

**Hungarian Academy of Fine Arts  
Doctoral Course Programme**

**EXAMINATION AND CONSERVATION POSSIBILITIES OF 16-17<sup>th</sup>  
CENTURY PAINTED PAPER-BASED OBJECTS**

**DLA THESIS**

**Katalin Orosz**

**2008**

**Supervisor: Dr. Márta Járó**

## INTRODUCTION

With the spreading of book and paper printing more and more books, maps, atlases, engravings were made, which were often coloured or painted. In the 16-17<sup>th</sup> centuries painting was, in general, done manually afterwards. The condition of these coloured or painted objects are often very different, moreover, very frequently we can meet pages in perfect condition and chemically deteriorated ones as well within the same book. The question arises, what causes the degradation of the components of the material, as well as the differences within one material. In the deterioration of the coloured paper-based objects, the paper support itself, the printing ink, the colour materials and the different additives can play a role. That is why these factors and their interactions should be examined. Paper is mainly damaged by acids and oxidative agents that were mostly used in the manufacturing process in the 18-19<sup>th</sup> centuries (e.g. chlorine bleaching, acid and basic digestion of cellulose fibres). But in the early period, in the 16-17<sup>th</sup> centuries, the above-mentioned substances very not used very often. As far as we know, the printing ink did not contain any component that could cause the degradation of the paper or colour materials. So the causes of the damage should firstly be searched in the substances used for painting and in their impact on each other and on the support.

Public and private collections store a big number of 16-17<sup>th</sup> centuries painted paper documents. Stopping their degradation is an important challenge for the restorer. For the successful conservation and restoration it is extremely important to know the processes taking place within the object as well as the causes of the degradation. International scientific literature provides but fragmental information about it. Scientists deal with special topics (e.g. role of metals in the degradation of cellulose) but there are still a lot of unknown areas. The synthesis of the knowledge and the widest possible knowledge of the potential causes are necessary in order to be able to treat these objects in a reassuring way. That is why I chose the examination of printed and painted documents of the 16-17<sup>th</sup> centuries for the topic of my research.

## THE OBJECTIVES OF THE THESIS

From the material, the manufacturing features, the type and extent of degradation of the painted paper objects we can draw conclusions concerning the history, the owner, the producer, the place of the production of the object, and the habits of its time. We can only have this information if we have a widespread knowledge about the substances used in the

time of the production and about the intervention, and if we “interrogate” the object with an adequate examination method. On the basis of this knowledge we can select the most adequate and the safest conservative treatment for the object and for the restorer as well.

Starting from what has been said so far one of the objectives of my thesis was the description of the preparation method of the painted and coloured paper objects of the 16-17<sup>th</sup> centuries on the basis of the original sources and the contemporary technical literature, including the publication of the receipts and descriptions of the time which have not been published in Hungarian yet and the summary of information taken from the examination of a book of the 16<sup>th</sup> century concerning the preparation of paper and paint layers.

Crumbling, powdering, crocking or bleeding of colour substances brought to the paper support, fading of colours and change of tone or colour is a frequent problem. These phenomena highlight the importance of knowing the dyes and paints applied in that time, and the scientific examination of the painted papers from such a point of view. Numerous analysing methods are known, from which the restorer should select the most adequate one. A guideline is available for the research of painting (pictures, canvases, wall paintings, and painted wooden sculptures) from such a point of view. But for the examination of the paper-based painted objects there is no “syllabus” in Hungary and as far as I know abroad either, which would help the restorers choose the adequate methods to plan the examination and to assess the results.

That is why I wanted to elaborate a protocol, which helps paper restorers in libraries, archives, museums and specialists carrying out analyses for them to do the preparation method and condition analysis of the painted paper objects. In my thesis I illustrated with concrete examples of what kind of information can be obtained with what methods and types of examination about the object and what kind of knowledge should a restorer or a scientist have for a successful examination.

We have more and more information concerning the degradation processes caused by coloured materials. Specialists try to use different types of compounds to set acids and metal ions, which cause the biggest problems. The question of the conservation of the works of art cannot be considered as fully answered yet. The findings of the researches and the

conservation methods in an experimental phase are unfortunately not sufficiently known among Hungarian restorers.

That is why my objectives are – beyond the above mentioned considerations – the revision of the known and available methods for conserving painted paper-based objects of the 16-17<sup>th</sup> centuries; the summarising and publishing in Hungarian language the available findings of the international research, as well as the elaboration of a possible new method with special regard to the treatment of the degradation caused by pigments containing metal.

## THE STRUCTURE OF THE THESIS

The thesis is composed of three major parts: materials and painting methods of painted paper-based objects of the 16-17<sup>th</sup> centuries, scientific examination methods for their analysis, and the presentation of the conservation experiments I know and practice.

In the first part of the thesis I present the paper production technology, the applied raw and auxiliary materials and the composition of the dyes and paints from the point of view of their ability to degrade or damage an object. I obtained the published findings by analysing the available international technical literature and original sources.

In the second major part of my work I give a short presentation of the examination methods that are applied today as a routine, or which are in an experimental phase; with the help of which the material of the painted paper-based objects can be identified and the causes of their degradation be explored. As my objective was to make a protocol for the assessment of the condition of 16-17<sup>th</sup> century painted paper-based objects, and for obtaining the necessary information for the conservation of them, I chose a work of art on which I could demonstrate the steps of an examination in practice. I analysed a book (and had it analysed) entitled „De re metallica” by Georgius Agricola printed in 1557 in German language and painted manually with the help of the scientific methods that were available for me. I present the findings in detail. By comparing and analysing the findings of the examination with the information concerning technical history, the preparation method and material composition obtained in the first phase of the research I explore and describe the possible causes of the degradation of the paper and paint layers considering the chemical background of the degradation and alteration.

Finally I deal with stopping degradations and the possibilities of conservation. I studied a wide range of international technical literature and I carried out my own experiments with special regard on blocking metal ions on paper.

I finish my thesis by concluding the findings of the work carried out, and I outline the protocol I elaborated.

## SUMMARY OF THE FINDINGS OF THE THESIS

Technical literature of that time and of today say that additives containing acid and metal, like alum, iron sulphate and copper sulphate, were used during the preparation of paper and treatment before painting in the 16-17<sup>th</sup> centuries. We even have data about the fact that mined alum contained iron contamination. Although this information can be regarded as well known, its role played in paper degradation has not been given enough attention. On the basis of the relevant data and the findings of the examination of the material concerning the degradation of the paper-based objects made in the examined period I came to the conclusion that we had to attach a much bigger importance to the acid and oxidative decay caused by alum and metal contamination than before. It also had a special importance from the point of view of my further findings.

During the research it became obvious that we have very little knowledge about dyes and auxiliary materials used for painting 16-17<sup>th</sup> -century papers and about the ways of preparing and using them. That is why I translated and published in the annex of my thesis more than one hundred recipes from the ones I found in the foreign technical literature mentioning the source. As far as I know, these recipes have not been available in Hungarian language. In addition to its importance from the point of view of technical history, the great value of the collection is given by the fact that it can explain further causes of the degradation of painted paper-based objects. The auxiliary substances often figuring in the descriptions are alum, different acids (e.g. acetic acid), and vitriols (metal-sulphates). These substances worsen the degrading impact of the alum, and metal ions, which had got into the paper during production accelerating acid hydrolysis and Fenton reaction. The studied recipes often describe the preparation method of the so-called “green water” which was made by grinding verdigris pigment into vinegar and then mixing it with gum arabic and alum. As it generates a solution, which is strongly acid containing copper, it can attack paper during application. I supposed that “green water” becomes brown by ageing so its colour changes. I proved my hypothesis with experiments. From the studied recipes it turned out that verdigris was often mixed with organic dye, which were extracted from plants with alum, and often precipitated on a substrate (e.g. starch). I proved this practice during the examination of the presented book of

the 16<sup>th</sup> century. It explains the differences in condition that can be observed within the same object.

Among the studied recipes I discovered the description concerning the preparation method of the brown copper-gall ink. As far as I know this compound that can be used as paint or ink as well, is not mentioned in the technical literature, its corrosive properties have not been dealt with. The paper degrading impact of dyes made according to the descriptions presented by Jehan le Begue and figuring in the Bologna manuscript is close to the impact of the well-known iron-gall ink. Presumably the chemical processes take place in a very similar way. I call attention to the fact that the author of the recipe in the Bologna manuscript proposes also the addition of alum, which makes ink shiny according to him. This further increases the acidity of the dyeing agent and of the material for writing and thus the degrading effect. As far as I know, specialists in their studies of gall-inks suppose the presence of iron in each case, and copper is considered as an auxiliary or contaminating material. It is probable that the brown substance does not always contain iron in a detectable quantity so paper degradation is caused by copper-gall ink. I detected its presence also in the book by Agricola, which explains the strong degradation of some pages. On the basis of these I think it is important to examine the copper content in each case before treating paper-based objects, which were written or painted with brown ink.

I identified the majority of the pigments, paints and binding agents used in the book by Agricola with a series of scientific examination methods chosen for studying painted paper-based objects. As a result of my knowledge obtained from the above mentioned recipes along with the examination data I could describe the preparation method of the book and prove that the painter changed methods during painting the 290 engravings. On the basis of the analyses I found an explanation of the different extent of the degradation of the first and second part of the book.

I tried to explore the possibilities of conservation with the help of the available technical literature and by the way of modelling. I examined the impact of bensotriazole, an inhibitor applied by metal restorers, on paints, dyes and pigments used in that period. With instrumental examination I succeeded to prove the existence of the chemical bond between verdigris pigments and bensotriazole, both in the case of treatment with the alcoholic solution of the inhibitor and with the so-called conservator paper, which is impregnated with the agent. At the same time it turned out that the long term impact of the complex cannot be examined by accelerated ageing, as it degrades between 40-60°C. A further problem arose during my

experiments, namely that the complex made a change of tone in the green paint layer and a change of colour in the case of copper-gall ink. I proved that bensotriazole does not prevent the paint layer from solving during water treatment. Thus on the basis of my modelling experiments I do not propose the application of bensotriazole for treating original painted documents. But during the experiments I carried out in the simultaneous presence of iron and copper ions, the combination of treatment with calcium-phytate and bensotriazole proved to be convenient for blocking metal ions of certain iron-copper-gall inks. In these cases I did not observe a visible change of tone or colour after the treatments, but further experiments and examinations are necessary for examining long term effects.

Finally the most valuable result of my work for the Hungarian paper restorers and scientists who help them is perhaps the protocol I composed and the outline of which is presented at the end of my thesis. Because, as I mentioned before, there is no available guideline in Hungarian language and, as far as I know, in other languages either, on the basis of which restorers could plan the examination of the preparation method of the degraded painted rag paper.