
# Innovation in Paper Preservation: Green Chemical Treatments - First Results

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## Abstract

Aim of the presented research is the exploitation of the effects of new sustainable compounds for paper restoration and protection: green ionic liquids (IL) and a polysaccharide extract from the cyanobacterium Arthrospira maxima (PE). The sustainability of the proposed compounds in paper treatment was taken into account with respect to operators and environment safeguard; further, all feedstocks are renewable so that also the economic aspect is positively considered.

Here the aim is to define a significant level of stress in paper, necessary for the successive testing of the effect of the proposed compounds: ionic liquids and polysaccharide extract. In this second stage a potential restoring effect is evaluated by comparing characteristics of aged samples before and after treatment with the compounds of interest; in parallel, a potential protective effect of the studied compounds is evaluated by comparing characteristics of treated samples before and after aging. The results deserve further deepening researches.

## Introduction

During natural ageing, paper undergoes colour changes and becomes brittle. This is mainly due to the degradation of cellulose, which suffers acid-catalysed hydrolysis and oxidation in a mixed mechanism [1-3], where the reactions are autocatalytically accelerated by protons and by reactive oxygen species. Current paper preservation is thus based, overall, on deacidification-treatments and physical reinforcement. The present work studies innovative and sustainable products for paper protection and restoration: cyanobacterial polysaccharides and green ionic liquids.

Polysaccharides contained in or produced (intra- or extracellularly) by algae and cyanobacteria for nutrition and/or defense are currently hot topics in research, because of their peculiar properties, longing from antiviral to antifungal to antioxidant. In this context, the ascertained antioxidant activity of the Arthrospira maxima polysaccharides [4] could have an interesting side effect.

IL are defined as liquid salts at room temperature, in fact they are also called Room Temperature Ionic Liquids (RTILs). Among a large number of ILs that have been synthesized and characterized, traditional ILs that consist of imidazolium or pyridinium cations and halide-containing anions have been demonstrated to be highly toxic and poorly biodegradable. The goal is to obtain ILs that can unite the most relevant properties with biocompatibility. For this reason, reaction media entirely composed of biomaterials have been developed. In our study we focus on ILs of this new type composed by choline, as cation, and aminoacids as anion. The sustainability of both proposed treatments was taken into account with respect to operators and environment safeguard; further both types of compounds are obtained from renewable feedstocks.

## Materials & Methods

Our work plan is composed by two steps: 1) accelerated aging of different paper samples; 2) assessment of treatment effects. Paper samples before and after treatment + accelerated aging and accelerated aging + treatment were compared using the same analytical techniques.

A spectrophotocolorimeter (CM-2600d by Minolta, Japan) was used to evaluate colour changes; pH-meter (Crison GLP-22, Spain; Metrohm 6.0227.100 flat pH-electrode, Switzerland) for pH determination (cold extraction); Attenuated total reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR) (Bruker Interferometer alpha, England) was used to track chemical changes; we use also a folding resistance test to track changes in physical properties.

Paper samples: Whatman filter paper (pure cellulose without sizing agents, 87 g/m$^2$) and two types of commercial white paper (Fedrigoni SpA, with sizing agents and different fiber composition,

90 g/m$^2$). Accelerated aging was carried out by UV irradiation (QUV Accelerated Weathering Tester, Q-PANEL Company, USA), or dry heat at 105°C in an oven (M-710 Thermostatic oven, Galli, Italy) in accordance to ISO 5630-1.

LIs and PEs were synthesized/extracted and characterized by ourself.

## Results

The folding resistance test, carried out on Whatman paper; new, aged at 105°C for 4 days or exposed to UVB radiation, were treated with IL or with PE and compared. For both treatments a positive effect, in terms of increased mechanical strength, was evidenced.

| | Unaged Whatman | Whatman heat-dry aged (4 days) | Whatman treated with polysaccharide extract and heat-dry aged (4 days) | Whatman treated with ionic liquid and heat-dry aged (4 days) |
|---|---|---|---|---|
| Average | **13.1** | **2.3** | **4.3** | **5.0** |
| Dev.std | 0.7 | 0.1 | 0.1 | 0.2 |

**Results of the mechanical test of strength double fold; a greater number of folds after breaking of the sample is due to a greater resistance of the paper. Comparing of unaged Whatman paper, aged in an oven for 4 days (days) and previously treated with algal extract or ionic liquid (LI). The averages shown are for 12 consecutive measurements.**

No significant variation of pH (cold extraction) come from the thermochemical aging (0, 4, 11, 44 days) and photochemical aging (0, 50, 100 hours) of all the paper samples.

A significant reduction of the spectral reflectance resulted for the Whatman paper, heat-dry aged already for 4 days, letting to an optical effect of yellowing. On paper treated with IL or PA the colour difference is minimal.

An increase of bands relating to the "fingerprint" zone of cellulose was evidenced by ATR-FTIR on unaged paper treated with algal extract. Considering variations in intensity of certain bands, such as that at 900cm$^{-1}$, as indicators of aging, it seems reasonable to assume that the prior treatment with algal extract has had a positive effect on the aging of the paper. The same result was also obtained on aged paper treated with IL.

## Conclusions

This research follows the current draft of the sustainable restoration, researching innovative and non-toxic products including ionic liquids and a new generation of algal extract for possible applications to the protection and restoration of the paper. The products were synthesized/extracted, characterized and now we are evaluating their effect. This evaluation uses treated and untreated samples and artificially aged on which were recorded the FTIR spectra, colour changes, pH and mechanical strength. To continue the process many experimental aspects are still to be assessed (the effects of different concentrations, biological evidence with respect to biodeterioration, etc.). However, the early results are encouraging, particularly in relation to the increasing on mechanical strength and the negligible aesthetic effect of treatments.

## References

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