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BEHAVIOR OF ARCHAEOLOGICAL PAPER AFTER CLEANING BY ORGANIC SOLVENTS UNDER HEAT ACCELERATED AGING

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ABSTRACT

The main goal of this study was to study and evaluate the organic solvent on the chemical composition of aged paper samples. chemical pulp wood samples, which were, have been cleaned with three types of solvent then a Measurement of mechanical properties, Measurement of color change by spectrophotometer, PH values, X-ray diffraction and infrared spectroscopy (FTIR) study were undertaken, to see if any significant structural or chemical differences could be detected between "untreated" and "treated" paper. Dramatic changes in functional groups on the paper surface, as monitored by FTIR, occurred in the samples before and after solvent cleaning. Mechanical properties, however, show that ethyl alcohol, toluene and acetone may give good results in cleaning paper surface, but the solvents accelerated oxidation and hydrolysis of paper samples under heat aging are another point to consider.

KEYWORDS: Cellulose, Mechanical properties, pH, Solvents, Accelerated aging, Color change

1. INTRODUCTION

For many centuries paper was the main material for recording cultural achievements all over the world. Paper is mostly made from cellulose with small amounts of organic and inorganic additives .Archaeological paper is formed from network structure between cellulose and non cellulose (hemicelluloses and lignin). These materials are held together with hydrogen bonds(Kamel, &Sakhawy,2004 ; Ward,1973) the mechanical properties of different paper samples are substantially influenced by the individual characteristics of cellulose fibers, by the nature, concentration and chemical properties of fillers and additives, as well as by the network structure of the paper (Caulfield& Gunderson, 1988; Havlínová,et al, 2009). Paper document has gathered a lot of dust and acquired some types of marks, spots or stains for example by pencil, ink, fungus, water need to be cleaned. Dirt and other surface deposits accumulated on archaeological paper can be removed mechanically by brushing with soft to hard brushes, scalpels, or by using abrasive blasting techniques Although mechanical cleaning should enable a degree of control over it, should avoid adding any substance that causes additional damage, like chemical cleaning, it has disadvantages too for several reasons: incorrect mechanical cleaning can lift or disturb fibers and cells, especially if the deposits adhere strongly to the paper surface. Moreover, the use of various tools in the mechanical cleaning can result in microscopic scratches on the surface of the paper (Hamed et al, 2013; Florian et al, 1990; Moncrieff& Weaver, 1993).

For conservation purposes, chemical cleaning is often applied, by using different reagents and solvents. In some cases the chosen concentrations are very low; in other cases the concentrations used may be too high and unsuitable (El Hadidi & Darwish, 2008), solvents are used for many purposes in conservation including cleaning and the application or removal of coatings, consolidates and adhesives. It may often be difficult to choose a solvent which is both effective and safe. Making the most of any solvent requires familiarity with the basic principles of molecular bonding and an understanding of how the structure of solvents affects their physical and chemical properties. Solvent Cleaning used in removed types of spots or stains such as stains penetrate in to paper fibres and cannot be easily removed .The basis of stain removal with solvent its solubility in the selected chemical, their efficacy will depend on the nature of the stains and nature of the paper (Grawal & Barkeshli, 1997; Kanegsberg, 2001; Petrulio, B. Kanegsberg, 1998). Chemical cleaning of paper surfaces involves the use of reagents, which are chemicals that break primary molecular bonds, converting dirt, and other unwanted material to a different form in order to remove it from the surface. After solvent cleaning, original material cannot be recovered in the same way as it was when the archaeological object was first made in the past. However, paper has giant molecules with either primary or strong secondary bonds linking them together. These are more difficult to dissolve than the small dirt molecules. It has always been believed that the consequence for cleaning non deteriorated paper is that organic solvents, in general, are likely to be innocuous as far as any risk of dissolving the main structural materials of paper such as cellulose and lignin.

One can be rather less sure about the supplementary materials of an object such as colors and pigments (Moncrieff and Weaver, 1994). Solvents are often used in conservation textiles (Abdel-Kareem, 2008), wood (Darwish & El Hadidi, 2008), mummies (Abdel-Maksoud & El-Aminb, 2013) to aid in cleaning and removal of dirt (Romão et al, 1990). In other hand, Thermal and accelerated aging has been shown to affect the void structure of cellulose and the ability of paper to retain water, thermal degradation of cellulosic materials is greater in present of air than in its absent, because of oxidation by atmospheric oxygen.in the other hand, thermal degradation is greater under steaming than under dry heating conditions. The activation energies for the degradation reactions are about half as large as under dry heating conditions (Stamm,1956). Also the large numbers of specific reactions and products involved in the thermal degradation of cellulose have been the subject of extensive studies. Mechanisms and Kinetics remain controversial, but it has been established that the first step in cellulose degradation is the production of laevoglucose which either decomposes to volatile fragments, or reacts further to produce (Madorsky,1964; TESORO,1976) .Therefore when dealing with valuable cultural heritage items, researchers have constraints in choosing the right solution for cleaning procedures, in order to obtain good results in removing the dirt and to produce no chemical or mechanical damage to the surface. Moreover, they should not to leave residues on the surface after the cleaning agent removal, but there is no previous study concerning the effect of solvents on chemical composition of paper under heat aging.

2. MATERIALS &METHODS

2.1. Materials:

Unbleached chemical sulphite pulp, upsized, 25gm-2 (approx. 7×15 cm), 0.05 mm thickness was selected for the study, with no further aging. Chemi-

cal pulp wood was used which commonly used widely beginning of the eighth century AD.

2.2. Cleaning agents:

Acetone (Fluka) was used as is, Ethyl alcohol (99.5% v/v was mixed with water so that final concentration was 50% v/v). Toluene was used as is.

2.3. Cleaning:

Cotton swab was used in cleaning the surface of the paper, as the stain removed .Samples were divided into 5 groups depending on the type of solvent used for cleaning, the grouping was as follows; sample (1) wood pulp paper record. The sample (2) untreated sample, (3) treated sample with acetone, (4) treated sample with toluene and (5) treated sample with ethyl alcohol. After the treatment is over, the paper samples are allowed to dry.

2.4. Accelerated aging of paper after cleaning:

In order to model the long-term degradation processes in an appropriate time scale, the paper samples 1-5 were exposed to heat accelerated-aging procedures. The dry-heat aging at 105 ◦C, was performed according to ISO 5630 (ISO 5630-1:1991; ISO 5630-4:1986) for 27 days.

2.5. Measurements of mechanical properties (tensile strength and elongation)

The samples were cut in the machine direction with15 cm length and 1.5 cm width as per the requirement of the test standard (T-494,1988),paper samples were conditioned according to ISO 187 (ISO 187:1990; ISO/DIS 15754, 2007), at a temperature of 23 ◦C and a RH of 50% over 24 hours(ISO 1924-2:1994; ISO 1924-3:2005) . The Samples were measured by testing machine type H5KT130-500N/E139-34A (Shimadzu, Kyoto, Japan).The tests were done according to TAPPI Standard TAPPI T494OM-88 (Junior, 1999). The crosshead speed was 100mm/min, Load Range: 400N, Extension Range: 100mm, Gauge Length: 100 mm.

2.6. Measurement of color change by spectrophotometer

The changes in the color parameters L, a, and b were measured with a Hunter lab colorimeter; L index of color represents black-to-white color, the index represents green-to-red color, and b index represents blue-to-yellow color. The overall change in color indices due to aging was expressed as _E according to the following for-mule (George,1995; El-Feky,et al ,2013) :

$$\Delta E=\sqrt{(\Delta L)^2+(\Delta a)^2+(\Delta b)^2}$$

Where _L, _a, and _b are the differences between the values of the color indices before and after aging.

2.7. Measurement of pH

Measurement of pH was performed on samples according to the procedure of Wouters(Wouters,1993,1994,1997; Larsen,2000). pH was measured at by using ML1010PH. Misura Line, Romania, between pH 4.01 and 7.01, at 20°C .

2.8. X- ray diffraction analysis (XRD) FOR determination of paper crystallinity

X-ray diffraction analysis(XRD) of the treated and untreated paper samples before and after heat aging was carried out on a Philips X-ray diffract meter, type PW 1840, giving 40 kV Cu Ka radiation at 25 mA. The crystallinity index is calculated according to equation:

$$CrI=\frac{I\,002-I\,am}{I002}\chi 100$$

Where:

CrI= crystallinity index

I 002 = intensity at approximately 22.6°2 θ

I am = intensity at approximately 19º2 θ

This method is as good as any other approach for the relative ranking of cellulose I crystallinities (Attalla,1984,1998; Abed-Maksoud,2010).

2.9. FTIR

FTIR was used for monitoring the chemical characterization and modification which occurred in the paper after treatment with solvent. So, the samples were analyzed before and after treatment with a FTIR spectrometer (Model 6100 Jasco, Japan). Each spectra was obtained in the transmission mode with TGS detector and by using KBr method and represents (2 mm/s) co -added scans at the spectral region ranging from 4000 to 400 cm^{-1} with resolution of4 cm^{-1}.

3. RESULTS & DISCUSSION

3.1. Mechanical properties of paper

Values of tensile strength reflect the detailed structure of the paper and the properties of its individual fibers, i.e., the dimension and strength of fibers, their arrangements, and inter fiber bonding (Caulfield& Gunderson,2008). Fig. 1 show the percent loss in tensile strength of paper samples1–5 monitored under heat accelerated aging after 27 days. The results confirmed a high sensitivity of tensile strength to the effects of dry-heat. Many authors have also confirmed these results, Zou et al; 1994 have recently shown that the effects of accelerated aging processes on paper are interpreted in terms of cellulose chain scission producing weaker fibers, and covalent crosslinking by the additional hydrogen bonds leading to increased brittleness (Zou et al ,1994).These results confirmed the strong impact of the treated paper's properties on the loss of tensile

strength upon accelerated aging. The application of dry cleaning caused a noticeable decrease of tensile strength of treated paper. However, solvent cleaning caused of a loss in stretch of 12% for treated paper with alcohol which may due to exposure the treated paper to water molecules. Water which is capable of swelling the carbohydrate components of celluloses and may accelerate further degradation, and can also dissolve and extract the starch, decayed hemicelluloses (Florian et al ,1990) .In other studies, Spiros Zervos (2013) confirmed that the causes of the strength loss after aqueous treatments, a tentative mechanism has been proposed, based on microstructural changes that adversely affect the bonding among cellulose fibres and/or fibrils(Zervos,2013) .Generally, the results confirmed that the organic solvents decrease the breaking length and elongation of the treated paper samples. In case of breaking length, the effect of the solvent is clear and causes a decrease in tear factor due to the decrease of the inter fiber bonding, one others hand, the solvent forms complexes with cellulose when unlimited swelling arises as a consequence of breaking the adjacent bonds. The extent of swelling depends on the solvent as well as on the nature of the cellulose sample. The resulting separation of the polymer chains indicates the beginning of the solubility. The dissolving ability entails formation of a complex with the two secondary hydroxyl groups in cellulose and with breaking of hydrogen bonds. The swelling and solubility of lignin is greater with hydroxylated solvents (swelling solvents), e.g., methanol, ethanol, phenol, and water than non-polar solvents (non -swelling solvents) like benzene and toluene. The hydrogen-bonding capacities of various solvents are proportional to the shift in wave length of the infrared region of the spectrum (Horvath,2006) .From the viewpoint of thermal degradation of paper, the combination of high temperature and moisture content may not be desirable. The thermal degradation, often manifested as loss of mass, signifi cantly impairs the mechanical properties of paper, The reduction in mechanical properties is in particular evident when specimens are compared at similar moisture content, instead of at similar ambient conditions, because mass loss often decreases hygroscopicity, thus reducing the moisture content of paper at constant ambient conditions. The decrease in hygroscopicity is mainly caused by the reduction of bonding sites available for water sorption that accompanies the degradation of hemicelluloses.

3.2. Change of color:

The effect of heat aging for 27 days on the change in color parameters (L, a, and b) of untreated and treated paper was studied. Tables 1 show the change in color (ΔE) of the different series as a result of heat aging. In sample 2 (untreated paper),a slight differences between the ΔE of blank paper was observed. This could be due to the fact that wood plup is made of cellulose and non cellulose (hemicelluloses and lignin, which is known to be durable under heat. Cellulose unit has groups absorbing heat. Thus, its thermal-degradation is induced by internal, external chromophoric impurities, or additives. The thermal-degradation processes involved in cellulose are main chain scission, dehydroxylation, dehydromethylation and dehydrogenation, which lead to formation of several free radicals that cause degradation and yellowing of cellulose (Fan et al ,2011) ,dramatic increase in ΔE of the treated sample with solvents are observed before and after aging. The increase in ΔE of aged treated samples as a result of the formation of a permanent cellulose-solvent complex. The formation of such a complex might increase the reactivity of the paper and accelerate its rate of aging (Wächter,1974). Generally, major changes in the paper samples are observed before and after cleaning.

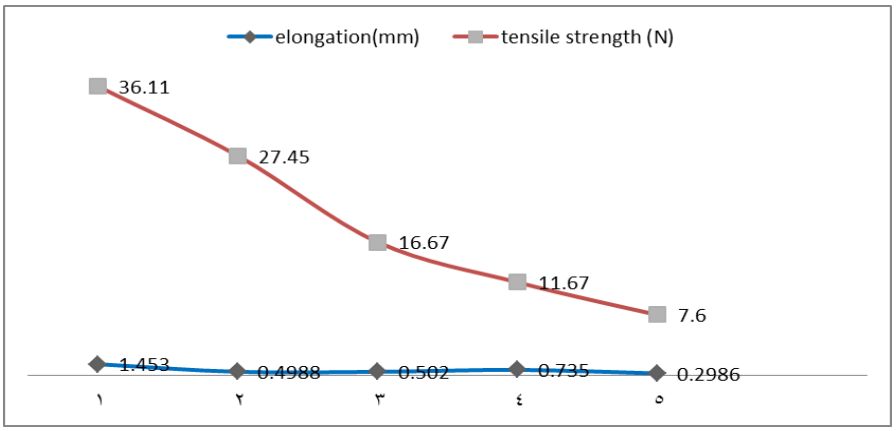

Fig . 1. Percent loss of tensile strength and elongation monitored for paper samples 1–5 exposed to heat accelerated aging

Table 1 The changes in the colour values for the paper samples after heat aging

samples	ΔL	Δa	Δb	ΔE
Blank	0	0	0	0
Aged untreated	-1.31	-0.08	1.51	2.00
Aged treated with acetone	-0.99	-0.24	2.57	2.76
Aged treated with toluene	-1.47	-0.29	2.25	2.97
Aged treated with alcohol	-1.34	-0.18	2.54	2.88

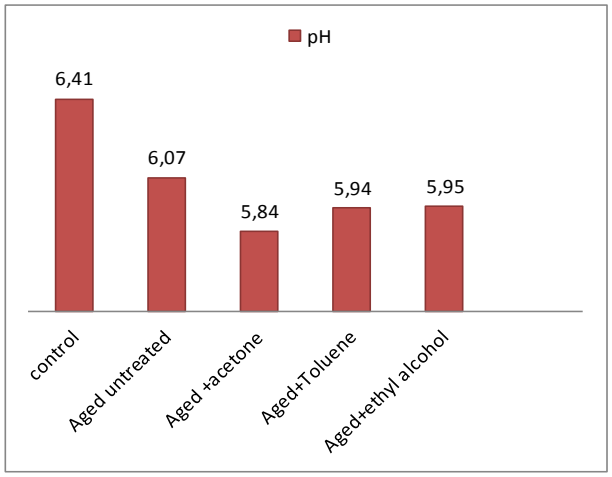

Figure 2. pH values of untreated& treated paper samples after heat accelerated aging

3.3. Measurement of pH

Figure .2 shows the effect of solvents on the acidity of paper. It can be observed that there is a slight decrease in the pH values of the treated samples after aging compared to the control sample. The decrease of untreated sample could be due to the effect of heat aging which caused some modifications in lignin structure including depolymerisation and condensation reactions, some researchers found that of the structural components, hemicelluloses are the most vulnerable to thermal degradation. Degradation rates of hemicelluloses have been reported to be four times higher at 150°C than α-cellulose and revealed that acetic and formic acids liberated from cellulose fibre during thermal treatment enhanced hydrolysis of hemicelluloses and cellulose (Nuopponen,2005; Sundqvist,2004) .After cleaning, dramatic changes was observed before and after aging, a slight decrease in pH values especially for treated samples with acetone which could be due to the decrease of water molecules as some acetone replaced water and formed cellulose-acetone complex. A complex vibrational pattern of various carbonyl groups due to partial cellulose oxidation products and accelerate hydrolysis of both cellulose and lignin Finally, acids, like formic, acetic, lactic, and oxalic acids were formed (Library of Congress,2006).

3.4. Crystallinity of paper

The results of XRD show that there are noticeable differences in the amorphous areas in the paper before and after the aging (see Figure.3 and Table .2). This indicates that the paper samples are less elastic after the treatment with solvents. Also the results show that there is change in XRD pattern of untreated and treated paper samples after the aging by heat, Crystalline regions of aged treated slightly decreased However, There is no need for the whole polymer part to be accessible to the solvent prior to dissolution ,due to the difficulties for dissolving or chemically treating cellulose, it has always been postulated, and taken for granted, that the whole cellulose part must be first brought accessible to the solvent by methods like (i) opening of the pores present in native or regenerated cellulose, (ii) swelling non-crystalline regions, (iii) breakage of the crystalline areas, (iv) weakening the hydrogen-bond array by chemical or physical treatments or (v) decreasing molecular weight by chemical (Le Moigne, 2008).

Table 2 Intensity and Crystallinity index of treated paper samples before and after heat accelerated aging

Samples	Intensity				Crystallinity index (%)
	Cellulose I				
	101	101	002	am	
The blank(1)	208	1.0	3.46	0.69	80
Aged untreated (2)	156	1.1	3.20	0.92	71.1
Aged cleaned with acetone(3)	182	0.89	2.56	0.75	70.3
Aged cleaned paper with toluene (4)	156	1.07	3.58	0.82	77.6
Aged treated with ethyl alcohol(5)	220	0. 96	3.03	0.65	78

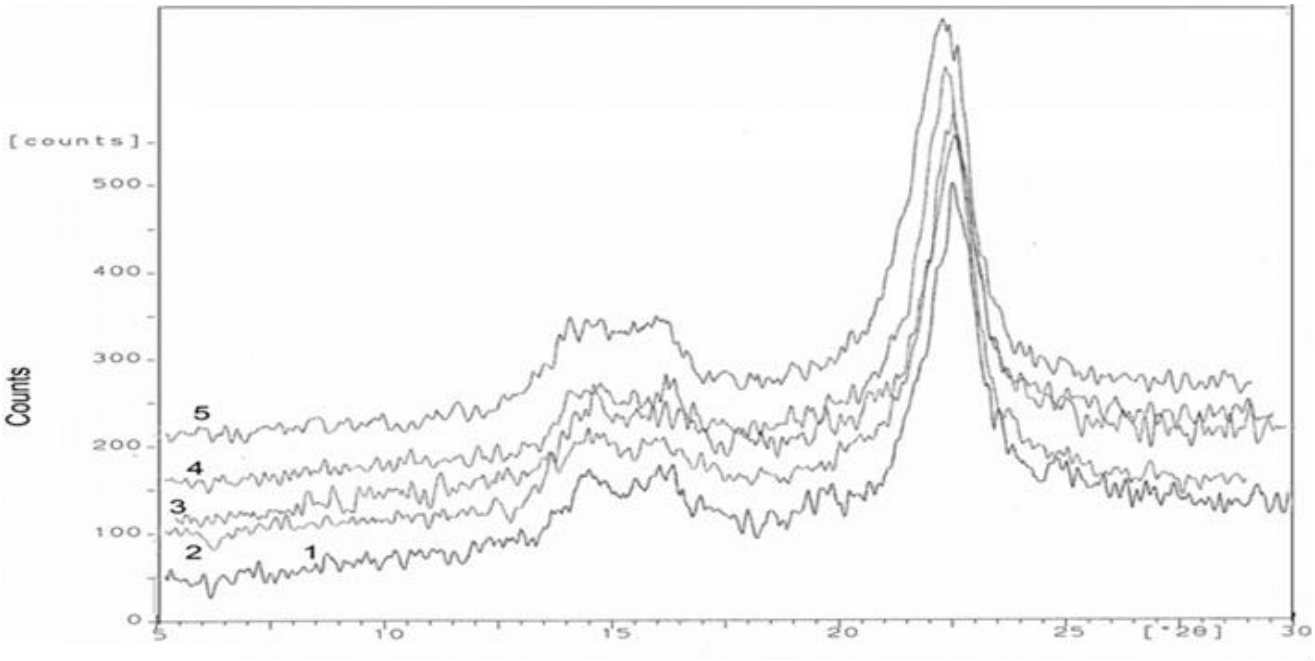

Figure 3. X-diffactogram of samples of paper before and after heat aging (1) The control, (2) Aged untreated (3) Aged treated with acetone (4) Aged treated with toluene,(5) Aged treated with ethyl alcohol

3.5. ETIR spectra of paper samples exposed to accelerated aging

Paper samples were also studied by FTIR spectroscopy before and after solvents cleaning and results were compared to monitor changes.

3.5.1. Un treated paper, aged untreated paper

The infrared spectra of paper show the same basic structure as all paper samples (Derrick,1998; Hinterstoisser,& Salme´n,2000) as assigned in Table.3. The relative intensities of Intermolecular hydrogen bonding OH stretching at 3498.8 cm^{-1} is higher in the paper, whereas bands at1107,1053.8,1031 cm^{-1} and 2894.7cm^{-1} are stronger. After aging new band at 900.6, 910.3&952.5 cm^{-1} appeared (in comparison to the untreated sample). It may be due to C–O group of ester formation or new C–OH groups resulting from opening of the pyranose ring. More carbonyl groups were formed as a result of further oxidation of C–OH groups' cellulose molecules(Lojewskaet al ,2005) and there has been the removal of the Association CH stretching, where the oxidation process of Cellulose to occur where heat oxidized hydroxyl group Cellulose molecule to the carbonyl and carboxyl group(Mohammad et al, 2000)

3.5.2. Treated paper after heat aging

Dramatic changes are observed after solvent cleaning (see fig.4), after cleaning with solvents there are some differences in the decrease of the relative intensity of the O–H group at 3400 cm^{-1}.

3.5.2.1. Heat aged acetone treated sample

After cleaning with acetone (fig.4) the O–H stretching band at due to bending modes of water molecules disappeared ,band at 1156 cm-1 appeared (in comparison to the untreated sample). It may be due to C-O group of ester formation or new C-OH groups resulting from opening of the pyranose ring. More carbonyl groups were formed as a result of further oxidation of C-OH groups of cellulose molecules the band C-H stretching, which is evidence of complete water desorption, a slight increase in the relative intensity of the 3400 cm^{-1} peak is observed.

3.5.2.2. Heat aged toluene treated sample

Heat aging of toluene treated samples showed slight variations compared to heat aged untreated ones .The 1733$cm^{-1}$and 1638cm $^{-1}$band which represent the C=O carbonyl group have increased in relative intensity, this could be interpreted as change some of C–O group to C=O group. We can also observe the existence of the strong peak at 1114 cm^{-1}.In addition, the O–H group at 3400 cm^{-1} disappeared.

3.5.2.3. Heat aged alcohol treated sample

New bands due to free OH stretching appeared in the region between 3710 and 3565 cm-1. Various carbonyl groupscm^{-1} is presumably from the ester groups which may arise at this position of the spectrum and may form in the reaction of the carboxylic groups with unreacted alcoholic group or with residual ethyl alcohol (Inari,2007) .Finally, we can say

that Infrared spectroscopy is a useful method for studying and understanding the chemical changes in paper, but since the chemical composition of paper varies with different source (cotton, hemp, ramie& flax), etc. The spectra also change a little if recorded in different positions. This means that any changes have to be quite pronounced for us to be sure that it is really from the solvent and not the paper.

Table 3 The functional groups in paper.

Wave number cm^{-1}	Functional group
3400-3409cm^{-1}	Very strong, broad hydrogen bonded (O-H) stretching absorption
2894.7cm^{-1}	C-H stretching due to aromatic and symmetric stretching
1107,1053.8,1031 cm^{-1}	C = O stretching vibration
744.38 cm^{-1}	C-H bending vibration

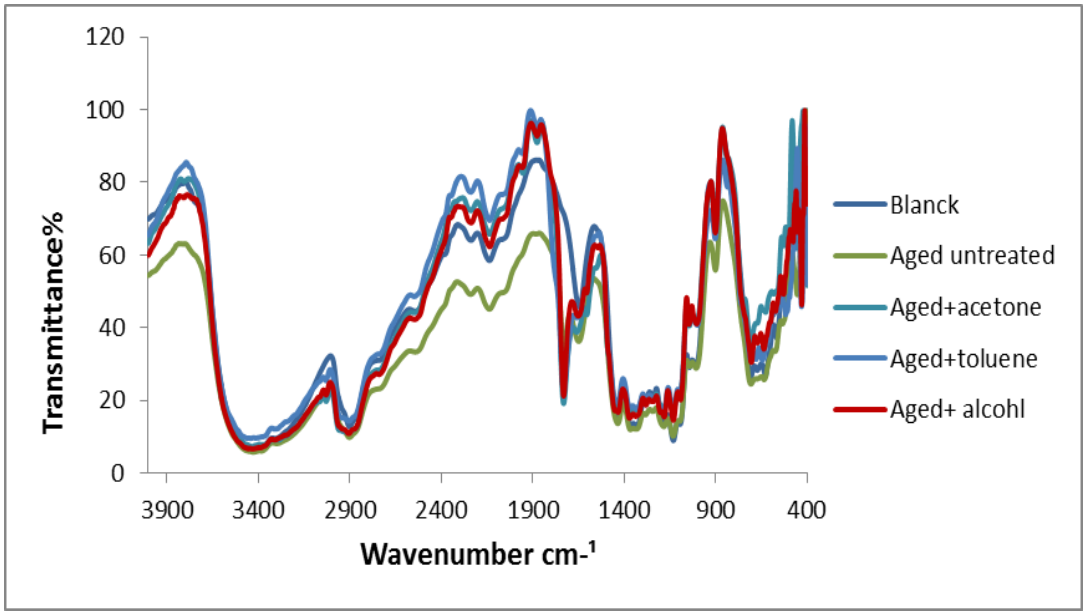

Figure 2 . FTIR Spectra of paper samples before and after cleaning with acetone, toluene and ethyl alcohol upon heat accelerated aging

4. PRACTICAL APPLICATIONS

Acetone, toluene and alcohol, seriously affect the properties and structure of paper, acetone showed a slight change compared to the other solvents used. So, it can be used safely in conservation treatment. It must be clear that the knowledge of the type and the chemical composition of cleaning material, which was used on the archaeological paper surface, in addition to its properties, lead to good results during cleaning, as it contributes in the selection of the best cleaning method to remove it and also reduces the amount of solvents used in the cleaning process, the length of time the paper is exposed to the solvent and the amount of mechanical action necessary to remove the foreign accumulation. It also increases the chances of a good cleaning. It must be clear that analyzing effects of chemical on archaeological paper, in addition to knowledge of these specific decay signs that provide important information to understand the paper condition after conservation treatment enable us to plan and determine appropriate lifting procedures as well as for selecting or developing conservation methods, and consolidation procedures or other treatments for each decay situation, to reduce the risks of losing historically important artifacts.

5. CONCLUSIONS

Using solvents in cleaning archaeological paper have been investigated using different experimental techniques including the mechanical properties, pH measurements, FTIR spectroscopy, Measurement of color change and X-ray diffraction after thermal accelerated aging. The conclusions that can be reached from this research can be summarized as follows:

Two mechanisms, such as degradation of structural components and formation of irreversible hydrogen bonds, are found to contribute to both the

hygroscopicity and the mechanical properties of aged paper.

It was found that the chemical composition of the paper components is affected by organic solvents commonly used in cleaning archaeological paper. Toluene and Ethyl alcohol accelerated oxidation and hydrolysis of paper samples. Acetone showed a slight change compared to the other solvents used. So, it can be used safely in conservation treatment, but the acetone increased the acidity of aged paper samples are another point to consider. Although the data obtained from both mechanical properties and pH were completely compatible, it is useful to note that sometimes there are changes in the chemical composition of archaeological paper observed using infrared spectroscopy.

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REFERENCES

Abdel-Kareem, O. Zidan, Y. Lokma, N. Ahmed, H; (2008) Conservation of a rare Painted Ancient Egyptian Textile Object form The Egyptian Museum, Cairo, *e-preservation Science,* 9-16.

Abdel-Maksoud , G;El-Aminb, A; (2013)The Investigation And Conservation of A gazelle Mummy from The Late Period in Ancient Egypt , *Mediterranean Archaeology and Archaeometry*, Vol.13, No 1, 45-67.

Abed-Maksoud, G (2010) Artificial Accelerated Aging and Investigation Method Used for the Evaluation of the Effectiveness of Polyurethane Applied for consolidation paper , *Journal of The Faculty of Archaeology* Vol . XIV. Cairo University Press, 85.

Attalla,R (1989) Patterns of Aggregation in Native Cellulose: Iimplication of Recent Spectroscopic Studies. In Kennedy J.f. Phillips G. o and Williams .P.A (eds) , *Cellulose* .Ellis Hour – wood , Chi Chester,61-67.

Attalla,R;Vander Hart, D (1984) Native Cellulose Composite of Two Distinct Crystalline Forms, *Science Journal* ,283 – 284.

Caulfield,D.F; Gunderson,D.E (1988) Paper Testing and Strength Characteristics, in: TAPPI *Proceedings of the 1988 Paper Preservation Symposium, Paper Preservation* (1988) 31–40, Available on http://www.fpl.fs.fed.us/documnts/pdf1988/caulf88b.pdf (May 08, 2008).

Darwish ,S.S. El Hadidi , N.M.N (2008) The Effect of Solvents on the Chemical Composition Of Archaeological Wood , *International conference of Giza though Ages*, Conservation Dept. - Faculty of Archaeology - Cairo University, 2-3.

Derrick,M. Stulik, D. Landry, J (1998) Infrared Spectroscopy in Conservation Science ,*The Getty Conservation Institute*, Los Angeles 182.

El Hadidi, N.M.N; Darwish, S.S (2008) The use of Acids and Alkalis in Cleaning Archaeological Wood, *Giza through the Age Conference*; Faculty of Archaeology, Cairo University.

El-Feky,O. M; Hassan, E.A; Fadel, S. M; Hassan, M. L (2013) Use of ZnO Nanoparticles for Protecting Oil Paintings on Paper Support Against Dirt, Fungal Attack, and UV Aging, *Journal of Cultural Heritage* xxx, xxx–xxx.

Fan,H. ; Li,G; Yang,F; Yang,L; Zhang,S (2011) Photodegradation of Cellulose Under UV Light Catalysed by TiO2, J. Chem. *Technol Biotechnol*. 86 ,1107-1112.

Florian,M; Dale, P.K; Norton, R.E. (1990) The Conservation of Artifacts Made from Plant Materials (First edition), *The Paul Getty Trust*, U.S.A, 215-216.

George,W (1995) Hand Book of Material Weathering, second ed., *Chem Tec*, Ontario, Canada.

Grawal,A; Barkeshli, p.O., (1997) Conservation of Books, Manuscripts and Paper Documents, *Indian Council of Conservation Institutes*, Lucknow ,111.

Hamed ,S.A; Ali,M.F; El Hadidi, N.M.N; (2013) Assessment of Commonly Used Cleaning Methods on The anatomical Structure of Archaeological Wood, *International journal of Conservation Science,* Volume 4, Issue 2, 153-160.

Havlínová, B. S; Katuˇsˇcák,M; Petroviˇcová,A. Maková,V. Brezová,A; (2009) A study of Mechanical Properties of Papers Exposed to Various Methods of Accelerated aging. Part I. The Effect of Heat and Humidity on Original Wood-Pulp Papers, *Journal of Cultural Heritage* ,10 ,222-231.

Hinterstoisser,B; Salme´n, L (2000) Application of Dynamic 2D FTIR to Cellulose, *Vibrational Spectroscopy 22*,111-118.

Horvath, A. L. (2006)Solubility of Structurally Complicated Materials, *J. Phys. Chem*. Ref. Data, Vol. 35, No. 1.

Inari,N. G.; Petrissans, M; Gerardin, P., (2007) Chemical Reactivity of Heat Treated Wood, *Wood Science and Technology*, Volume 41, no.2, (12),157-168.

ISO 187 (1990) Paper, board and pulps – Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples, *International Organization for Standardization*, Geneva, Switzerland.

ISO 1924-2 (1994) Paper and board – Determination of tensile properties – Part 2: Constant rate of elongation method, *International Organization for Standardization*, Geneva, Switzerland.

ISO 1924-3(2005) Paper and board – Determination of tensile properties– Part 3: Constant rate of elongation method (100 mm/min), *International Organization for Standardization*, Geneva, Switzerland.

ISO 5630-1 (1991) Paper and Board – Accelerated Aging – Part 1: Dry Heat Treatment at 105 ◦C, *International Organization for Standardization*, Geneva, Switzerland.

ISO 5630-4 (1986). Paper and Board – Accelerated Aging – Part 4: Dry heat treatment at 120 or 150 ◦C, *International Organization for Standardization*, Geneva, Switzerland.

ISO/DIS 15754 (2007) Paper and board – Determination of z-directional tensile strength, International Organization for Standardization, Geneva, Switzerland .

Junior,H.L (1999) The Development of Micro-Analytical Methodologies for Characterization of The Condition of Paper, *9th International Congress of IADA*, Copenhagen, August 15-21, 3920-3926.

Kamel,S; El-Sakhawy,M;, Nada, A.M.A (2004) Mechanical properties of The Paper Sheets Treated with Different Polymers, *Thermochimica Acta*, 421, 81–85.

Kanegsberg ,B (2001) What is Critical Cleaning ?, Handbook for critical cleaning. London, 12.

Larsen,R (2000) Experiments and Observations in The Study of Environmental Impact on Historical Vegetable Tanned Leather, *Thermochimica Acta* 365, 85-99.

Le Moigne ,N.M (2008) Swelling and Dissolution Mechanisms of Cellulose Fibres, Ecole Doctorale 364 : Sciences Fondamentales et Appliquées, *l'Ecole Nationale Supérieure des Mines* de Paris62.

Lojewska ,J.; Lubanska, A; Lojewski, T.; Miskowiec, P; Proniewicz, L. M., ,(2005) Kinetic Approach to Degradation of Paper. In situ FTIR Transmission Studies on Hydrolysis and Oxidation, *Directory of Open Access Journal*, 21-12.

Madorsky, M (1964) Thermal Degradation of Organic Polymers, *Wiley-Interscience*, New York.

Mohammad , H; Roger ,M ; Maim , A; Samira ,F; (2000) Thermo Plasticization of Bagasse. Preparation and Characterization of Etherified Bagasse Fibers, *Journal Applied Polymer Science.* Vol (76),561-576.

Moncrieff,A; Weaver,G. (1983) Cleaning (First edition), *Crafts Council Conservation Science*, London, 28- 31.

Moncrieff, A., Weaver, G.; (1994) Cleaning, Science for Conservators, vol.2,*The Conservation Unit & Routledge*, 13-15.

Nuopponen,M;(2005) Thermal Modification of Wood and FT-IR and UV Raman Spectroscopic Studies of its Extractable Compounds, PhD Thesis, *Helsinki University of Technology Laboratory of Forest Products Chemistry*, Reports, Series A 23, Espoo, Finland.

Petrulio,D;Kanegsberg, B;(1998) The Care and Feeding of A vapor Degreaser with New Solvents, Proc. Nap Con West 98. *Anaheim*, CA,16.

Romão, P.M.S., Alarcão, A.M., Viana, C.A.N;(1990) Human Salvia as a Cleaning Agent for Dirty Surfaces. *Study in Conservation* 35 (3), 153-155.

Stamm ,J.A; (1956) Thermal Degradation of Wood Cellulose, Forest Products Laboratory, Forest Service, U.S. *Department of Agriculture,Madison*,Wis. 413-418.

Sundqvist,B;(2004) Colour Changes and Acid Formation in Wood During Heating, Doctoral Thesis, *Luleå University of Technology*, Sweden, 50.

T-494(1988) om-88, Tensile Breaking Properties of Paper and Paper Board, Tappi Test Standards, *Tappi Technology Park*, Atlanta ,GA, USA.

Tesoro,G; (1976) Current Research on Chemical Modification of Cellulose, Pure & App L Chem., Vol. 46, *Pergamon Press*,239—245.

The Library of Congress (2006) Preservation, The deterioration and Preservation of paper: Some Essential Facts, http:// www.Loc.gov/preserv18octber.

Wächter,H; (1974),Cellulose, *Mitteilungen*, 4(4), 189.

Ward, K.J ; (1973) Chemical Modification of Paper Making, *Marcel Dekker*, New York ,23.

Wouters,J; (1993) ICOM Committee for Conservation, *10th Triennial Meeting* (Preprints), Dresden ,669.

Wouters,J; (1994) STEP Leather Project, European Commission DG XII, Research Report No .1 ,*The Royal Danish Academy of Fine Arts, School of Conservation*, Copenhagen,91.

Wouters,J; Bos, M; Claeys,V. J; Oostvogels, A; (1997) Environment Leather Project, European Commission DG XII, Research Report No. 6, *The Royal Danish Academy of Fine Arts, School of Conservation*, Copenhagen, 103.

Zervos,S; (2013) Revising Established Tenets in Paper Conservation, Procedia - *Social and Behavioral Sciences* 73, 35 – 42.

Zou,N; Gurnagul, T; Uesaka, J; (1994) Bouchard, Accelerated Aging of Papers of Pure Cellulose: Mechanism of Cellulose Degradation and Paper Embrittlement, *Polymer Degradation and Stability* 43, 393–402.