THE INVENTORY AND CLASSIFICATION OF TYPES OF DAMAGE TO OBJECTS FROM ETHNOGRAPHIC COLLECTIONS

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***Rezumat*:** *Lucrarea cuprinde o parte din cercetările efectuate în cadrul proiectului Tehnici complexe de investigare, evaluare, conservare şi restaurare a materialelor colagenice etnografice, finanţat prin Centrul Naţional de Management Programe. Sunt prezentate principalele cauze ale deteriorării, factorii de deteriorare şi tipurile de deteriorări produse patrimoniului etnografic pe suport colagenic.*

***Abstract*:** *This article includes part of the research carried out within the project 'Complex techniques of investigation, evaluation, conservation and restoration of collagenic ethnographic materials', financed by the National Centre of Management Programs. The main causes of deterioration, factors in degradation and types of damage affecting ethnographic collagenic heritage are presented.*

Résumé: *L'ouvrage ci-joint comprend une partie des recherches effectuées dans le cadre du projet Techniques complexes d'investigation, évaluation, conservation et restauration des matériaux collagèniques, financé par le Centre National de Management Programmes. On y a présenté les principales causes de la détérioration, les facteurs de détérioration et les types de détériorations produites au patrimoine ethnographique sur support collagènique.*

***Keywords*:** *inventory, classification, damage, collagenic materials, heritage, ethnographic.*

Amongst the important creations of popular art in Bucovina, the manufacture of leather occupies a pre-eminent place through the diversity, originality and unusualness of its decorative value. Due to its beauty, ornamental richness and colourful harmony, it has attracted the attention of researchers and lovers of traditional art. The ethnographic section of the Museum Complex Bucovina includes a rich ethnographic heritage comprised of works of decorative and applied art from glass, ceramics, metal, wood, textiles, domestic and household items, furnishings, clothing, leather, religious objects, embroidery, musical instruments, old books, props for winter traditions, hunting trophies, bone and horn pieces, photographs, monuments and sites of ethnographic objects (open-air ethnographic museum).

Procedures in the manufacture of leather in the region of Bucovina

In order to be able to investigate, conserve or restore collagenic heritage objects, knowledge of the old techniques of manufacture is necessary, as much of the degradation that appears is caused by deficiencies in manufacture. Therefore, the main techniques of manufacture of collagenic materials are presented using as support ethnographic museum objects from the region of Bucovina.

In the collective of Bogdăneşti, Suceava County, tanning solution was prepared from oak, alder and fir bark, which were ripped from the trunks, dried and ground in a mill until they became flour. Several large wooden buckets were then taken and in them were placed a layer of skin and one of bark, alternately, until they were full, after which they were filled with warm water. In the resulting solution, called 'dubala' (a type of tanning solution), the skins were kept six weeks. When taken out, the skins had a reddish colour. The next step was the removal of the hair that is the taking of the hair from the skin: the skin was stretched out on even ground and with a hair brush moistened in melted potash alum (aluminium potassium sulphate), was scrubbed until it obtained a black colour.

Another similar procedure cited by Tudor Pamfile in his work[1] 'Romanian domestic industry' is the following: take a kilogram of red alder bark (*alnus incana*), over which you sprinkle a handful of ash, then pour over two litres of boiled water; leave to cool. This solution is called 'tabaceala' or tanning solution. The skins are introduced into the vessel with the solution and are kept 24 hours until they obtain a light-red hue. They are then taken out and left to dry.

From black alder (*alnus glutinosa*) take a kilogram and a half of bark, which after it has been torn into pieces the size of two fingers, place into a special vessel for the preparation of the tanning solution. Boil two litres of water and pour over the bark. The liquid has a dark-red hue. In Bucovina, there were villages in which the majority of households knew how to tan sheep, goat, fox skins, etc. The tanning of skins was done in the following way: boil salt water (water from a salt source), pour it into a vessel and to leave it to cool. In the warm salt water place oatmeal and a little of the heart of the grain, i.e. grain bran second and mix well. Stretch out the skin on the ground, put the tanning solution on top, then fold in two and leave it three days, after which check that it is tanned. The tanned skin is kept to dry.

Also in the village Bogdăneşti in Suceava County, exists the following procedure of preparation of skins for sheepskin coat/waistcoat and hats: the skins are raised and then left to dry, after which they are washed with warm water to remove the wool sweat; then wrung out and put in the tanning solution. The tanning solution is made from salted whey. After several days, the skins are taken out, stretched out well and left to dry.

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[1]Tudor Pamfile, *Industria casnică la Români - Trecutul şi starea ei de astăzi, contribuțiuni de artă şi tehnică populară* [*Romanian domestic industry - past and present state, contributions in art and popular technique*], Bucureşti, Tipografia "Cooperativa" Academia Română, 1910, p. 41-44.

Before cleaning the skin of the rest of the flesh, it's stretched in length with a hook. The skin is suspended on a line secured to a loft nail. It's held by hand from the bottom of the skin, again with the other end in the hook handle.

After it has been cleaned of flesh, the skin is stretched with the help of *skin-stretching frames*. The frames are fitted with a tongue, which goes under a chiselled hole on the frames. The skin is put on the frame, placed in the stiff tongue of the frame and then stretched by hand. The categories of leather used in the manufacture of clothing are of diverse qualities and thicknesses, beginning with the very thick for peasant sandals and ending with thin, elastic leather linings, dyed green, brown, black or red serving in particular as decoration for sheepskin coats/waistcoats and girdles.

Damage to ethnographic leathers

However, leather ethnographic objects can be conserved in much better conditions than archaeological ones, which have several characteristics that increase the risk of deterioration. Many of them occur in un-tanned or semi-tanned skins, being more sensitive to fluctuations in humidity than completely tanned materials. The situation of excessive fat content is also often encountered, due to regular impregnation with oils (the original use of the object or older, inadequate, curative treatments). Ethnographic objects often also contain other elements inclusive of: feathers, fur, hair, unprocessed skin, wood, which attract insects.

With regards to the analysis of the deterioration of the duo tannin-collagen two main causes are distinguished: *hydrolysis* and *oxidation.* Both are influenced by the surrounding environment in which the skin is located: water, heat, light, pH, gases, etc. Both can act on tanning materials as well as on amino acids and collagen peptides. The two main causes of degradation are nonetheless different in their mechanism and result. Recent studies show that the ***'hydrolysis' decomposition*** of vegetable-tanned leather is attributed primarily to the presence of sulphur dioxide and nitrogen dioxide from the polluted atmosphere.

Oxidised decomposition is due to the radical high energy effects of light with oxygen, oils and reactions leading to the triggering of an altered internal chemical structure. Tanning agents self decompose in conditions of oxidation and acid-hydrolysis, also the resulting products can lead to oxidative and hydrolytic decomposition of the collagen[2].

Deterioration factors and the result of their action

1. Faulty manufacture

Almost any stage of the manufacture of leather carried out unsatisfactorily can cause defects in the quality of the objects. We will cite several of the typical, mistaken applications as well as the result that follows them:

- Improper treatment with *chalk*, that leads to the hardening of the leather
- The use of *strong mineral acids* leads to the weakening of the leather's structure

[2] M. Kite, R. Thomson, *Conservation of Leather and Related Materials,* Oxford, Butterborth-Heinemann, Elsevier, p. 181.

• The use of *iron and copper salts* as colouring agents can accelerate oxidative degradation.

Brittleness can be caused by the deposit between the fibres of the leather of different materials, such as: calcium carbonate or plaster (resulting from treatment with chalk), aluminium, products from damage caused by some of the tanning agents, etc. The second cause of brittleness can be the prolonged treatment of the leather before tanning.

Both the conservation of the leather as well as the softening, the cremation, the bating, when they are not controlled, attack the collagen fibre resulting in brittle leather. The residual of the strong acids next to the accumulation of the iron and copper salts also leads to brittleness[3].

• Weak penetration by the tanning agents into the interior of the leather consequently causes foliated peeling and the cleaving of the leather into two layers.

Photo 1. Deterioration due to faulty manufacture.

2. The effects of water and humidity on leather

At relatively normal temperature and humidity there are two types of water present in permeable organic materials such as leather: physically retained water – *free water* and chemically *bound water* at the molecular level.

Bound water is present in the form of several aggregated parts of the structure of the collagen, which the physical and chemical properties influence. The elimination of the bound water alters the arrangement of the intra and intermolecular bonds, producing irreversible stiffening[4].

Free water is localised in the network of interlacing bonds of collagen. It is weakly tied through hydrogen and van der Waals bonds.

Free water can penetrate the leather and increase the rate of chemical reactions, such as *hydrolysis* and *oxidation.* The loss produces stiffening, still reversible, by an increase in relative humidity, as long as the physical structure of re-accumulation

[3] L. Miu, P. Budrugeac, *Evaluarea degradării obiectelor de patrimoniu din piele şi pergament* [*Degradation assessment of heritage items made of leather and parchment*], Bucureşti, Editura Performantica, p. 41.

[4] *Ibidem*, p. 45.

wasn't destroyed[5]. Both a reduced *relative humidity*, as well as an increased one can be harmful to the leather, but more serious is the fluctuation between them, determining in the case of organic materials the fluctuating loss or accumulation of humidity to achieve equilibrium with the surrounding environment (exo-, endothermic reaction, which amplifies the deterioration caused by heat). Insufficient humidity leads to dehydration, again in extreme cases to irreversible changes such as contraction, deformity, stiffening, cracking and peeling.

The fluctuation of the humidity content following temperature changes and relative humidity often causes stiffening and leads the leather to become fragile. After the repetition of further cycles of absorption-desorption, the material loses the capacity to absorb water – *hysteresis* – resulting in an inflexible character that can turn into the rearrangement of polymers and their hydrogen bonds, using the space initially destined to bind the water. At the same time, as a result of the numerous polar groups, the collagen is capable of absorbing a large quantity of water that leads to swelling. *The excess of water* can break the chemical bonds between collagen and the tanning materials, can extract the vegetable tannates, aluminium and chalk of a fibrous structure, exposing the collagen to hydrolytic decomposition. Thus, the water increases the rate of chemical reactions and also plays an important role in the phenomenon of photolysis, favouring damage caused by light.

Another aspect of the influence of water is linked to the disappearance of certain components. Several salts from the skin can migrate and form condensed water intensifying the damage. This phenomenon called *sweating* isn't connected to temperature and relative humidity.

The proteins have a maximum stability in their pH isoelectric area. While the new skin is stable at a pH between 3 and 6, for art objects made from leather a pH between 5 and 7 is recommended, because their state of conservation is more precarious and they have a heightened sensitivity.

The content of the water will also dictate the pH of the complex. Through the usual loss of water owing to natural ageing of the material, the pH can fall following an increase in the concentration of any acid present. In alkaline or acidic environments hydrolysis can have a place in the protean chain that leads to the destruction of chemical structures.

A heightened, constant humidity facilitates attack on the microorganisms, which is primarily on dusty surfaces and those treated with chalk. It can also appear on clean leather, to a relative humidity of over 75%, causing staining, relative softening and the weakening of the leather owing to acid deterioration. On furs, the bacteria attack the roots of the fur, causing it to fall out.[6]

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[5] A. Bernath, L. Miu, M. Guttmann, *Identifications, Microanalysis, Evaluations and Diagnosis of an Ethnographical Leather Object,* Sibiu, Art2008 Book of Abstracts and CD of the Proceedings, p. 47.

[6] Doina Maria Creangă, *Conservarea,investigarea şi restaurarea bunurilor de patrimoniu pe suport din piele* [*Conservation, investigation and restoration of heritage assets on leather backing*], Suceava, Editura Universității, 2006, p.124.

Photo 2. Deterioration due to the effects of water and humidity.

3. The effects of fatty materials

Fatty materials have an important role as they lubricate the fibres, maintaining a degree of flexibility and softness, being used both in manufacture and also in the periodic maintenance of leather objects. The most common fats and oils are triglycerides, which are molecules made from a molecule of glycerol, to which adhere three fatty acids, saturated or non-saturated. All non-saturated fatty acids are susceptible to *self-oxidation* (less so the saturated ones), to whose chain reactions are linked complex phenomena, potentially catalysed by oxygen, ozone, nitrogen dioxide, sulphur dioxide, metals.[7]

The results of deteriorations caused by fatty materials can be recognised thus:

- The follicular layer can become fragile owing to the excess of fat. In this case the fat doesn't work as a lubricant, but on the contrary glues the fibres together.
- Free fatty acids increase the acidity in the leather.
- Free fatty acids attack the copper auxiliaries; also the green products of corrosion can cause harm to the surface of the leather.
- Free fatty acids, solid at room temperature, tend to form a white deposit on the face of the leather – *fat sweat,* (this is often confused with mould, but under the microscope can be confirmed with ease – with a warm spatula the melting of the fat can be observed).
- Drying oils make the leather very coarse, rigid and dark.
- The fat can cause the accumulation of dust and favours biological attack.

[7] A. Moldoveanu, *Conservarea preventivă a bunurilor culturale* [*Preventive Conservation of Cultural Assets*], Bucureşti, 1999, p. 121.

Photo 3. Deterioration due to the effects of fatty materials.

4. The effects of organic solvents

The majority of organic solvents succeed in repelling the materials used for treating leathers; again some of them can deteriorate the finish of the surface of these.

Alcohol with a low molecular weight can dry the leather through the absorption of chemically bound water.

Photo 4. Deterioration due to the effects of organic solvents.

5. The effects of metals

Iron and ions of copper can accelerate the *oxidation* and *per/pro-oxidation* of the fatty materials (polyunsaturated fatty acids). Iron is a contaminant normally met in the process of tanning and the extract of vegetable tannates.

In a damp environment, products from the corrosion of iron cause *automatic damage* by increasing their volume in the process of hydration.

Products from the corrosion of iron, copper and silver can colour the surface of the leather.

Photo 5. Deterioration due to the effects of metals.

6. Dust and pollution agents

Ozone is a powerful agent of *self-oxidation* of unsaturated fatty acids, being the most reactive component amongst atmospheric pollutants. Sulphur dioxide from a polluted atmosphere can, alongside sunlight, become a powerful agent of *oxidation*.

Sulphuric acid from leather, resulting from the absorption of the sulphur dioxide is considered the primary agent of *acid hydrolysis* of historic leather (leading to damage known under the name of 'red rot') and the sulphuric acid formed in conditions of humidity reduces the pH of the leather.

Atmospheric dust absorbs humidity and fatty materials, leading to the drying of the leather. The dust always contains metal particles that have the capacity to act as catalysts of oxidation. The dust also acts as an abrasive material on the face of the leather.

Photo 6. Deterioration due to dust and pollution agents.

7. Light, ultraviolet radiations

The deteriorations provoked by light are cumulative and irreversible.

UV radiations are the most aggressive and they accelerate the degradation of organic materials (collagen, tannates, fatty materials, etc.). The colours and pigments that contain iron or copper increase the photosensitivity of collagen. The light can cause the discolouration of the dyed leather.

Photo 7. Deterioration due to light, ultraviolet radiations.

8. Biological damage

Biological damage to leather objects is caused mainly by insects, fungi and bacteria. Insects appear especially in dark environments, in which they don't wander frequently between the objects. The most often met harmful species to raw skin, tanned leathers and furs are carpet and skin beetles (the species Anthrenus, Attagenus and Daermestide).

Moths (Tinea pellionella, Tineola bisselliella) attack and destroy firstly furs and hair, but they are also dangerous to partially tanned leather. The insects produce the greatest havoc at the time of their larval stage.

Photo 8. Deterioration due to biological agents.

9. Human activity

Functional damage takes place through wear and tear of objects in use.

The inadequate handling, depositing and display in museum collections, just as the improper conservation and restoration, can be the cause of serious damage.

Photo 9. Deterioration due to human activity.

Collagenic materials are very susceptible to diverse categories of factors of degradation and the effects produced by these are of a significant severity producing important deteriorations on patrimonial collagenic objects. The great richness and diversity of ethnographic patrimonial leather objects, just as the increased degree of susceptibility to different types of attack, make the process of conservation-restoration of ethnographic leather a complex one and a great responsibility for their preservation.

Conclusions

The inventory of types of existing degradation to heritage objects of a collagenic base from ethnographic collections has led to the following conclusions:

1. Collagenic materials are highly susceptible to diverse categories of factors of degradation but the effects produced by these are of an exceptional gravity producing significant deterioration of heritage objects of a collagenic base.

2. The inventory of the main types of degradation present in ethnographic objects of a collagenic base can be classified into three broad groups: physical, chemical and biological. The biological types being the most frequent.

3. Bearing in mind the typological diversity of the heritage objects of a collagenic base and the conservation treatments, there is a need for the following differentiation: 3.1. For leather with fur, two aspects of conservation will be born in mind, namely: - the prevention and arrest of moth attack, this being the main factor of degradation, by finding biocide substances with a high grade of retentivity, which doesn't affect the material base and don't present a grade of toxicity for the conservator; - the finding of solutions for the protection and cleaning of leather used in the making of ethnographic objects, as being white in colour, ornamented coloured threads, they become dirty and stain, being difficult or almost impossible to clean. 3.2. For leather without fur, from the point of view of protection to bear in mind the finding of solutions which create a transparent, reversible skin and which include also a biocide applied by brush to the surface of the object.

4. The results of this phase consisted of the finding of non-invasive methods of investigating ethnographic heritage of a collagenic base and the identification and classification of the main types of degradation.