Facile and Scalable Conservation of Chinese Ancient Paintings Using Water-Borne Fluoropolymer

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ABSTRACT: In China, alum-gelatin aqueous solution is historically used to prevent falling off of mineral pigments from paintings and to enhance strength of their paper matrices in the restoration process. However, after a long period of time of preservation, alum-gelatin aqueous solution applied to paintings will hydrolyze and produce free acid, which accelerates aging. To resolve this issue, instead of using alum-gelatin aqueous solution, here we report a new method of hydrolysis and producing free acid, which accelerates aging. To resolve this issue, of time of preservation, alum-gelatin aqueous solution applied to paintings will of their paper matrices in the restoration process. However, after a long period the di

1. INTRODUCTION

Chinese ancient paintings are important cultural heritage, with high values for history, art, and culture research. Traditionally, for these paintings, handmade papers are used as carrier on which contents are drawn with inks and mineral pigments of the different colors. Using handmade papers without proper pretreatment, inks, and pigments will fast disperse and penetrate into paper fibers during the painting process but will lead to undesired diffusion. To this end, in the ancient times, handmade papers were usually pretreated with alum-gelatin aqueous solution as a surface-sizing agent in order to decrease hydrophilicity and thus decrease diffusion rate of inks and pigments on the paper. This would allow painting processes in a well-controlled manner. However, the alum is prone to hydrolyze to produce acids, which will catalyze the hydrolysis and aging of cellulose, causing Chinese ancient paintings to suffer from acidification, yellowing, and embrittlement. For this reason, many Chinese ancient paintings of Ming and Qing Dynasty in museums have become yellow, brittle and easy to break, and even pulverized. The conservation and restoration of such ancient paintings are imminent. In China, traditional mounting technique is a common and effective restoration technique, which has a long history of more than 2000 years, mainly including the procedures such as cleaning, uncovering, mending, mounting, and color compensating (Figure 1).

Cleaning refers to wash painting by using water. Harmful degradation substances of paintings will dissolve into water and then be taken away. However, water cleaning will decrease interfacial binding between applied inks and/or pigments and a handmade paper, leading to falling off of pigment and decrease in mechanical properties of the paper. As a result, quite similar to pretreatment of handmade papers for original painting, alum-gelatin aqueous solution composed of alum and gelatin according to a certain ratio was used to reinforce paintings prior to cleaning, a well-established procedure from as early as in the Tang Dynasty (618–907 A.D.). In alum-gelatin solution, gelatin is mainly made up of collagen whose amino, hydroxyl, and amide groups can be associated with each other to form a protective film on papers. Alum (KAl(SO_4)_2·12H_2O) can further promote adhesion between gelatin and pigments.

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and papers.\textsuperscript{14,15} However, alum will liberate free acid due to hydrolysis of alum, thereby accelerating oxidative degradation of paper cellulose and thus deteriorating the long-term preservation of paintings.\textsuperscript{16−20} Even worse, gelatin is prone to aging and decomposing. These issues have long existed but really challenging, and their solution that relays on developing new reinforcing materials of high durability in place of alum are commonly synthesized from copolymerization of fluoroethylene-vinyl, which are commonly synthesized from copolymerization of fluoroolefin monomers such as chlorotrifluoroethylene (CTFE) or tetrafluoroethylene (TFE) with vinyl ether and/or ester monomers. FEVE’s main chains commonly consist of \(-\text{CF}_2-\text{CFX}-\) (where \(X\) is a halogen) with functional groups such as \(-\text{COR}, -\text{OR}, -\text{R}_1\text{OH}, \text{ and } -\text{R}_2\text{COOH}\) as side chains where \(R_1=R_2=\text{alkyl and others}\).\textsuperscript{21,22} The F atom has the strongest electronegativity with a small atomic radius, leading to very high dissociative energy F−C bond. As a result, FEVE displays excellent chemical and thermal stability, aging resistance, and fire retardancy.\textsuperscript{23,24} FEVEs are widely used as durable protective coatings in many fields, such as architectural paint, vehicles, heavy-duty coating, and insulation systems.\textsuperscript{25,26} FEVE can be classified into solvent-based and water-borne ones, and the latter can be dispersed into water resulting in significant environmental benefits especially for coating applications.\textsuperscript{27} So, water-borne FEVE receive a lot of research interests in recent years in the academia and industry and find important applications in protective and decorative coatings for steel, aluminum, plastic, cement, and furniture wood. So far, the application of water-borne FEVE in reinforcing ancient paintings is rarely reported in the open literature, and FEVE are expected to be able to deliver some desired results. In the present study, we selected a commercial water-borne FEVE (ZB-F600) and they were applied to reinforce paintings on papers. As illustrated in Figure 2, ZB-F600 is a copolymer of trifluorochloroethylene, vinyl acetate, allyl alcohol, and fatty acid. The trifluorochloroethylene units provide the weatherability and durability, the vinyl ester units provide the good solubility and transparency; the allyl alcohol’s hydroxyl groups provide cross-linkable sites; and the fatty acid units provide wettability and adhesion. These characteristics rationalize the capability of ZB-F600 to be suitable for protecting ancient paintings. To test this hypothesis, we applied ZB-F600 not only to simulated paintings but also to real ancient paintings. We examine related antipeeling property of pigment, paper mechanical properties, colorimetric parameters, surface morphology, and water contact angle. The results show that ZB-F600 endows the treated paintings with the good comprehensive performances, preventing falling off of mineral pigments without a significant alternation of the traditional mounting process. Our work provides a new, facile, effective, and harmless approach to better protect historical paintings.

2. EXPERIMENTAL SECTION

2.1. Materials. The water-borne fluoro carbon emulsion ZB-F600 was obtained from Dalian Zhenbang Fluorine Paint Co., Ltd. (China). The key physical and chemical properties of ZB-F600 from the vendor are listed in Table 1. ZB-F600 is a water emulsion with a solid content of \(~42\) wt %, an average particle size of \(100−200\) nm, and a viscosity of \(30−40\) cps. So, ZB-F600 has good fluidity and dispersion stability. Also, its pH value is \(~7−9\), which will not increase acidity of papers. The four kinds of mineral pigments, which are cinnabar, ultramarine, malachite, and carbon black, were purchased from Beijing Jindizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China). Gelatins were bought from Jinbizhai Art Pigment Factory (China).

Figure 1. The typical process of traditional mounting technique. (a) Cleaning is to remove contaminants on ancient paintings; (b) uncovering is to remove back mounting paper of the paintings and supporting paper for the core area of the paintings, named the life paper; (c) mending is to repair the damaged areas of the uncovered paintings; (d) mounting is to paste a new supporting paper for the repaired paintings and (e) color compensation is to use original painting pigments to compensate the lost pigments on the paintings if necessary.

Figure 2. Schematic molecular structure of ZB-F600.
from Tianjin Chemical Reagent Co., Ltd. (China). Ethanol (A.R.) was from Sinopharm Chemical Reagent Co., Ltd. (China). The deckle edge papers were sourced from Anhui Jingyang County Xuan Paper Factory (China).

2.2. Preparation of Simulated Ancient Paintings. Deckle edge paper, known as bamboo paper, belongs to a Chinese traditional handmade paper used for ancient paintings.28 This paper painted with pigments was used to simulate ancient paintings, as specified below. The paper sample was brushed twice with alum-gelatin aqueous solution containing 8 wt % gelatin and 3 wt % alum and dried at room temperature. Then, the paper sample was aged at 105 °C for 72 h. On the other hand, 3 wt % gelatin solution and the mineral pigments (5:3 by mass) were mixed homogenously and dried at room temperature. This procedure was repeated twice. The samples were cut into strips (100 × 150 mm) for further testing.

2.3. Water-Borne FEVE Coating Treatment. Eight grams of ZB-F600 emulsion was diluted with 100 mL of water/ethanol (6:4, wt/wt) with stirring for 30 min. The diluted emulsion was applied to the paintings using a brush and dried at room temperature. This procedure was repeated once. After that, the paintings were cut into strips (100 × 150 mm) for further testing.

2.4. Cleaning Procedure. The untreated and treated paintings were sprayed with distilled water until completely infiltrated to remove dirt and free acid. Excessive water was removed using a towel after 15 min. The operation was repeated twice. The samples were dried in air for 24 h.

2.5. Mechanical Performances. 2.5.1. Antipeeling Property. The paintings were wet by spraying with distilled water. A filter paper was used to wipe wet paintings. Four pigments with different colors were examined respectively to check their retention.

2.5.2. Tensile Properties. The tensile strengths of the paintings were measured according to the international standard (ISO 1924-2:1994) by using a universal testing machine (QT-1136, Dongguan Gaotai Testing Instrument Co., Ltd., China) at room temperature. Tensile speed was 5 mm/min, and 10 specimens were tested to obtain statistical data.

2.5.3. Folding Resistance. The folding resistance of the paintings were determined according to the standard (ISO 5626:1993) using a folding endurance tester (LB-MIT13S, Shenzhen Lanbo Testing Instrument Co., Ltd., China). The applied force was 4.9 N, and 10 specimens were examined.

2.6. Thermal Stability Properties. In order to evaluate the effect of ZB-F600 on the thermal stability of paper, the TG was performed on treated samples (in Section 2.3 for the treatment method), untreated samples, and pure ZB-F600 with a heated rate of 20 °C/min from 25 to 800 °C.

2.7. Surface Properties. 2.7.1. Scanning Electron Microscopy. A scanning electron microscope (Quant 200, FEI, USA) was used to examine the surface morphology of the paintings before and after treatment. The samples were sputtered with gold, magnification was 1200X, and accelerating voltage was 20.0 kV.

2.7.2. Water Contact Angle. The contact angles of untreated and treated paintings were measured using a contact angle system (OCA 20, Dataphysics Instruments GmbH, Germany) with a fixed water volume of 2 μL. The contact angles took the average of three measurements.

2.7.3. Color Difference. The color changes of the paintings were recorded by VS-450 (X-Rite, USA) from 400 to 700 nm, by the Commission Internationale de l’Eclairage (CIE) L* a* b* system according to ISO11 467:2000, and D65 standard light source was adopted.

2.7.4. pH Measurement. pH measurements of untreated and treated samples after cleaning were carried out by a Mettler Toledo SevenCompact pH S210.

2.8. Artificial Aging Procedure. The durability of the samples was evaluated from dry and heat accelerated tests according to ISO 5630-1:1991. The tests were performed in an aging chamber at 105 °C for 72 h, corresponding to 25 years of natural aging.29

2.9. Applications in Real Cases. The developed method was applied to real ancient paintings from the ceiling of Dayu Temple built in Yuan Dynasty (1271–1368 A.D.). There are 6
rows and 28 columns of paintings (28.5 × 27 cm), with total members of 168. The pigments used are mainly green, red, white, black, and blue, and the patterns mainly consist of flowers, grasses, fish, insects, figures, historical allusions, and life scenes to fully reflect the cultural diversity and profound humanistic spirit of ancient Chinese architecture. At present, these paintings show serious acidification, yellowing, and embrittlement (Figure 3).

3. RESULTS AND DISCUSSION

3.1. Antipeeling Property of Pigments. Figure 4 shows results from the antipeeling property tests of untreated and treated pigments with ZB-F600. The pigment of the untreated sample stuck on a filter paper, which suggests the poor antipeeling property of the pigment. After treatment with ZB-F600, no pigment on the filter paper was observed, indicating good antipeeling property of the pigments because ZB-F600 can form a protective film on the pigments and thus increase adhesion between the pigments and the paper matrix. This finding may support that the application of ZB-F600 is able to increase the retention ability of the pigments on the paper matrix.

3.2. Scanning Electron Microscopy. The surface morphologies of the untreated and the treated samples were examined using SEM; see Figure 5. Before treatment, the pigment particles and part of the fiber surface in untreated paper showed cracks and holes, indicating the poor connection among the pigment particles. After the treatment, a smoother surface morphology is observed without any cracks hand holes because ZB-F600 infiltrated the gaps among the pigment particles and paper fibers. Moreover, a protective film was formed on the pigment surface. Therefore, ZB-F600 shows a good compatibility with paper fibers and increases the fixability of the pigments. This finding is consistent with the result from the antipeeling property of pigment test.

3.3. Hydrophilic Test. The most used adhesive in the mounting process of traditional ancient paintings is starch paste. In the paper and starch paste adhesive mechanism, the hydroxyl group in starch molecules forms a hydrogen bond with the hydroxyl group in paper cellulose molecule, which plays a bonding role. Therefore, the hydrophilicity of paper is indispensable for the following traditional mounting technique. The surface hydrophilicity of the untreated and treated samples was obtained. The measured water contact angles can qualitatively demonstrate wetting ability of the paintings. For example, a material is hydrophilic if the contact angle is <90° or hydrophobic if the contact angle is >90°. Figure 6 shows the contact angle of untreated samples sharply decreased from 65 to 0° in 40 s, indicating the strong hydrophilicity. In contrast, the treatment of the paintings results in a decrease in the contact angle from 81.8 to 0° in 140 s, as a result of the decreased hydrophilicity. But the treated samples still retained somewhat hydrophilicity instead of complete hydrophobicity. In other words, although ZB-F600 forms a protective film on the surface of the paper, water is still able to penetrate into the paper fibers through this film in a relatively short time, which will not change the traditional mounting technology of paintings.

![Figure 4](https://example.com/figure4.png)

Figure 4. Photograph of antipeeling property of pigments from untreated (A1, B1, C1, and D1) and treated (A2, B2, C2, and D2) paintings with ZB-F600. Four different mineral pigments (red - cinnabar, green - ultramarine, blue - malachite, and black - carbon black) on the paintings are wet and then used a filter paper to rub the surface to check the adhesion pigments on the filter paper.

![Figure 5](https://example.com/figure5.png)

Figure 5. SEM photographs of paintings with four different mineral pigments with a magnification of 1200. Before treated (a1 - cinnabar, b1 - ultramarine, c1 - malachite, and d1 - carbon black) and after treated with ZB-F600 (a2 - cinnabar, b2 - ultramarine, c2 - malachite, and d2 - carbon black).
3.4. Color Change. Ancient paintings are of high artistic values, so their treatments should not modify their visualization without significant color change, which is an important principle during the conservation of ancient paintings. The CIE L* a* b* system is widely used to evaluate the color difference of pigments. The color difference in the CIELAB space is given by

$$\Delta E^* = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

In eq 1, $\Delta E^*$ is the total color change, $\Delta L$, $\Delta a$, and $\Delta b$ are the change of the color lightness ($L^*$), position between red and green ($a^*$), and position between yellow and blue ($b^*$), respectively. The smaller the value of $\Delta E^*$, the less color difference between treated and untreated pigment samples.

Here, the $\Delta E^*$ values of the four kinds of pigments are compared in Table 2. $\Delta E^*_1$ is the color difference between before and after treated samples; $\Delta E^*_2$ is the color difference between before and after aging of the untreated samples; and $\Delta E^*_3$ represents the color change before and after aging of the treated samples. In general, for $\Delta E^*_2 > 1$, the change is discriminated by the eyes. Here, the color changes ($\Delta E^*_i$) of the four treated samples are lower than 0.6, so that the appearance of the related paintings paper shows a slight change. After the dry heating aging, untreated samples showed significantly increased color difference ($\Delta E^*_i$), whereas the treated samples display reduced changes ($\Delta E^*_1 < 1$). The change of the treated samples cannot be detected by the eyes. Note that this dry heating aging process is corresponding to 25 years of aging under normal condition. Therefore, such treatment did not affect the appearance of the paintings and will be of great help for long-term conversion.

3.5. Surface pH Test. The degradation substances of ancient paintings mainly due to acid-catalyzed hydrolysis, which is promoted by the addition of alum. Free acids could increase the acidity of paper causing the acceleration of fragility and yellowing of paintings, which negatively influence the appearance and deteriorate the mechanical properties of the paintings. Therefore, to remove free acids of the ancient paintings as a result of cellulose degradation, water cleaning is necessary in painting conservation. So, the samples were cleaned with deionized water, and then the acidity was tested by using a plane electrode. Figure 7 displays the change of the obtained pH values of untreated and treated samples. Water washing leads to the increase in pH value, which indicates effective removal of free acids. Moreover, the treated and untreated samples show a very similar pH value of ~6, so that the application of ZB-F600 slightly affects the removal of acid during the water cleaning process. The reason lies that ZB-F600 provides the sufficient water hydrophilicity, which facilitates the transfer of the water through the paper fibers.

3.6. Tensile Strength Test. Figure 8 compares the tensile properties of untreated and treated papers before and after aging. A considerable improvement in a parallel tensile strength from 0.6 to 1.67 N/m of papers before and after treatment is found. Correspondingly, the vertical tensile strength increases from 0.34 to 1.0. N/m because ZB-F600 fills paper fiber internal pores and improves the strength of the paper. After aging, the tensile strength of untreated paper samples was slightly decreased by about 10%, while the treated paper samples still maintained more than 98% of their tensile strength, which indicated that the treated paper samples retained much better tensile strength. Furthermore, the above results show that ZB-F600 plays an important role in facilitating the transfer of the water through the paper fibers.

![Figure 7](https://dx.doi.org/10.1021/acsomega.0c04827)  
Figure 7. pH value changes of untreated and treated paintings with ZB-F600 before (blank) and after cleaning (shadow).

![Figure 6](https://dx.doi.org/10.1021/acsomega.0c04827)  
Figure 6. Water contact angles of the untreated and treated paintings with ZB-F600 at different times.

|     | untreated, no aging | treated, no aging | untreated, 3 days aging | treated, 3 days aging |
|-----|---------------------|-------------------|-------------------------|-----------------------|
|     | L*      | a*       | b*       | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta E^*$ | L*      | a*       | b*       | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta E^*$ |
| red | 46.49   | 51.78    | 29.15    | −0.34      | −0.19       | −0.15       | 0.42        | −0.70    | 0.03      | 1.02      | 1.24       | −0.37       | 0.49        | 0.10        | 0.62    |
| green | 69.85   | −28.32   | 12.81    | −0.17      | 0.48        | −0.01       | 0.51        | 0.77      | 1.17      | 0.03      | 1.4        | 0.41        | −0.07       | −0.73       | 0.84    |
| blue | 33.59   | 2.94     | −35.13   | 0.23       | 0.08        | −0.53       | 0.58        | −0.97    | −0.09     | 0.57      | 1.13       | 0.92        | 0.06        | 0.06        | 0.93    |
| black | 21.1    | −0.02    | −0.18    | 0.38       | −0.01       | 0.13        | 0.4         | −0.92    | 0.06      | −0.16     | 0.94       | −0.86       | −0.16       | −0.03       | 0.87    |

Table 2. Color Change of $\Delta E^*$ before and after Treated (105 °C/3 days) Simulated Ancient Paintings
improving the mechanical properties of the paper and also has excellent antiaging performance, which is conducive to the long-term preservation of the ancient painting.

3.7. Folding Endurance Test. Folding endurance represents the most sensitive indicator of paper breakage. Figure 9 shows the folding endurance of untreated and treated samples before and after aging, respectively. The folding endurance parallel to the direction of tensile displacement leads to the complete loss of the folding endurance for untreated samples, whereas the treated samples retain a considerable folding endurance. More notable difference is observed for the retreated and untreated samples before and after aging. The treated samples show the superior folding endurance to the untreated samples, especially after aging.

3.8. Thermal Stability. As shown in Figure 10, the temperature at 5% loss, \( T_{5\%} \), of the untreated paper is 62.0 °C, due to the liberation of the absorbed water of the paper. In contrast, the \( T_{5\%} \) of ZB-F600 film is high rather high (272.0 °C), due to the thermal decomposition of the polymer, which indicates ZB-F600 has strong hydrophobicity. The \( T_{5\%} \) of treated paper with ZB-F600 increased to 75.6 °C, which indicates that the hydropilicity is slightly changed. In this case, water molecules are still able to penetrate into the paper fibers through the ZB-F600 film. This observation is consistent with the slightly increased water contact angle of the paintings. ZB-F600 leads to the increased onset decomposition temperature, \( T_{\text{onset}} \) and the maximum thermal decomposition temperature, \( T_{\text{max}} \) of the treated paper by 34.2 and 43.5 °C, respectively, because ZB-F600 has a higher thermal stability than the treated and pristine papers. The increased thermal stability agrees with the enhanced thermal aging properties of the treated paper. In addition, the char residual yield (700 °C in \( N_2 \)) of the treated samples is slightly decreased. To conclude, the ZB-F600 not only provides the paper with acceptable hydropilicity but also increases the thermal stability of its treated paper.

3.9. Applications of ZB-F600 Coatings on Ancient Chinese Paintings. From the above analysis, the ZB-F600 coatings function well in the conservation of the simulated paintings. Furthermore, to examine the real situation of ancient painting conservation, the coating is applied to a Chinese painting of the Yuan Dynasty (1271–1368 A.D.), as shown in Figure 11. After the pigment on the original painting was wet by spraying distilled water, the pigment was pressed on a filter paper. The stuck pigment on the filter can be observed, indicating poor adhesion between the pigment and paper of the painting. After treatment using the coating by a writing brush as seen in Figure 11c, there is no observed pigment on the filter paper in Figure 11d, indicating the enhanced adhesion of the pigment on the painting. Therefore, this fluoropolymer coating can be successfully used as a very effective material for conservation of real ancient paintings with an approval.

4. CONCLUSIONS

This work examined the application of a commercial water-borne fluoropolymer coating as a new pigment reinforcement material for restoration of Chinese ancient paintings. The coating was applied not only to simulated paintings but to real ancient paintings as well. The coated paintings were found to be able to compatible with the well-established mounting techniques for Chinese traditional paintings, especially the water clearing process. From the antipeeling property test of pigments, ZB-F600 caused no pigment falling off compared with the untreated ones because of the better adhesion between the pigment and paper of the painting. SEM results demonstrated that the fluoropolymer could fill holes and gaps among the pigment particles, thus consolidating the pigments of the paintings. The coating led to the increased water contact angles, but the treated paintings still retained adequate hydrophilicity, without affecting the subsequent removal of degradation substances by water cleaning according to the mounting techniques. The coating slightly affected the surface acidity after water cleaning, which will greatly facilitate removal of free acids from the paintings. The colorimetric analysis of treated paintings showed that their appearance slightly changed even after aging, and the tensile and folding
endurance properties were also improved. To conclude, after trailing on the simulated paintings, very positive results were obtained. Subsequently, the ZB-F600 was successfully applied to real Chinese paintings (168) of the Yuan Dynasty (1271∼1368 A.D.) with an approval. Our work provides a simple, useful, and scalable method to protect paintings with the good compatibility with the traditional mounting techniques of ancient painting protection.

Figure 10. The TG and DTG curves of untreated and treated papers with ZB-F600 and pure ZB-F600 under nitrogen at a heating rate of 20 °C/min.

Figure 11. Application of the ZB-F600 coating to conserve the Chinese ancient paintings. (a) Original ancient painting on a wood board, (b) filter paper pressed on the wet paintings with the stuck pigments found, (c) application of coating on the pigments, (d) filter paper pressed on the wet paintings without the stuck pigments found, (e) original ancient painting on a wood board, (f) restored paintings, (g) original ancient painting on a wood board, and (h) restored paintings.

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Author Contributions
J.L.W. conceived the research, designed research methodology, performed experiments and data acquisition and processing, conducted data analysis, and wrote the manuscript. D.D.H. discussed the results and conducted data analysis. H.P.X. discussed the results, conducted data analysis, and reviewed and corrected the manuscript. Y. P. Q. performed experiments and data acquisition and processing, discussed the results, and

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conducted data analysis. Y.H.L. designed research methodology and discussed the results.

Notes
The authors declare no competing financial interest.

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**REFERENCES**

(1) Missori, M.; Righini, M.; Dupont, A.-L. Gelatine sizing and discoloration: A comparative study of optical spectra obtained from ancient and artificially aged modern papers. Opt. Comun. 2006, 263, 289–294.

(2) Benetti, F.; Marchettini, N.; Atrei, A. ToF-SIMS and XPS study of ancient papers. Appl. Surf. Sci. 2011, 257, 2142–2147.

(3) Dupont, A.-L. Study of the degradation of gelatin in paper upon aging using aqueous size-exclusion chromatography. J. Chromatogr. A 2002, 950, 113–124.

(4) Wang, G.; Peng, J. Influence of Bauxite Water on the Performance of Drawing Paper. Pap. Sci. Technol. 2019, 38, 66–70.

(5) Jablonsky, M.; Sima, J.; Lelovský, M. Considerations on factors influencing the degradation of cellulose in aluminosilicate sized paper. Carbohydr. Polym. 2020, 245, 116534.

(6) Carter, H. A. The Chemistry of Paper Preservation: Part 2. The Yellowing of Paper and Conservation Bleaching. J. Chem. Educ. 1996, 73, 1068–1073.

(7) Carter, H. A. The Chemistry of Paper Preservation: Part I. The Aging of Paper and Conservation Techniques. J. Chem. Educ. 1996, 73, 417–420.

(8) He, W.; Zhang, J.; Chen, X. Exploring Scientificization of Traditional Painting and Calligraphy Mounting Technique: An Example of Nanjing Museum. Southeast Cult. 2014, 25–30.

(9) Mazzucca, C.; Micheli, L.; Carbone, M.; Basoli, F.; Cervelli, E.; Iannuccelli, S.; Sottini, S.; Palleschi, A. Gellan hydrogel as a powerful tool in paper cleaning process: A detailed study. J. Colloid Interface Sci. 2014, 416, 205–211.

(10) Casoli, A.; Isca, C.; De Iasio, S.; Botti, L.; Iannuccelli, S.; Residori, L.; Ruggiero, D.; Sottini, S. Analytical evaluation, by GC/MS, of gelatine removal from ancient papers induced by wet cleaning: A comparison between immersion treatment and application of rigid Gellan gum gel. Microchem. J. 2014, 117, 61–67.

(11) Shi, Q.; Tie, F.; Gou, J. The Impact of Gelatin and Alum Concentration on Xuan Paper. J. Natl. Mus. China 2013, 2, 136–149.

(12) Xu, X. The effect of aluminum potassium sulfate (PAS) on the durability of Xuan paper. Sci. Conserv. Archaeol. 2008, 20, 47–50.

(13) Xu, X.; Wang, J.; He, Q. The Influence of Alum Alum Gelatin solution on Cellulose, Calcium Carbonate and Gelatin in XUAN Paper. Spectrosc. Spectral Anal. 2018, 38, 1829–1833.

(14) Barbabietola, N.; Tasso, F.; Alisi, C.; Marconi, P.; Perito, B.; Pasquariello, G.; Sprocati, A. R. A safe microbe-based procedure for a gentle removal of aged animal glues from ancient paper. Int. Biodeterior. Biodegrad. 2016, 109, 53–60.

(15) Huanhuan, W.; Changgai, W. The influence of Alum Gelatin Solution on the performance of traditional papers. J. Cult. Herit. Sci. Res. 2014, 1, 76–79.

(16) Amornkitbamrung, L.; Mamul, M.-C.; Palani, T.; Hribernik, S.; Kovalcik, A.; Karig, R.; Stana-Kleinschek, K.; Mohan, T. Strengthening of paper by treatment with a suspension of alkaline nanoparticles stabilized by trimethylisilyl cellulose. Nano-Struct. Nano-Objects 2018, 16, 363–370.