Title: NEW FEATURES IN LEATHER PRESERVATION

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Abstract:

Description of an international project sponsored by the E.E.C. Coordinated by the School of Conservation, Copenhagen, Denmark. Involved are five European institutions experienced in the conservation and research on leather.
The main goal of the project is to set the parameters and criteria for a standard ageing method for leather based upon the results of extensive analytical examination of natural deteriorated historical leather and artificially aged new leather. The project, starting March 1991 will cover a period of three years, resulting in a reliable and standardized method to evaluate the usefulness of conservation methods and materials.

Keywords: Leather, artificial ageing, analysis, project, tanning.

At present we may conclude that there seems to be a period of stabilization in the development of conservation materials and recipes concerning the treatment of leather objects in general. Already for some time there is a clear emphasis on the application of exsisting methods and recipes developped in earlier years, illustrated by literature and papers from meetings dealing with mainly case studies and comparative investigations. At the same time one may ascertain the existence of a growing feeling of doubt and dissatisfaction concerning the usefulness of the applied preservation methods and materials. In this respect I am referring to the use of fatting media, buffering materials, impregnation materials and moisturizers.

Although in the past couple of years there has been a continuous evalution of the above mentioned recipes and materials, resulting in a more or less pronounced preference, this has so far only been based on the results of several competitive examinations.
One may establish the fact that there is a clear lack of absolute data concerning the effectiveness of treatments of leather objects in relation to the prolongation of the viability of the material, deceleration of the natural degradation processes and to the protection offered against the attack of atmospheric pollution on the material itself.
The main reason for this development was that in the past there was a clear emphasis on the treatment of objects, conservators had to preserve by means of some kind of treatment and encouraged by the large amount of objects presumably in direct need of preservation there was a growing pressure on the few scientists involved in leather research for the development of preservation materials and methods. This tendency was intensified by reports on the destructive influence of air pollution components on materials of art objects. Protection of the objects by means of treatment had absolute priority.

The last few years one may notice a change in direction. A lot of measures has been taken by governments and industries to get airpollution under control and this accent on environment had his impact on the care for art

objects in museums and other buildings. A general understanding originated that is was much more profitable first to take care of the environment where art objects are in. This would take away the inmediate need for treatment of each object separately and would provide time and opportunity to design criteria for separation of objects in different conditions and in different need for preservation. It is much more profitable to spend the available amount of money for preservation of objects on creating an environment in buildings, storage accommodations and showcases that is as harmless for the materials of art objects as possible, because in this way a great quantity of objects are stabilized at the same time. The already stated lack of absolute data on the effectiveness of leather preservation treatments has resulted in the development of a research project, sponsored by the Commission of the European Communities, Department Science and Technology for Environmental Protection.
The idee to set up this project originated in Denmark in the School of Conservation connected to the Royal Danish Academy of Fine Arts as a result of the work on the analyses of amino acids in decayed leather, executed there. It appeared to be possible by means of amino acid analysis performed with HPLC ion-exchange chromatography and detection by fluorescence to characterize corium collagen in leather. The presence of tanning materials or degradation products did not interfere with the method of total hydrolysis used to dissolve the material and the chemicals used in connection with the HPLC chromatography method. This was confirmed by means of comparing samples of tanned and untanned leather of the same animal origin.
There appeared to exist significant differences between the amino acid distributions of new leather and historical leather in an advanced state of degradation. It is shown that proline and lysine are the two amino acids mostly affected by deterioration. These two amino acids together with a third amino acid present in the leather collagen, isoleucine, may in connection with the state of deterioration of the material, provide a statistical method to establish the animal origin of the leather. Preliminary attempts with accelerated ageing methods performed on new leather were leading to comparable results as with historical leather.

The above mentioned project entitled: "Evaluation of the correlation between natural and artificial ageing of vegetable tanned leather and determination of parameters for standardization of an artificial ageing method" will cover a period of three years and will be executed in close cooperation between Five European Institutes which are or have been dealing with leather conservation problems and research.
These five institutes are:
1. The School of Conservation, Copenhagen, Denmark, who is coordinating the project.
2. The Centre de Recherches sur la Conservation des Documents Graphiques, Paris, France.
3. Central Research Laboratory for Objects of Art and Science, Amsterdam, Holland.
4. The Leather Conservation Centre, Northampton, England.
5. The Royal Library, Den Haag, Holland.

Connected to the Leather Conservation Centre in Northampton are several other Institutes as subcontractors, also subcontractors are connected to the School of Conservation, Copenhagen.

Some general information about the project

The serious deterioration, commonly known as "red rot" of many vegetable

tanned leather objects, including bookbindings has been known since last century. The cause of this particular kind of decay has been ascribed in general mainly to air pollution. So far many attempts have been made to develop artificial ageing methods to examine the durability of leather and to be able to predict and to assess the effectiveness of conservation methods and materials. None of the existing methods so far has been recognized as a reliable standard method. The proposed project is concerned with vegetable tanned calf leather, mainly in order to restrict the number of samples which have to be analysed, but in principle the applied methods may be used for all kinds of leather and other protein based materials.
In general the main goals and objectives of the proposed project are:

- To get as much information as possible by means of physical and chemical tests about the deterioration products present in naturally degraded leather, the identification and quantification of these compounds linked to the changes that has taken place in the material due to natural ageing, atmospheric attack and environmental factors (temperature, humidity). Structural changes to the two main constituents of vegetable tanned leather will be examined, namely changes in the collagen proteins and changes in the vegetable tannins.

- To establish the parameters of pollutants, temperature, U.V.-light and humidity which will cause changes in new vegetably tanned calfskin leather that will correspond to the in the first stage of the project assessed physical and chemical changes in naturally aged leather, when new leather is artificially aged in a deterioration chamber.

- The definition of a standard method for testing leather which will give information about the resistance against destructive environmental factors and chemicals in order to assess the suitability of leather for conservation purposes as well as to test the effectiveness of current and newly devised conservation methods and materials which are suppose to stabilize or prevent further deterioration.
  The preliminary tests will be made on deteriorated historical vegetable tanned calf leather collected in each of the four countries involved in the project.

Production of new vegetably tanned calfskin leather will be performed by the participants in Denmark and England. All the partners in the project will examine different samples of the same material, both with regard to analyses and artificial ageing.
Proven and well-defined analytical methods are used for the examination of the samples which supplement each other in order to characterize both deteriorated and non-deteriorated materials as extensive as possible.
Artificial ageing is carried out in England and France where facilities such as deterioration chambers are available, a possibility to with a introduce known concentrations of sulfurdioxide and of nitrogenoxide.
The physical and chemical tests which will be used in this specific project are:

- Amino acid analysis by means of ion-exchange high performance liquid chromatography (HPLC).
  The amino acid distribution describes the differences in the collagen composition between natural deteriorated leather and new unaged tanned and untanned materials. The changes in the amino acid composition achieved by accelerated ageing will be the main starting point in the assessment and changing of ageing parameters. Amino acid analysis will

also be usefull in the quantification of the deterioration and the identification of breakdown products.

- Identification of breakdown products by Gas Chromatography combined with Mass Spectrometry (G.C.-M.S.).
  The most sensitive method at the moment for the identification of organic compounds. The amount of breakdown products found in deteriorated materials will be a measure of the stage of decay.

- Determination of nitrogen-terminal groups in the collagen by means of HPLC.
  Leather suffering from "red rot" is characterized by desintegration of the structure due to splitting of the collagen chains. The amount of N-groups present will be a quantitative measure of the stage of decay.

- Measurement of the isoelectric point by means of isoelectric focusing.
  Changes in the amino acid composition due to oxidative conversion of some sensitive amino acids combined with splitting of the collagen chains will cause changes in the isoelectric point of the collagen.
  This will lead to chemical and physical instability of the leather resulting in lowering of the shrinkage temperature, tear strength, and to changes in the moisture release and uptake balance. Hopefully changes in the isoelectric point will correspond with the stage of decay of the leather.

- Examination of changes in the vegetable tannin structure by means of HPLC.
  The vegetable tannins are classified in two groups, the hydrolysable type and the condensed type respectively.
  From literature it is known that the condensed type of tanning material is accelerating the deterioration of leather. The determination of the type of tanning material originally used in historic material is important for the understanding of the deterioration mechanism and possible interactions between tanning material and collagen, different from the binding that takes place in the tanning stage of the leather.

- Determination of the relation between moisture uptake and release.
  The ability of the leather to take up moisture and to release it under different atmospheric conditions changes with the rate of deterioration. A disturbed moisture balance causes physical stress between the fibres and desiccation of the material as such. Measurements of the change in moisture content of samples in a controlled environment (different relative humidity and constant temperature) will provide an indication of the degree of instability of the leather.

- Determination of degree of acidity and sulfate content will provide information of the presence of strong mineral acid and determination of soluble and volatile nitrogen will be a quantitative measure of the degree of collagen breakdown.
- Determination of denaturation temperature by means of differential scanning calorimetry.

- Determination of the shrinkage temperature.

- Physical tests by means of standarized methods normally used in leather technology.

The results of the above mentioned methods of analysis will be compiled in different stages of the project, from the historical material and after each step in the process of artificial ageing from new leather, manufactured under controlled circumstances.
The influence of micro-organisms on the deterioration process will not be included in this project.
It is expected that the characterization of deteriorated historical leather will be almost completed after the first year. The second year will comprise comparison of the results of the analyses of the historical leather and data obtained from the first experiments with artificial ageing of new leather. The third year will offer the possibilities to adept the parameters of the artificial ageing method in order to get data which are as close as possible to the analyses results of the historical leather. A interim report on current progress will be made at the end of each year of the project.

As I mentioned earlier the strong deterioration ("red rot") of many leather objects was connected to mainly metropolitan airpollution already in the last century in Europe. Then, as is now, the problem was must pronounced in archives and libraries. In particular leather bindings, but in general vegetable leather from last century presents clearly the greatest deterioration problem. The cause of the decay is ascribed mainly to airpollution, but partly also to factors connected to the manufacture of leather. This fact coincides with the introduction of new methods and materials for leather production by European tanneries in the last century. However the deterioration generally occurs among vegetable tanned leather on the whole. Large collections of gilt leather from the 18^{th} and 19^{th} century have thus deteriorated considerably. So far no satisfactory conservatory solution has been found to the problem. The scientific development within conservation has reached a stage where new and decisive progress can only be achieved through utilization of export knowledge and modern advanced analytical equipment. The recources required to realize such progress cannot be covered financially by a single country. Projects like the one proposed may contribute to develop and strengthen the co-operation between the European States and the sense of community.

In the meantime the different Institutions concerned with the conservation of leather objects continue their efforts for the development of better methods and materials. In relation to the production of materials especially concerning libraries and archives there has been a large emphasis on the production of new leather for bookbindings conforming to the requirements as they are drafted by the conservators. This means that this type of leather should fulfill some special requirements that differ from the qualifications of a commercial new leather regarding compatibility with the object, expectation of life, flexibility, resistance against environmental attack etc.

In some European countries this type of special bookbinding leathers are commercially available, more or less meeting the above mentioned requirements.

Last year the Central Research Laboratory for Objects of Art and Science together with the Royal Library conducted an inquiry among conservators from libraries and archives to find out about their experiences with available new bookbinding leather.
One general remark that emerged from the answers was that the data

available from the new leather were incomplete for instance with regard to the applied tanning materials.
Because of the fact that a majority of the conservators stated that there was a marked difference between leather from bookbindings manufactured according to traditional methods and recipes that appeared to be much more resistant to atmospheric pollution compared with leather manufactured in the industrial era and later.

As a result of this inquiry we contacted several leather manufacturers and tanneries with the question if they were able to produce a new calfskin leather according to the old recipes, without the use of any sulfur containing chemicals and strong mineral acids, completely vegetable tanned (so no combination tanning) with the right type of tanning material.
After a lot of problems and misunderstandings one small tannery succeeded in the production of a new calfskin leather according to the old recipes. Specimens of this leather are going to be chemically and physically tested and conservators of the Royal Library in The Hague are going to use this leather for conservation purposes to test the suitability as such. When more data are available we will report about the results.

Conclusion

It is expected that the described project will provide essential information concerning the complex composition of deteriorated leather, the contribution of internal and external factors to the degree and rapidity of decay and that the results will be a startingpoint for further research aimed to the improvement of exsisting preservation methods and materials and the development of new ones.
It is the intention of the project to promote international and inter-disciplinary cooperation.

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