of the pouch laid on top of the dyed cotton lining fabric

FIGURE 8. The skin remaining on the reverse of the pouch: the flap to one side has been encased as described in the text

of the dyed nylon net used in the repair of the front flap was coated with a 10% v/v solution of 498 HV adhesive in distilled water using a wide brush and allowed to dry against polythene sheeting. Two pieces of adhesive net were cut to shape to fit the missing areas of the front and back of the bag, leaving an area of overlap on the outer surface of the bag to protect the friable edges.

FIGURE 9. Detail of the pouch with the flap open showing the new cotton lining fabric

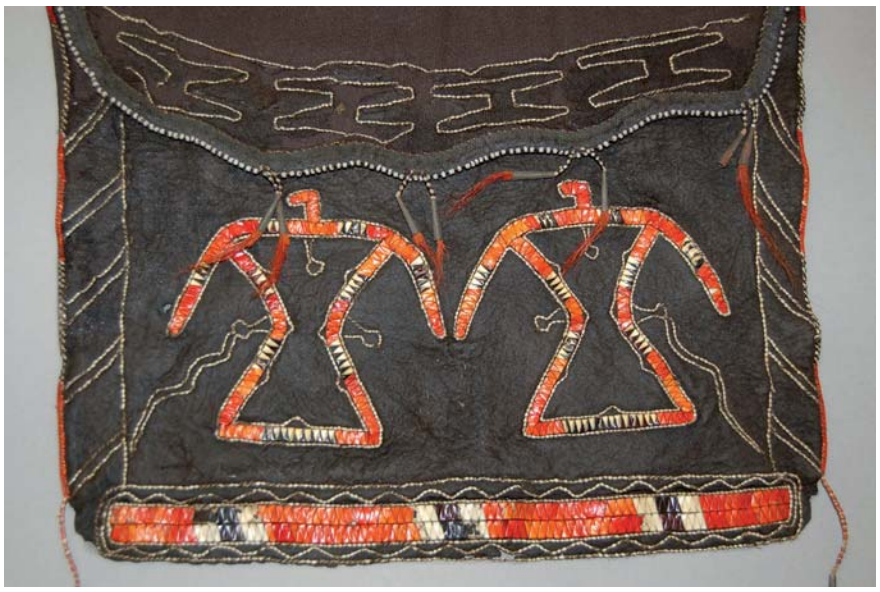

FIGURE 10. Detail of front of the pouch with the flap closed

The adhesive-coated net was carefully positioned on the outer surfaces of the bag, and gradually secured by local reactivation through a Gore-Tex® membrane using blotters cut to shape and moistened with IMS. After applying the blotters for three minutes the net was covered with polythene to slow down evaporation and gentle finger pressure was applied until the area was dry. The loose pieces of skin from the upper edge of the bag were repositioned during this process. The adhesive net overlay was secured to both the cotton fabric lining and the edges of the outer skin of the bag. The outer edging of the bag at the top left corner (as viewed) was additionally secured to the net by overstitching with the dyed silk thread. Should it prove necessary to remove the nylon net in future the Lascaux 498 HV adhesive can be dissolved in acetone.

The dyed cotton fabric and adhesive net overlay were trimmed to the shape of the edges of the bag, but allowing extra fabric to turn under along the edges. Finally, the seams of the bag were rejoined by stitching with the dyed silk thread and the flap was joined to the main body of the bag by stitching through the cotton fabric that replaced the missing skin at the upper edge of the bag, Figures 1, 9 and 10.

STABILIZATION OF BLACK-DYED SKINS

Preventive conservation

All artefacts that have been treated with iron/tannin type black dyes degrade faster than those that are undyed and are a cause of concern for conservators. Iron gall ink drawings and manuscripts have received much attention over the last decade and the vast majority of research on iron/tannin blacks has been directed toward ink on paper or parchment [28].

Although it can be confidently predicted that the rate of deterioration of any object can be decreased by lowering the storage temperature, the effect of lowering relative humidity (RH) is more contentious. Those deterioration reactions that involve the presence of water will be slowed down by decreasing the RH, but there can be unwanted side effects; for example, leather becomes more brittle when RH decreases as the water it contains acts as a plasticizer. While less humid conditions will probably decrease the rate of acid-catalyzed hydrolysis, the effect of RH on oxidation processes can be unpredictable.

The use of antioxidants has not been shown to be effective, but an alternative strategy is to store the object in an oxygen-free environment. Several practical solutions have been developed in recent years. Most involve the use of bags made from oxygen-impermeable film into which objects are placed, along with sachets of an oxygen-absorbing compound, before sealing; in most cases an oxygen-indicator 'tablet' is also included to show that the level of oxygen is minimal [29, 30].

Chemical stabilization

Chemical stabilization processes can lower the concentration of the agents responsible for deterioration. Deacidification is possible, and widely used in book and paper treatments, but it is not often used on proteins because its usefulness has not yet been proven. It also has the side effect that an increase in pH can be associated with a change of colour, as black dyes often become brown in slightly alkaline conditions. Although it is generally considered that iron that is tightly bound in a dye complex is unable to participate in degradation processes, the degradation of the iron/tannin complex can, as mentioned above, release free iron(II) ions that are particularly aggressive in promoting further degradation leading to an autocatalytic reaction. A promising approach is, therefore, the use of agents that reduce the concentration of free iron in the substrate. Neevel has suggested the use of phytates [31], but these have so far only been tested and used in aqueous solutions, which limits their applicability in situations where moisture is also known to be an agent of deterioration.

A potentially useful range of stabilization treatments based on immidazolium antioxidants has been proposed by Kolar *et al.* [32], although these and the majority of other treatments have been developed to address the degradation of paper by iron gall inks. To assess existing or new treatments and develop solutions for the deterioration caused by iron/tannin colorants on other organic substrates, such as the skin in the pouch considered here, a three-year collaborative research project has been initiated by the British Museum and the University of Manchester.

CONCLUSIONS

Conservation of the pouch has ensured that all the remaining sections are held together and that further fragments will not be lost. Although display should be restricted to minimize any further degradation, information about the pouch will be available in the *Collection Database* on the British Museum website.[1] In addition, the early watercolour gives an idea of its original appearance. Scientific analysis carried out on the skin has added to the knowledge of how such iron/tannin dyes affect skin, and will contribute to research into non-aqueous methods of chemical stabilization for cellulose and protein artefacts affected by such black dye degradation that is now under way.

ACKNOWLEDGEMENTS

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MATERIALS AND SUPPLIERS

- Beva® 371, Klucel G, Lascaux 498 HV, Paraloid® F10 and Pliantex: Conservation Resources (UK), Ltd., Unit 2, Ashville Way, Off Watlington Road, Cowley, Oxford OX4 6TU, UK; www.conservationresources.com.
- Gore-Tex®: Talas, 330 Morgan Avenue, Brooklyn, NY 11211, USA; www.talasonline.com.
- Lanaset® and Solophenyl® dyes: Huntsman Textile Effects, Unit B, Adlington Court, London Road, Adlington, Cheshire SK10 4NL, UK; www.huntsman.com.

AUTHORS

Pippa Cruickshank (pcruickshank@thebritishmuseum.ac.uk) is a conservator and Vincent Daniels (vdaniels@thebritishmuseum.ac.uk) an emeritus researcher, both in the Department of Conservation and Scientific Research. Jonathan C.H. King (jking@thebritishmuseum.ac.uk) is Keeper of the Department of Africa, Oceania and the Americas at the British Museum.

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NOTE

1. www.britishmuseum.org/research/search_the_collection_database.aspx (accessed 17 June 2009).