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STUDY ON SOME RESIZING AND CONSOLIDATION METHODS OF OLD PAPER SUPPORT

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Abstract

This paper focuses on the study of new, non-conventional evaluation methods, for resizing and consolidation of archives documents. These methods are new in comparison with the classic methods and are based in principal on the utilization of cellulose derivatives.

Keywords: paper conservation, resizing, chitosan, AKD

1. Introduction

Paper is an essential part in cultural and economic progress of humanity. The books, meticulous illustrate manuscripts, printing press, the papers, archives documents are a precious thesaurus, which must be conserved and transmitted to the next generation. The paper is an organic material and it is under the action of many degradation factors: physical, chemical, biological or social.

Under the action of degradation factors the support paper is straining, decolorizing, closing at colour, cracking, melding or is attacked by insects.

An aspect of paper deterioration is loosing the sizing agent. The losing of sizing agent is a consequence of humidity attacker, which is dissolving the sizing agents after cleaning operation. The paper with an affected sizing agent became absorbing, lose the characteristic noise and is more expose at the physical, chemical and biological factors (Figure 1).

For preventing total deterioration of the documents, usually are applied consolidation treatments, which have the following objectives: replace the lost sizing agent, improve the mechanical properties and rigidity of sheet paper, give characteristic noise, stop bleeding ink on the document surface, give strength under acids action, give strength at oil penetration, reduce sticky dust on document surface.

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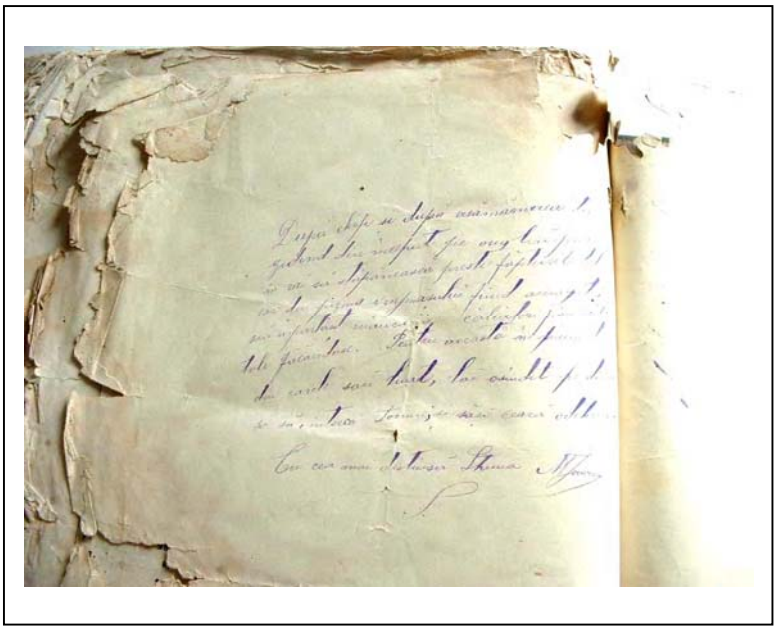


Figure 1. Document with affected sizing agent (Pidalion, 1844).

The consolidation treatments have two aspects:

1. Resizing stage: the document is covered with a sizing agent, in purpose of replacement the lost sizing agent;
2. Consolidation stage: the document is partial or totally covered with different films or materials in view of improvement the mechanical properties [1].

By many years, conservators and restaurateurs from Europe and USA use cellulose ethers in the domain of paper restoration, especially sodium chloride of carboxymethylcellulose (CMC) and methylcellulose (MC), (the first one has been used mainly in Europe, and the second one by specialists from USA) [2].

The treatments of consolidation, which use these ethers of cellulose, have some limits, one of these being the poor improvement of the strength at liquids penetration. Keeping in mind all these facts, we decided to test other materials like consolidation agents for paper.

2. Experimental

2.1. Materials

The support is a manual paper from the 19th century, without patrimony value, made from textile fibres, the sizing being made with gelatine.

The following materials were used for consolidation and sizing:

- Conventional: methylcellulose (MC) and carboxymethylcellulose (CMC) in water solution, with concentration of 1%;

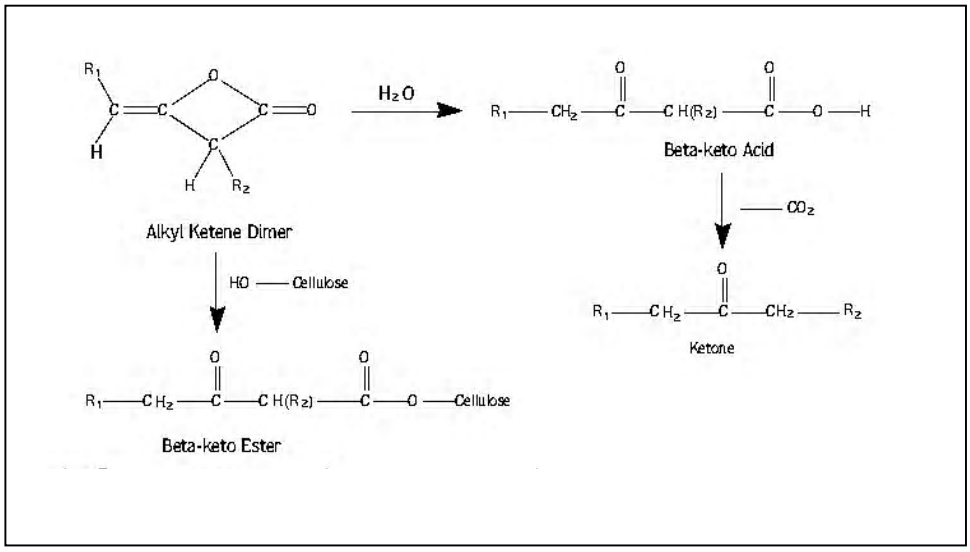
- Non-conventional: cationic starch (AC), alkyl ketene dimmers (AKD) and chitosan (CH) in different combinations.

AKD's are waxy materials which are insoluble in water and have a melting point around 50^0 C depending on chain length. Commercial AKD's are prepared from natural fatty acid sources and stearic acid, by the dimerisation of acid chlorides and they are used in neutral systems of paper sizing. Industrial AKD's might have a different side chain lengths due to the fact that the source material itself could have a variety of chain lengths [3].

AKD are described as having:

- Hydrophobic character: the AKD molecules contain relatively inert hydrocarbonate chains, which give the hydrophobic properties;
- Uniform distribution at the fibbers surface: in order to obtain good distribution of these materials at surface of the fibres, the solid substance is emulsified as very small particles (<1μm) and is stabilized with cationic starch;
- Stabilization of sizing particles: the AKD molecules have a reactive part that reacts with the hydroxyl groups on the fibbers surface forming covalent bond;
- Sizing action inert to the liquids: this characteristic is the result of the solid molecules consolidation at the fibbers surface as well as of the capacity of hydrocarbonate chains to cover larger surfaces [4].

The reaction between cellulose and AKD was performed at a low rate and was catalyzed by alkalinity (Scheme 1).



Scheme 1. Reaction of AKD with cellulose and water [5].

Chitosan is one of natural polymers with important applications in medicine, pharmaceutics industry, biotechnological, cellulose and pulp industry, textile industry, cosmetic. Studied since 1970, it was discovered in the exo-skeleton of the crustaceans.

Chitosan is a carbohydrate polymer derivate from chitin, with straight structure formed by units of D–glucosamine, has aminoreactive groups that give them a cationic character (Figure 2). It also contains hydroxyl groups that give them the ability to from hydrogen bond; is biodegradable, biocompatible and bioactive.

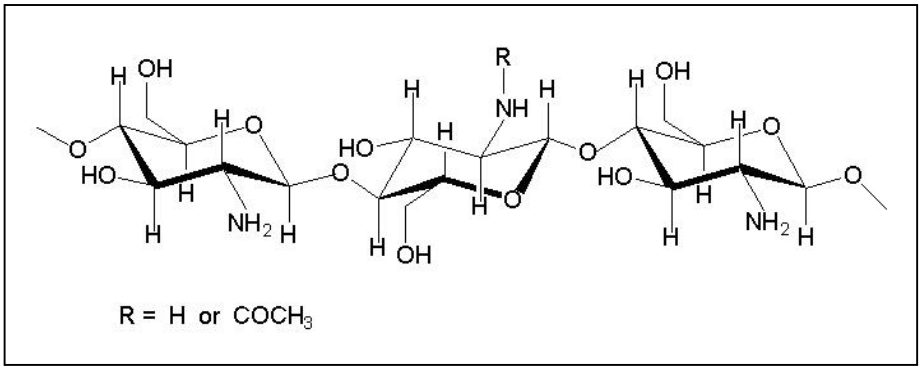


Figure 2. Schematic illustration of chitosan's structure [6].

In papermaking, chitosan is used due to the similitude with the structure of the cellulose molecules. The paper with chitosan has a smoother surface and they are more resistance at the humidity action. When added, chitosan offers the opportunity of economizing the chemical additives used in papermaking and contributes to the productivity increase [7-9].

2.2. Working methods

The paper samples have been washed with distillate water and deacidified by a calcium hydroxide solution. The sizing–consolidation treatments were made on the washed samples and deacidified trough applying the treating solution with a brush on both faces of the paper. The method was detailed described elsewhere [10].

The sizing-consolidation on the proposed solutions are:

- Solution of CMC,
- Solution of MC,
- Solution of AC + CMC,
- Solution of AC + AKD,
- Solution of AC + AKD + CH.

The total amount of solution and of dry substance from each sample (X), has been gravimetrically determined:

$$X = (m_1 - m_0) \cdot c_i / m_0 \quad (1)$$

The determinations were made for the original paper samples, which were washed and deacidified, then treated with conventional and non-conventional materials.

For the washed, deacidified and chemically treated samples were physico-mechanical analyses were performed, determining the following parameters:

- pH of water extract,
- sizing degree – Cobb number (T441 om-90),
- bursting strength and
- tensile strength.

The samples treated with different sizing–consolidation solutions, have been dried in air and conditioned for 4 hours in standard conditions.

3. Results and discussion

3.1. Evolution of the pH of water extract

The progress of the pH of water extract, during the consolidation treatments with different agents is represented in Figure 3. We observe that the deacidification treatment gives a small increase of the pH, which will rise during the consolidation treatments with different agents. The CMC solution, with the highest contribution to alkalinity leads to the highest pH increase.

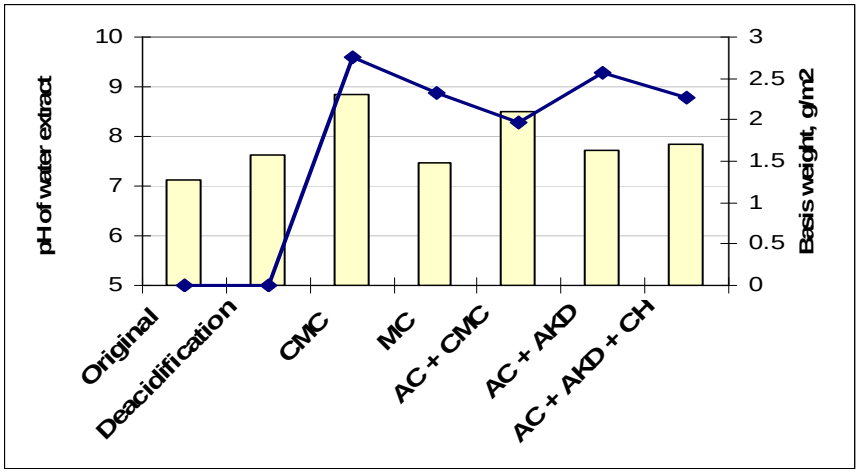


Figure 3. Evolution of pH for the samples treated with different solutions.

3.2. Cobb number

As we expected, the deacidification and the treatments with cellulose derivatives, in special CMC gives a rise on the suction capacity of water. The only treatment, which gives a decrease of Cobb number, is the one based on AC, AKD and CH.

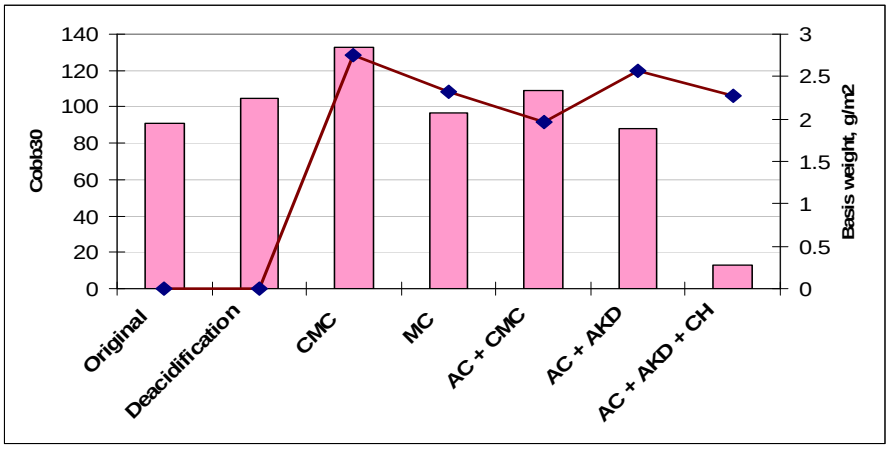


Figure 4. Evolution of Cobb number.

3.3. Bursting strength

The treatment with CMC results in the highest weight of the film and determinate an improvement of strength at bursting, but the other compositions have consolidation effect too.

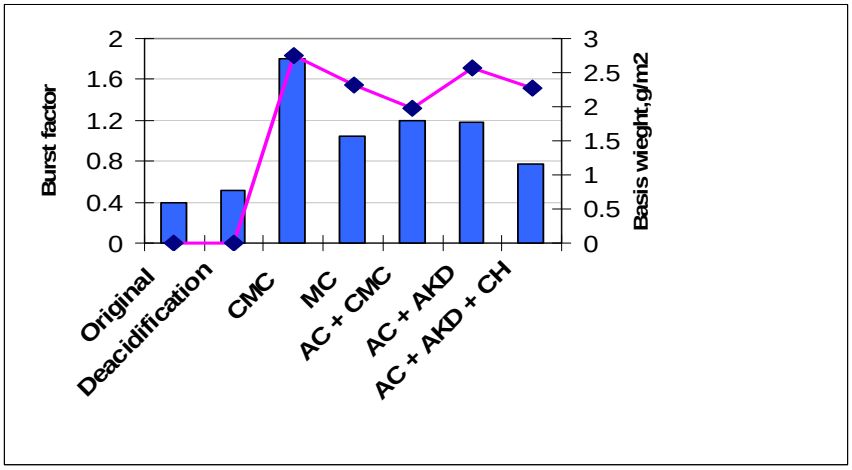


Figure 5. Evolution of bursting strength.

3.4. Tensile strength

The treatment with CMC improves the tensile strength by four times. The other composition gives an important rise of strength, specially on the longitudinal direction.

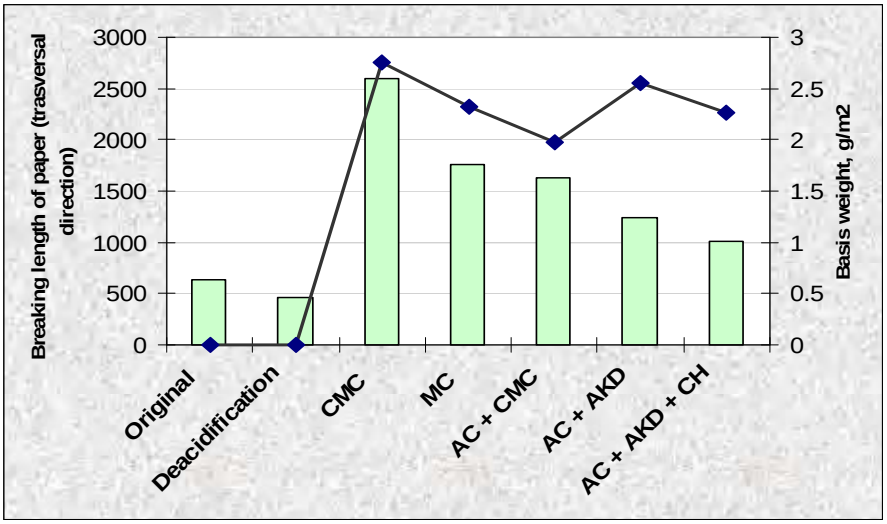


Figure 6. Tensile length – frontal.

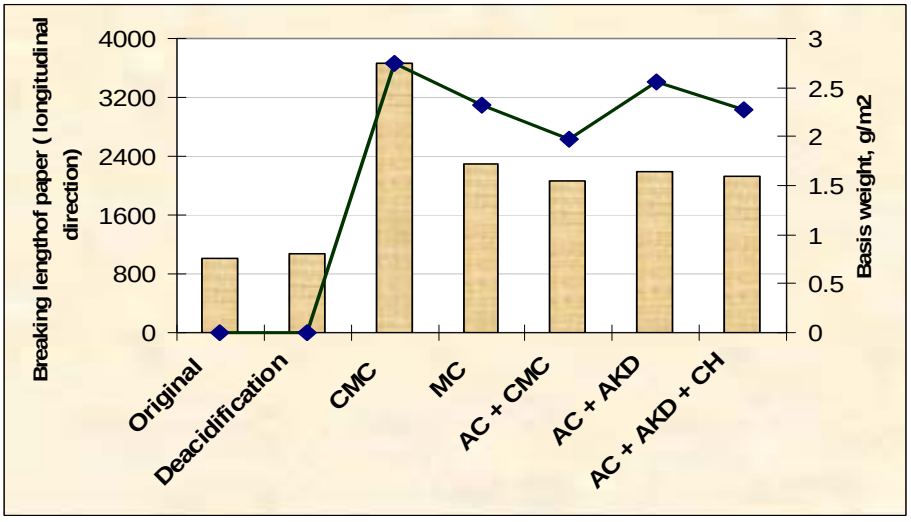


Figure 7. Tensile length – longitudinal.

4. Conclusions

The derivatives of cellulose, conventional materials used in restoration of documents, especially CMC, are very efficient in consolidation and in rise of mechanical strength of the old paper.

Derivatives of cellulose do not improve the sizing degree, but on the contrary they produce a rise of the water penetration capacity.

Non-conventional formula of paper treatment (AC/CMC, AC/AKD, AC/CH) gives the following results:

- the AC/CMC formula improves the strength of paper, but raise the capacity of water suction;
- the AC/AKD formula improves the strength without rising the water suction degree, like in case of conventional formula;
- the AC/CH formula gives a very good degree of sizing and a resizing degree strength similar with another formula based on cationic starch, as well as those based on MC.

The use of chitosan as well as of the AKD in the domain of the paper conservation and restoration is an objective perspective, but there are other aspects that must been studied: the compatibility with different components of paper; the behaviour regarding the action of different degradation factors; the behaviour of supports treated for accelerated aging.

The general conclusions of these experiments are that the conventional treatment of paper consolidation, based on derivatives of cellulose, can develop a new formula based on combination by of cellulose derivatives and sizing agents of documents on the paper support.

References

[1] V. Vinas and R. Vinas, *Les tehniques traditionnelles de restauration: un etude RAMP*, UNESCO, Paris, 1992, 34.

[2] R.L. Feller and M. Wilt, *Evaluation of Cellulose Ethers for Conservation*, The Getty Conservation Institute, Los Angeles, 1990, 105.

[3] J.C. Roberts, *Neutral and alkaline sizing*, in Paper Chemistry, J.C. Roberts (ed.), 2nd edn., Blacklie A&P, Glasgow, 1996, 140.

[4] E. Bobu and V. Popa, Procese chimico–coloidale la fabricarea hârtiei, Cermi, Iaşi, 1998, 162.

[5] K.J. Bottroff and M.J. Sullivan, Nord. Pulp Paper Res., **8** (1993) 86.

[6] M. Hiorth, A.-L. Kjøniksen, K.D. Knudsen, S.A. Sande, and B. Nyström, Eur. Polym. J., **41(8)** (2005) 1718.

[7] C.D. Kienzle-Sterner, D. Rodriguez-Sanchez and C.K.Rha., *Solution properties of chitosan chain conformation*, in Chitin, chitosan and related enzymes, Academic Press, New York, 1984, 383

[8] G.G. Allan, J.R. Fox, G.D. Crosby, and K.V. Sarkanen, *Chitosan, a mediator for fiber-water interactions in paper*, College of Forest Resources. University of Washington Press, Seattle, 1977, 125.

[9] M. Del Pilar Ponce -Jiménez, F. A. López-Dellamary Toral and E. Delgrado Fornué, Journal of the American Institute of Conservation, **41(3)** (2002) 243.

[10] C. Crespo and V. Vinas, *La preservation et la restauration des documents et ouvrages en papier*, UNESCO, Paris, 1984, 78.