Zno Nanocomposites: Control of Enviromental Effects for Preservation of old Manuscripts

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***Abstract*—**We investigate the ZnO role in the inherent protection of old manuscripts to protect them against environmental damaging effect of ultraviolet radiation, pollutant gasses, mold and bacteria. In this study a cellulosic nanocomposite of ZnO were used as protective coating on the surface of paper fibers. This layered nanocomposite can act as a consolidate materials too. Furthermore, to determine how well paper works screen objects from the damaging effects, two accelerated aging mechanisms due to light and heat are discussed. Results show good stability of papers with nanocomposite coating. Also, a good light stability was shown in the colored paper that treated with this nanocomposite. Furthermore, to demonstrate the degree of antifungal and antibacterial properties of coated papers, papers was treated with four common molds and bacteria and the good preventive effects of coated paper against molds and bacteria are described.

***Keywords*—**Enviromental effects, Manuscript, Nanocomposite, Zinc oxide.

I. Introduction

PAPER -art-works such as old manuscripts are susceptible objects that need to protect from damaging effect of ultraviolet radiation, visible light, air pollutant, mold and bacteria [1-3]. Preventive conservation is an important element of museum policy and collections care. It is an essential to create and maintain a protective situation for the collections in their care. Since ZnO is broadly used in modern and contemporary pictorial art, acting both as a pure white pigment or a moderator of hue and saturation, the present paper is trying to investigate the ZnO role in the inherent protection of paper works of art. Zinc oxide is considered a safe substance and harmless to human. ZnO coatings have received much attention as photocatalysts in practical applications such as environmental purification, deodorization, sterilization and self-cleaning [4,5]. The photocatalytic reactivity of zinc oxide can be applied for the reduction or elimination of polluted compounds in air such as nitrogenous and sulfurous compounds, greenhouse gases and cigarette smoke, as well as volatile compounds arising from various construction materials, atmospheric constituents such as chlorofluorocarbons undergoes photochemical reactions either directly or indirectly [6,7]. This technology is also very effective at killing a variety of bacteria and molds [8,9]. A variety of physical and chemical approaches have been used to prepare zinc oxide coating [10,11].

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However, the preparation of ZnO thin coatings is usually achieved at relatively high temperature or mechanical impact condition. Using this coating in the substrates with low thermal and mechanical resistance such as old manuscripts needs more attention. Non-impact spray based techniques are generally preferred to avoid breaks and streak defects. Also paper objects should be placed far enough away from display cases that oxide does not affect on the chemical and physical properties of fibers over time.To demonstrate the suitability of our coating method to protective the paper, first we have chosen a filter paper (Whatman) to test the coating procedure, then some pages of ancient manuscript was examined. Zinc oxide nanoparticles were dispersed in ethanol by using ultrasonic instrument and used for coating the selected papers. Many pieces were cut from paper and one set was reserved without any treatment for comparison. Another set of samples prepared by coating the surface of paper by Klucel and then spray the zinc oxide nanodispersion on the cellulosic polymer (Klucel) (Fig. 1). This layered nanocomposite can act as a consolidate materials as well as protecting papers from UV light, air pollutant, mold and bacteria.

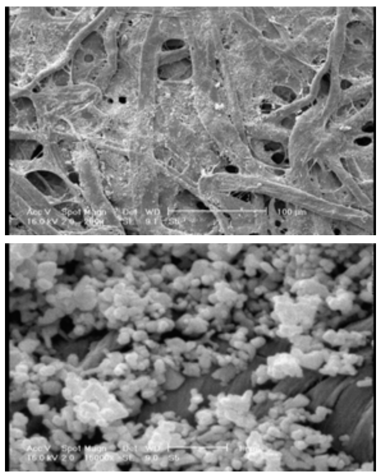

Fig. 1 SEM images of ZnO coating on the surface of paper

The SEM of coated sample showed ZnO nanoparticles which identified by EDX too (Fig 1). SEM analysis also showed that no degradation of the fiber structure has occurred during coating. The FTIR specta of the papers obtained from coating of ZnO nanocomposite clearly shows the ZnO absorption band. As you seen, the absorption band of Zn-O in coated paper was shifted to higher frequencies. This observation accepted chemical bonding between ZnO and cellulosic surfaces.

As we know, when considering the use of new materials for conservation of art works, it is important to understand the probable long-term effects of treatments. The chemical and physical properties of art works must be remain stable long enough. So accelerated ageing are designed to find materials which can be safe for long-term use and would not cause degradation of treated papers. Accelerated ageing techniques are useful for detecting physical and chemical changes released by conservation materials after a long time. In these studies on the aging of paper materials, the two accelerated aging mechanisms described are those due to light and heat. The FTIR spectra of coated papers compared with uncoated one after accelerated ageing clearly show that nanocomposite coating can successfully preserve paper from cellulose degradation. The bands at 1740 and 1630 cm-1 have proved the degradation of paper by oxidation of cellulose under ageing condition that are assigned to C=O vibrations. These bands in coated paper with ZnO nanocomposites are so weak. This observation shows a little degradation of cellulose in coated paper with ZnO nanocomposite. Additionally, degradation of mechanical properties of papers with aging has been measured by tensile strength to evaluate the effects of thermal aging on the properties of coated papers. Mechanical tests highlight that artificially aged paper are coated with ZnO, retained good resistance to tensile strength. On the other hand, the uncoated papers showed a strong decrease in mechanical resistance after aging (Fig.2).

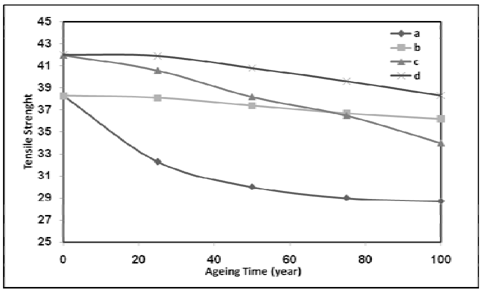

Fig. 2 Tensile strenght of (a) uncoated paper, coated paper by (b) ZnO nanoparticles, (c) Klucel, (d) ZnO nanocomposite

Also, the UV-absorber property of zinc oxide coating was evaluated by testing the rate of fading of colored paper under UV exposure. Light is a common cause of damage to library and archival collections. Paper, bindings, and media (inks, photographic emulsions, dyes, and pigments, and many other materials used to create words and images) are particularly sensitive to light. Light damage manifests itself in many ways. Light can cause paper to bleach, yellow, or darken, and it can weaken and embitter the cellulose fibers that make up paper. It can cause media and dyes used in documents, photographs, and art works to fade or change color. Light energy is absorbed by molecules within an object. This absorption of light energy can start many possible sequences of chemical reactions, all of which damage paper.

The performance of ZnO nanoparticles as UV-absorbers can be efficiently transferred to papers through the application of ZnO nanoparticles on the surface of coated paper. This property of zinc oxide nanoparticles can be exploited for the protection of the art works against light. To determine how well paper works screen objects from the damaging effects of ultraviolet radiation, a selection of colored papers were exposed to light and the fading of color are discussed. The fading rate of the colorant-on-paper samples can be characterized by the change over time of their visible reflectance spectra. The diffuse reflectance spectra of these samples were measured before and at intervals during the UV exposure experiment. The traditional artists' colorant, Alizarin Lake, was used as a model of a fugitive organic pigment, applied in coloring the paper samples. As the physical-chemical principles that govern the fading of pigments have been difficult to discover solely by visual observation of changes in color. We use of precise spectrophotometric reflectance measurements to demonstrate that the decrease in concentration of Alizarin Lake (fading) during exposure. This result suggests that the colorant molecules on the surface of the samples, which are easily brought into contact with UV light, are consumed quickly. So, the rate of fading in uncoated paper is more than nanocomposite coated paper. This slowing of the fading process in nanocomposite coated paper over time is expected because the remaining colorant embedded under the layer of cellulosic polymer and absorbing of UV light by ZnO nanoparticles becomes more difficult to reach the UV light to colored paper. Furthermore, to demonstrate the degree of antifungal and antibacterial properties of coated papers, samples were treated with two common molds (Aspergillus Niger and Penesilium) and two bacteria (Escherichia coli and Staphylococcus aureus) the preventive effects of coated paper against molds and bacteria are discussed. Paper is subjected to numerous biodeterioration processes, which may cause the irreversible degradation of important documents and works of art. Many chemical and physical factors can affect these processes and their behavior, and fungi seem to play a key role in biodeterioration of paper works. This study is mainly aimed at verifying the antifungal and antibacterial properties of zinc oxide coating. It was found that ZnO possess substantial antibacterial and antifungal properties in light and dark. These results suggest that a ZnO coating may have prevented the formation of a protective biofilm of adsorbed bacteria and fungi rather than actively killing them. Results show that in coated paper, the bacteria and fungi growth was significantly decreased compared with uncoated sample.

II. Conclusion

Paper is subjected to numerous deterioration processes, which may cause the irreversible degradation of important documents and works of art. In this study, we investigate the TiO2 role in the inherent protection of paper works of art to protect them against damaging effect of ultraviolet radiation, pollutant gasses, mold and bacteria. Layered cellulosic nanocomposite of TiO2 was used as protective coating on the surface of paper fibers. This layered nanocomposite can protect the paper from damaging effects of UV light, air pollutant, mold and bacteria. Furthermore, to determine how well paper works screen objects from the damaging effects, two accelerated aging mechanisms due to light and heat are discussed. Degradation of mechanical properties of paper with thermal aging has been measured in tensile strength of papers. Results show good stability of papers with nanocomposite coating. For aged samples, the strength drops down drastically with ageing time as paper becomes brittle due to variation in structure of the paper. Also, a good light stability was shown in the colored paper that treated with this nanocomposite. Furthermore, to demonstrate the degree of antifungal properties of coated papers, samples was treated with two common molds and the good preventive effect of coated paper against molds is described.

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REFERENCES

[1] P. Begin, S. Deschateletes, D. Grattan, N. Gurnagul, J. Iraci, E. Kaminska, D. Woods, X. Zou, *Restaurator* vol. 20, pp.1-7, 1999.

[2] M. Strlic, J. Kolar, *Fifth EC Conf. Cultural Herit. Res.: Pan-Eur. Challenge*, Cracow, Poland, 2002, pp. 79-86.

[3] S. Margutti, G. Conio, P. Calvini, E. Pedemonte, *Restaurator* vol. 22, pp. 67-83, 2001.

[4] A. Fujishima, T.N. Rao., D.A. Tryk, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* vol. 1, pp. 1-21, 2000.

[5] Fujishima, A., Hashimoto, K., Watanabe, T., *TiO2 Photocatalysis; Fundamentals and Applications. Best Knowledge Center* (BKC), Tokyo, Japan, 1999.

[6] J.M. Herrmann, *Catalysis Today* vol. 53, pp. 115-129, 1999.

[7] J. M. Daisey, A. T.Hodgson, W. J. Fisk, M. J. Mendell, J. Tenbrinke, *Atmos. Environ*. Vol. 28, pp. 3557-3559, 1994.

[8] Walid A. Daoud, John H. Xin, Yi-He Zhang, *Surface Science* vol. 599, pp. 69-75, 2005.

[9] P.C. Maness, S. Smolinski, D.M. Blake, Z. Huang, E.J. Wolfrum, W.A. Jacoby, *Appl. Environ. Microbiol*. Vol. 65, pp. 4094-4098, 1999.

[10] C.R. Bickmore, K.F. Waldner, R. Baranwal, T. Hinklin, D.R. Treadwell, R.M. Laine, *J. Eur. Ceram. Soc*. Vol. 18, pp. 287-301, 1998.

[11] A. Sandell, M.P. Andersson, M.K.J. Johansson, P.G. Karlsson, Y. Alfredsson, J. Schnadt, H. Siegbahn, P. Uvdal, *Surf. Sci.* vol. 530, pp. 63-68, 2003.