# CLEANING OF PAPER WORKS WITH SELEC-TIVE SOLVENT METHODS

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INTRODUCTION

The aim of this work was the study of the weathering processes due to the use of adhesive tape for the restoration of paper and for temporary exhibitions and to try their removal from the paper works through the use of selective solvent methods. Before the experimental tests a research on the production sources and on the technical studies of the adhesive tapes was carried out (Smith Merilly et al., 1983; Bicchieri et al., 1984; Dauga Nadège, 1997; Botti et al. 2000).

The adhesive tapes were often used in the restoration of paper works but during the natural ageing the tape support becomes hard and brittle; it comes off the adhesive and following an oxidative process it penetrates into the paper fibers giving rise to the formation of stains (figure 1). Besides the tapes can cause the deformation of the paper work since they have got an expansion coefficient different from that of paper (Roserba, 2007).

The recent acrylic adhesive tapes are more difficult to remove because they are composed by anti-ageing, softening, anti-oxidative and plasticizing agents in addition to the acrylic resins. These adhesive tapes undergo oxidative processes in spite of the presence of stabilizing agents. In fact the presence of tackfiers (viscosity modifying) and plasticizing agents (generally benzyl butyl phthalate) causes the adhesive instability and accelerates the oxidative processes. The acrylic adhesives are trasparent and they have no clear tendency to yellow, but with the ageing process they penetrate into the paper supports and the adhesive becomes more and more insoluble in the common organic solvents. So the removal of the acrylic adhesive residues from the paper works can become very hard.

In this preliminary research we try to reproduce the deterioration processes of some common adhesive tapes and to evaluate their effects on some industrial and handmade papers. The tape-paper systems were investigated in relation to the temperature, to the relative humidity and to the radiation exposure conditions.

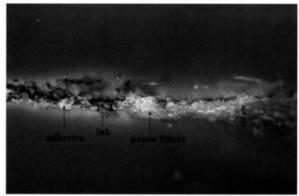


Fig. 1: Cross section of a print document (1905) restored in the Laboratory of Province of Viterbo. The removal of the adhesive tapes was tried out with sepiolite imbibed of acetone. UV light, magnification 10x.

After the ageing tests adhesive-paper samples had undergone some cleaning tests using different solvent mixtures with and without thickening agents.

MATERIALS AND METHODOS

The following adhesive tapes were analyzed: Tesa Adhesive and Biadhesive, Eurocel Ecophan and Eurocel Biadhesive, 3M Magic 810 and 3M Biadhesive.

The adhesive tapes were analysed by means of µ-FTIR. The papers used in this research are: Kinugawa Japanise Paper 632 161 (KJP); Fabriano Rome Paper (FRP); Canson Laid Paper (CLP); hand-made paper Moulin Du Verger (MDV). The Naturally Aged Parchment (NAP) was also tested. The paper and parchment samples and the adhesive tapes were analysed before the ageing tests. Colour measurements of the papers and of the parchment sample

were taken by means of a reflectance spectrocolorimeter X-Rite mod CA22 according to CIE 1976 coordinates. The papers and parchment were also analysed through u-FTIR using a Centaurus microscope equipped with a MCT detector. Roughness, pH, ash% and DRIFT-FTIR of the ash were also measured for each paper and for the parchment. Roughness was easured by means of an HOMMEL LV 15 roughness tester, pH measureaments were taken by means of a Crison pH-meter with a flat membrane electrode. DRIFT-FTIR spectra of the ashes were obtained by means of a Nicolet Avatar 360 IR spectrometer equipped with a DTGS detector. A temperature of 30 °C with UR 90% for 30 days was tested on paper and parchment samples, with the attached adhesive tapes, in a climatic box equipped with a 70 W Xenon lamp (OSRAM Power Star HQI-T), UVA 210x10-3W/m2 and 3500 lux. The experimental tests were tried out with 4x14,5 cm samples. The distance of the samples from the lamp was 30 cm.

The colour changes were assessed by means of colour

measures, taken before and after the artificial ageing. The colour measurements were taken in CIE 1976 coordinates (L\*a\*b\*), ¢E and ¢L were calculated according to UNI-NORMAL 43/93. Cleaning tests were carried out with the following solvents and thickening agents: white spirit, acetone, ethanol, MEK and acetonalcool applied with and without sepiolite.

### RESULTS AND DISCUSSION

### a - FTIR analyses

The  $\mu$ -FT-IR spectra of the paper samples show the presence of cellulose as main component and of calcium carbonate, silicates and sulphates probably employed as inorganic charges (figure 2). NAP sample is obviously composed of animal proteins (see the absorbion bands of amide group I and II in the region of 1550-1690 cm-1, figure 3); the spectrum shows the presence of sulphates. The DRIFT-FTIR spectra of the paper ashes show that MDV and FRP contain only

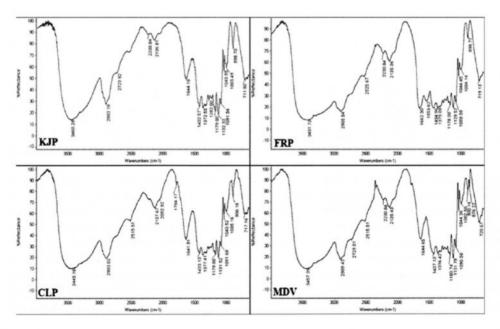


Fig. 2:  $\mu$ -FTIR spectra of the four examined paper samples.

CaCO3 and iron oxide (the colour of MDV ash is light red; that of FRP ash is red) as indicated by the absoption in the 400-600 cm-1 region of the spectrum. FRP paper contains also traces of sulphates (figure 4).

The percentage of the ashes of the paper and parchment samples is carried in table 1. MDV and CLP samples show high values of ash contents; only for FRP the percentage of ashes is very low. KJP, CLP and NAP (fig. 5) ashs contain sulphates (calcium and/or barium) and silicates (probably kaolin) as inorganic charges. The ash of these samples are white (KJP), whitish (NAP) or pink (CLP). The µ-FT-IR spectra of the adhesive tapes are characterized by the strong stretching band of the C=O group typical of acrylic compound at about 1730 cm-1. The solubility of the adhesives was tested before the ageing process by means of five solvents with different polarity: white spirit, acetone, ethanol, MEK (methyl ethyl ketone) and a 1:1 v/v acetone:alcool mixture (named AA mixture). In table 2 the results of the solubility tests are reported in comparison with that of the adhesives carried out after the ageing procedure.

MEK is generally the best solvent for the all the adhesive tested before the ageing. Acetone and AA mixture show their effectiveness only for some of the adhesives. White spirit is not a good solvent probably for its low polarity compared with that of the adhesive components. At last ethanol is a good solvent only for Tesa Adhesive and 3M Magic 810 Scotch.

# b - Ageing and solubility tests

The artificial ageing caused some changes in the colour and solubility properties of the paper and parchment samples and adhesive tapes.

The graph of figure 6 shows the difference in the a\*b\* coordinates: in the case of NAP there are significant variations of the chromatic parameters following up the ageing process. Both a\* and b\* values increased giving rise to a yellowing of the parchment. MDV hand-made paper had a similar behaviour but with a lower variation of the chromatic parameters. For KJP paper both a\* and b\* coordinates decreased giving

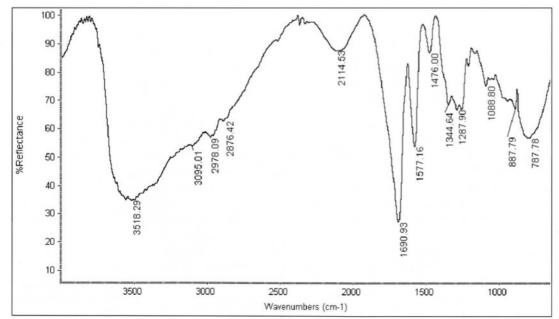


Fig. 3: μ-FTIR spectrum of the parchment sample.

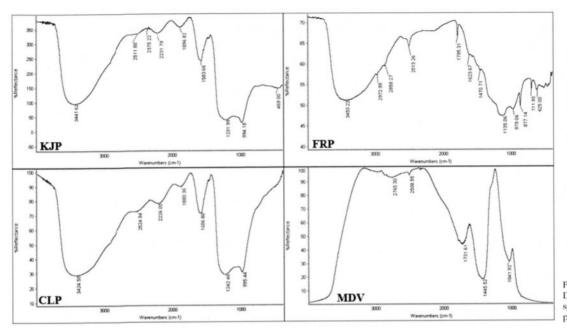


Fig. 4: DRIFT FTIR spec tra of the paper ashes.

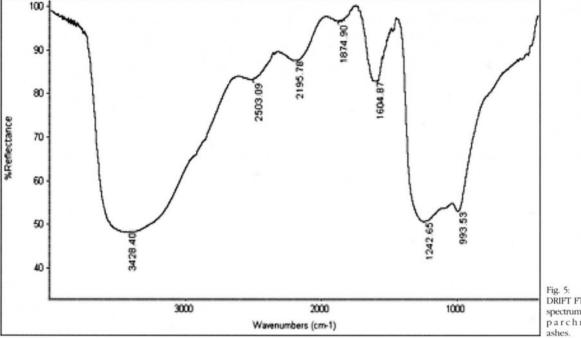
SAMPLE	% of ashes	ДрН	∆Ra (µm)	ΔL	ΔE
NAP	3,47	0,42	2,36	-8,25	11,93
CLP	5,49	0,27	0,345	-3,65	4,42
KJP	2,01	-0,6	1,39	-5,38	8,53
FRP	0,32	-0,38	0,705	-3,66	4,15
MDV	5,32	0,03	-0,135	-3,66	3,74

Table 1: Percentage of ashes; pH, roughness and colour differences of the paper and parchment samples following up the ageing process

rise to a grey tone. FRP and CLP didn't undergo significant variations of the chromatic parameters. Total colour, pH and roughness differences are showed in table 1, together with the percentage of the ashes of the paper and parchment samples. The larger total colour difference (AE) occurs in NAP (11,93) and KJP (8,53). The AL values are always negative indicating a general decrease of brilliance of the samples following up the ageing process.

The pH values had no considerable variations following up the ageing tests. The roughness underwent significant changes for NAP (ΔRa=2,36 μm) and for KJP (ΔRa=1,39 μm).

Other ageing tests should be carried out in order to better understand the role of relative humidity, temperature, radiation intensity and time of exposure on the chemical modifications of the papers and the adhesives tapes. After the ageing tests, the adhesive



DRIFT FTIR spectrum of the parchment

tapes were observed under a videomicroscope in order to evaluate the microscopic alterations of the support or of the adhesive. Some of the examined adhesive tapes underwent significant yellowing, for example Eurocell Biadhesive especially with high basis weight FRP and CLP papers. Other

adhesive tapes formed manifest craquelures; in particular Tesa Biadhesive tape showed many evident craquelures with all papers, especially with KIP and NAP. At last Tesa and Eurocel Biadhesive tapes underwent a loss of their adhesive power; the biadhesive supports became hard and brittle and they tended to come off the adhesives. Only 3M Magic 810 and 3M Biadhesive didn't show significant alterations of the support and of the adhesive. The cleaning tests showed that the best solvent also after the ageing tests was MEK (see table 2). The removal of the aged adhesive tapes is easier for FRP, a special produced

paper suitable for conservation works. The stability and behaviour of this paper as regards its interaction with the adhesive tapes is a significant result. The 3M Biadhesive, in spite of its apparent stability, is very difficult to remove from all the paper samples in comparison with the other adhesive tapes. Tesa Adhesive, Eurocel Ecophan Adhesive and Eurocel Biadhesive solubility remained almost unchanged at the end of the ageing test compared with the beginning of the process. Tesa Biadhesive solubility increased with polar solvents following up the ageing test. Nevertheless this Biadhesive is difficult to remove from the paper and parchment samples except for FRP. 3M Magic Adhesive solubility decreased with the ageing process and MEK was the only solvent able to dissolve this adhesive.

The use of thickening agents, like sepiolite, improves the removal process because it extends the contact

	White Spirit	Ethanol
Tesa adhesive	swells up	soluble
Aged Tesa adhesive	swell up a lot	soluble
Tesa Biadhesive	insoluble	insoluble
Aged Tesa Biadhesive	insoluble	soluble
Eurocel Ecophan	swells up	swells up
Aged Eurocel Ecophan	swells up	slightly soluble
Eurocel Biadhesive	swells up	insoluble
Aged Eurocel Biadhesive	insoluble	no much soluble
3M Magic 810	swells up	quite soluble
Aged 3M Magic 810	swells up	insoluble
3M Biadhesive	soluble	insoluble
Aged 3M Biadhesive	swells up	insoluble

Table 2. Solubility tests before and after the ageing process

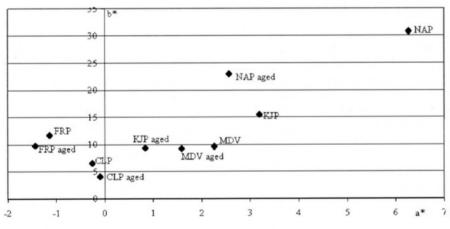


Fig. 6: a\*b\* graph of the papers and of the parchment before and after the ageing test

time of the solvents with the paper. Moreover sepiolite is a clay material and so it possesses an absorbing power due to its chemical characteristics. Nevertheless, the removal of adhesive tapes both from natural aged papers and artifi-cial ones was not completely successful. Infact the industrial paper, like that restored in the Laboratory of the Province of Viterbo dated 1905, was not completely cleaned from the adhesive residues probably for its more close weft

that doesn't allow the sepiolite to absorb the materials penetrated in the paper fibers. Further experimental tests should be carried out in order to obtain a better knowledge of the adhesive tapes behaviour and to understand the possibility of removal the naturally aged adhesive matter from the paper works using other thickening agents and also techniques different from the solvent systems, for instance laser cleaning.

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