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Original article

Alcoholic deacidification and simultaneous deacidification-reduction of paper evaluated after artificial and natural aging

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ABSTRACT

Cellulose oxidative and hydrolytical degradation is one of the greatest problems for the conservation of paper supports. To contrast these degradation processes, both deacidification and reduction of the oxidized functions are needed. Dealing with original documents, it is often impossible to perform the two mentioned treatments in aqueous solutions and in a distinct subsequent way, because of the fragility of the artifacts. After studying, in a separate way, an effective deacidifier (calcium propionate) soluble in ethyl alcohol and many reducers (boron complexes), able to act in different non-aqueous solvents, it was decided to test a simultaneous method of deacidification and reduction in ethanol. This paper presents the chemical-physical results obtained by applying simple deacidification and simultaneous deacidification-reduction on laboratory paper samples that were artificially aged and then re-measured after 10 and 15 years of natural aging. Results show that all alcoholic treatments are very effective: papers are stable also after a long period of both artificial and natural aging.

1. Research aims

This paper tries to answer to the needs of conservators of books, archival materials and graphic works of art, who need sometime to use non-aqueous solutions in treating original documents to prevent the dissolution of the graphic media, the alteration of the paper structure and the loss of the printing impression. Moreover, it is often necessary to work on bound books to maintain the original bindings untouched. Also in this case, water solutions could not be used.

All the analyses and the used complementary techniques were applied in order to ascertain the effectiveness of a simultaneous non-aqueous deacidification and reduction treatment on artificially and naturally aged papers.

2. Introduction

Cellulose oxidative and hydrolytical degradation is one of the greatest problems for the conservation of paper supports such as archival documents, books and graphic works. Degraded papers show an evident fragility and a yellowing, compromising in some cases the readability of the text or the graphic sign.

Many deacidifier can be used [1], but only few reducers can be directly applied on paper documents without damaging the fiber structure and the graphic media.

Boron compounds and complexes are very effective and chemoselective in reducing carbonyls that are the most important oxidized groups in the cellulose polymer chain [2–4].

During the reduction reactions, hydrogen is produced and, if the reaction rate is too high, the cellulose fiber wall could be broken [5] by the large amount of hydrogen generated in a short time. This effect has been observed when sodium borohydride, the first reducer used in conservation field, was used as reducing product in the treatment of strongly oxidized papers [6]. Therefore, to minimize this negative effect, mild and "slow" reducers should be chosen, such as the boron-amine complexes. Furthermore, to avoid β-alkoxyelimination reaction, which occurs at ambient temperature in high alkaline environment (greater than 10.5) when a polymeric chain contains a large amount of carbonyl groups, the employed reducers should have a pH lower than 10 when applied in water solution [1].

In 1997, we published the first results on the application of borane tert-butylamine complex [$(CH_3)_3CNH_2{\cdot}BH_3$, TBAB] for the reduction of carbonyl groups in oxidized paper [7].

Almost in the same period, TBAB was proposed for the bleaching of pulp in the paper industry. Amine boranes appeared to behave

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better than sodium borohydride and even than sodium hydrosulphite for obtaining a more stable, white and not-degraded cellulose pulp [8].

In a second time, we investigated the possibility of a non-aqueous application of different boron compound for reducing purposes [9] and the applicability of a simultaneous non-aqueous deacidification with ethanol solution of calcium propionate $[Ca(CH_3CH_2COO)_2]$ and reduction with borane-ammonia complex $[NH_3BH_3]$ [10]. Non-aqueous treatments are in fact requested in case of restoration of originals containing water-soluble graphic media or when it is mandatory to treat books keeping intact the bookbinding.

Due to instability of borane-ammonia complex and the difficulties in its handling by restorers, we decided to perform a new series of studies on TBAB, whose interactions with cellulose are reported in [11], and to use it for a new series of tests on alcoholic deacidification and reduction.

This paper presents the comparison between the data obtained on artificially aged samples and those collected on the same samples after natural aging in uncontrolled conditions for 10 and 15 years.

Before presenting the results of this work and their discussion, some points need to be underlined.

Looking at the specific literature [12 and related references], it seems that conservators are more interested in "bleaching" of paper – that is only a side effect of the reducing treatment – than in the most important result that is the stabilization of the cellulosic support and the increase of its expected life.

Despite the researches carried out on different boron complexes, outside Italy only sodium borohydride is used, whose effect on strongly oxidized papers can be dramatic, causing the mechanical breaking of the paper [5]. Another reducer, sodium dithionite [12], has a mild brightening effect on paper, but is very effective in the reduction of iron (III) ions. This makes the dithionite not applicable to all manuscripts containing iron-based inks or pigments, which could disappear after the treatment.

Moreover, the articles concerned with chemical methods for paper restoration often report results based on mechanical and optical measurements. Significant variations of mechanical properties need very long time (See supplementary material S1). On the contrary even light chemical variations can cause strong degradation.

This implies that potentially harmful treatments – such as reduction with sodium borohydride or deacidification with calcium hydroxide at too high pH – are commonly accepted. For these reasons, we focused our attention on the chemical behavior of the investigated items to perform a rational and scientific acceptance or rejection of the treatment. Therefore, the characterization was carried out by applying chemical methods (pH, carbonyl content and degree of polymerization), spectroscopic techniques (Raman spectroscopy) and optical methods (color coordinates and Optical density measurements).

3. Materials and methods

Materials, methods and techniques used in this work are briefly described below.

3.1. Materials

- Whatman® cellulose chromatography paper grade 1; 46 cm × 57 cm, a pure cotton and cotton linters cellulose.
- hydrochloric acid 37% [HCl] (Aldrich ACS grade) used to simulate "original" acidic samples subjected to hydrolytic degradation.
- 0.015 M aqueous solution of potassium meta-periodate $[KIO_4]$ (powder, Merck 99.8%) brought to pH 5 with HCl 10^{-2} M in order to simulate "original" samples subjected to oxidative degradation.
- 3.0 g/L solution of calcium propionate $[Ca(CH_3CH_2COO)_2]$ (Aldrich 95%) in ethyl alcohol (Aldrich 96%). The solution was used to carry out simple non-aqueous deacidification treatments.
- 3.0 g/L solution of calcium propionate in ethyl alcohol + borane tert-butylamine complex $[(CH_3)_3CNH_2{\cdot}BH_3]$ (Aldrich 97%). The resulting solution is 0.2 M in borane complex. The solution was used to carry out simultaneous deacidification and reduction.
- 0.2% w/V water solution of 2,3,5 triphenyl-2H-tetrazolium chloride (TTC, Aldrich 98%).
- 0.5 M cupriethylenediamine solution (Carlo Erba for analysis).

3.2. Preparation of paper samples

Three sets of laboratory paper samples were considered in the present work; each one was successively divided in three series, as described below:

- one set was oxidized by immersion for 15 minutes in a KIO_4 0.015 M water solution, at pH = 5.0, and then rinsed by two immersions, 5 minutes each, in distilled water. This treatment was used to simulate "original" papers presenting a strong degradative oxidation. After the treatment, one series was kept as prepared (Ox series in the following); a second one was immersed in the alcoholic deacidification solution of calcium propionate (Ox-D series in the following) as described in a previous work [10] so to have a comparison with established restoration treatments, and the third one underwent a simultaneous non aqueous deacidification and reduction treatment (Ox-DR series in the following);
- one set was hydrolyzed by 1 h exposition to fuming HCl vapors, to simulate acidic "original" documents. After hydrolysis, a series was kept as prepared (Hy series in the following), a series was deacidified (Hy-D series in the following) and the third one deacidified and reduced (Hy-DR series in the following);
- one set of Whatman N.1 samples (not treated, deacidified and deacidified/reduced) was included in the experiment as control samples (respectively C, C-D and C-DR series in the following).

All laboratory samples were artificially aged in climate chamber (Angelantoni Challenge E300) for 35 days, according to International Organization for Standardization ISO 5630-3:1996 at 65% R.H. and 80 °C and characterized each 7 days of ageing with destructive and non-destructive techniques. The chosen temperature is compatible with the stability of TBAB: amine-boranes prepared from primary and secondary amines are stable up to 110 °C [13].

After the artificial ageing experiment, for each set and series, the "zero-time" samples and those artificially aged for 35 days, were left on library shelves for 10 years in order to simulate a non-controlled storage. After their retrieval, the samples were once more characterized and left for other 5 years in uncontrolled ambient for a third characterization.

Chemical, optical and spectrometric tests were performed after each cycle of artificial and natural aging. Oxidation and hydrolysis induced by environmental conditions, in fact, cause important chemical and structural modifications with great impact on paper permanence and durability, even if mechanical characteristics are not particularly affected in the short term. Decrease in the degree of polymerization is related to hydrolytic degradation, whereas increase in carbonylic functions is due to oxidative processes. Structural changes produce modification in the Raman spectra of paper.