



Analytic study and restoration of leather shoes from 18th Century burials

Joan Enrich i Hoja, BASF Curtex S.A.

Joaquim Font I Vallés, EUETII (UPC)

M^a Lledó Barreda i Casanova, Sant Boi de Llobregat Museum

In 1991, when the pavement of the parish church of Sant Baldiri in Sant Boi de Llobregat, Barcelona, was replaced, three 18th Century graves were revealed. In one tomb a pair of leather shoes was found; the following article describes the results of the analysis and restoration of the shoes.

Dating the burials

This Baroque church was consecrated in 1734. However, on April 3, 1787, King Charles III of Spain decreed that burials inside the churches would be prohibited—except for those of prominent persons. These three ordinary burials, therefore, must have taken place between these dates.

Leather in archaeological excavations

The presence of leather in archaeological excavations is very

exceptional as decomposition normally occurs over a long period. Nevertheless, leathers can be preserved by exceptional environmental conditions, either when extremely wet or dry. In extremely dry conditions, as in this case, leathers undergo a series of variations such as:

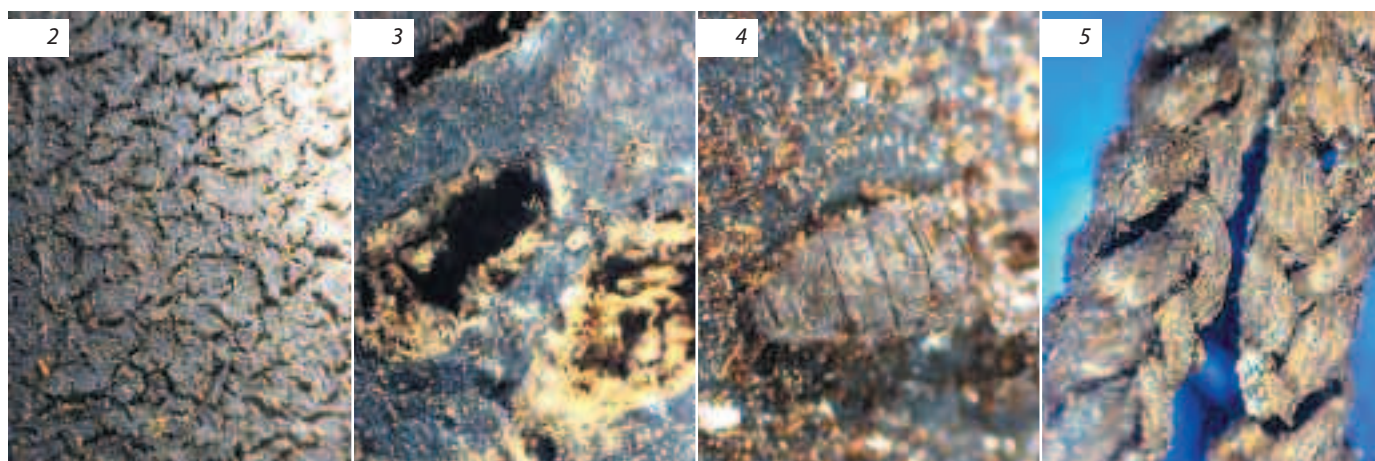
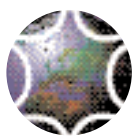
- The loss or oxidation of tannins in vegetable tanned leathers
- Changes in the original fatliquor due to oxidation of tannins and fatliquors
- A fragility due to a loss of softness and flexibility as a result of a drying up of fibres and fibrils
- Intense dehydration

The analytic study

Before starting the restoration process, separate analyses were



Shoes as found in their original condition.



Revealed by microscopic examination (2) grain degradation, (3) needle damage from original construction, (4) an insect, and (5) shoelaces made of wool.

performed on 40-50 grams of both the sole and shoe upper leathers. Samples were taken from the pair of shoes in worst condition. Knowledge of the ancient tanning process was valuable in this case to help to determine the most appropriate approach to restoration.

TYPE OF LEATHER

Because of the thickness of the leather, it was concluded that the sole is bovine leather. Similarly, the shoe uppers also seem to be bovine, though the use of goat or sheep leather cannot be ruled out.

TYPE OF TANNINS

The appearance of the leather is characteristic of tannages using vegetable extracts.

Analysis (absorption, UV, ferric chloride) confirmed this initial hypothesis. Alternative systems, such as oil, were excluded because the amount of oil found was too low.

A low aluminium content was, however, detected but only 10-20 times higher than the content of leathers currently tanned with aluminium-free chemicals. Part of this aluminium content could arise from both impurities in the tanning materials used at that time, and a 'mineralisation process'. This means that since the shoes were made there had been a decrease in organic components, with a gradual development of inorganic components.

Contamination has also to be taken into account, because exchange with substances from the ground may have occurred. Most types of earth have an aluminium content, and exchange could have taken place, especially in wet weather.

However, these reasons do not entirely justify the amount of aluminium found in the samples, particularly in the shoe uppers. It has to be borne in mind that alum-tanning agents were known in Ancient Egypt and Mesopotamia, and in Roman times this process became very popular. Vegetable alum-tannins that were well known at those times may have been used and would justify the data obtained from this study.

TYPE OF FATLIQUORS USED

The upper leathers

Lipoidal substances also undergo decomposition. Among degradation processes—hydrolysis, oxidation and microbiologic degradation—oxidation needs to be taken into close account. The composition of fatty acids, extracted from the samples of

upper leather, shows a very low unsaturated acids content (oleic, linoleic) being only 11.9%. No oil or natural fat accounts for such a low rate. The lowest unsaturated acids content, amounting to 40/50 %, is attributed to land-based mammal fats.

It is recognised that the double bonds are more susceptible to oxidation. Consequently, unsaturated fatty acids undergo a greater degradation. In turn, these become hydroacids and chemically fix with collagen. In this situation, combinations are formed that cannot be extracted from the leather in an analysis. This may explain in part the 0.86% low rate of oil content found in the upper leather. This low amount of extractable fats could also be produced by the continued exposure of the long-used shoes, to light and humidity.

Analysis also showed a ratio of stearic acid to palmitic acid (*s/p ratio*) of 1:1.34. As no double bonds are present, it is believed that this amount has not been substantially modified by degradation. However, this is not a common ratio, and studies of oils and fats of both animal and vegetable origins show a predominantly greater amount of palmitic than stearic acid. The *s/p ratio* is less than 1:1, with the exception of cocoa butter, neem oil (from India) and sheep fat.

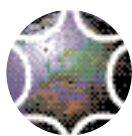
Because of their exotic origin, the use of cocoa butter and neem oil as fatliquors is unlikely. The stearic/palmitic ratio of sheep fat is, according to Wolff, 1:1.58 whereas Mehlenbacher places it down to 1:1.21. The two authors respectively attribute to bovine fat a 1:0.4 and 1:0.9 *s/p ratio*. Accordingly, it is believed that either sheep fat was used for softening or perhaps the uppers were sheepskins.

The sole leathers

As expected, the amount of fat extracted from the sole was lower than that extracted from the upper leather. Because of its function, sole leather requires none or a very light fatliquoring, in order to be tough and firm. The analysis revealed an unsaturated acids content of 26.5%. The better fat preservation in the sole leather is probably due to its thickness, as this provides a higher fat protection from surface phenomena such as oxidation. The 1:0.33 *s/p ratio* is a characteristic ratio of bovine fat, so it is most likely that the soles were produced from cattle hide.

TYPES OF DYES

Aqueous extracts obtained from the study of the tannage applied do not indicate any dye or natural colouring. However, analysis shows a very high content of iron.



Details of restored shoes.

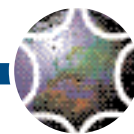
Leathers tanned today contain some iron, mainly produced from product impurities or machine use. But the historic upper and sole leather samples respectively revealed values 10-40 and 50-60 times higher than today's equivalents (0.02-0.08% and 0.006-0.010 % Fe_2O_3).

Additionally, the effects of mineralisation also need taking into account. Nevertheless, values are high enough to suggest the use of ferric salts for fixing tannins or for colouring the upper leathers black. The lower concentration found in the sole may be either due to a lower penetration in a thicker leather, or to a lighter original application.

Restoration and conservation

Restoration and conservation were based on the following:

- Before handling, the shoes were exposed to UV for 2-3 minutes to avoid biological risk.
- The shoes were photographed in their original condition as shown in *photographs 1a,b,c,d & e*.
- The shoes were subjected to microscopic examination to determine their state of conservation and detected:
 - ♦ "Craquelé" effects in the epidermis and dermis due to surface dryness *photograph 2* (x10).



Details of restored shoes.

- ♦ Broken fibres as result of the original sewing of the shoes *photograph 3* (x20).
 - ♦ An insect imbedded in the epidermis of the leather, shown in *photograph 4* (x25).
 - ♦ The shoelaces, shown in *photograph 5* (x 12.5).
- It was determined that the shoelaces were made of wool. A sample flame test (combustion) produced a strong smell of burned keratin but no flame. In addition, surface cuticles typical of wool were revealed by microscopic examination.
- Before the re-hydration/restoration process, the uppers and soles were hand washed in distilled water to remove osseous

remains, dust, salts and insects.

- Both soles and uppers were introduced for rehydration in a solution of:
 - ♦ PEG 400 (*Polyethleneglycol*): 300 grams
 - ♦ Distilled water: 700 grams
 - ♦ Cortymol BAC (*microbiocide*): 2 grams
 - ♦ Cortymol FUN (*fungicide*): 1 gram.

The leathers required rehydration before handling and restoration. Although the shoes were fragile, flexibility and softness were recovered by moistening the fibres with distilled water. A twenty-four hour treatment was needed to rehydrate



the heels and soles and eight hours for the shoe uppers. An excessive soaking had to be avoided in order not to alter the fibres and protofibrils.

- Once soaked, the soles and uppers were dried at 25°C, 60% humidity. Before drying was completed the uppers were carefully moulded on a wooden last to give shape and the soles and heels placed on a flat surface covered with blotting paper and weighted down to keep them flat.
- As the leather was extremely fragile, two or three brush applications of fatliquor were needed. The original dark brown colour of the shoes darkened after this treatment. The solution consisted of:
 - ♦ *Perpristol U* (Synthetic mineral oil): 700 grams
 - ♦ *Eukesol Wax SF* (a mixture of oils and waxes that do not oxidise): 300 grams.
- Three days after the fatliquoring application the shoes were sewn together. The soles and reinforcements were first sewn with cotton thread, then the different parts that made up the shoe uppers. Finally, the soles and uppers were sewn together. Photographs were taken to document this process, and details of the restored shoes are shown in *photographs 6a, b, c, & d*.
- To avoid deformation, the shoes were placed on expanded polyurethane lasts to recover their original form.
- Finally, in order to keep the shoes in good condition, they were placed in microperforated polyethylene bags (to let them breathe) and stored in cardboard boxes under conditions recommended of 16±2°C and 52±5% atmospheric humidity. 🌸

Bibliography:

1. BASF Curtex (1995): *Información técnica.- L'Hospitalet de Llobregat*
2. BASF (1997): *Información técnica - Química textil y del cuero.- Ludwigshafen/Germany.*
3. BARREDA Ma. LL. (1992): "Memoria de l'excavació d'urgència realitzada al jaciment arqueològic del Barri de Sant Boi de Llobregat"-sector Interior Església de Sant Baldiri 1991. Sant Boi de Llobregat – Ajuntament. Inèdit.
4. EVERSLED, R.P. et alii (1992): "Proceedings of British Academy", 77, p.187.
5. FONT; J. ENRICH; J. MURIELS, S. (2002): "Estudi analític i restauració d'un conjunt de sabates de cuir procedents de l'Església de Sant Baldiri (segle XVIII)" - Sant Boi de Llobregat – Igualada: Inèdit
6. FONT, J. GÓNZALEZ M. (1991): "Estudio del contenido de hierro del cuero". AQEIC, 42 pages 17-24
7. FORBES R.J. (1996): "Studies in Ancient Technology". Volume V. Leiden: Brill.
8. GRASSMANN W; SPRINGER-VERLAZ, W. (1994): "Handbuch der Gerbereichemie und Lederfabrikation" – Vienna.
9. GRATACOS E. et alii (1962) "Tecnología química del cuero".
10. IZQUIERDO L. (2002): "Acabar pieles con ceras y aceites". En "Preactas del Congreso de la Asociación Química Española de la Industria del Cuero" – 2002 – Inédito
11. MEHLENBACHER V.C. (1979): "Análisis de grasas y aceites" – Bilbao: Urmo pages 497-503
12. PARIS J.C. (1992): "Determinación de aluminio en piel por espectrofotometría de absorción atómica". AQEIC, 43. p. 276.
13. RUSSELL A.E. et alii (1967) "Further studies in vegetable tannage" J. Soc., Leather Tech., Ch.51, p. 349.
14. SÁNCHEZ A.; CAÑABATE M.L. (1998): "Indicadores químicos para la arqueología"- Jaén: Universidad de Jaén.
15. WILLS B. (2001): "Leather wet and dry" – London: Archetype Publications, Ltd.
16. WOLFF J.P. (1968): "Manuel d'analyse des corps gras"-Paris: Azoulay, pages 373-385.