

## EXAMINATION OF EROSION IN USAGE OF CHEMICAL ANTISEPTIC IN HISTORICAL PAPERS DOCUMENTS

Haideh KHAMSEH<sup>1,\*</sup>

<sup>1</sup> Department of History and Archaeology, Science and Research Branch, Islamic Azad University, Tehran, Iran

### **Abstract**

*According to historical documents, the identity of a nation or ethnic group in each period is determined. Maintain these documents according to their structural nature that was so vulnerable to deterioration of the utmost importance. What factors should be considered Identify damaging agents and attempts to reduce it. Biological degradation is the main cause of damage to paper documents. To solve this problem, various methods were used. The most common method is using chemical antiseptic such as thymol, para chloro benzene dioxide, ethylene oxide etc. But what this study will examine the effects of abuse on the structure of these materials is cellulose paper such as ethylene oxide, indicating improper methods to remove the erosion and provide a convenient method, including freezing in order to reduce these damages. In this paper, 673 paper samples were studied, of the type of documents, which were identified first by the chemical laboratory method and then based on the information obtained from the results of tests with laboratory devices (FTIR, pH-meter). as well as by other methods. Aging, acidity and the effect of disinfectants on the structure of documents and fibers have been analyzed. In this research, which was tested on 673 paper samples, the type of dough was first identified by chemical laboratory method and then with the information obtained from the test results by laboratory devices (pH, FTIR meter) as well as methods. Aging, acidity and the effect of disinfectants on the structure of documents and fibers have been analyzed.*

**Keywords:** FTIR; Documents; Chemical; Antiseptic acidity; pH

### **Introduction**

Paper in every culture era as a written document Could bring on its own value. The organic matter in different historical periods has been used with a variety of structure. Since not only the historical aspects of the social, cultural, are considered, but also in terms of its structural materials can be research. The most important factor in the erosion rate of the paper is biological agents such as fungi. Fungi are important biodegrading and are considered as serious degrading agents where the presence of vegetative cells or spores on the surface of wood or other materials like paper may indicate a possible degradation in the future [1, 2]. The best way to avoid and eradicate the fungal infestation which cause degradation of different materials is to use antifungal compounds of botanical origin that are generally considered safe for human health and the environment. They are also used to preserve museum exhibits and antique book collections, important documents and different materials [3-6].

In order to eliminate biological factors, the common method is used chemical antiseptic, Such as para-chloro-benzene dioxide, thymol, methyl bromide and ethylene dioxide. This

\* Corresponding author: hkhamsheh72@yahoo.com

method of reduce the biological damage but damage to cellulose fibers [7]. This paper is based on impact of these factors on the primary structure of the paper are examined and the results are obtained from the use of this method is that the reason or is rejected and the main question in this paper was: "Do chemical disinfectants increase the acidity of the paper?" Erosion and environmental control in museum are very complex and the various methods in library, archive are used. Although most of these methods have positive effects but there are side effects. Antiseptic methods divided into several categories [8, 9], therefore, some usual method which are used in documents archive are as follow:

*Mechanical* (the removal of physical and biological factors). Paper was cleaned mechanically by soft brushes in the direction of the fibers from the middle toward the edges, beside using tweezers, a spatula, and air pump sometimes [10].

*Physical*, include methods of radiation (UV, gamma rays, beta rays, microwave radiation), freezing, and so on.

*Chemical* (the use of antiseptic and fungicide). Each method has advantages and disadvantages that may limit their use. The chemical method used in this research study material used for antiseptic in three phases are solid, liquid or gas [11, 12].

Solid as: Para dychloro benzene, thymol, ortho - phenyl – phenol;

Liquid as: Carbon tetrachloride;

Gas as: Ethylene oxide, hydrogen cyanide, methyl bromide.

In that case, the gas is more effective pesticide and disinfectant. This research examined Ethylene oxide and Thymol will be studied [13, 14].

## Experimental psrt

### *Materials*

#### *Ethylene oxide and Thymol*

Ethylene oxide  $\text{CH}_2\text{CH}_2\text{O}$  was used as disinfectant, began in 1928 as an agricultural insecticide fumigation gaseous disinfectant is a standard library and usually 10 to 12% concentration in the gas containing carbon dioxide or Freon are used. Ethylene oxide on eggs and larvae and adult stages of insects and fungi is effective. Bacteria can also be disinfected, 1.0ppm limit value is set at 8 hours. Preliminary results have shown that this substance causes reaction with metals, Cellulose and protein. Disinfected after removal of impurities is less variation. Its smell is the limit 24ppm. The gas does not ignite and 50cm in depth is required [15-17].

Thymol (2-isopropyl-5-methylphenol) is the main monoterpene phenol occurring in essential oils isolated from plants belonging to the Lamiaceae family (Thymus, Ocimum, Origanum, and Monarda genera), and other plants such as those belonging to the Verbenaceae, Scrophulariaceae, Ranunculaceae, and Apiaceae families. These essential oils are used in the food industry for their flavouring and preservative properties, in commercial mosquito repellent formulations for their natural repellent effect, in aromatherapy, and in traditional medicine for the treatment of headaches, coughs, and diarrhea. Many different activities of thymol such as antioxidant, anti-inflammatory, local anaesthetic, antinociceptive, cicatrizing, antiseptic, and especially antibacterial and antifungal properties have been shown [18-21].

Thymol in the form of libraries and documentation fumigations (steam) is used, but owners of small libraries or small collections better of thymol as paper impregnated. Among the books or documents to which it is put to use. The disadvantage is the toxicity of thymol.

#### *Chemical test for fiber identification*

673 types of documents in the National Archives and Library of Iran were identified through chemical testing according to the standard of the Iranian Standard Organization 17-14 and according to the obtained pulps, a high percentage was obtained (Fig. 1).

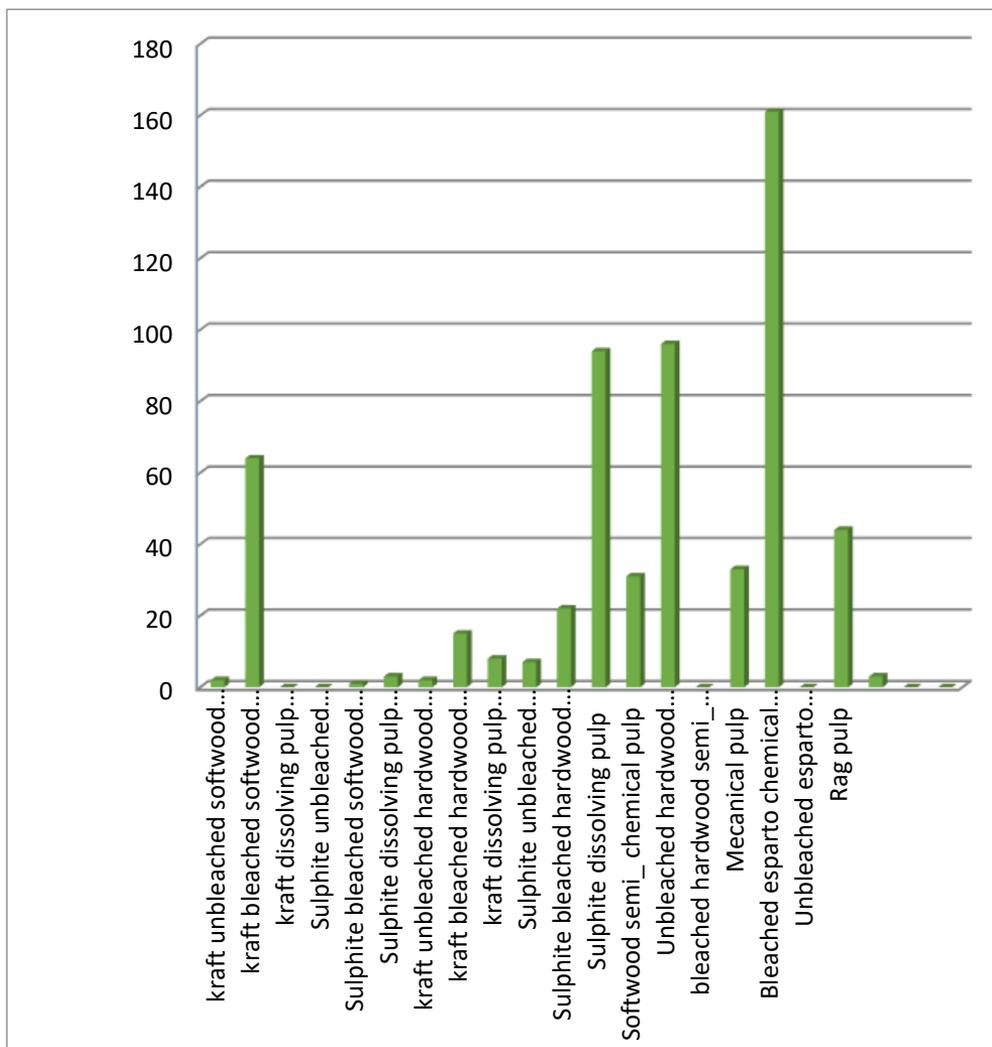


Fig. 1. Pulp papers

### Methods and techniques

Tests on samples of studies included the following measurements: determined paper pulp, antiseptic with ethylene oxide, aging, Infrared Spectroscopy, pH. Thus, it has been determined that the type of paper pulp, so the pulp is from softwoods, hardwoods, fabrics and esparto. This test is used detectors from the reagents graph C, Herzberg and fushin [21]. Condition with ethylene oxide antiseptic unit volume of  $5\text{m}^3$  and 34g of gas. are injected into the system in a vacuum environment. Disinfection time is 7h. In four stages of air vacuum is performed and to be removed from quarantine after 48h.

After disinfection of the aging tests were performed on samples that with  $23^\circ\text{C}$  temperature and 50% humidity aging device starts [22].

### FT-IR analysis

The main aim of using the analysis in this study is to know functional group, which is used the cellulose decomposition of the manuscript paper.

The Equinox 55 model is made by the German company BRUKER was used. Using this device, the FTIR range of samples in the range of  $400\text{-}4000\text{cm}^{-1}$  is obtained. The tests that must

be done on the sample before starting work are: samples do not have water and moisture; film samples should be in the form of a thin and transparent film so that light can pass well; the thickness of the film should not be more than 30 microns; powder samples should be fine and dry powder.

FTIR Spectrum shows the peaks in the region 1000 to 1500, 3500 and 1432cm<sup>-1</sup> have the highest peak in the state sterilized with ethylene oxide (Fig. 2).

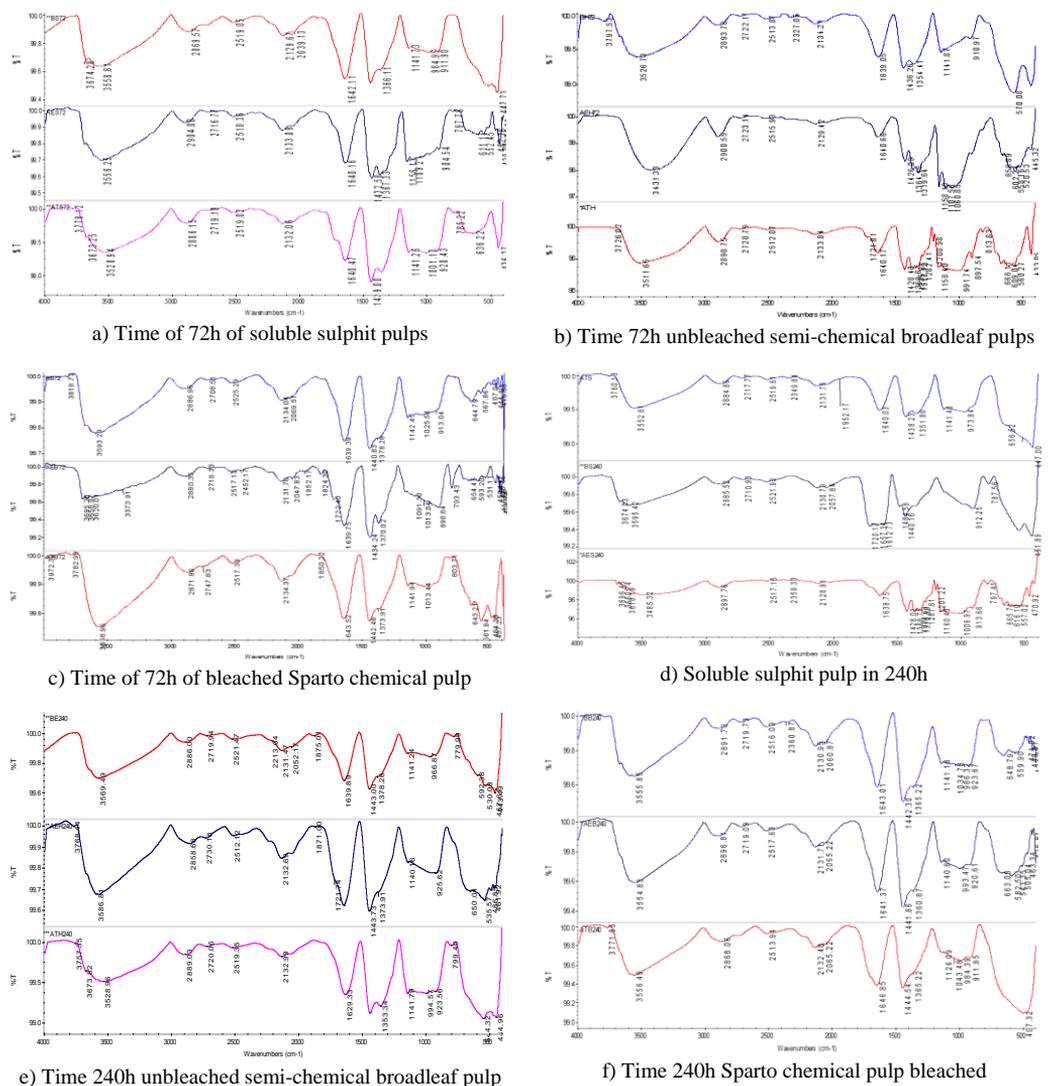


Fig. 2. FTIR Spectres results in 6 pulps

*Determination of the pH*

Paper pH knowledge is a simple but a very useful tool to define the paper conservation status. The method used determines the pH value of a thin water layer laid on a surface by a potentiometric measurement. The water allows the substances present in the superficial paper layer to cross into the water solution. These substances affect pH values. The pH value was determined by using a portable pH-meter (Digi-Sense, USA) connected to a plane electrode of contact [23].

Acidity increases during aging is shown (Fig. 3).

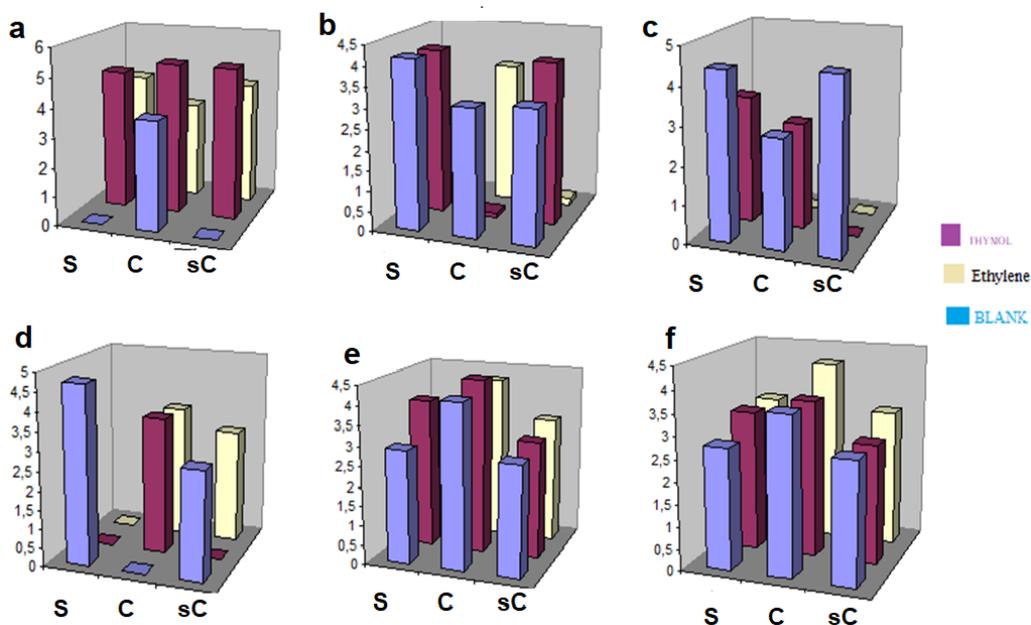


Fig. 3. The pH tests: a – at beginning, b – after 24h, c – after 72h, d – after 144h, e – after 192 h, f – after 240h.

## Results and discussion

Based on the peaks obtained from soluble sulphit pulp in area  $3500\text{cm}^{-1}$ , we have the highest peak in the case of fumigation with ethylene oxide. In figure 2a, the areas between  $3500$  and  $1500\text{cm}^{-1}$  do not change much and the most change is observed in ethylene oxide in areas of  $1432\text{cm}^{-1}$ . The presence of these peaks in these areas is the reason for the presence of methylene  $\text{CH}_3$ -functional groups. The greatest change is in the range between  $1000$  and  $1500\text{cm}^{-1}$ , which we have changed in all groups. And does not give much information. The change in sulfite paste with ethylene oxide is more than thymol. In general, it can be said that according to the obtained diagrams, the aging changes of 72h do not show a significant difference in sulfite paste.

In 72h (Fig. 2b), unbleached semi-chemical broadleaf pulps. In the range between  $3000$  and  $3500\text{cm}^{-1}$  there is no significant change in all three cases. The diagram shows the IR spectrum of the pulps made from unbleached broadleaf, which also shows the strong spectra of the  $3500\text{cm}^{-1}$  regions, which correspond to the previous pulps (sulphit). The graphs show that no significant change is observed in the spectra, except for the areas  $1000$  to  $1500\text{cm}^{-1}$ , which belong to the groups of alkenes, which are the result of chemical changes or the use of ethylene oxide or thymol.

In figure 2c, for 72h of bleached Sparto chemical pulp, the spectra show that the spectra in the  $3500\text{cm}^{-1}$  regions have undergone slight changes that could be due to chemical changes in this synthetic sample of paper with ethylene oxide, although they do not show very marked changes and the dough is clearly identical in disinfection with thymol and shows no disinfectant. Examination of the spectra shows changes in the range of  $500$  to  $1000\text{cm}^{-1}$  (off-plane bending alkenes) in ethylene oxide impregnated paper and the sample if these changes in the impregnated paper Thymol is much higher, it can be seen that some weak peaks have been removed in this area.

Soluble sulphit pulp in 240h (Fig. 2d), the diagrams show that no comorbid changes are observed in the main paper texture after the application of ethylene oxide and thymol. The only change observed in this study is in the IR spectra. In the range of 1000 to 1500 $\text{cm}^{-1}$ , small absorptions are observed, which can be related to changes in the chemical structure of the paper. This change was not observed in thymol-impregnated paper and there was no significant difference between the control paper and the thymol-stained sample.

In 240h, Unbleached semi-chemical broadleaf pulp (Fig. 2e), these spectra show that no significant changes have been observed in the structure of this type of paper and the use of thymol and ethylene oxide disinfectants seems to be harmless.

In 240h Sparto chemical pulp bleached (Fig. 2f), these spectra show that we do not see any significant sturcker changes in thymol and ethylene oxide papers and samples.

As can be seen in the 72h charts discussed, small chemical changes were observed in semi-chemical papers with ethylene oxide, which could not be traced or tracked in 240h papers, which could result in It is possible that ethylene oxide is present in the pores or structure of the remaining paper in the IR spectrum of these compounds, which after 240h is removed from the paper texture and again the same spectrum is observed between the three paper samples.

According to the pH values, the acidity increases during aging is shown in figure 3 [24].

## Conclusions

Methylene  $\text{CH}_2$  groups have a characteristic adsorption of about 1450 $\text{cm}^{-1}$ . Methylene  $\text{CH}_3$  groups have adsorption in the area of 1375 $\text{cm}^{-1}$ . Alkenes C-H = plane bending at 650-1000 $\text{cm}^{-1}$  has adsorption. Methyl and methylene groups can be identified by examining the area of 1365-1465 $\text{cm}^{-1}$ . The scissors related  $\text{CH}_2$  spectrum appears in the 1465 $\text{cm}^{-1}$  area.

These bands indicate the presence of methylene and methyl groups in the infrared spectrum.

Cis-trans doped 1,2-heterogeneous bonds: the cis form is shown on a strong double-bonded pound near 700 $\text{cm}^{-1}$ . The transform absorbs near 970 $\text{cm}^{-1}$ , which is important for the diagnosis of stereochemistry, indicating substitution by disinfectant agents or functional groups.

The acidic agent 3400-2400 $\text{cm}^{-1}$  hydrogen bond has a very wide and strong adsorption that the spectrum of acidity increases with increasing aging hours.

The obtained results demonstrated from experiment IR has a very broad and strong absorption of hydrogen bond acidity of 3400-2400 $\text{cm}^{-1}$ . The spectrum with increasing aging time increased acidity. So, this result paper was made with ethylene oxide sterilization after time with aging test and PH test their acidity has increased.

By measuring the amount of acidity in the obtained values, it showed that with increasing aging time, its acidic value increased and became acidic.

Based on the results, the chemical assay method is not a suitable method for antiseptic decontamination.

It is indicated to use the vacuum, freezing and plant disinfectants methods.

## Acknowledgments

The authors are grateful to Polymer and Petrochemical Research Institute of Iran Laboratory for the FTIR examination which was conducted at National Library of Iran.

## References

- [1] A.A. Fabbri, A. Ricelli, S. Brasini, C. Fanelli, *Effect of different antifungals on the control of paper biodeterioration caused by fungi*, **International Biodeterioration and Biodegradation**, **57**, 1997, pp. 61–65.

- [2] N. Mesquita, A. Portugal, S. Videira, S. Rodríguez-Echeverría, A.M.L. Bandeira, M.J.A. Santos, H. Freitas, *Fungal diversity in ancient documents. A case study on the Archive of the University of Coimbra*, **International Biodeterioration and Biodegradation**, 63, 2009, pp. 626–629.
- [3] S. Borrego, S Gómez De Saravia, O. Valdés I, I. Vivar I, P. Battistoni, P. Guiamet, *Biocidal Activity of Two Essential Oils on Fungi that Cause Degradation of Paper Documents*, **International Journal of Conservation Science**, 7(2), 2016, pp. 369-380.
- [4] O. Florescu, R. Hritac, M. Haulica, I. Sandu, I. Stanculescu, V. Vasilache, *Determination of the Conservation State of Some Documents Written on Cellulosic Support in the Poni-Cernatescu Museum, Iasi City in Romania*, **Applied Sciences-Basel**, 11(18), 2021, Article Number: 8726. DOI: 10.3390/app11188726.
- [5] M. Boutiuc (Haulica), O. Florescu, V. Vasilache, I. Sandu, *The Comparative Study of the State of Conservation of Two Medieval Documents on Parchment from Different Historical Periods*, **Materials**, 13(21), 2020, Article Number: 4766. DOI: 10.3390/ma13214766
- [6] M. Boutiuc (Haulica), V. Vasilache, O. Florescu, M. Brebu, I. Sandu, P.O. Tanasa, J.C. Negru, *Study of the Effects of Skin Surface Lipids on Old Cellulose-Support Documents*, **International Journal of Conservation Science**, 11(3), 2020, pp. 731-746.
- [7] W.W. Allen, *Fumigation for cyclamen mite: Fumigation for cyclamen mite: Methyl bromide fumigation can give good control of pest on strawberries when treatment is properly timed and applied*, **Hilgardia**, 11(9), 1957, pp. 9-15.
- [8] H.A.U. Monro, *Manual of fumigation for insect control*, **FAO Agricultural Studies No. 79, FAO Plant Production and Protection Series No. 20**, 1969, pp. 142-146.
- [9] W.J. HAYES, *Clinical handbook on economic poisons*, **U.S. Public Health Service, Publication No. 476 Rev.** Washington, D.C., 1963.
- [10] S. Zervos, *Natural and accelerated ageing of cellulose and paper: A literature review, Cellulose: Structure and properties, derivatives and industrial uses*, **Nova Publishing**, New York, 2010, pp. 155-203.
- [11] P. Engel, K. Sterflinger, R. Eckhart, *Ethyleneoxide Fumigation for Mouldy Archival Material*, **Österreichische Restauratorenblätter (Paper Conservation News)**, 2014, pp. 241-255.
- [12] R.A. Higham, **A Handbook of Paper Making**, Oxford University Press, 1968, p. 282.
- [13] A. Liénardy, P. van Damme, *Resultats de recherches experimentales sur le blanchiment du papier*, **Studies in Conservation**, 34(3), 2013, pp. 123-136.
- [14] R.L. Feller, M. Wilt, **Evaluation of Cellulose Ethers for Conservation**, Getty Conservation Institute, 1990.
- [15] C. Snyder, S. Springer, *Putting the Wiki Platform to Work: Sharing Material Testing Results*, **Conservation & Exhibition Planning: Material Testing for Design, Display & Packing**. Abstracts, Smithsonian American Art Museum, 2015, pp. 5-6.
- [16] S. Springer, *Putting the Wiki Platform to Work: Sharing Material Testing Results*, **Selected Proceedings of Advances in Conservation**, [S.l.], nov. 2017. Available at: <<https://epubs.utah.edu/index.php/waac/article/view/4021>>. [Date accessed: 24 oct. 2020].
- [17] T.A. Salah, *investigation and restoration of a 17th century ad manuscript at al-azhar library in egypt*, **International Journal of Conservation Science**, 9(1), 2018, pp. 117-126.
- [18] G. Giovani, L.A.C. Souza, Y. Froner, A. Rosado, *The use of industrial paint on wood by Lygia Clark*, **Studies in Conservation**, 61(2), 2016, pp. 291-293.
- [18] O. Borhan, A. Muresan, C.D. Radu, E. Muresan, C. Rimbu, I.G. Sandu, *Silver Nanoparticles Used to Obtain Cellulosic Materials with Antibacterial Properties*, **Revista de Chimie**, 66(11), 2015, pp. 1796-1801.

- [19] R.V. Lupusoru, L. Simion, I. Sandu, D.A. Pricop, A. Chiriac, V. Poroach, *Aging Study of Gold Nanoparticles Functionalized with Chitosan in Aqueous Solutions*, **Revista de Chimie**, **68**(10), 2017, pp. 2385-2388.
  - [20] C.V. Houry, **Materials Used in the Restoration of Organic Solvents Ashesives and Varnishes**, Tehran University, 1999, pp.110- 115.
  - [21] A. Marchese, I. Erdogan Orhan, M. Daglia, R. Barbieri, S. M Nabavi, *Antibacterial and antifungal activities of thymol: A brief review of the literature*, **Food Chemistry**, **210**, 2016, pp. 402-414.
  - [22] A. Kelaydezil, **Chemical Materials Used in Restoration**, Translated by Mariyam Baba Shahi, University of Art, Tehran, 2000, pp. 152-153.
  - [23] S. Manente, A. Micheluz, R. Ganzerla, G. Ravagnan, A. Gambado, *Chemical and biological characterization of paper: A case study using a proposed methodological approach*, **International Biodeterioration and Biodegradation**, **74**, 2012, pp. 99-108.
  - [24] G. Crazy, J. Vivian, D. Pavia, G. Lampman, **A Perspective on Donald Pavia Spectroscopy Translated by Brahman Authentic**, Publisher Scientific and Technical, 2006, pp. 30-32.
- 

*Received: October 10, 2020*

*Accepted: October 2, 2021*