PAPERTECH

6th Framework Programme

European Commission

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PAPERTECH

INNOVATIVE MATERIALS AND TECHNOLOGIES FOR THE CONSERVATION OF PAPER OF HISTORICAL, ARTISTIC AND ARCHAEOLOGICAL VALUE

BOOK OF CONCLUSIONS

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PART-A

INTRODUCTION TO PAPERTECH PROJECT AND SCIENTIFIC AND TECHNOLOGICAL ANTEFACTS

CHAPTER-A.1:

The "PAPERTECH" Project: Innovative materials and technologies for the conservation of paper of historical, artistic and archaelogical value. Structure, Partnership, Objectives and Outputs.

By Domenico Acierno and Ezio Martuscelli

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Works on paper of artistic and historical value (prints, drawings, photographs, maps, letters, certificates, legal documents, seals, stamps, ledgers, books and bound items), as any other piece of art, are unique and cannot be substituted. Moreover any kind of harm producing the spoiling of those objects irremediably reduce their artistic and economic value. In absence of remediation interventions degradation processes may lead to the complete destruction or disintegration of the items with no possibility for the future generation to make profit of their knowledge, lecture and view.
Millions of works on paper are literally disintegrated into pieces every day. It was ascertained that in Germany and in USA, around 1995, almost 100 billions of volumes were no more available for consultation due to their high level of deterioration [1].
The problem of the conservation of objects stored in public or private libraries must be accepted as a relevant issue for every country by recognizing that through paper documents and books it has been possible to transmit and preserve the knowledge and the history of mankind [2].
Examples of heavily degraded books and archival documents are exhibited in figure 1 [3].

The European Union reserved to the issue of paper conservation a great attention as demonstrated by the relevant number of projects financed in the period 1995-2006 in the framework of several different type of programs (see figures 2 and 3) [4,5].

The ascertainment that the preservation of archival paper materials is a need, even if hard and difficult task to be reached, represented a spur to undertake a wide research project finalized to development of innovative materials and chemical technologies procedures especially suitable for the conservation of paper of historical, artistic and archaeological value (PAPERTECH-Project) whose structure and objectives are hereafter described [6].

PAPERTECH is a specific targeted research projects, INCO-CT-2004-509095, financed by the EU Commission, 6th-Framerwork Programme (priority 10, specific measures in support of international co-operation with Mediterranean partner countries).
PAPERTECH, that started on July 1, 2004 and ended on December 31, 2007, as evidenced by table 1, is based on a Euro-Mediterranean *Thematic trans-National Research Network* with 11 Partners belonging to European and non European Mediterranean countries.

The goals, the structure and the overall approach of PAPERTECH agree with the general objectives of international cooperation activities proposed by EU within the Sixth Framework Program finalized to open up the European Research Area to the Southern Mediterranean Area in fields of common particular interest for the Region such as that of the *Conservation of Cultural Heritage*.

Moreover the project was elaborated in agreement with the thematic issues described for INCO-MPC projects in the Cultural Heritage field (B2) in which it is textually reported that:

<the protection and conservation of Cultural Heritage ...requires a large multidisciplinary and integrated approach to research on the use of modern methods and new technologies for the study of materials, artifacts and monuments>.

The activities of PAPERTECH were organized according to 6 operative Work Packages, each of one is subdivided in various tasks as reported in table 2.

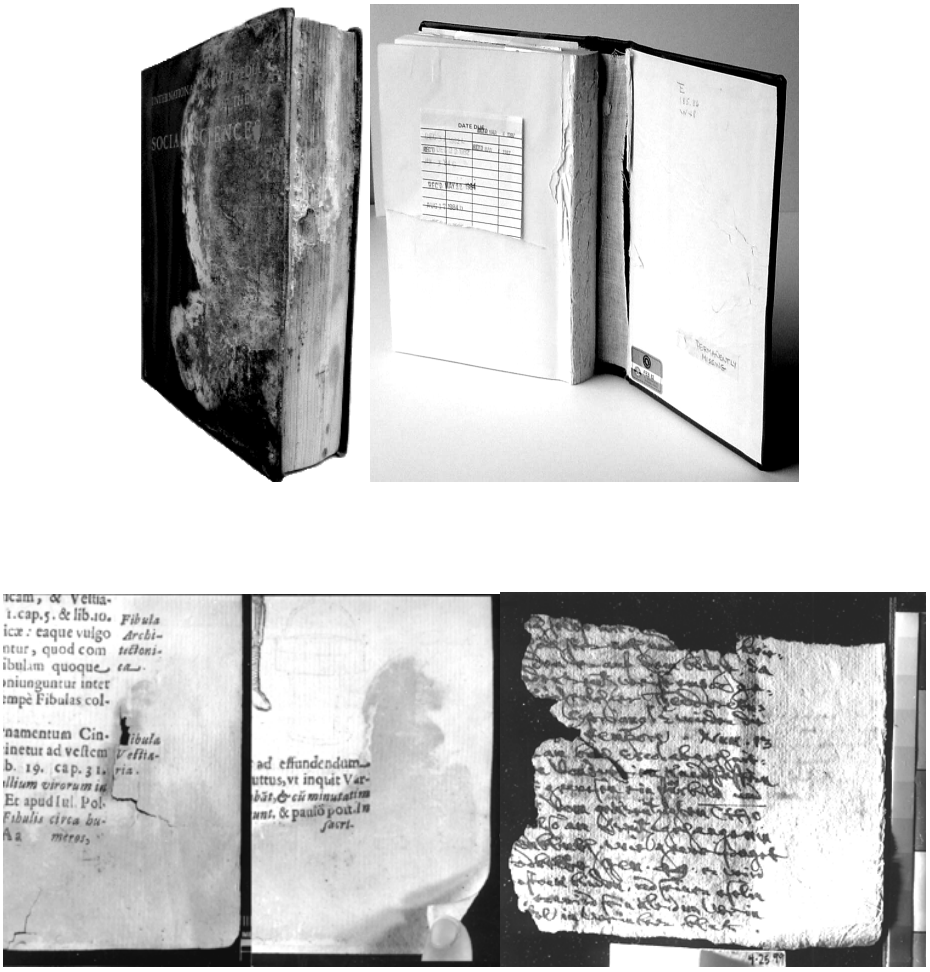

FIGURE 1: Examples of deteriorated books and paper documents of archives [3].

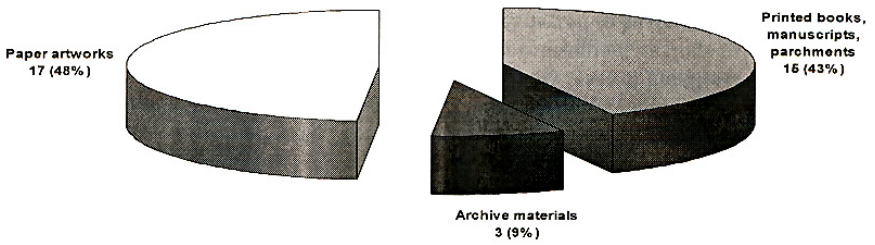

FIGURE 2: Distribution, per use function of artifacts, of projects on conservation of paper based items financed by EU, period 1995-2006, in the framework of different type of programs [4,5]

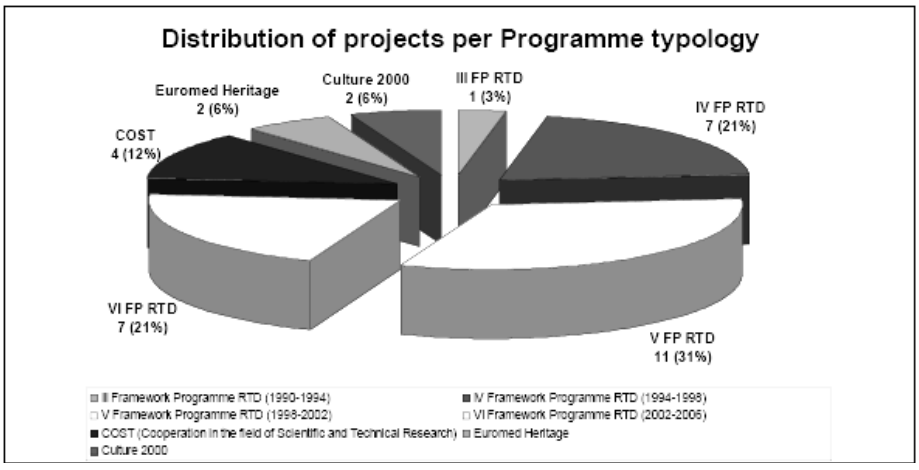

FIGURE 3: Distribution , per Program typology, of projects on conservation of paper based items, financed by EU, period 1995-2006, in the framework of different type of programs [4,5].

TABLE 1: PAPERTECH Partnership

no.	PARTNER	Short name	Country
1	Consorzio sulle applicazioni delle materie plastiche e per i problemi di difesa dalla corrosione s.c.r.l.	CAMPEC	ITALY
2	Università di Genova – Dipartimento di Chimica e Chimica Industriale	DCCI	ITALY
3	Consiglio Nazionale delle Ricerche, a) Istituto di Metodologie Chimiche, and b) Dipartimento Attività Internazionali, III Divisione, Mediterranean and Middle East	CNR	ITALY
4	Mubarak City for Scientific Research and Technology Applications	MUCSAT	EGYPT
5	Universidad del Pais Vasco / Euskal Herriko Unibertsitatea	UPV-EHU	SPAIN
6	Faculdade de Ciencias da Universidade de Lisboa	FCT-CFA	PORTUGAL
7	Centre National de la Recherche Scientifique - Delegation Provence	CNRS-BIP	FRANCE
8	Universite Sidi Mohamed Ben Abdellah - Ecole Superieure de Technologie - Laboratoire de Transmission et de Traitement d'Image	LTTI	MOROCCO
9	Yarmouk University - Institute of Archaeology and Anthropology	YU-IAA	JORDAN
10	Supreme Council of Antiquities	SCA	EGYPT
11	Cairo University	CU-FA	EGYPT

TABLE 2: Structure of PAPERTECH in Work Packages and Tasks

--Work package-1, ***INNOVATIVE DIAGNOSTIC TECHNIQUES***
-Tasks: Documentation of the objects; NMR relaxometry; NMR MOUSE; Thermal characterization; Identification of inks and additives.

--Work package-2, ***ANCIENT AND MODEL SAMPLES***
-Tasks: Selection of ancient items; Analysis of ancient items; Model-samples through weathering.

--Work package-3, ***NEW MATERIALS AND TECHNOLOGIES***
-Tasks: Materials for coating and adhesives; Technology for consolidation; New synthetic antimicrobial agents; Efficiency and limits of laser cleaning.

--Work package-4, ***EFFICIENCY AND DURABILITY OF THE CONSERVATION TREATMENTS***
-Tasks: Evaluation of coating and adhesives; Evaluation of consolidating technologies; Efficiency of the new antimicrobial agents; Efficiency and limits of laser cleaning.

--Work package-5, ***DISSEMINATION AND EXPLOITATION OF THE RESULTS***
-Tasks: Network for dissemination of information; Restoration treatments on ancient items; Exploitation of the results.

--Work package-6, ***PROJECT MANAGEMENT***
-Tasks: Managerial Board; Secretariat Office; Intellectual Properties Protection Actions.

The main objectives of PAPERTECH may be summarized as follows:

▲ the development of innovative diagnostic techniques to evaluate the deterioration degree of paper items of historical, artistic and archaeological value;

▲ the selection and the characterization of paper/papyri samples of artistic and historical value and the set up of model paper samples, i.e. modern samples artificially aged reproducing the degradation degrees of the ancient samples;

▲ the development of innovative materials and technologies for the conservation of paper;

▲ the evaluation of the efficiency of conservative treatments and the endurance with reference to the chemical-physical characteristics of modern papers;

▲ the spreading out and the exploitation of results;

▲ the elaboration and diffusion of maintenance and preservation protocol for the works on paper.

The activities to be performed in each of the Work Packages are below described in details.

--Work package-1, ***INNOVATIVE DIAGNOSTIC TECHNIQUES***

- new analytical methods to evaluate the state of conservation of paper/papyri items of historical and artistic value;
- new documentation techniques of image analysis to obtain detailed maps of ancient items;
- NMR relaxometry measurements to evaluate the degradation level of ancient paper and/or papyri;
- development of an innovative mobile NMR instrument (NMR MOUSE) for the "*in situ*" characterization of ancient paper and/or papyri;
- enhanced methods of thermal characterization of paper samples of historical and artistic value;
- protocol of analysis (non destructive and micro destructive) for the deep characterization of paper items;
- database of the Infrared and RAMAN spectra of inks and additives for their identification on ancient items.

--Work package-2, ***ANCIENT AND MODEL SAMPLES***

- select ancient paper and/or papyri samples to be used to set up the analytical techniques described in WP1 and to test the materials and the technology described in WP3;
- accurate characterization of the selected ancient samples to plan conservative interventions for them;
- model samples, i.e. modern paper/papyri samples in different states of conservation, to be used for the setting up of the analytical techniques described in WP1 and the materials and the technology described in WP3.

--Work package-3, ***NEW MATERIALS AND TECHNOLOGIES***

- new materials to be used as coating or adhesive agents on ancient items;
- new technologies for their consolidation;

- to study the effects of new materials to prevent and contrast the biological attacks;
- new cleaning technology for ancient items;

--Work package-4, ***EFFICIENCY AND DURABILITY OF THE CONSERVATION TREATMENTS***

- new materials to be used as coating or adhesive agents on ancient items;
- new technology for their consolidation;
- new materials to prevent and contrast the biological attacks;
- new cleaning technology for ancient items;
- protocol of innovative interventions to improve the mechanical properties and the photo-oxidative stability of degraded items.

--Work package-5, ***DISSEMINATION AND EXPLOITATION OF THE RESULTS***

- network of excellence for the study of the degradation mechanisms and the planning of the restoration interventions on ancient paper items;
- to plan and carry out restorative interventions on the ancient items selected in WP2, through the analytical protocol suggested in WP1 and the protocol of interventions suggested in WP4
- to spread out and to exploit the experimental results.

--Work package-6, ***PROJECT MANAGEMENT***

- to coordinate all the activities of the Consortium through continuous contacts and periodic meetings of the Managerial Board
- to support all the research groups through the activities of the Secretariat Office, responsible for all the exchange of the information among the partners.
- to study actions to protect the results of the researches carried out by filing patents of the materials and technologies set up.

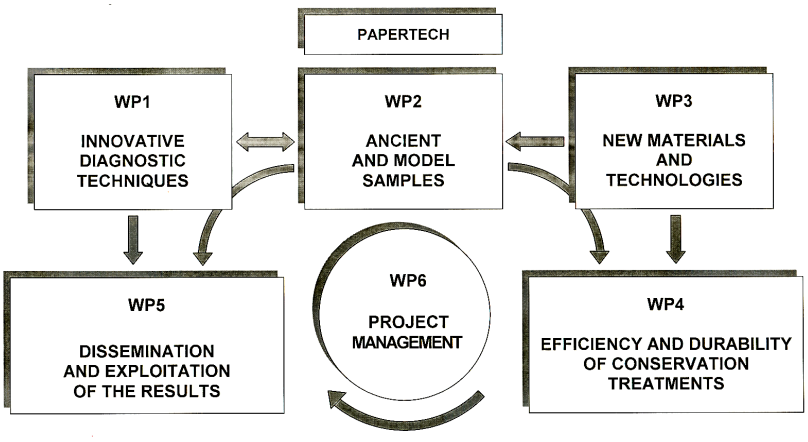

FIGURE 4: Interconnections between various Work packages in Papertech and flow of information transfer.

The inter-connections between the various Work packages including the in/out flow of information are schematically represented by the block diagram reported in figure 4.

From scientific point of view the activities of PAPERTECH are essentially congruent with a *virtuous cycle* (see figure 5) where two main *Research-Pillars* (Chemical Analytical Diagnostics and Innovative Materials Technologies) are developed taking into consideration from one side environmental factors of degradation and from the other consistent and durable conservation procedures.
In particular the research was focused in find out new polymer based materials and procedures of consolidation that take profit of the innovative means of a modern macromolecular chemistry.
The first pillar foresees the set up of new analytical chemistry diagnostic methods as well as their innovative applications useful for the assessment of:

--nature of components in a work on paper;
--typologies of damages, factors and mechanism of action;
--mechanisms of reaction and molecular structure of synthesized polymer materials;
--chemical compatibility with paper components;
--durability, functionality and reactivity against degradation factors.

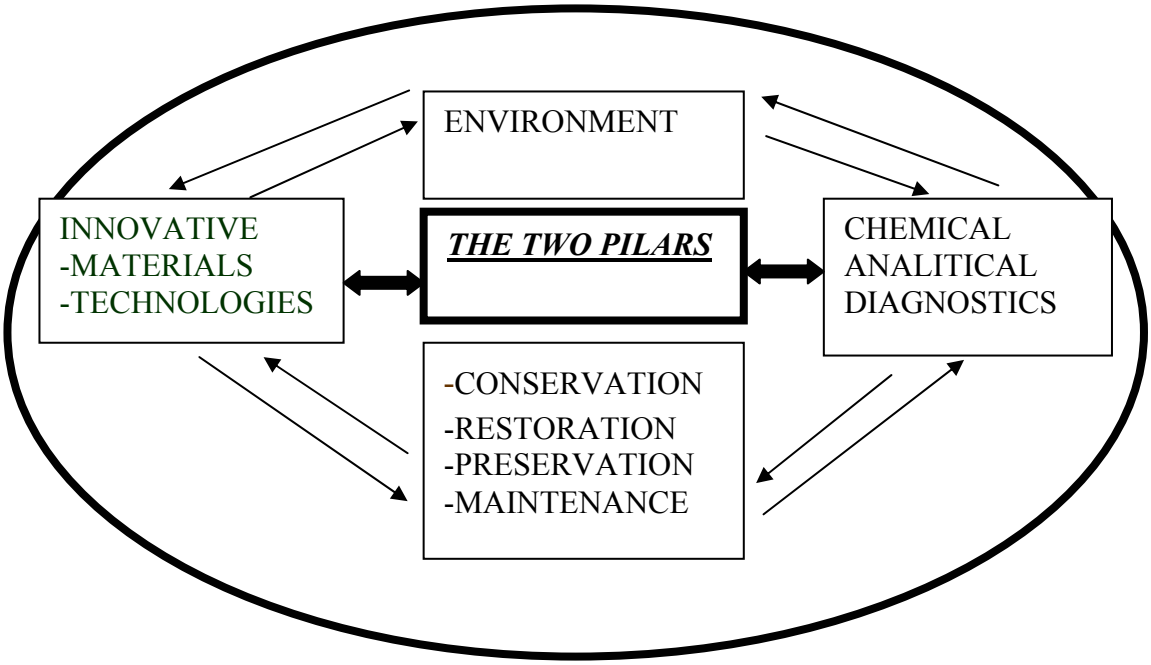

FIGURE 5: The virtuous cycle of PAPERTERCH.

The second pillar saw the concentration of efforts finalized to the development of better adapted polymers materials, obtained through tailor poly(copoly)merization processes, able to be used in the consolidation and/or protection of paper based artifacts and characterized by:

--easy applicability and durability;
--multi-functionality and chemical resistance;
--radiation and thermal resistance.

Preliminary actions have been focused on the selection of paper items recovered in different areas of the Mediterranean Basin. These items were characterized by means of non-destructive and micro-destructive methods in order to:

- identify the materials and the technologies used in their manufacture;
- evaluate their origin/provenance;
- determine the inks and pigments eventually present;
- analyze the deterioration morphologies;
- study the causes and mechanisms of degradation;
- plan suitable and eco-sustainable restorative interventions;
- develop, inter-calibration and validation of non-destructive techniques for "in situ" analysis.

All the samples received from most of the countries participating to the Projects have been collected and their characteristics and conservation state described in detail in a CATALOGUE published on the Web-site dedicated to PAPERTECH (see details on the dedicated Web-site).
Two examples of works on paper being part of the Catalogue are reproduced in Plate A.1.1[7].

OUTPUTS OF PAPERTECH AND EXPLOITATION AND DIFFUSION OF RESULTS

Dissemination and exploitation actions were planned to be mainly directed towards:

- Restorers, conservationists and chemists;
- Managers and directors of historical and archaeological sites and museums, and directors of libraries;
- Students (PhD students, Attendants to Masters in Conservation, Students of Faculties involved in Conservation of Historical Artifacts);
- Users.

In order to tailor the dissemination and transfer of know-how, the exploitation and spin-off of results for each of the countries participating a significant number of stakeholders was identified. For sake of simplicity they were grouped according to the following categories:

- Public and private research centres and universities active on conservation of paper items;
- Archives, libraries and museums with operative laboratories for the conservation of paper items;
- Private restorers and conservators;
- Industries which produce materials for the conservation of paper items;
- Paper industries and related industries of additives**.**

The collected data allows the creation of an Euro-Mediterranean *stakeholders database*, including 94 entities from France, 142 from Italy, 28 from Egypt, 25 from Portugal, 36 from Morocco, 17 from Jordan and 86 entities from Spain (see details in a following chapter).

Some of the most relevant types of outcomes and dissemination actions undertaken in the framework of the project are hereafter described.

1) Scientific and technical Deliverables

According to the Work program all the deliverables, being of public type, are susceptible to be diffuse. Essentially they concern the following relevant topics:

1) Preliminary evaluation of the ancient objects selected for the characterization and the restoration.
2) Results of the documentation of the ancient items through image analysis.
3) Results of the measurements carried out by means of NMR relaxometry technique on ancient items.
4) Set up of model samples: accelerated aging processes of modern items.
5) Identification of inks and additives present on modern and ancient sample.
6) Enhanced methods of thermal characterisation: results of the analysis of ancient and model samples.
7) Results of the development of the mobile NMR instrument (NMR-MOUSE) and characterization of some ancient and model samples.
8) Summary on the analytical results of the diagnostic techniques applied on ancient and model sample and suggestions for a protocol of analysis for the characterization of ancient items.
9) Synthesis of new polymeric materials to be used as coatings and adhesives for restoration interventions on degraded samples.
10) Model samples treated with new water-dispersed polyurethanes.
11) Consolidative treatments of model samples through cross-linking and grafting reactions.
12) Model samples consolidated through cross-linking and grafting reactions.
13) New anti microbial agents for the protection of paper.
14) Laser cleaning technique applied to model samples.
15) Model samples cleaned by means of laser techniques.
16) Summary on the results of the new materials and technologies set up for the conservation of ancient items.
17) Evaluation of the efficiency and durability of new materials and technologies for the conservation of ancient items and suggestions for a protocol of methodologies to restore them.
18) Report on the restoration interventions carried out on selected ancient items.
19) CD ROM: Innovative Materials and technologies for the conservation of paper and papyri of historical, artistic and archaeological value.
20) Summary of the scientific papers (from 5 to 10) published by the partners on national and international scientific and disseminative magazines.
21) Exhibition: Innovative Materials and technologies for the conservation of paper and papyri of historical, artistic and archaeological value.

2) Scientific and technical Publications

Highly qualified national and international magazines have been identified for the publication of scientific papers describing the results of the project.
In order to asses the productivity of the project the technical and scientific outputs of PAPERTECH were subdivided according to the following categories:

1) publications in international magazines;
2) publications in proceedings of conferences;
3) participation in conferences: oral/poster communications;
4) master degree thesis;
5) chapters in books;
6) books.

From figure 6, where the relative distribution of the various typologies of the technical and scientific outputs are shown, it emerges that, at February 2008, an overall number of 89 scientific and technical outcomes has been issued. This number will presumably still increase in the next months.
The text of all publications are available for consultation on request on the Web-site.

3) The web site (http://www.papertech-inco.eu/home.asp)

The publication of a web-site represents one of the main step in the exploitation and dissemination activities as well as the *fulcrum* of the network for the exchange of information among the partners.
Most scientific results are available to people interested in the paper conservation through the publication of the activities reports in the web-site of the project.
All the outcomes of the projects are /will be available on the web-site and, on demand, by mail to interested people.
The final goal of the realization of such a electronic platform will be the chance for people interested in the topics related to the conservation of paper to be informed on the state of the research during the lifetime of the project. This platform will be active for at least three years after the end of the project.
The web address is **http://www.papertech-inco.eu/home.asp**

4) Exhibitions and Catalogue, Conferences and Workshops

An: ***Exhibition/Conference on:***

Innovative Materials and Technologies for the conservation of paper of historical, artistic and archaeological value
was organized in Naples- December/03/04/2007.
The event, foreseen by the Work-program ***as part of a required disseminatio /transfer activity***, was finalized to the presentation of the results, know-how and enabling technologies developed by PAPERTECH actions to the stakeholders of paper sector.
The main topics treated are summarized in table 3. Each of the topics was introduced by a Rapporteur member of PAPERTECH. Invited lectures, given by authoritative scientists followed.

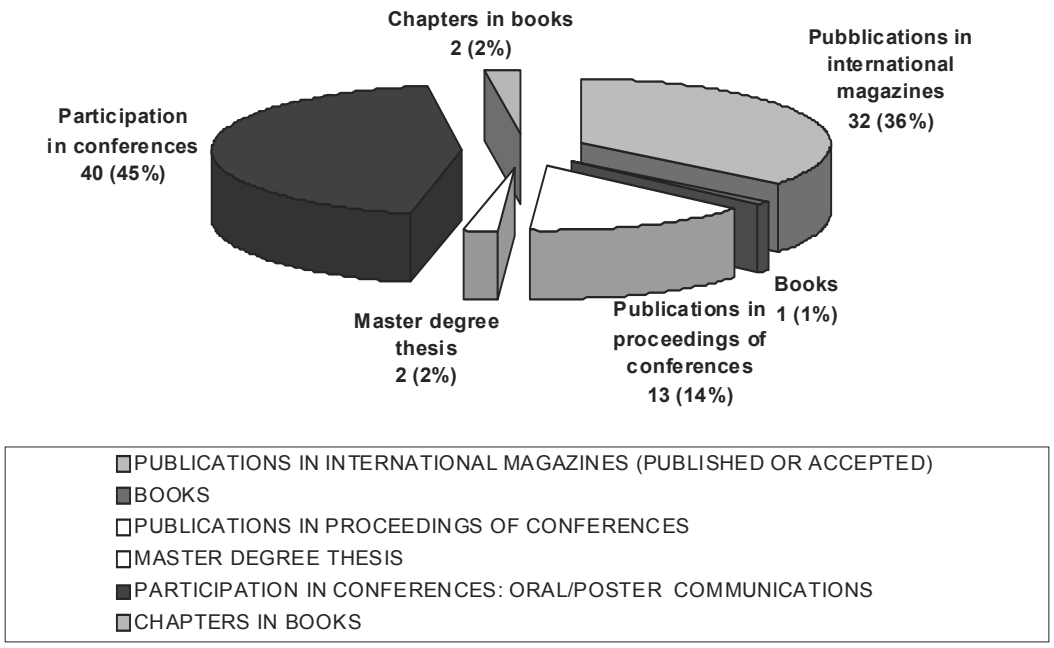

FIGURE 6: Scientific and technical publication issued in the framework of PAPERTECH at February 2008

TABLE 3:Main Topics discussed at the Exhibition/Conference organized in Naples- December/03/2007.

PAPERTECH PROJECT: ***objectives and achievements***

TOPIC-1: *Innovative diagnostic methodologies to assess:*
- *nature of components;*
- *degree and factors of deterioration;*
- *state of conservation of paper Items.*

TOPIC-2: *Innovative materials and technologies for the stabilization, consolidation, protection and conservation of paper.*

TOPIC-3: *Procedures of consolidation, stabilization and protection of paper based items of historical and artistic value.*

TOPIC-4: *Innovative pre-treatment procedures of modern paper in order to impart better resistance to degradation and to use conditions.*

5) ***Recommendations and Guide lines for best practices***

All the scientific reports and deliverables contain a section where best practices for diagnostic techniques and for consolidations procedures are evidenced.

A specific publication aimed at the diffusion of recommendations and guide lines concerning essentially the best conditions of ***"Maintenance and Preservation of works on paper"*** was separately elaborated and published.
This protocols, edited by CNR-SMED will be freely distributed to all stakeholders and Institution interested. Moreover it will be published on the project Web-site.

The studies undertaken in the framework of PAPERTECH project led to the development of innovative diagnostic techniques to evaluate the deterioration degree of works on paper of historical and artistic value and to the set up of innovative materials and technologies for their consolidation based on the utilization of new procedures of polymerisation tailored to the types of paper and to the degradative mechanisms occurring during internal and external ageing processes of degradation. Moreover, the performed evaluation of efficiency and durability of the developed treatments allows to select the best:

1) coatings and strengthen materials;
2) reagents and techniques for consolidation;
3) antifungal agents.

The detailed description of the most relevant results attained with PAPERETECH will be reported in the following chapters of the present book together with the presentation of the specific activity performed by each of the Partner Units.
Copies of this book will be freely distributed to Partners and Stakeholders of the sector as part of a diffusion action foreseen by the Work Program of PAPERTECH project.

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7) Papertech-Catalogue, http://www.papertech-inco.eu/home.asp

CHAPTER A.2:

The chemistry of treatments of consolidation and strengthening of works on paper based on the use of polymers (Status of art)

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The de-acidification and lamination/mounting procedures are suitable at retarding the deterioration of items in paper; unfortunately they are unable to restore loss strength into document[1].
The necessity to restore, at least partially, the mechanical strength to works on paper, which have been deteriorated as a consequence of exposure to unfavourable conditions, may be afforded by impregnating the surfaces of fragile and friable paper items with polymers having suitable chemical structures and physical chemistry properties. The consolidation processes that use synthetic polymers to strengthen fragile paper based documents may be divided in four different types [2,3,4,5].

Process of type-1
It is based upon the following phases:

a) Dissolution or dispersion of a pre-formed polymer in appropriate solvent;
b) Impregnation of the surface of the object with the polymer solution/dispersion;
c) Evaporation of the solvent allowing the polymer macromolecules to interact with cellulose fibres thus exerting a consolidation and protective effect.

According to such a method a consolidating polymer compound is applied directly on the "Recto" of the paper document. The impregnation is effected by using suitable synthetic resins in order to impart to the works on paper higher resistance to traction and to tear.
The direct impregnation requires an heating press to bring the resin above its softening /melting point and to force the penetration of the reinforcing molecules deep between the cellulose fibres of the paper support. Some of the procedures are based on the following polymers:

i) Cellullose acetate (press temperature: 90°C);
ii) Polyethylene (press temperature: 115°C) [3].

Derivatives of cellulose, soluble in water, such as the ether derivatives, methyl and ethyl cellulose and the derivate known as sodium carboxy methyl cellulose (CMC) find large applications as general purpose adhesives in the consolidation procedures for paper based items.
The CMC as sodium salt is obtained by reaction between cellulose sodium hydroxide and mono-chloroacetic acid under controlled conditions [6,7].
<*The major use of CMC in conservation has been on paper, as an adhesive, as a moisture-holding gel during aqueous surface treatment, as pigment fixative and as paper consolidant*> [8].
In presence of ink or soluble dyes a vaporization technique may be also used.
The efficacy of water dispersion polymers, based on acrylic and acetovinylic monomers, having different molecular structure, in consolidating treatments of cotton fibres, before and after artificial aging in HCl solution, was assessed by E. Martuscelli and Others [9,10].

The water dispersions used were based upon the following different polymers:
--- Acrilem RP 6005 (polyethylacrylate).
--- Acrylem 674 (ethylacrylate-co-methylmethacrylate).
--- Primal AC 33 (ethylacrylate-co-methylmethacrylate).
--- Mowilith DMC 2 (vinylacetate-co-di-n-butylmaleate).
--- Mowilith SDM 5 (vinylacetate-co-di-n-butylacrylate).

The efficiency of the various polymer dispersion was evaluated by measuring the "Recovery in the specific stress at maximum load (R stress, %)" for HCl-degraded cotton yarns, as function of the relative amount of polymer absorbed after impregnation (A %). Moreover the adhesion between polymers and fibre was qualitatively assessed by scanning electron microscopy.
From the study it was possible to demonstrate that:

i) all polymers above indicated show consolidating effects whose entity depends upon the amount of polymer absorbed and by its molecular structure (see figure 1);
ii) the formation of bridges constituted by polymeric thin fibrils joining adjacent cellulose fibres contribute to the enhancement of mechanical properties (see figure 2) [9,10].

Process of type-2 (Parylene process)
In general it consists of:
a) The treatment of the document with a monomer substance in a vapour phase.
b) The in site polymerisation of the monomer with formation of a thin coating of a highly stable polymer throughout all the specimen able to protect fragile pages of books or single sheet documents.
Hereafter the Parylene process is described in details.
Parylene is the generic name for the poly-para-xylylenes, the various members of a family of polymers developed by Union Carbide Corporation, able to form, following a vapour deposition polymerization, coatings and films made up of linear highly-crystalline polymers. The most used terms of the family are:
--Parylene C, the mono-chloro substituted compound.
--Parylene N, the un-substituted compound, characterized by high-frequency dielectric properties, better penetrating power of coating.
--Parylene D, the di-chloro-substituted compound, with high temperature resistance [11,12].

The phases of the Parylene process, by referring to Plate A.2.1, may be summarized as follows.

I) Sublimation at about 150°C of the high purity crystalline dimer di-p-xylylene (see Plate A.2.1 on the left side).
II) Pyrolyses of the vapour at ~ 650°C to form the gaseous monomer which has an olefinic structure (Plate A.2.1, middle).
III) The monomer in the vapour state moves to the coating chamber, kept at room temperature, where it <*condenses on all surfaces equally and can pass through holes as small as 1μ. It then spontaneously polymerises to form a product with a high degree of crystallinity. The coating is absolutely conformal and can be laid down in thickness from a few angstroms to 50 microns or more depending on the requirements of the end use*> [12]. (Plate A.2.1, right side)

Some of most relevant characteristics of Parylene polymer films/coatings may be summarized as follows:

** Extremely resistant to chemical attack and insoluble in most chemicals.
** Exhibit a poly-crystalline structure which is highly resistant to moisture (Contact Angle = 87°); highly hydrophobic materials).
** Remain stable at continuous temperatures as high as 130°C in air or 220°C in the absence of oxygen showing high mechanical strength and flexibility.

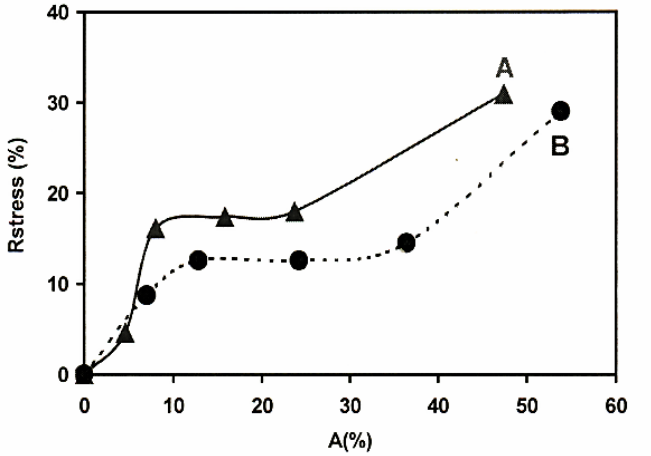

FIGURE 1: Recovery in the specific stress at maximum load (Rstress, %) for HCl-degraded cotton yarns impregnated with different relative amount (A %) of vinylacetate (A) and acrylate (B) based polymers [9,10]

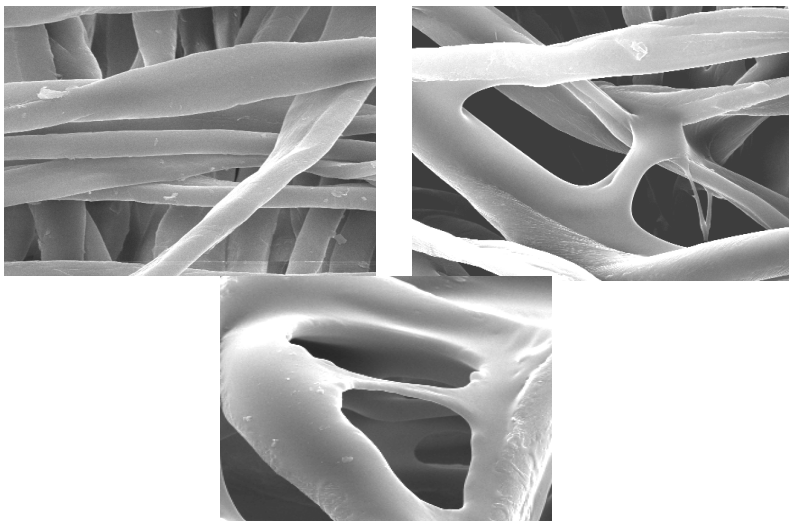

FIGURE 2: SEM micrographs of cotton fibres untreated (A) and treated by immersion in water dispersions of vinylacetate (B) and acrylate (C) based polymers [9,10].

The Parylene process due to the unique application conditions and characteristics of the formed films/coatings (barrier properties, mechanical strength, chemical characteristics, adhesion to the substrate, etc.) found interesting applications in strengthening paper in degraded old books and archival documentations and manuscripts [11,12].
Studies about the suitability of Parylene process in the consolidation /protection of various type of items, including works on paper, were performed at the J. Paul Getty Conservation Institute and at the Library of Congress (USA). In the latter case investigations were addressed towards the possibility of using the Parylene process as a potential means of mass consolidation.
Bruce J. Humphrey was the one of the first in to propose that Parylene vapour polymerization might have applications in the consolidation of bound books whose pages have become weakened or embrittled due to the high acidity of the paper, even taken into account the irreversibility of the treatment [11]. At the beginning the experiments were performed by placing books directly in the coating/polymerization chamber. First of all it was observed that as the air is evacuated the single pages automatically arranged themselves in a fanlike manner.
Nevertheless it emerged that once the bound book was submitted to Parylene treatment the polymer did not penetrate equally on all region of the leaves (see figure 3) [11].
Thus the Author reached the conclusion that <*Uniform coatings of any desired thickness can be obtained by disbinding the book and processing the individual pages on trays 3–5 mm apart—a rather costly procedure*> [11].

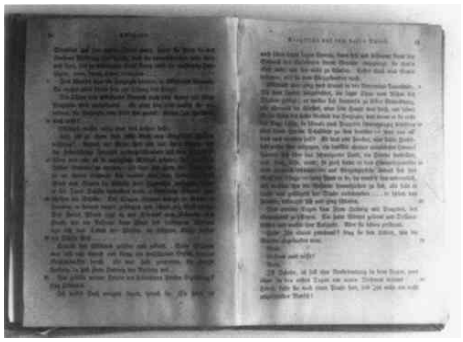

FIGURE 3: Test book after immersion in water. Dark areas indicate water penetration due to absence of parylene [11].

Nevertheless from the studies conducted on bound books it was evidenced:

1) the lack of swelling with no proof of water damage following immersion tests on the part of parylene treated books (see figures 4 and 5);
2) no water spotting or discoloration of the coated pages nor was there any evident weakening of the paper;
3) that a coating as thin as 2500 angstroms can double the tensile strength [11].

Moreover it was observed a very close physical contact between parylene coating and the paper based substrate. This behavior makes irreversible the treatment (Parylene coating can be removed only by treating with hot orthodichlorobenzene or chloronapthalene (at ~ 180°C), thus the taking away of the Parylene, without damaging the paper leaves would be impracticable).
The results of the above cited studies give indication that the gas phase in site polymerization of Parylene may induce a consolidate effect suitable to extend the useful life of embrittled and/or

weakened books or single sheeted archival documents.
Tsang-Chyi Shiah and others, quite recently have conducted an investigation to test the applicability of Parylene technology to the preservation of brittle books and archives [13].
The research was aimed at finding the optimum treatment conditions by evaluating the strength, accelerated aging behaviour, and colour changes of Parylene-coated paper items.
The main findings are hereafter summarized:

i) The Parylene treatment causes a generalized increase in paper strength mostly to be attributed to the fact that the vaporized para-xylylene monomers penetrate into the paper structure where they polymerise giving rise to a coating strongly adhering with the cellulose fibre network (see SEM micrographs in figure 6).

ii) The folding endurance and zero-span tensile strength improved noticeably in paper samples treated with Parylene.

iii) Parylene C showed a less paper brightness losses and colour variations compared to Parylene N-treated specimens (see photos in Plate A.2.2).

FIGURE 4: Untreated book after 4 months of immersion in water followed by 3 months of storage while still wet [11].

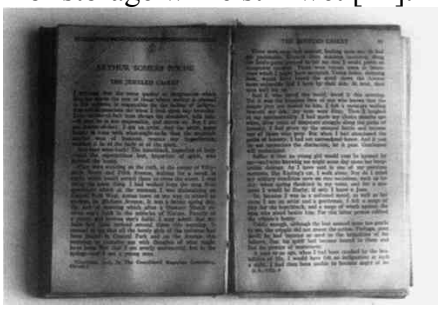

FIGURE 5: Treated book after 4 months of immersion in water followed by 3 months of storage while still wet [11].

iv) Water dropping test led to the observation that Parylene treatments induce a better water resistance to paper surfaces coated with Parylene-N and Parylene-C (Plate A.2.3). Moreover it was observed that Parylene C-treated samples exhibited higher water resistance compared to Parylene N-treated items.

v) Paper surfaces with a 5-μm thick polyparaxylene coating develop a higher resistance against the degradative attack of 5 common molds (*Aspergillus niger, A. flavus, Penicillium sp., Rhizopus sp., and Trichoderma virid*). Samples treated with Parylene C showed better fungal resistance than those treated with Parylene N [13].

Finally it was observed that the efficiency of parylene technology depends upon the type, structure and physical characteristics of the treated papers.
According to what reported in reference [14] the Parylene process, at that time, was <... *offered commercially by a library binding company (ICI) for strengthening the pages of entire books, one or several books at a time*>.
H.D Burgess and D. W. Grattan, have studied the efficiency of Parylene process on two different types of paper sheets, namely: a porous ligneous unsized book paper and a heavily calendared, lignin-free, sized ledger paper [15].
Single-sheet papers were first treated with Parylene-N (one set was treated at normal pressure to yield a coating of average porosity and one at high pressure to generate a more porous coating) and successively subjected to water washing, bleaching or deacidification.
The investigation led to the following observations:

1) In both cases the treatment caused an improvement in the strength of samples; a larger effect being observed for the porous ligneous book-leaves.

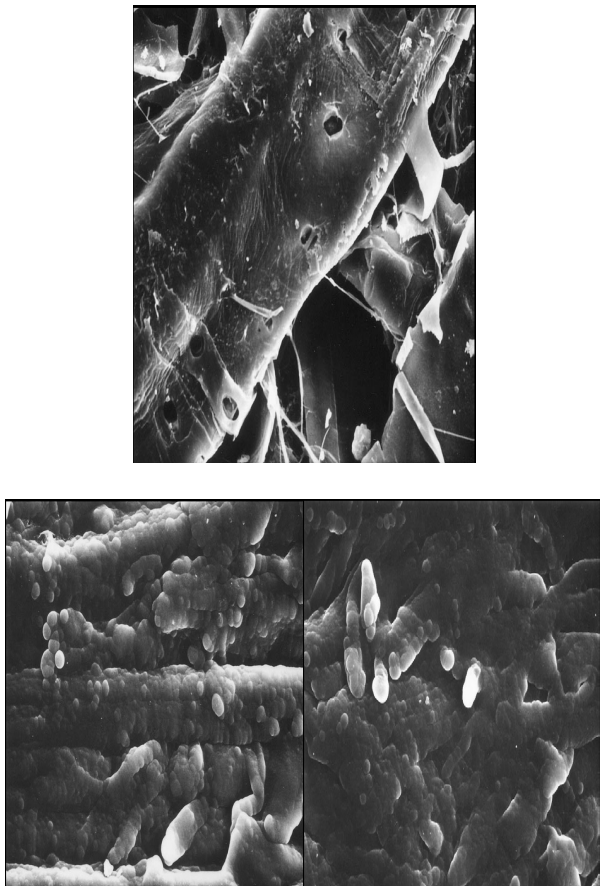

FIGURE 6: SEM micrographs of newsprint paper surfaces coated withParylene-N and Parylene-C. Top: no-treatment. Bottom-Left: Parylene-C.Bottom –Right: Parylene-N [13]

2) Aqueous washing and bleaching processes had almost no effects on the colour and strength of all treated samples.
3) The coating processes seemed to facilitate the deacidification treatments, the extent depending on the nature of paper component [1. 5]

Process of type-3 (*internal polymerization* of acrylic monomers)
It foresees:

a) The impregnation of the surfaces of the deteriorated paper document with reactive liquid acrylic monomers or with their solutions or suspension in a proper liquid phase;
b) The in site induced polymerisation of monomers;
c) Evaporation of the solvent and polymer-coating formation .

The mass paper-strengthening procedure, based on the principle of *internal polymerization* of acrylic monomers, developed by the British Library in London belongs to type-3 process [16].
Acrylic monomers (methyl acrylate, methyl metha-acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, etc.) are highly reactive liquid chemicals whose molecules readily combine with themselves or with other functional monomers to form linear high molecular weight macromolecules. Some relevant physical properties of commonly used acrylic monomers are reported in table 1 [17].
The mass treatment, suitable in principle for books and single documents is essentially based on the following procedure:

i) Infiltration of a mixture of acrylic monomers to the interior of the leaves of books stacked in a suitable container where previously nitrogen, to remove air and free oxygen, was pumped.
ii) Diffusion of the monomers and uniform distribution throughout the pages of books.
iii) Exposition of the monomers absorbed on the pages of the books to γ-radiations.
iv) Polymerization of monomers, in site, induced by γ-radiations.
v) Formation of polymer chains some of which may be also chemically grafted to cellulose fibres.
vi) Removal of the monomer residue by using a flux of air [16].

TABLE 1: Physical properties of some acrylic monomers [17].

	Methyl Acrylate	Ethyl Acrylate	Butyl Acrylate	2-Ethylhexyl Acrylate
Molecular Formula	$C_4H_60_2$	$C_5H_8O_2$	$C_7H_{12}O_2$	$C_{11}H_{20}O_2$
Molecular Weight	86	100	128	184
Boiling Point (°C)	80	100	148	216
Freezing Point (°C)	<-76	<-72	<-65	<-76
Density (20/20 °C)	0.957	0.923	0.900	0.886
Flash Point	-3	8	41	87

The above treatment seems to be able to strengthen the paper substrate delaying further degradation. According to reference [17], *<this could be achieved by the absorption of polymers into the substratum, thus strengthening and protecting each individual paper fibre>*.
Moreover it was also found that by combining a de-acidification treatment with that of internal polymerization the strengthening effects is further enhanced. The trends of the curves in figure 7 seem to confirm the above statements [1].

Process of type-4 (Graft in site copolymerisation)
This procedure is based on the capacity of reactive side groups, present along cellulose chains, including those resulting from degradation reactions, to graft high-molecular weight macromolecules thus giving rise to fibres with a chemically modified surface. The steps of the methodology are:

a) The surface of a degraded paper item is impregnated with a reactive monomer or a tailored mixture of co-monomers in a liquid state or in solution or in a vapour phase;
b) The reaction of polymerization /copolymerisation is induced by radiations having suitable wave length (i.e. weak gamma-rays or UV-light);

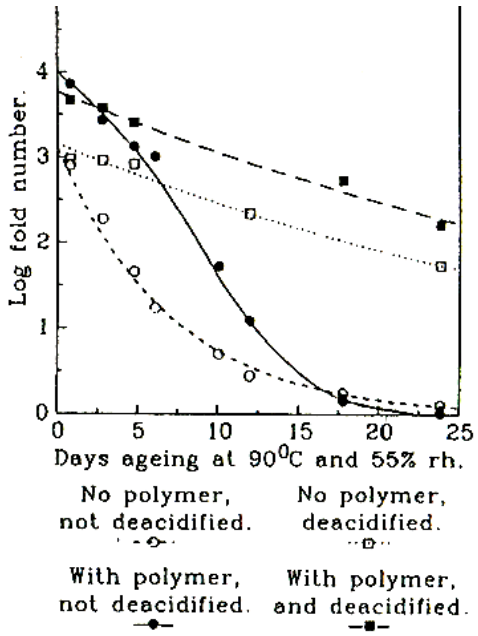

FIGURE 7: Accelerated ageing performed at the British Library on paper samples treated with the internal polymerization method. The mechanical strength, measured by the folding endurance, is plotted against time. The curves refer to different type of samples (see legend on the bottom and the text) [1].

c) Due to the presence of functional reactive groups along the degraded chains of cellulose monomers or oligomers are chemically grafted on the cellulose chains. The polymerisation may continue giving rise to the formation of grafted fibres (see Plate-A.2.4) [2,3].

Some of the procedures adopted to graft polymer chains onto the surface of cellulose fibres are below described.

♦♦ The co-continuous approach: consists of grafting pre-formed high-molecular weight polymers with reactive end chain terminal groups directly to the fibre surface of cellulose fibres . Polypropylene glycol mono-butyl ether (PPG), Polycaprolactone (PCL), and Polytetrahydrofuran (PTHF) are examples of such kind of polymers (see molecular structures in figure 8) [18].
The grafting process is described in reference [18] as follows:
<…. *one of the two reactive chain ends …is blocked using a monoisocyanate (phenylisocyanate). The other reactive chain end is subsequently reacted with a diisocyanate of which only one moiety reacts. The other remains unreacted and is used in the last step to react with the hydroxyl groups at the cellulose surface. The reaction is followed by infrared spectroscopy……. One can clearly see the existence of urethane bonds due to the different grafting reactions, while the remaining isocyanate signal indicates the existence of unreacted isocyantes to be used for grafting to the cellulose surface hydroxyl groups*> [18].
The modification of the surface of cellulose fibres, following grafting treatments have been evidenced, by scanning electron microscopy.

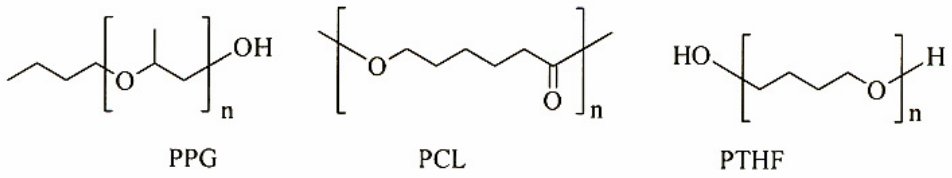

FIGURE 8: Polypropylene glycol mono-butyl ether (PPG), Polycaprolactone (PCL), and Polytetrahydrofuran (PTHF) as examples of preformed polymers that can be grafted to the surface of cellulose fibers (see text) [18].

It was observed that following grafting the morphology of fibre surfaces is deeply modified, the type of modification depending on the graft agent used(see micrographs in figure 9) [18].
In the case of PCL treatment a prominent level of modification was attained with an almost homogeneously covered fiber surface. Samples grafted with PPG, on the contrary showed only a discrete coverage [18].
According to the Authors the above results <*confirm earlier presented results based on contact angle and infrared spectroscopy experiments. These experiments showed a hydrophobisation of the fibre surface upon grafting, as well as the appearance of infrared signals consistent with grafting*> [18].

♦♦ The co-polymerisation approach. Small bi-functional molecules, with a rigid backbone structure, are previously grafted onto surface of cellulose fibers being sure that only one functionality will react during grafting, leaving the other one free to react with the reactive groups of a preformed polymer.
Examples of grafting agents are: 1,4-phenylene di-isocyanate (PPDI), pyromellitic di-anhydride (PMDA), and benzophenone-3,3′,4,4′-tetracarboxylic di-anhydride (BPTC) (the molecular structures are reported in figure 10) [18].
Cellulose fiber, including those contained in paper based items, after modification with the above bi-functional molecules showed the capacity to graft different types of pre-formed polymers [18].

♦♦ Graft-copolymerisation of acrylic monomers, from the vapour phase, directly onto degraded paper substrates. Studies finalized to establish operative procedures to graft, in site, polyacrylic chains onto the cellulose fibres of paper based items were conducted by E. Pedemonte, E. Princi, S Vicini and Others. The objective of the research was the development of a method appropriate for the consolidation/stabilization of degraded works on paper.
Preliminary studies led to development of a procedure based essentially on the hereafter described steps [19,20,21].

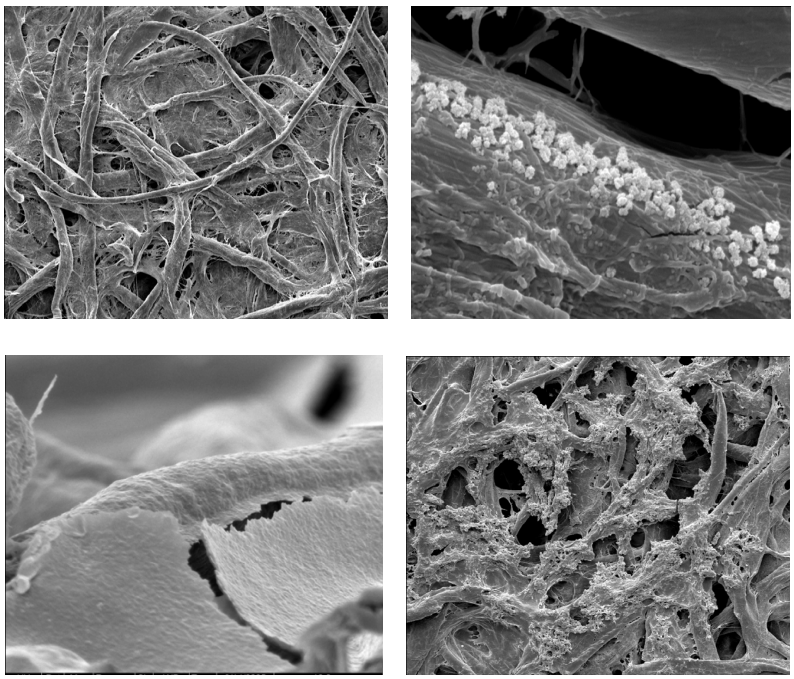

FIGURE 9: Scanning electron micrographs showing the surface of cellulose fibres before and after graft treatments:
Top-left- Non-modified Whatman paper. Top-right- Whatman paper Modified with PPG. Bottom-left- Whatman Paper modified with PCL. Bottom-right- Whatman paper modified using PTHF (see text)[18].

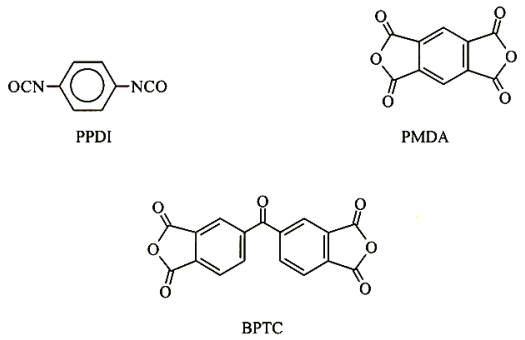

FIGURE 10: Molecular structures of grafting agent for cellulose fibers used in the co-polymerisation approach: 1,4-phenylene diisocyanate (PPDI), pyromellitic di-anhydride (PMDA), and benzophenone-3,3′,4,4′-tetracarboxylic di-anhydride (BPTC) [18].

First step: It consists in the formation of photosensitive groups along the cellulose macromolecules necessary to the free radicals UV-photo-induced polymerization of acrylic comonomers and grafting reaction. To do this samples of Whatman, no. 1 filter paper (pure cellulose, DP= 1,230), are oxidized by treating them with solutions of sodium metaperiodate ($NaIO_4$).
Such a treatment, as shown by figure 11, specifically causes the cleavage of the C_2-C_3 bond of the glycoside ring with the conversion of the 2- and 3- hydroxyls in two aldehyde side groups.
At the end of the oxidative reaction the paper samples are washed with de-ionised water up to a neutral pH and afterward dried.
Second step: Oxidized paper samples, in order to open up the structure and thus to facilitate the uniform penetration of the gaseous acrylic co-monomers, are swollen in de-ionised water. Then still wet are positioned in a polymerisation reactor chamber (see figure 12). The chamber is kept at relatively low pressure, then the acrylic liquid monomers mixture is in let. Under the conditions selected the acrylic monomers vaporize and penetrate deeply the network of cellulose fibers.

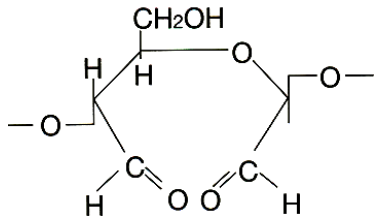

FIGURE 11: Oxidation and cleavage of carbon 2 carbon 3 bond of the β-D-glucopyranose ring of the cellulose chain with formation two aldehyde side groups [19,20,21].

Third step: The paper samples impregnated by vapors of acrylic monomers are exposed, at room temperature, to UV radiation to initiate the photo-induced radical polymerization of acrylic monomers including the reaction of grafting on the activated oxidized aldehyde groups previously produced along the cellulose chains. After a suitable time the polymerization is stopped, the un-reacted monomer is removed and the sample is washed with a mixture of methanol and water.
Fourth step: From the dried paper sample the free acrylic copolymer chains are removed by treating with acetone at RT. After this procedure only copolymer grafted to cellulose fibers is left on the paper items.
The Grafted Yield (%) (GY %) of the reaction is measured through the following equation:
(GY %) = [(W_2−W_1)x 100] / W_1
where W_1 and W_2 are the initial and the final weight of the paper sample respectively.
The efficiency of the grafting reaction (E-Grafting %) is given by the ratio between the amount of the grafted monomer and that of the total monomer polymerised (free homopolymer + grafted polymer):
(E-Grafting %) = (W_2−W_1) / (W_e−W_1)x100
"We" being the weight of the paper sample after reaction and before the extraction of the homopolymer [21].

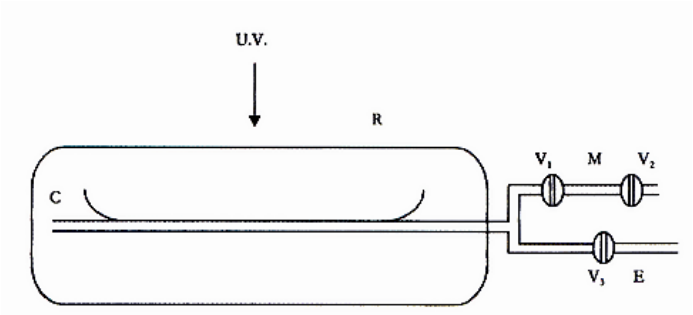

FIGURE 12: Scheme of the early reactor for graft-copolymerisation of acrylic monomers, from the vapour phase, directly onto paper substrates. R: vessel in quartz glass; C: paper sample; M: way for monomer in let; E: vacuum connection; V_1, V_2, V_3: cocks (see text) [21].

Keeping constant the temperature and the pressure then the main factors upon which the efficiency of the grafting reaction is dependent are:
▼- Concentration of the $NaIO_4$ solution.
▼- Treatment-Time of cellulose fibers with $NaIO_4$ solutions.
▼- Polymerization time of acrylic comonomers.
▼- Molecular structure of acrylic comonomers.
▼- Molecular ratio of comonomeric unities.

As shown by the data reported in figure 13 both the viscosity [η] and degree of polymerization (DP) of treated fibres diminish with the increase of the oxidation time and the concentration of $NaIO_4$ indicating that oxidative reactions even if specific for the cleavage of carbon 2 carbon 3 bond

of the β-D-glucopyranose ring of the cellulose chain with formation two aldehyde groups may also give rise to chain ruptures. Thus to reduce this effects relatively low times and $NaIO_4$ concentrations should be used. The concentration of $NaIO_4$ solutions seems to influence also the values of the grafted yield and of the efficiency of the grafting reaction. As matter of fact as reported in figure 14 increasing the concentration of $NaIO_4$ solutions the above mentioned quantities increase [21].
The grafted yield of methylmethacrylate (MMA) on Whatman paper first increases with the time of polymerization then level off after 10hrs (see figure 15). As far as the efficiency of the grafting reaction is concerned it can be observed that it keeps almost constant with the time increase [21].
The results above presented show that the ratio between the amount of polymer grafted to cellulose and the total amount of monomer converted in polymer is practically constant. Moreover it was found that the amount of homopolymer is around 15% indicating that the grafting reaction prevails over the homopolymerization. The yield of the grafting reaction can be still improved by pre-irradiating the oxidized cellulose by UV exposition that causes an activation of aldehyde functions [21].
The applicability of the procedure was assessed on a naturally aged paper sample of the eighteen century. This sample, assuming that due to degradation processes active sites have been produced along the cellulose chain, after UV pre-irradiation were submitted to the photo-induced radical polymerization of acrylic monomers. The results showed that after one hour a value of the grafted yield equal to the 19% was attained. Such a result was a demonstration that the procedure could be applied even to ancient degraded works on paper [21].
With reference to the influence of the molecular structure of acrylic monomer it was found that by using ethyl acrylate (EA) instead of MMA the yield of the graft reaction can be enhanced.
Even the mechanical properties of the treated Whatman paper resulted to be dependent upon the molecular structure of the acrylic monomer used. In fact it was observed that cellulose-grafted with polyethyl acrylate (PEA) show a lower Young modulus and an higher elongation at break in comparison with samples grafted with PMMA [21]. Such different behaviors were ascribed to the diverse Tg values of PMMA and PEA polymers.
The studies showed that acrylic monomers such as methyl methacrylate (MMA) and ethylacrylate (EA) are appropriate for grafting reactions onto cellulose fibres but the grafting procedure turned to be not suitable for an effective consolidation/stabilization of paper based items. As matter of fact the first monomer because of the high Tg of the corresponding poly(methyl methacrylate) polymer (PMMA) (Tg = ≈ 105°C) induces brittleness and rigidity to the cellulose support. The inappropriateness of the second monomer is, instead, connected to the relatively low Tg of the poly(ethyl acrylate) (PEA) (Tg = ≈ - 24°C) and to its gummy characteristics. On the contrary it was found that degraded textiles supports, consisting of cellulose fibres, after being grafted with an EA/MMA copolymer 75/25 wt % (tg =≈ 10°C), directly from the vapour phase, showed improved mechanical properties with no changes in the characteristic of flexibility [22].

The above mentioned findings were the reasons why a mixture of EA and MMA acrylic monomers with a 75/25 wt % ratio, to which a EA/MMA copolymer with a Tg of = ≈ 10°C corresponds, was considered interesting to carrying out tests finalized to the consolidation/stabilization of degraded paper items by graft-copolymerisation reaction directly from the vapour phase [23].
Such a study was developed with success in the framework of Papertech-Project and the results will be presented in details in the next parts of the present book.

$t_{ossidazione}$ (h)	[η] (dl/g)	DP	[η] (dl/g)	DP	[η] (dl/g)	DP
0	8,20	1.230	8,20	1.230	8,20	1.230
1	5,93	890	3,06	460	1,60	241
2	2,60	390	1,95	293	1,23	185
3,75	2,20	330	1,66	250	1,13	170
5	2,00	300	1,60	240	1,10	165
24	1,60	250	1,42	214	1,07	160
48	1,46	240	1,40	210	1,07	160

* $NaIO_4$ 0,01 M, $NaIO_4$ 0,03 M, $NaIO_4$ 0,1M

FIGURE 13: Influence of the concentration of the $NaIO_4$ solutions and of the oxidation time (t) on the viscosity [η] and degree of polymerization (DP) of cellulose fibers present in Whatman paper samples [21].

$NaIO_4$	% grafting	% efficienza del graffaggio
0	0	0
0,01	0,36	77
0,1	11	82

* Oxidation time= 2hrs; monomer/cellulose ratio= 1,35molMMA/100g of paper sample; polymerization time= 1hr

FIGURE 14: Grafted Yield (%) and efficiency of the grafting reaction of methylmethacrylate (MMA) on Whatman paper as function of concentration of the $NaIO_4$ solution [21].

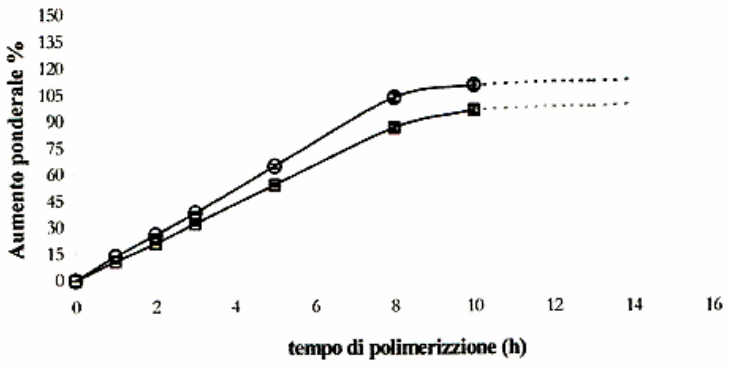

FIGURE 15: Weight increase of paper samples as function of the time of polymerization of MMA monomer: ● = before extraction of the homopolymer; ■ = after extraction [21].

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CHAPTER A.3:

The selection of works on paper: Ancient and modern samples.
Natural and artificial weathering and techniques for paper and papyrus characterisation and for assessing the conservative treatments

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The selection of reference works on paper

In a research regarding writing materials of different type, provenience and composition, it is fundamental to be able to carry out experiments involving several samples. Often, destructive testing is needed to systematically evaluate new analytical methods and treatments, before applying them to originals: therefore the composition and the behaviour of the selected writing materials should be representative of ancient samples to be tested and treated. Moreover, in order to understand and explain the degradation processes occurring on paper during its life, it is necessary to perform a complete study of well-defined specimens, subjected to artificial weathering carried out in strictly controlled conditions.
In this research the attention has been focused on different paper grades and on papyrus, defined throughout the research as "model samples", having different composition, properties and manufacturing. It is worth to note that the word "grade" identifies a class of papers with the same composition and characteristics; it can also refer to the quality level of the paper.
Among the so-called "model samples", two categories can be distinguished: new writing materials, to be submitted to artificial weathering, and naturally aged samples, without any historical or artistic value.
At the first category belong the following writing materials, not died and/or printed, used during the research as received from the factories:

- ***Whatman paper for chromatography*** (Carlo Erba, Italy; grammage: 70 g/m^2). Manufactured from high quality cotton linters (minimum α-cellulose content: 98%), without additives.
  Whatman paper has been extensively used since many years in paper research science, thanks to its large availability, easy use and reproducibility. Nevertheless, it should be kept in mind that this paper is dramatically different from the paper found in archives or libraries. Therefore, at a certain stage, the extrapolation of the results obtained on such papers to historical ones can not be longer legitimate. One of the main differences lies in the fact that, being Whatman paper a filter paper, it contains no sizing agents, giving rise to a distinctively behaviour during a consolidation treatment. Another main difference concerns the fibre composition: Whatman paper comes from cotton linters or bleached rags, whereas the most common paper grades come from pulpwood.

- ***Murillo paperboard*** (Fabriano Factory, Italy; grammage: 360 g/m^2). Uncoated paper, made with 100 % of bleached short fibres, coming from trees. The product is acid free, with alkaline reserve, guaranteeing long life. It contains cellulose, no lignin and about the 10 % of inorganic fillers. What differentiates paperboard from paper is the weight of the sheet; indeed Murillo is a heavy weight, thick and rigid paper.

- ***Watercolour paperboard*** (Fabriano Factory, Italy; grammage 200 g/m^2). Acid free paper, made with 25 % of cotton fibres, 15 % long fibres pulp and 70 % short fibres pulp. The product has alkaline reserve, guaranteeing long life and it contains cellulose, no lignin and about the 5% of inorganic fillers.

- ***Paper for conservation*** (Fabriano Factory, Italy; grammage 390 g/m^2). Natural white, moulmade watermarked paper, made of 100 % totally chlorine-free pulp of cotton. The product is wood and acid free, with alkaline reserve, to guarantee the longest life; it contains cellulose, no lignin and about the 6 % of inorganic fillers.

- ***Newsprint paper*** (Cartiere Burgo, Italy; grammage 65 g/m^2). Made largely from mechanical pulp and/or waste paper; it contains blanched cellulose, recycled fibres after deinking, starch, a noticeable amount of fillers (≅ 20 %) and optical correctors. **It** is one of the least expensive printing papers.

- ***Papyrus*** (Siracusa, Italy; grammage: 85 g/m^2). Due to its provenience the main constituents are cellulose and lignin. In general, this material suffers the same deterioration processes as cellulose of paper. However, the presence of lignin increases the effects of the ageing processes due to the acidity that lignin provides.

The selected naturally aged paper samples, belonging to the second category, have different provenience, age and composition; therefore these samples give the possibility to investigate the effect of the natural weathering at various level of degradation (see Figures 1 and 2).

Figure 1: Blue cover of and white page of "L'Illustrazione Italiana" (magazine)

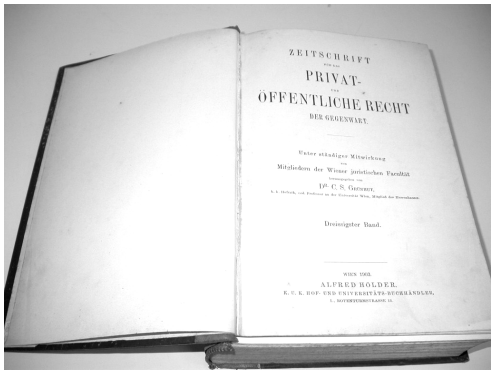


Figure 2: Austrian Book

All these printed samples present evident traces of photodegradation and oxidation (yellowing and browning), due both to the additives used in the production (inks, sizing, fillers, etc.) and to the storage conditions. In table 1 the main characteristics of the naturally aged model samples are collected.

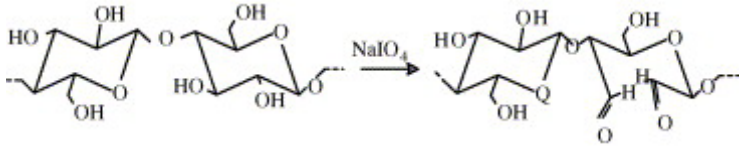
N°	Type	Age	Provenience	Description
1	Book "Privat und offentliche recht der gegenwart"	1903	Austria	Printed sheets, with evident traces of oxidation on the borders
2	Magazine "L'illustrazione Italiana"	1919	Italy	Printed white pages and a blue cover with evident traces of oxidation on the borders
3	Magazine "Rivista di diritto commerciale"	1941	Italy	Printed sheets, with traces of oxidation on the borders

Table 1: List and description of the naturally aged model samples

The artificial weathering

Ageing may be defined as the irreversible change that occurs slowly over time on materials. Generally this term connotes degradation and deterioration phenomena that are measured in relation to a specific state, either the original state or that at a fixed time. Over long term it is necessary to attempt to reduce, minimize or eliminate the effects of ageing on the materials. In order to achieve this, it is helpful to understand what the ageing process consists, what factors affect and what effects induce [1].
Usually, to investigate the ageing phenomena as they normally occur, any material is submitted to weathering processes, speeded up so that measurable changes take place within a reasonable time. The accelerated ageing is an attempt to simulate in a short time what happens during long periods of natural ageing. It is worth to note that each ageing accelerated test can not reproduce accurately what happens in nature, because during the natural weathering many factors act cooperatively and sometime it is difficult to predict particular events. The weathering experiments consist in the exposure to any combination of potentially damaging environmentally factors as heat, humidity, light, oxygen and pollutants, speeding up the decaying phenomena occurring during the natural ageing [1].
In the case of cellulose, the main component of paper and papyrus, the ageing processes is generally very slow because cellulose is a stable material. As extensively described in Chapter 3, paper degradation is due to a high number of reactions that determine physical and chemical changes mainly in the cellulose matrix and, if present, also in the other components. At macroscopic level, the paper appears not only weaker, because its mechanical resistance is noticeably reduced, but also sometime the appearance becomes completely different from the original one [2].
To study the effect of both the degradative agents and the storage environments on paper life, it is necessary to replicate in a laboratory setting, for few weeks or months, the natural ageing of paper, which takes place in real life over several decades [3]. However, the set up of accelerated testing for paper is much more complicated than for other products, because the same test should work with a wide variety of papers. Accelerated-aging tests are often used as well to predict the long-term effects of a particular conservation treatment. However, there are many questions about the actual predictive value of these tests.
There are two schools of thought on accelerated ageing of paper, those who think that it provided a

reliable tool, and others who believe that it do not and could never duplicate natural ageing. Nevertheless, recent studies highlighted that accelerated aging can be considered as a reliable approximation of natural ageing for predicting paper longevity [4-6], even if it is impossible simulate exactly what happens in the nature when the weathering occurs.
The ways in which the degradation experiments can be performed are variable; the choice depends on the requested final goals of the study. In this research it has been investigated how fluctuations of temperature, humidity and light exposition can affect paper and papyrus: the influence and the effects of these external conditions significantly depend on the quality of material itself.
The monitoring of effects of weathering on paper and papyrus components is the base to elaborate a diagnostic approach to the problem of degradation, as it will be broadly demonstrated in Chapter 5.
Three "physical" and one "chemical" methods to age the model paper samples have been selected: at the first group belong the treatments in oven, in solarbox and in climatic chamber, whereas the chemical treatment consists in the oxidation with sodium metaperiodate ($NaIO_4$).
Periodate oxidation is a highly regioselective reaction: the oxidative agent opens the pyranose ring and attacks merely the C2-C3 bond on the ring, converting the 1,2-dihydroxyl groups in two aldehyde groups, without modify the glucosidic bonds and without significant side reactions (Figure 3) [7,8]. The resulting product is the dialdehyde cellulose (DAC). The high selectivity is easy to explain: the oxidation mechanism requires vicinal hydroxyls and such groups are located in cellulose at the C-2 and C-3 positions. The oxidation reaction is thought to proceed via a cyclic diester of periodic acid with vicinal hydroxyls, which subsequently undergoes an intra-molecular redox process with C–C bond cleavage according to a concerted mechanism [9].



Cellulose 2, 3- dialdehyde cellulose

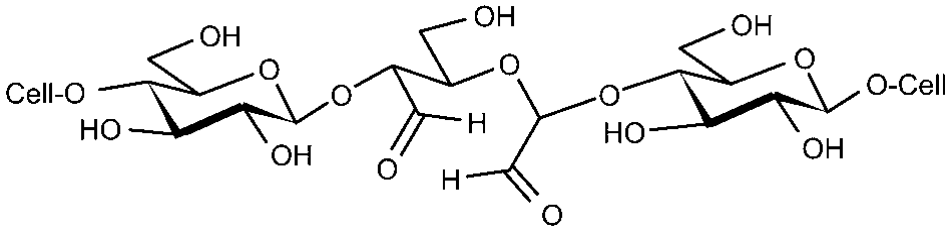


Figure 3: Regioselective oxidation of cellulose by $NaIO_4$ (top)
and scheme of the resulting partially periodate-oxidised cellulose (bottom)

Periodate oxidation of cellulose proceeds not only on amorphous region, but also the crystalline phase cellulose exhibit a particular reactivity [9]. Prolonged reaction time and higher oxidant concentration are necessary to access into the inner region of the polymer; in this way cellulose becomes increasingly amorphous.
For verifying if this treatment can be considered as a correct way to simulate the degradation occurring on the paper stored in normal archives conditions, the oxidative reaction with sodium metaperiodate has been performed in mild conditions. Indeed in a previous study [10] we demonstrated how prolonged reaction time and high oxidant concentration lead to a progressive and deep destruction of cellulose based materials that lose their typical characteristics and properties. Therefore, starting from these results, in the present research the oxidative treatment has been

carried out in the following conditions: [$NaIO_4$] 0.1 M for 2 hours; this can be considered suitable for our aims.
Periodate oxidation represents a key reaction also for the set up of the grafting polymerisation of acrylic monomers onto the cellulose chains. Indeed, the carbonyl functions formed during the oxidative process are the photosensitive groups that allow the formation of radical sites where the UV photoinduced grafting process starts. It is necessary to point out that the creation of aldehyde functions onto cellulose chains is indispensable because grafting can occur onto the raw (unaged) writing materials, as the model samples, that do not have these groups, deriving from the weathering. On the contrary, the naturally aged papers do not require any former oxidative treatment before the polymerisation, because they already present the photosensitive sites.
To summarise, all the model samples have been weathered in the following experimental ways:

- In oven (ISCO NSV 9035) at 100 °C for 500 hours in the dark
- In solarbox Angelantoni SB3000E at 65 °C (R. H. 25 %) for 500 hours, under a Xe-arc lamp (power 1000 W/m^2)
- In climatic chamber Angelantoni Challenge 250 E at 60 °C (R. H. 70 %) for 500 hours, under a UV lamp (power 150 W/m^2)
- Chemical oxidation with sodium metaperiodate ($NaIO_4$). The ratio sample/solution has been kept for all experiments 1 g of sample for 100 ml of water. The samples have been mixed in a closed vessel with the metaperiodate solution 0.1 M and the mixture has been stirred gently at room temperature in the dark for two hours. At the end of the oxidation processes the samples have been filtered, washed with deionised water up to neutral conditions (pH 7) and dried.

Ancient samples

Once the diagnostic approach has been established by studying the model paper samples before and after artificial weathering, it has been applied on ancient papers in order to assess their conservation state and the degradation level.
The selection of ancient paper samples has been performed, considering the following criteria:

- geographic provenience of the objects;
- estimated ages;
- state of conservation;
- different nature of the object (archaeological sample, manuscript, drawing).

The selected ancient specimens belong to different archaeological and historical periods, as well as to different geographical areas, particularly Egypt, Jordan and Spain. The Egyptian fragments are clear examples of biodegraded paper, whereas the wallpapers, produced by xilographic printing of glue tempera with a cylinder, show the effect of dyeing with inorganic pigments on paper endurance. The other printed samples present evident traces of photodegradation and oxidation (yellowing and browning); the last one is ascribed both to the additives used in the production (inks, size, fillers, etc.) and to the storage conditions. Also two ancient maps have been investigated.
Micro fragments have been cut from each ancient sample, avoiding damaging the papers.

Jordan papers
In around 1870, the Ottoman government started, as a part of administrative reforms, a new distribution of landownership in the countries belonging to the Ottoman Empire. The new ownership of land was recorded in official documents, called Ottoman records. The paper of these documents is ca. 130 years old and it has been stored in a very aggressive environment. Although some documents are still in a relatively good condition, many show obvious traces of ageing and

deterioration. Seven degraded pages of records coming from the Ottoman archive of the Jordanian Department of Lands and Survey have been available for this research; among them, two have been completely characterised.
In figure 4 an example of Ottoman record (Code 1-1) is shown (original size: 28x40 cm; current size: 28x37 cm). This is an example of industrial paper, superficially coated; the superficial coating makes the surface translucent and avoided the ink spreading, since these sheets were prepared to be used for handwriting.

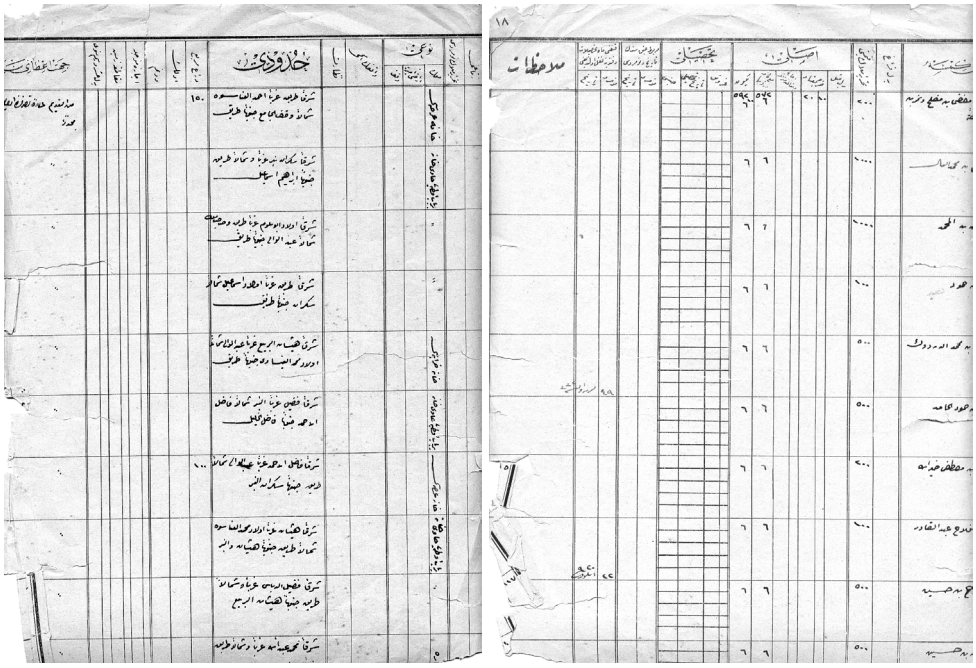


Figure 4: Recto and verso of the Document 1-1 of Ottoman records (1870)

Egyptian fragments
Fragments of two manuscripts coming from the Archives of Supreme Council of Antiquities have been analysed. These manuscripts belong to the collection of 120 books found in the El Gouhary mosque, situated in the centre of ancient Cairo; they are dated in 1751 - 1758 A.D. They are parts of the Holy Qur'an and are older than the mosque itself. In Plate A.3.1 three fragments coming from the Holy Qur'an manuscript dated 1761 are shown (Code 3-16, 3-18 and 3-19 respectively).

Spanish wallpapers [11]
Five wallpapers coming from the Santa Isabel factory in Vitoria-Gazteis (Basque Country) have been characterised.
In Plates A.3.2 and A.3.3 two examples of wallpapers, coded as 4-29 and 4-30, manufactured around 1850 are shown, respectively. Both the wallpapers show a very rich iconography, with flowers and medallions in undulating arrangement in blue, green, white, red, yellow, orange, brown and grey colours, most of them in at least two different shades, set alternatively over a white, brilliant background colour. The state of conservation is really poor; indeed, in some areas of the sample cracks and loses of polychromy are detectable. On the verso evident traces of oxidation, due to the pigment migration, are present.
The skirting border (wallpaper 4-31), in which the iconography shows a repeated pattern of squares, is dated second half of 19th century. Also in this case loses of polychromy are detectable in some areas, together with the red pigment migration on the verso.

Another skirting border of the first half of 19th century (wallpaper 4-33), showing a repeated pattern of flowers in yellow and orange, is in a modest state of conservation. The vertical bands (wallpaper 4-32) characterised by a repeated pattern of vases and flowers in black and yellow (second half of 19th century) are in a good state of conservation, even if the colour migration on the verso is observed (Plate A.3.4) on the contrary, those dated 20th century (wallpaper 4-34), in which the iconography represents a landscape with flowers and some buildings are in a bad conservation state

Maps
The map in Plate A.3.5 showing the Italian region of Vicenza (code 4-35) was made on handcrafted paper by using the technique known as etching engraving (black ink); it map was also painted by hand in several colours. This map was part of one of the most important atlas from the XVII century, the Atlas Major, due to Willem Janszoon Blaeu (1571-1638) and his son Joan Blaeu (1596-1673), the most widely known cartographic publishers of the seventeenth century. This atlas was the most expensive printed book of the XVII century (it cost 460 florins, nowadays about 20.000 Euros), consisting of nearly 600 double-page maps and 3000 pages of text. The analysed map (415x494 mm) was published in one of the volumes in 1640.

Techniques for paper and papyrus characterisation and for assessing the conservative treatments

In line with the complexity of writing materials, the methodologies used for paper and papyrus characterisation have been numerous. A multi-analytical approach has been selected to perform the diagnostic work; physical, mechanical and spectroscopic tests have been carried out before and after artificial weathering to determine the effects of ageing on the material structure, properties and durability. This approach makes use of several techniques: Thermogravimetry (TGA), Differential Scanning Calorimetry (DSC), Raman micro-probe spectroscopy, Infrared spectroscopy (Reflectance, ATR and FTIR), micro X-Ray Fluorescence (μXRF), X-Ray Diffraction, Optical Microscopy, Scanning Electron Microscopy (SEM) coupled to Energy Dispersive X-Ray Spectrometer (EDS) (followed by image analysis) and Nuclear Magnetic Resonance (^{13}C CP-MAS NMR). The most important characteristics of the selected instrumentation and techniques consist on their portability, the non-destruction of the samples and non-invasiveness of many of them during the analytical work. Besides, the evaluation of the mechanical properties, the degree of polymerisation (DP) and the colour measurements has been also performed.
It is worth to note that some of these methodologies have been applied to monitor the effects of enzymatic attack on writing materials, as well.

Thermal analysis: TGA and DSC
Thermal stability has been evaluated with a Perkin Elmer TGA 7 with nitrogen flow (4 cm^3 min^{-1}); the samples (3-5 mg) have been heated from 50 °C to 900 °C with the heating rate of 10 °C min^{-1}. The weight loss and its first derivative have been recorded simultaneously as a function of temperature.
A DSC Mettler Toledo 821e has been used with oxygen flow (120 cm^3 min^{-1}); the analysis was performed between room temperature and 650 °C with the heating rate of 5 °C min^{-1}, on 5-10 mg samples in an aluminium holder.

Optical Microscopy
The preliminary morphological characterisation of writing materials has been performed by optical microscopy, using magnifications: 14X, 20X, 40X and 90X. The microscope employed is an Optech PL 2000 (Germany) coupled with a digital camera Nikon Coolpix 4500.

Scanning Electron Microscopy (SEM-EDS)

The morphological observation has been carried out by Scanning electron microscopy (SEM) associated with EDS microprobe (Energy Dispersive Spectrometry). SEM images have been recorded using the Secondary Electron detector at three different magnifications: 500X, 1000X and 2000X. in the case of ancient samples observations at specific magnifications have been carried out.

EDS allows determining the elemental composition of each sample, in order to identify the nature of fillers. A Scanning electron microscope Stereoscan 440 Leica-Cambridge associated with an EDS microprobe Link-Gun Oxford have been used, after metallization of the specimen with a very thin layer of graphite, to obtain a good conductivity.

On SEM images of paper cross sections has been carried out the image analysis, in collaboration with the Université Sidi Mohamed Ben Abdellah, Fes, Morocco. Image analysis allows characterising the structural details of paper and papyrus, as the pore and filler distribution, the paper thickness and its surface roughness.

In order to obtain high-quality cross sections, suitable for the observation and the following image processing, an innovative method has been set up, based on the cold mounting of samples in a Struers® epoxy resin, mixed with a curing agent. Curing lasts 12 hours at room temperature; after, once the sample has been flatted, it is ready for the SEM observation at the most suitable magnification.

Colour Measurements

With optical measurement methods, the uniformity of colour can be objectively evaluated and presented as L^*, a^* and b^* coordinates named by CIEL*a*b* colour space values. These coordinates let to describe any colour and its perception in a three dimensional space (Figure 5), taking into account the "standard human eye response".

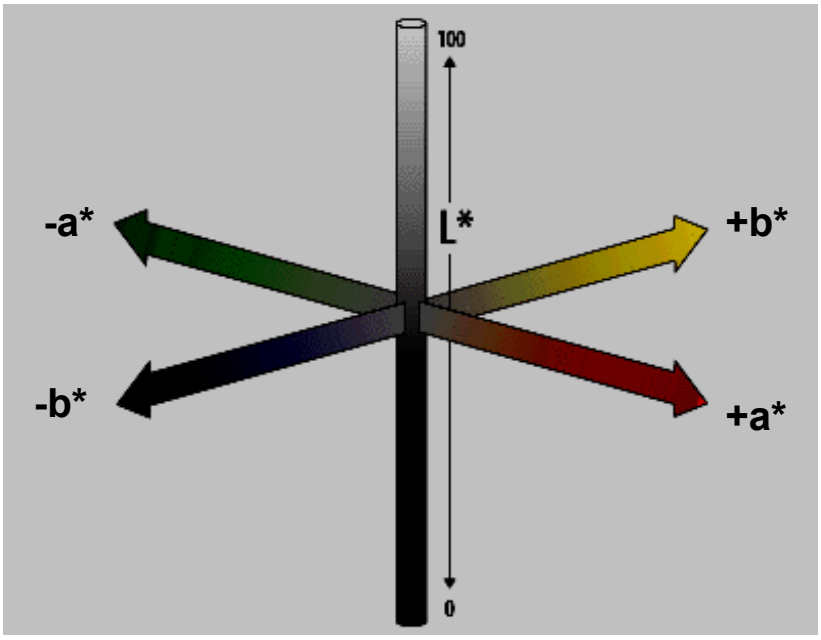


Figure 5: L*a*b* colour space

In this research a spectrophotometer Minolta CM-2600d with appropriate software (Spectra Magic 3.5) for the acquisition and the elaboration of data has been employed. The instrument has been calibrated with a white calibration plate CM-A415 (Minolta). Colour measurements (five tests for each sample) have been performed using a target mask with 3 mm viewing aperture, specular

component included (SCI), illuminant D65, and observer angle 10°. The colour parameters corresponding to the uniform colour space CIEL*a*b* have been obtained directly from the spectrophotometer.
The coordinate a^* is the degree of redness and greenness and it takes positive values for reddish colours and negative values for the greenish ones. The coordinate b^* is the degree of yellowness and blueness and it takes positive values for yellowish colours and negative values for the bluish ones. The coordinate L^* is the degree of lightness; it is an approximate measurement of luminosity, which is the property according to which each colour can be considered as equivalent to a member of the grey scale, between black and white, taking values within the range 0–100 [12].
Positive values of Δa* and Δb* indicate that the samples are more red and yellow, respectively, than the reference surface. Negative Δ*L** values indicate that the analysed area reflects less light than the reference surface.
Colour differences, which are very important to evaluate relationships between visual and numerical analyses, are calculated as the Euclidean distance between two points in the three-dimensional space defined by L^*, a^* and b^*:

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Polymerisation Degree Evaluation
The determination of the Polymerisation Degree (DP) has been carried out by viscosity measurements, performed at 25°C using a 0.5 M solution of cupriethylendiamine $[Cu(H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2)_2]^{2+}$ in water as solvent.
The viscosity values are related to the DP through the Mark-Houwink-Sakurada equation:

$$DP = K[\eta]^a$$

where K and a are experimental constants and [η] is the intrinsic viscosity.
Different equations have been proposed to evaluate the polymerisation degree, as that collected in the UNITEX CH 33 project [10] and that indicated by Evans and Wallis [14]. In our research, DP values have been calculated considering the equation proposed by the Scandinavian Pulp, Paper Board Testing Committee [13], in which the intrinsic viscosity is expressed in dl/g:.

$$DP = (35.7*[\eta])^{1/0.76}$$

Micro X-Ray Fluorescence (μXRF)
The elemental concentrations of paper and papyrus samples have been obtained by Energy Dispersive X Ray Fluorescence technique (EDXRF), in collaboration with the University of Lisbon.
The energy of emission lines in a XRF spectrum reveals the identity of the target atom (qualitative analysis), whereas the peak intensity is proportional to the quantity of atoms.
The spectrometer used in this work consists of an X-ray tube of tungsten, equipped with a changeable secondary target, normally molybdenum. This arrangement allows to obtain a monochromatic source and to select the secondary target in order to get the best excitation conditions for a special sample. The X-ray tube, the secondary target and the sample are in a triaxial geometry. With this arrangement the background decreases, taking the advantage of the effect of the partial polarisation of the incident X-ray beam from the tube, and thus, improving the detection limits.
The characteristic radiation emitted by the elements present in each sample has been detected by a Si(Li) detector, with a 30 mm^2 active area and 8 μm beryllium window. The energy resolution was

130 eV at 5.9 keV. The X-ray generator operated at 50 kV and 20 mA, with a typical acquisition time of 1000 seconds. A collimator of silver was placed in front of the detector in order to restrict the effective area of the detector to 25 mm^2, excluding the edges. All samples (minimum of seven measurements for each one) have been directly analysed without any kind of preparation.
Quantitative calculations have been made through the fundamental parameters method [15,16]. The relation between the measured peak intensity (I_i) and the concentration of an element C_i is given by the equation:

$$I_i=I_o m K_i C_i A_i$$

where I_o is the intensity of the X-ray beam, m is the sample thickness, K_i is an experimental calibration factor which depends on the spectrometer geometry, detector efficiency, detector solid angle and cross-sections for producing characteristic X-rays, and together with I_o is obtained by analysis of standard reference samples. A_i is the self-attenuation factor.
In table 4.2 the detection limits (DL) for the all the detected elements are reported; EDXRF is sensitive enough to detect almost all the heavy metals in biological samples, at concentration levels of 1μg/g (ppm).

	K	Ca	Mn	Fe	Cu	Zn	As	Rb	Sr	Co	Ni	Se	Pb
DL	70	50	4.0	3.1	1.2	1.2	0.5	1.2	0.6	1.2	1.5	0.8	1.9

Table 4.2: Detection Limits (μg/g) for EDXRF

X-Ray Diffraction
The X-ray diffraction spectra have been obtained in Bragg- Brentano geometry; the used equipment is an X ray Diffraction D5000 Siemens, with a copper anode and a monocrhomator for Cu Kα radiation (λ=1.5406Aº). The working conditions were 40 kV and 30 mA. The 2θ region was between 10º and 50º. The angle was changed in steps of 0.004º for 0.24 seconds.
Various methods and approaches for determining the percentage of crystallinity of the sample on the basis of the diffractograms obtained have been proposed in literature. A simple approach used by many authors (Bailey, Browning, Buschle, Roberts and Segal) [17] consists of taking from the diffractogram a suitable maximum and a minimum intensity to give a 'crystallinity value' (CrI), defined as:

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} 100$$

where I_{002} is the intensity of the crystalline peak at the maximum at 2θ between 22º and 23° for cellulose I (between 18º and 22° for cellulose II) and I_{am} is the intensity of the amorphous reflection at the minimum at 2θ between 18º and 19° for cellulose I (between 13º and 15° for cellulose II).

IR Spectroscopy
Infrared spectroscopy is practically indispensable for studying polymers, as cellulose, and their degradation, because it offers real insights concerning what happens at molecular level, whereas, for example, DP determination provides only a measure of the overall effects of degradation. Two ways of analysis can be followed:

- ⇨ in transmittance: Fourier Transform Infrared Spectroscopy (FT IR)
- ⇨ in reflectance: Attenuated Total Reflectance Spectroscopy (ATR) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).

In FT IR the analysed samples, in the form of self-supporting thin discs (KBr pellets), are crossed by the infrared beam; therefore the beam is firstly transmitted through the sample and after it is examined by the spectrometer.
ATR spectroscopy is used for analysis of materials surface; no sample preparation is required. It is suitable for the characterisation of materials which are either too thick or too strong absorbing to be analysed by transmission spectroscopy.
DRIFTS is a technique that collects and analyses scattered IR energy. It is used for measurement of fine particles and powders, as well as rough surface. Sampling is fast and easy because little or no sample preparation is required.
In this research IR analysis has been carried out in DRIFT and ATR modes both from 4000 cm^{-1} to 650 cm^{-1} at a spectral resolution of 4 cm^{-1}, recording 120 scans for each spectrum. IlluminatIR spectrometer by SensIR Technologies was used coupled to an Olympus BX51 microscope that implements a 15x IR reflectance objective and a 15x ATR objective. The spot of the IR beam was 100 μm to assure a good sensibility. The samples were analysed directly without any sampling or pellet preparation. This last characteristic is very useful when analysing real artworks in order to achieve non-destructive analysis.
The FT IR spectra have been recorded with a FT-IR Bruker IFS 66 spectrometer with a Globar source (silicon carbide brought up to incandescence), equipped with a water cooling system and OPUS data processing program. Samples have been analysed in transmittance, with accumulation of 50 scans and a resolution of 2 cm^{-1}. In this case approximately 1 mg of sample was used for the pellet preparation with KBr. Firstly, to reduce the humidity content in the cellulose and thus to prevent the overlapping between water and carbonyl bands in the spectra, a thermal treatment of pellets in oven at 80 ◦C for 2 days was carried out [13].

Raman Spectroscopy
A Renishaw RA100 System coupled to a Raman fibre optics micro-probe (785 nm diode laser, CCD detector) has been used (in collaboration with the University of Basque Country). Neutral density filters with an optical throughput of 1% and 10% implemented in the system were used to attenuate the laser power on the samples. Integration times of 30 seconds and 100 scans per spectrum have been accumulated to have a good signal-to-noise ratio. The head of the micro-probe implemented the 20X enlargement objective as well as a micro-video camera that helped to focus on the area under analysis. One of the main advantages of this device is the possibility to perform a totally non-destructive analysis directly over the samples, without any kind of sampling.

^{13}C CP-MAS NMR Spectroscopy
Samples have been finely cut and packed into 4 mm zirconia rotors and sealed with Kel-F caps. Solid-state ^{13}C CP-MAS NMR spectra have been performed at 50.13 MHz on a Bruker ASX-200 spectrometer. The spin-rate was always kept at 9 kHz. The 90° pulse width was 3.5 μs, the relaxation delay was 3 seconds, the contact time for the cross-polarization was 2 ms. The cross-polarization has been performed applying the variable spin-lock sequence RAMP–CP-MAS [18,19]; the RAMP was applied on the ^{1}H channel, the centre of the RAMP was set to the first matching sideband taking advantage of the faster cross-polarisation rate compared to that of the matching centre band. Spectra have been collected using 1024 data points in the time domain, zero-filled and Fourier transformed to a size of 2048 data points. The spectra deconvolution has been performed using the dm2004 program [20], selecting the Gaussian/Lorentzian model. Each resonance was modelled by the following parameters: amplitude, position and width at half height. Applying the best fit procedure the area and the chemical shift of all resonances have been calculated. The area of all resonances was normalised to 100.
Measurements have been carried out in collaboration with the ICM-CNR of Rome.

Mechanical properties

The normal use of paper includes its handling; therefore the evaluation of mechanical properties should be one of the principal focuses of all stability studies. In this research two mechanical tests specific for paper, evaluating the folding endurance and the tearing resistance have been performed, in collaboration with the University of Udine.

For the determination of mechanical characteristics big samples and in large amount are frequently needed, to ensure repeatability and reproducibility in the measurements. Therefore, mechanical tests can not be applied on ancient paper artworks, for which only very small fragment are usually available for the analysis.

Folding endurance is the paper capability of withstanding multiple folds before breaking. It is very useful in measuring the deterioration of paper after ageing and/or consolidation. Folding endurance is defined as the number of double folds that a strip of 15 mm wide and 102 mm length can withstand under a specified load before breaking. An harmonic Schopper-type tester has been used on strips of paper (10 cm in length and 15 mm in width), following the procedural standards described in the TAPPI Test Method T423 cm-98 "Folding endurance of paper (Schopper-type tester)". To perform a correct experiment, each sample is analysed both in a right-angled orientation according to the Machine Direction (MD) and in orientation according to the Cross Direction (CD). Results are expressed in terms of the folding number converted into the logarithmic form (Log_{10}MD and Log_{10}CD).

Tearing resistance represents the force required to tear a paper sheet. As reported in the TAPPI Test Method T414 om-98 "Internal tearing resistance of paper (Elmendorf-type method)", the right-angled dimensions of every specimen must be rigorously 63 mm x 53 mm; the tester is a pendulum type instrument, TMI testing machines Inc., Elmendorf tear tester, which measures the force perpendicular to the plane of paper required to tear the paper through a fixed distance. As for the folding endurance test, also in this case the samples were orientated according to both the Machine Direction (MD) and the Cross Direction (CD). The tearing resistance, expressed in mN, is calculated by the following equation:

$$\text{Average tearing resistance} = (16 * 9.81 * \text{average reading})/ \text{n° of plies}$$

Also mechanical tests till breaking have been performed with an Instron 5574 tensile testing machine, operating with 5 mm gauge length, cross-head speed of 10 mm/min at 25°C and relative humidity of 60 %. Before testing, samples were conditioned for 24 hours at 60 % relative humidity and 25 °C. An average of 15 tests for specimen type was used to calculate the tensile properties.

Techniques for assessing the efficacy of the conservative treatments and for monitoring their durability

Specific techniques, in addition to those reported in the previous paragraph have been applied to asses the efficacy of the conservative treatments and to monitor their durability when the writing materials are submitted to an enzymatic attack (see Chapter 10) and to artificial weathering in two different ways:

- ⇨ In climatic box at 80 °C, RH 65%, without light radiations and air polluting, for 12, 30 and 60 days
- ⇨ In accelerated ageing chamber XENOTEST ISO ST at 50 °C, with RH cycling between 50 and 70 % each 12 hours, for 10 days, under a xenon light source (power 5000W).

The consolidate samples have been submitted to the ageing treatment following a procedure

consisting in three phases of extraction at 12, 30 and 60 days.
Particularly, the wetting behaviour of treated writing materials before and after weathering has been evaluated by water absorption and contact angle measurements.
Specific measurements of paper porosity have been carried out and Synchrotron X-ray powder diffraction patterns have been collected on the consolidate samples.

Water absorption
To evaluate the protective effect of any conservative treatment onto the writing materials, a water absorption test has been carried out, on three specimens (2 x 1 cm^2) of each sample of paper and papyrus to ensure reproducibility.
Each specimen is soaked in deionised water; the amount of water absorbed is determined by weighing the specimen after 10, 20, 30, 40 and 50 minutes and 1, 2, 3, 4, 5, 6, 8, 24 and 48 hours, to obtain the wet specimen mass (± 0.0001 g). The amount of absorbed water Q_i, at the time t_i is defined as:

$$Q_i = (M_i - M_0) / M_0$$

where M_i is the specimen mass (g) at the time t_i and M_0 is the dry specimen mass (g). The Q_i values are plotted against the time to give the water absorption curve; by comparing untreated and treated materials, the improvement of water repellence can be evaluated.

Contact Angle measurements
Contact angles have been measured with an optical Kruss goniometer, model G-1 N° 88127. A 1.5-2 mm diameter drop of water, dripped from a microsiringe, has been put on the sample surface, and immediately the value of the contact angle between the water drop and the material has been measured.

Synchrotron X-ray powder diffraction
Synchrotron X-ray powder diffraction patterns have been collected on the High-resolution Powder diffractometer of the beam line ID31 at ESRF (Grenoble, France) with a wavelength λ = 0.79483 A.
ID31 is dedicated to High-resolution Powder diffraction; it is placed on an insertion device, with three undulators, allowing the energy range from 5 keV to 60 keV. Energy (or wavelength) of the incoming X-ray beam is selected with a double-crystal Si(111) monochromator, calibrated and refined using Si NIST powder (a = 5.43094 Å) from the position of the first 10 Si reflections. Fragments of paper have been rolled and placed in brass sample holders (~2 mm diameter), mounted on the axis of the diffractometer and spun during measurements at about 1000 Hz. Data have been collected for about one hour each sample, and rebinned into steps of 2θ = 0.025 deg. A bank of nine YAP detectors (Yttrium Aluminium Perovskite scintillators) was scanned to measure the diffracted intensity as a function of 2θ. Detectors are ~2° apart; each is preceded by a Si(111) analyser crystal. The nine crystals are scanned together, as a unit, effectively measuring nine high resolution diffraction pattern in parallel, with 2° between them [21].

Porosity
Porosity has been calculated following the Gurley Method (TAPPI T 460 om-06 "Air Resistance of Paper Test Method", in which the resistance to the passage of air, offered by the paper structure, when a pressure difference exists between two sides of paper, is evaluated. It is measured as the time (in seconds) for a given volume of air (100 cm^3) to flow through a specimen (with circular section of 10 cm^2 surface) under specified conditions (P = 4.88 water inch). The result indicates the

seconds needed to the 100 cm^3 of air to pass throughout the paper depending on the amount of voids present on it (porosity).

Techniques for characterising the polymeric materials

The most part of the techniques usually employed to characterise any material have been described. However, to know exactly the properties and the behaviour of polymers, usually also additional methods are used. In this research the complete characterisation of polymers used as consolidating products that is acrylics and polyurethanes, has been performed with the following techniques:

- *Differential scanning Calorimetry (DSC)*
  The glass transition temperature have been evaluated with a TA Instruments (Newcastle, DE) DSC 2010 differential scanning calorimeter at a heating rate of 20°C/min; traces were recorded in the temperature range of -120 to 150°C. To eliminate any effect of the thermal history, Tg measurements were made from a second heating cycle, after the heating of the sample up to 150°C at 20°C/min, followed by quenching down to -100°C.

- *AFM observation*
  AFM is an ideal tool for studying film formation of polymeric dispersions such as latex coatings. The technique has high spatial resolution, is fast and non-destructive, and measurements can be carried out in both air and liquid.
  The polymeric substrates have been studied by atomic force microscopy (AFM) in air by tapping mode, using a AFM PSIA XE-100 operating in air and using a probe with a conical tip in silicon assembled on a Mikromasch cantilever. Tapping mode is an extremely useful technique for topographical imaging of soft samples (latex films, paper coatings, etc.), because it effectively eliminates lateral and shear forces. The tip gently taps the surface while resonating at a certain frequency, thus significantly reducing the contact time. AFM scans of the surface have been performed with a scan rate of 0.5 Hz and driving amplitude of the cantilever of 25 mV. Performing the scans at relatively low scanning rates and driving amplitudes minimised possible artefacts due to tip contamination. Experiments have been carried out at 22 °C with about 40% RH, in collaboration with the University of Turin.

- *TEM observations*
  TEM analysis has been carried out at 80 kV with a Zeiss EM 900. Ultrathin sections (50 nm thickness) of the specimens, cooled at −80 °C, were obtained by cryoultramicrotomy with a diamond knife cooled at −60 °C.

- *Dynamic-mechanical thermal analysis*
  DMA was carried out with a TA Instruments DMA 2980 dynamic mechanical analyser. The samples have been run in the tension mode operating at an oscillating frequency of 3 Hz and a heating rate of 2°C/min under nitrogen. The samples were approximately 10 mm wide, 20 mm long and 0.3 mm thick. Tan δ was recorded from -80 to 100°C.

- *NMR spectroscopy*
  The investigation of the hard /soft ratio in the PU waterbornes with different hard segment content has been carried out performing ^1H low resolution NMR measurements. ^1H low resolution NMR measurements were carried out at 18MHz on a commercial spectrometer Spin Master2000 (SM2000), Stelar Mede Pavia (Italy). Paper samples were introduced into standard 5mmNMR tubes, and the height of samples was kept well within the NMR coil (5 mm).

- *SAXS and WAXS*
  SAXS and WAXS intensity profiles of polyurethanes have been collected in transmission by a PW 1710 Philips Diffractometer (CuKα Ni filtered radiation, λ = 0.15418 nm). High voltage was 40 KV and tube current was 30 mA. SAXS measurements have been performed at 2θ between 0.2° and 4°, whereas WAXS at 2θ between 2.5° and 60° (step width 0.03° and counting time 10 s).

Other methodologies as:

- *Thermogravimetric analysis*
- *FTIR and Raman spectroscopy*
- *SEM observations*
- *Colorimetric analysis*

Have been also used.

In addition, other characteristics have been evaluated, as:

- *Evaporation kinetic*
  The amount of solids present in each PU waterborne has been determined by controlled casting at room temperature; in this way evaporation curves, highlighting the evaporation kinetic, have been obtained. Casting has been carried out putting the waterborne in a Teflon box and covering it with an aluminium foil with 15, 30 and 50 holes respectively. For comparison films have been prepared also in open Teflon box.

- *Solubility*
  Test on solubility have been carried out on film obtained from the PU waterbornes, looking at the possible reversibility of the polymers when applied on paper artworks. Small fragments of each film (~ 100 mg) have been immersed in 10 ml of the selected solvents: acetone, dimethyl formamide and N.methylpyrrolidone. Solubility has been checked after 1, 7 and 15 days.

- *Mechanical properties*
  Mechanical tests till breaking have been performed with an Instron 5574 tensile testing machine, operating with 5 mm gauge length, cross-head speed of 20 mm/min at 25°C and relative humidity of 60 %. An average of 15 tests for specimen type was used to calculate the tensile properties.

- *Resistance to abrasion*
  The resistance to abrasion of polymeric coatings has been evaluated following the standard test method ASTM D 968-81 (1986). This test allows the determination of the resistance of organic coatings, as polymer films, to abrasion produced by abrasive falling of a standard abrasive, as silica sand of well defined granulometry. A given volume of abrasive (2 litres) falls from a specified height trough a guide tube onto a panel on which the analysed polymer has been coated. The resistance to abrasion is measured as the variation in the thickness of coating (ΔS) due to the abrasive action of sand.

- *Contact angle*

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PART-A

COLORED PLATES, MENTIONED IN THE TEXT BUT HEREAFTER VISIBLE, OUT OF THE TEXT, GROUPED ACCORDING TO THE CHAPTER OF AFFERENCE

CHAPTER A.1:

The "PAPERTECH" Project: Innovative materials and technologies for the conservation of paper of historical, artistic and archaelogical value.
Structure, Partenership, Objectives and Outputs.

By Domenico Acierno and Ezio Martuscelli

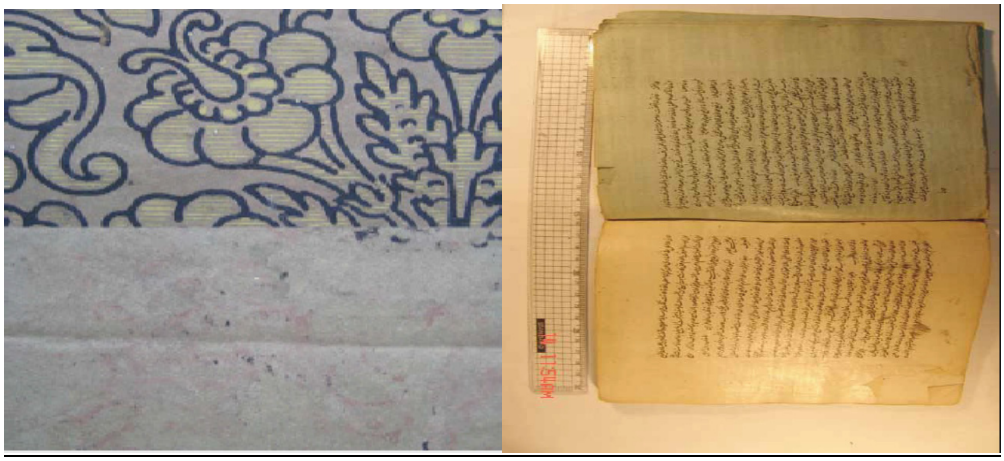


PLATE A.1.1 : Samples of works on paper part of PAPERTECH Catalogue. Left: Wallpaper (Vertical bands on the wall) from Santa Isabel wallpaper factory (Vitoria-Gazteis, Basque Country, Spain). Second half of XIX$_{th}$ century, Code: 4/32. Right: Arabic manuscript from the Central Library of Cairo University, Department of Ancient Manuscript, Code: 2/8 [7].

CHAPTER A.2:

The chemistry of treatments of consolidation and strengthening of works on paper based on the use of polymers (Status of art)

By Ezio Martuscelli

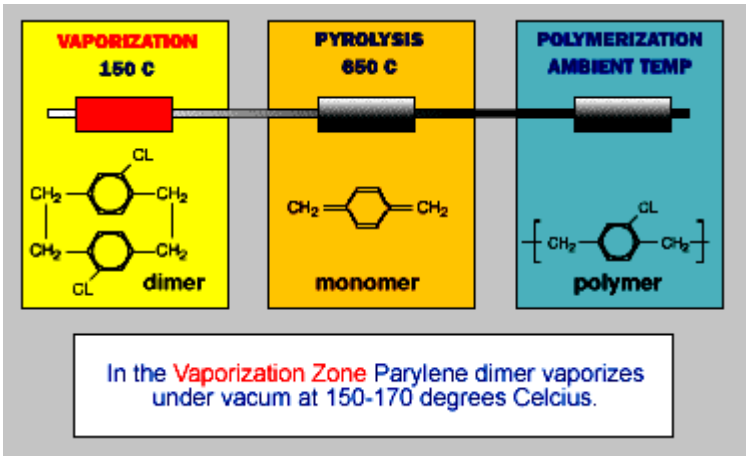


PLATE A-2.1: The phases of the Parylene process, based on a vapour deposition polymerization technology (see text) [12].

PLATE A.2.2: Photo of Taiwan Plant Atlas plates (published in 1911) coated with:Left, Parylene-C; Right, Parylene-N [13].

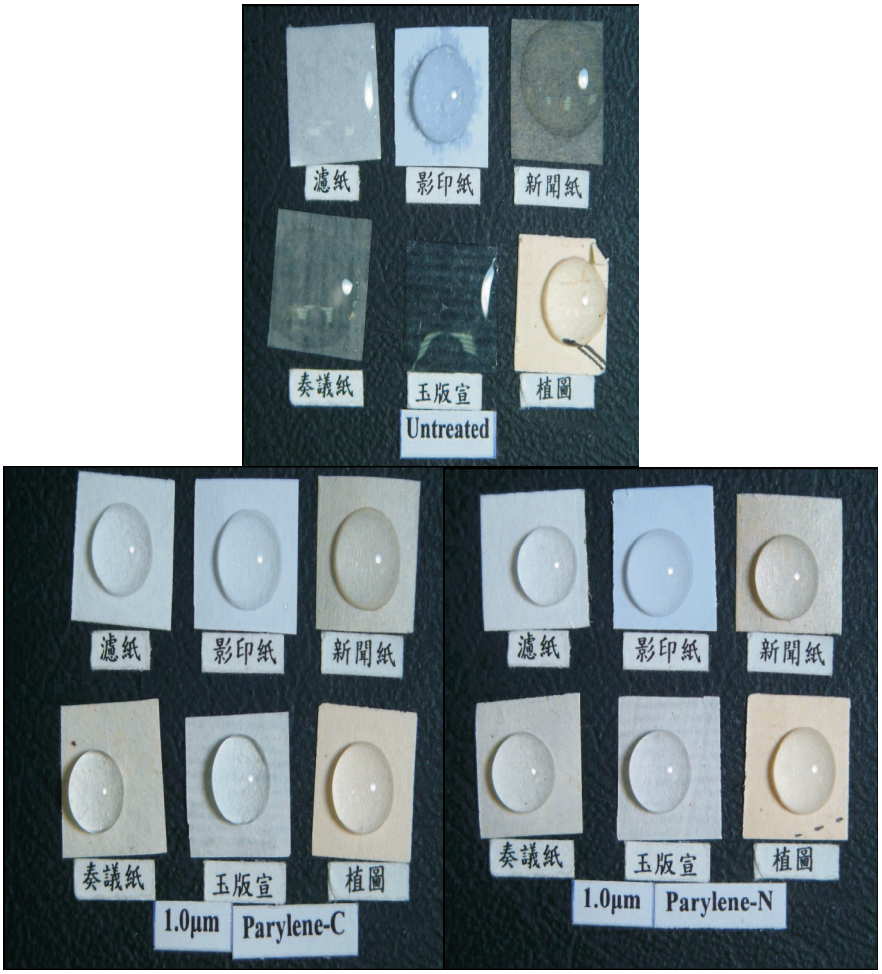


PLATE A.2.3: Water dropping test on Parylene-N and Parylene-C coated paper surfaces. Top, no-treatment; Down-left, Parylene-N at 1 μm; Down-right, Parylene-C at 1 μm [13].

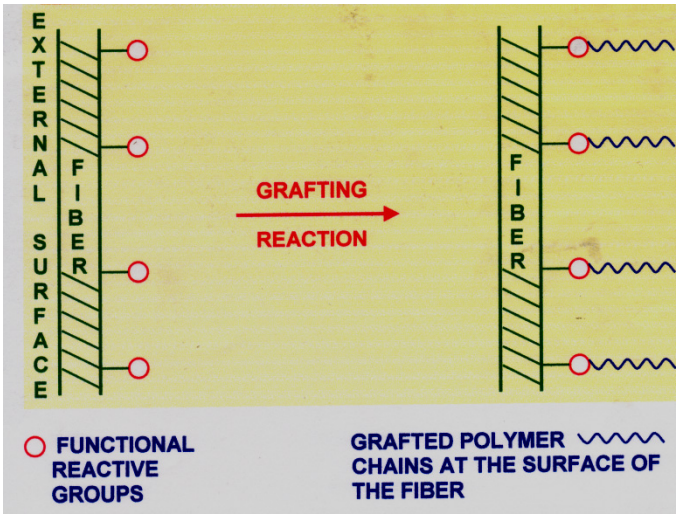
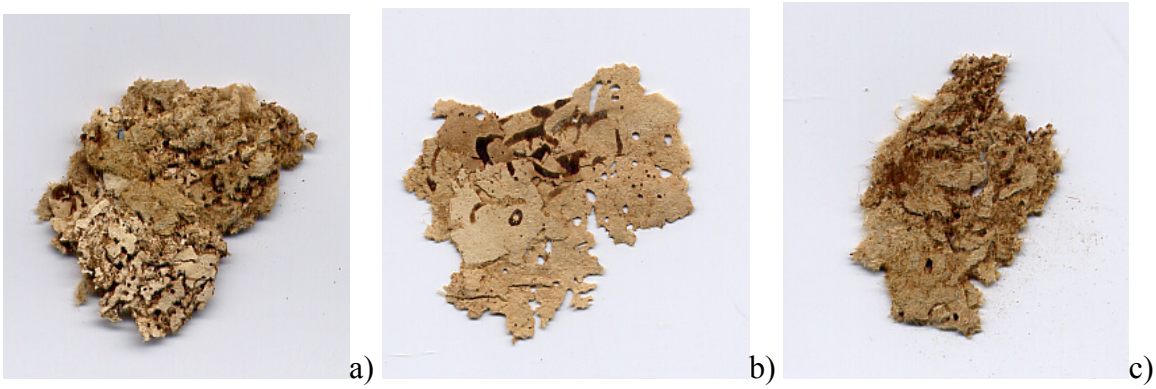


PLATE A.2.4: Schematic view showing the grafting formation of a cellulose fibre[2,3].

CHAPTER A.3:

The selection of works on paper: Ancient and modern samples.
Natural and artificial weathering and techniques for paper and papyrus characterisation and for assessing the conservative treatments

By Elisabetta Princi



a) b) c)

PLATE A.3.1: Fragments coming from the manuscript dated 1761:
a) 3-16, b) 3-18 c) 3-

PLATE A.3.2: Recto and verso of wallpaper 4-29

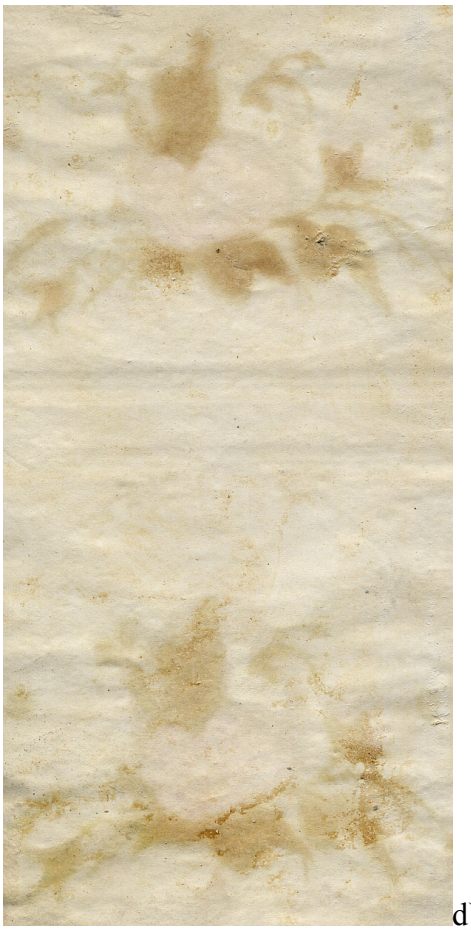

c)

d)

PLATE A.3.3: Recto and verso of wallpaper 4-30

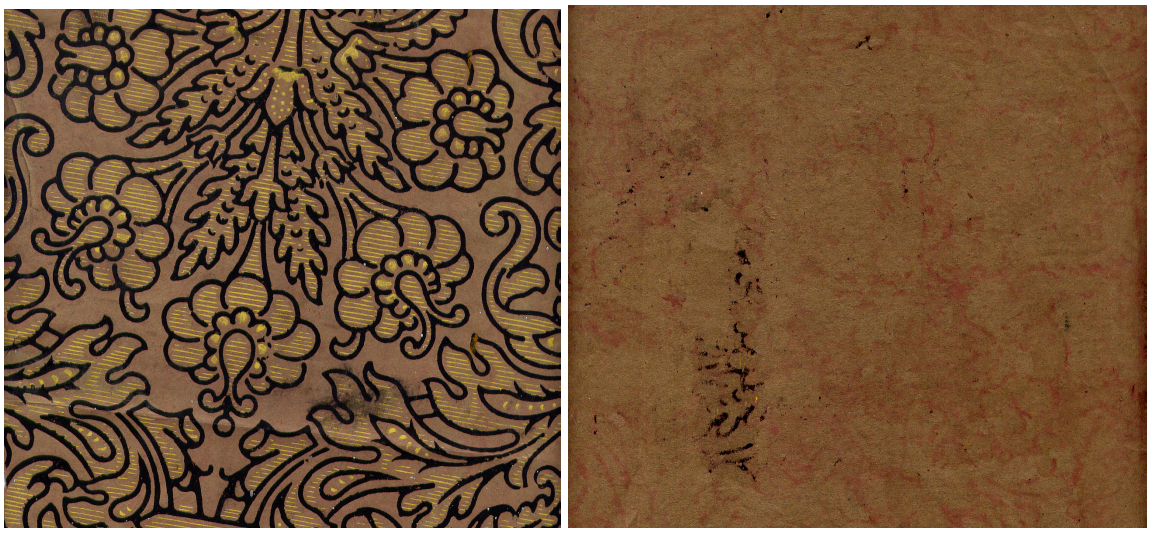


PLATE A.3.4: Recto and verso of wallpaper 4-32

PLATE A.3.5: Vicenza map (4-35); on the right a particular with evident traces of oxidation induced by the green pigments