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Pyrolysis of Precious Chinese Xuan Paper Containing Ammonium Phytate as a Flame Retardant

Yinchun Fang,* Jianguo Wu, Weihao Sun, and Xinhua Liu*

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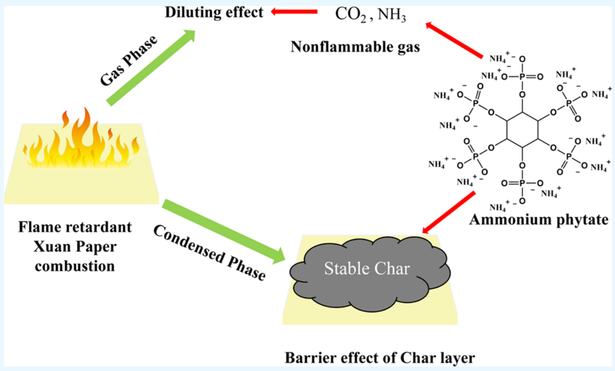
ABSTRACT: Xuan paper with outstanding cultural and artistic values is one of the most precious Chinese handmade papers and is widely used in traditional calligraphy and painting. However, the highly combustible cellulosic raw materials of Xuan paper present potential fire hazards. Ammonium phytate (AP) originating from biosourced phytic acid has been used for the flame-retardant treatment of Chinese Xuan paper by facile spray coating. The limiting oxygen index value of the treated Xuan paper increased to higher than 40%, demonstrating that the flammability of Xuan paper was greatly reduced by this treatment. The excellent flame retardancy afforded by this treatment was confirmed by cone calorimetry. TGA was used to demonstrate that the presence of AP changed the thermal decomposition process to promote char formation during the degradation of Xuan paper. The flame-retardant mode of action of phytate-coated Xuan paper was investigated using TG-FTIR, SEM, and XPS spectra. A P−N cooperative effect was proposed to account for both the condensed phase and gas-phase flame-retardant actions. The phosphorus component promotes char formation in the condensed phase, while the nitrogen component releases inert species to dilute the fuel load in the gas phase. The ink-wetting property of the coated Xuan paper was influenced negligibly by the coating process. The development of fire-resistant Xuan paper using ecofriendly flame retardants through simple and convenient spray coating has been demonstrated.



1. INTRODUCTON

Paper occupies an important place in the cultural heritage of modern society.[1] Chinese Xuan paper is one of the outstanding representatives and is widely used in traditional calligraphy and painting. The traditional handicraft of making Xuan paper was listed in the UNESCO Intangible Cultural Heritage of Humanity in 2009.[2] Xuan paper is regarded as "the king of paper that lasts for thousands of years" due to the advantages of high durability, aging resistance, and resistance to color change .[3] A great number of artworks with precious cultural and artistic values produced on Xuan paper over the past hundreds of years have been preserved well until now.[4,5]

Fire disasters have accompanied human civilization since the beginning of the use of fire; such events not only seriously threaten the economy but also directly endanger the development of human history and culture. Countless art treasures have been destroyed in fire disasters.[6] The Brazil National Museum Fire in 2018 and the huge fire at Paris Notre Dame Cathedral in 2019 represent the major cultural disasters. A large number of precious historical objects were lost in these two big fire disasters. In order to avoid the fire hazards, substrates with low flammability are extremely important for the artworks. Xuan paper, as a favorite material for artists, must be treated with appropriate additives to endow flame retardancy due to the high flammability of the cellulosic raw materials from which it is produced.[7−9]

Incorporation of inorganic flame retardants into the pulp fibers during the paper-making process is the traditional method used to enhance the flame retardancy of paper. However, the level usage of flame-retardant additives is usually large.[10] Various methods have been developed for applications to the surface of flame-retardant coating materials, such as dip coating, layer-by-layer deposition, plasma treatment, and sol−gel process. Spray coating is one of the most important and effective methods for the application of a flame-retardant coating to a surface, particularly for cellulosic materials.[11,12] However, the preparation of flame-retardant paper using the spray-coating method has not been widely reported. Halogen- and phosphorus-containing flame retardants have been utilized in flame-retardant coatings.[13,14] The use of these flame retardants may lead to

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severe environmental pollution problems and consequent human exposure and health damage. When subjected to high temperature, or in a fire, halogen-based flame retardants may produce volatile dioxins and other very toxic gases. Further, they may leach from the items discarded in a landfill, enter the environment where they are stable, bioaccumulate, and may enter the human food chain. For these reasons, the use of these materials has been restricted around the world.[15,16] Ecofriendly and high-efficiency inorganic and organic composite flame retardants or flame-retardant systems have received more and more attention in the last few decades. These include the nacre-mimetic organic/inorganic hybrid flame-retardant system.[17,18]

The construction of an ecofriendly nacre-mimetic organic/inorganic hybrid composite flame-retardant system from chitosan and montmorillonite and its use for improving the flame retardancy of Xuan paper have previously been reported.[19] Coating with this flame-retardant system endowed Xuan paper with excellent flame retardancy. However, the physical properties of Xuan paper were negatively influenced, such as color- and ink-wetting properties. In recent years, biobased flame retardants have been studied extensively due to the advantages of green and environmental friendly characteristics.[20] Phytic acid (PA) with a high content of phosphorus originates from natural plants as an energy storage material in seeds. It may be used as an ecofriendly and high-efficient flame retardant.[21] PA and its modified derivatives have been utilized as flame retardants for textiles (cotton, silk, and wool) and polypropylene.[22−25] The presence of these additives endow the textiles with excellent flame retardancy. The utilization of phytic acid or its derivatives as flame retardants for Xuan paper has not been reported previously.

Phytic acid is a relatively strong acid which may cause severe damage to cellulosic Xuan paper. Therefore, the neutral ammonium salt of phytic acid (ammonium phytate, AP) has been used for flame-retarding Xuan paper. Xuan paper was treated by spray coating with different concentrations of aqueous AP solution. The flammability of coated Xuan paper was determined using limiting oxygen index (LOI) and vertical flame test (VFT). Cone calorimetry was used to investigate the burning behavior of coated Xuan paper. The thermal stability of Xuan paper before and after treatment was evaluated using thermogravimetric analysis (TGA). The flame-retardant mode of action for coated Xuan paper was studied using TG-FTIR, SEM, and XPS analyses. The ink-wetting properties of the coated paper were also assessed.

2. RESULTS AND DISCUSSION

2.1. FTIR and SEM Analyses of Xuan Paper before and after Treatment. Figure 1 shows the FTIR spectra of untreated and treated Xuan papers. In the spectra of untreated paper, there exist absorption peaks at 3440 and 1650 cm^{-1} which are ascribed to the stretching vibrations of O−H bond in the cellulose macromolecules of the paper fiber and the absorption peak of adsorbed water, respectively.[19] These two peaks also exist in the spectra of treated Xuan paper. There are new peaks in the spectra of treated Xuan paper. The peak at 1412 cm^{-1} is assigned to the absorption peak of NH_4^+ which is due to the formation of AP by adding ammonium hydroxide solution in PA solution.[26] The peaks at 1160, 1110, and 1076 cm^{-1} are ascribed to the absorption peaks of P=O and P−O−C belonging to PA. There exist these characteristic absorption peaks, even when Xuan paper was treated by 4% AP solution. The results showed that AP has been successfully applied on Xuan paper.

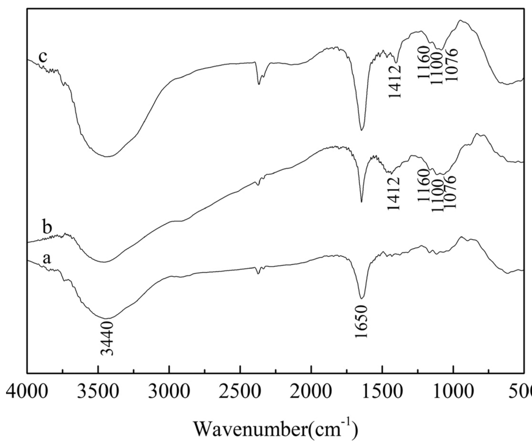

Figure 1. FTIR spectra of Xuan papers: (a) untreated, (b) X-AP4, and (c) X-AP10.

The surface morphologies of Xuan papers before and after treatment are shown in Figure 2.

The surface morphology of treated Xuan paper changed obviously when compared with the untreated one. The surface of treated paper was a rough covering with a coated layer. As shown in the cross-sectional images of Xuan papers, the thickness of the coating on the paper fiber increased with the concentration of AP solution. The results of FTIR and SEM analyses demonstrated that AP has been successfully applied on Xuan paper. Due to the 2D spreading property of Xuan paper that arose from the unique lamellar microporous and nanoporous composite structures,[27] AP also penetrates into the interior of the paper fiber, enhancing the flame retardancy. Therefore, AP was successfully applied on the surface and the fiber interior of Xuan paper.

2.2. Flame Retardancy of Xuan Paper before and after Treatment. Table 1 shows the LOI values and the results of VFT. Table 1 also lists the add-ons of treated Xuan paper. The digital photographs of Xuan papers after VFT are shown in Figure 3.

As can be seen from Table 1, the LOI values of treated Xuan papers increased with the concentration of AP solution and add-ons. The LOI value of untreated Xuan paper was only 19.0%, while it increased to 24.8% for X-AP2. Both untreated Xuan paper and X-AP2 were burned out. When the concentration of AP solution was 4 wt %, the LOI value of treated paper reached 29.8%, with the char length decreasing to 19 cm, revealing good flame retardancy. Further, the LOI value continued to increase with the AP solution concentration. The LOI value of X-AP10 reached 41.8%, with the char length of 9 cm, showing excellent flame retardancy when it was treated by 10 wt % AP solution. Both the after-flame time and after-glow time of treated Xuan papers reduced to 0 s.

Figure 3 shows the digital photographs of untreated and treated papers using different concentrations of AP solution after VFT. The untreated paper was burned out with no residue; the paper of X-AP2 was also burned out, while the shape was kept integral with the char residue. The char length of Xuan paper decreased with the increasing AP solution concentration.

Therefore, the flammability of Xuan paper was greatly reduced after the flame-retardant treatment by spray coating AP solution. Xuan paper achieved excellent flame retardancy when it was treated with higher than 6 wt % AP solution.

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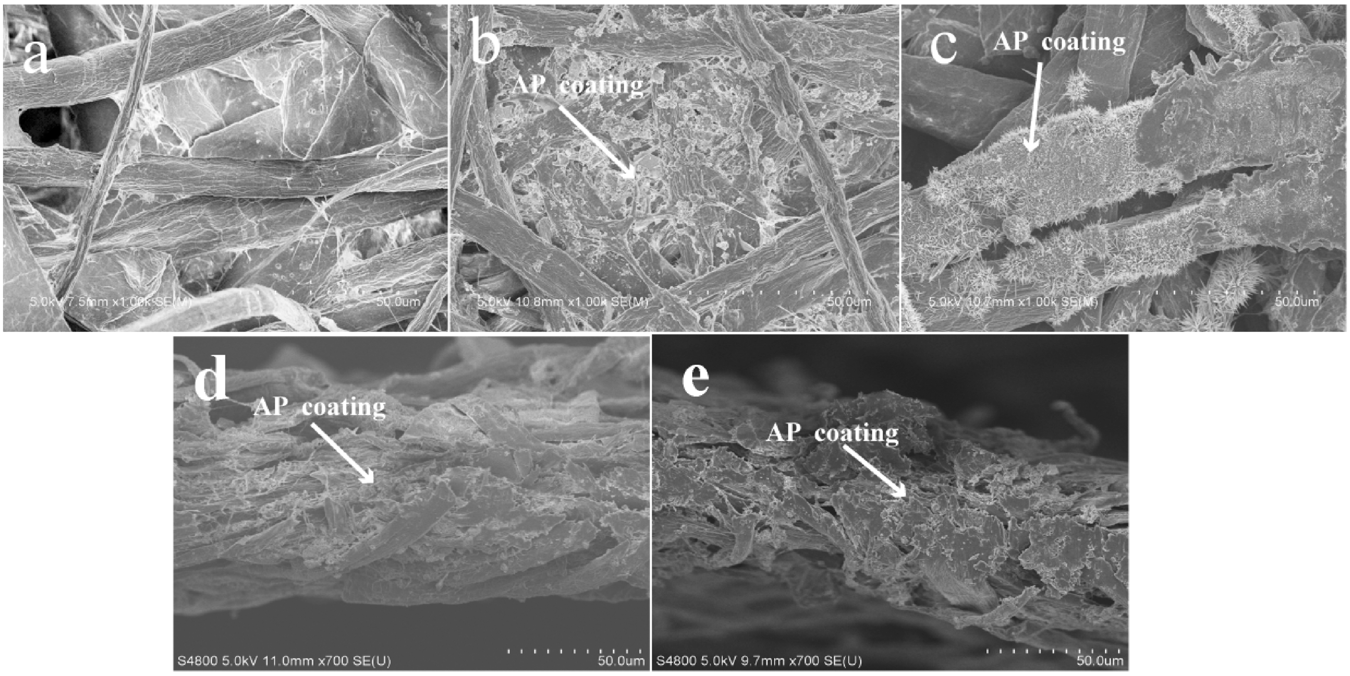

Figure 2. Surface morphologies of Xuan papers: (a) untreated, (b) X-AP6, (c) X-AP10, and cross sections of (d) X-AP6 and (e) X-AP10.

Table 1. Flame Retardancy of Xuan Papers before and after Treatment

sample	add-on (%)	LOI (%)	VFT		
			char length (cm)	after-flame time (s)	after-glow time (s)
untreated		19.0	burn out	0	4.0
X-AP2	4.84	24.8	burn out	0	0
X-AP4	5.95	29.8	19.0	0	0
X-AP6	7.26	31.5	12.0	0	0
X-AP8	9.91	37.3	11.0	0	0
X-AP10	12.11	41.8	9.0	0	0

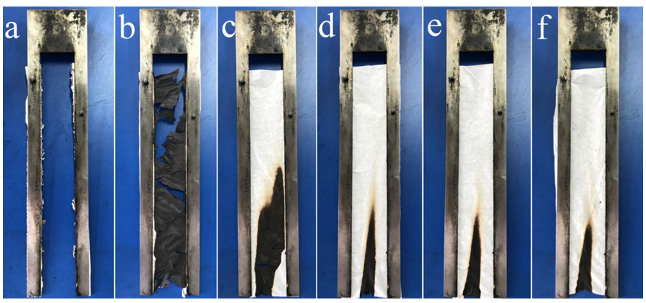

Figure 3. Digital images of Xuan papers after VFT: (a) untreated, (b) X-AP2, (c) X-AP4, (d) X-AP6, (e) X-AP8, and (f) X-AP10.

2.3. Cone Calorimetry Test. Cone calorimetry test (CCT) is performed to evaluate the burning behaviors of materials in the lab scale. The heat release rate (HRR) and total heat release (THR) curves of Xuan papers before and after treatment are shown in Figure 4. The related data are listed in Table 2. The data show the time to ignition (TTI), peak HRR (pHRR), time to pHRR (t-pHRR), THR, fire growth rate (FGR = pHRR/t-pHRR), average effective heat of combustion (av-EHC) (which was calculated as the heat released per kilogram of volatile released), and CO_2/CO.

As can be seen from Figure 4 and Table 2, the TTI of untreated Xuan paper was 7 s, while that of flame-retardant-treated paper will not be ignited. The pHRR and THR values of treated Xuan papers were 17.93 kW/m^2 and 3.84 MJ/m^2, respectively, which were much lower than that of the untreated one of 159.22 kW/m^2 and 4.97 MJ/m^2, decreasing by 88.7 and 23.0% for each. The results revealed that the fire diffuses much harder in treated Xuan paper than in the untreated one.[28] The flame-retardant-treated Xuan paper promoted the char formation, thus increasing the residual mass. The more char residues of treated Xuan paper resulted in lower pHRR and THR values, with the reduction of the combustible volatile products.[29] The FGR of treated Xuan paper was 0.40 $kW/(m^2 \cdot s)$, which was much lower than that of the untreated one of 6.37 $kW/(m^2 \cdot s)$. These results showed that the flame-retardant treatment of Xuan paper suppressed the spreading of fire, thus improving the possibility of escape from fire disasters.[30] av-EHC shows the combustion degree of volatiles in the gas phase, which was used as a parameter for the analysis of gas flame-retardant mechanism. The av-EHC value of treated Xuan paper (12.54 MJ/kg) was lower than that of untreated one (17.55 MJ/kg), suggesting that the flame-retardant-treated Xuan paper shows the gas-phase flame-retardant action.[31] The CO_2/CO ratio reflects the combustion efficiency, which is a parameter to analyze the gas-phase flame-retardant action.[32] The CO_2/CO ratio of treated paper was 1.92, which was much lower than that of untreated one of 15.3, revealing the gas-phase flame-retardant action of treated Xuan paper. The CCT results further confirmed the spray coating of Xuan paper by AP reducing the flammability obviously.

2.4. Thermal Stability of Xuan Paper. The TGA results of Xuan papers before and after treatment, both under nitrogen and air atmosphere, are shown in Figure 5 and Table 3.

As shown in Figure 5a and Table 3, there are two mass loss stages for both untreated and treated Xuan papers under nitrogen atmosphere. The $T_{-10\%}$ values of treated Xuan papers reduced to 190 and 185 °C for X-AP6 and X-AP10, which were

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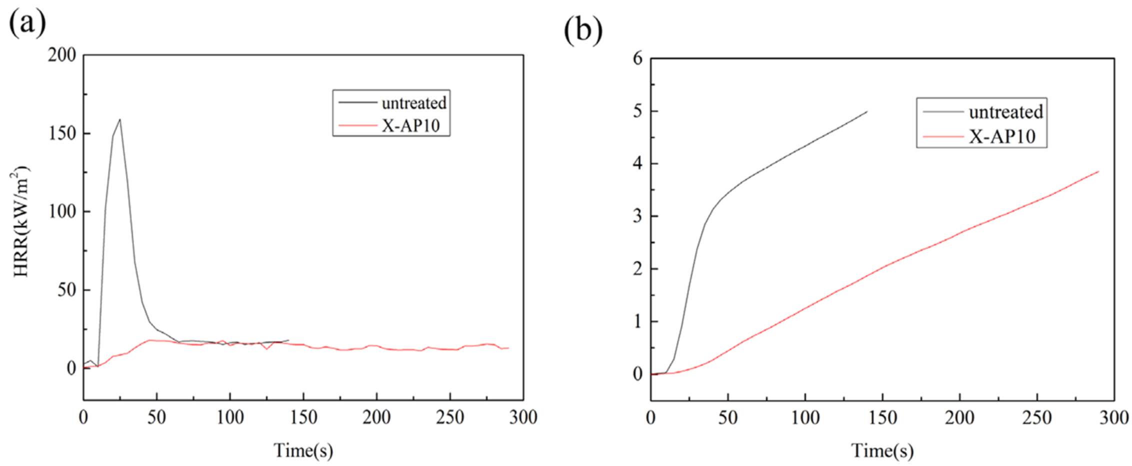

Figure 4. Heat release rate (a) and total heat release curves (b) of untreated and flame-retardant-treated Xuan papers.

Table 2. CCT Data of Untreated and Treated Xuan Papers

sample	TTI (s)	pHRR (kW/m^2)	t-pHRR (s)	THR (MJ/m^2)	FGR (kW/m^2·s)	av-EHC (MJ/kg)	CO_2/CO	residual mass (%)
untreated	7	159.22	25	4.99	6.37	17.55	15.34	10.30
X-AP10		17.93	45	3.84	0.40	12.54	1.92	15.27

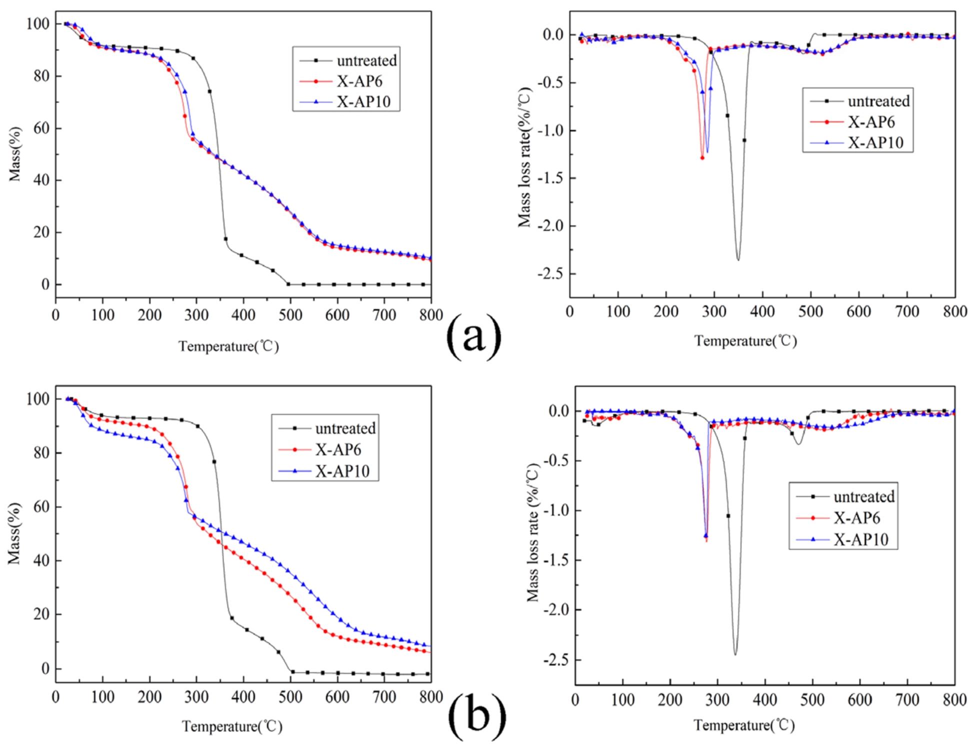

Figure 5. TG and DTG curves of untreated and treated Xuan papers under (a) nitrogen and (b) air atmosphere.

much lower than those of the untreated one (248 °C). The T_{max} values of the first decomposition stage of treated Xuan papers were also lower than those of the untreated one. This may have arisen from the lower onset decomposition temperature of AP and the promotion decomposition of Xuan paper by AP. However, the T_{max} value of the second decomposition stage of treated Xuan papers was higher than that of the untreated one. The mass loss rates at T_{max} of treated papers were much lower than that of the untreated one. This revealed that the flame-retardant treatment of Xuan paper enhanced the high-temperature thermal stability. There is no char residue of untreated paper at 800 °C, while the char residues of X-AP6 and X-AP10 were 9.45 and 10.59%, respectively. This result demonstrated that the flame-retardant treatment of Xuan paper promoted the char formation.

There also existed two mass loss stages for both untreated and treated Xuan papers under air atmosphere, as shown in Figure 5b and Table 3. The $T_{-10\%}$ and T_{max} values of treated Xuan papers showed the same trend with that under nitrogen atmosphere. The char residues of X-AP6 and X-AP10 at 800 °C were 5.95 and 8.45% compared with the no char residue of untreated paper. This also revealed that the flame-retardant

Table 3. TGA Data of Untreated and Treated Xuan Papers under Nitrogen and Air Atmosphere[a]

			stage 1		stage 2		
atmosphere	samples	$T_{-10\%}$ (°C)	T_{max} (°C)	mass loss rate at T_{max} (%/°C)	T_{max} (°C)	mass loss rate at T_{max} (%/°C)	residue at 800 °C (wt%)
N_2	untreated	248	346	2.36	500	0.20	0
	X-AP6	190	276	1.28	510	0.18	9.45
	X-AP10	185	285	1.23	512	0.18	10.59
air	untreated	286	338	2.45	472	0.33	0
	X-AP6	210	277	1.32	530	0.19	5.95
	X-AP10	180	275	1.27	535	0.16	8.45

[a] $T_{-10\%}$ represents the onset decomposition temperature which is defined as the temperature of 10 wt % mass loss, and T_{max} is defined as the temperature of maximum mass loss rate.

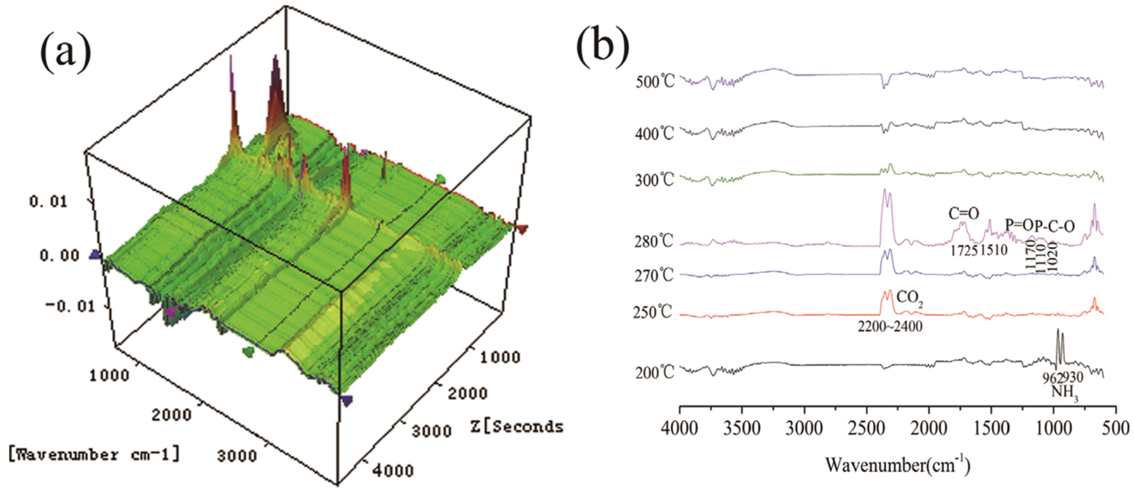

Figure 6. Three-dimensional diagram (a) and FTIR spectra (b) of volatiles of treated Xuan paper (X-AP10) at different temperatures.

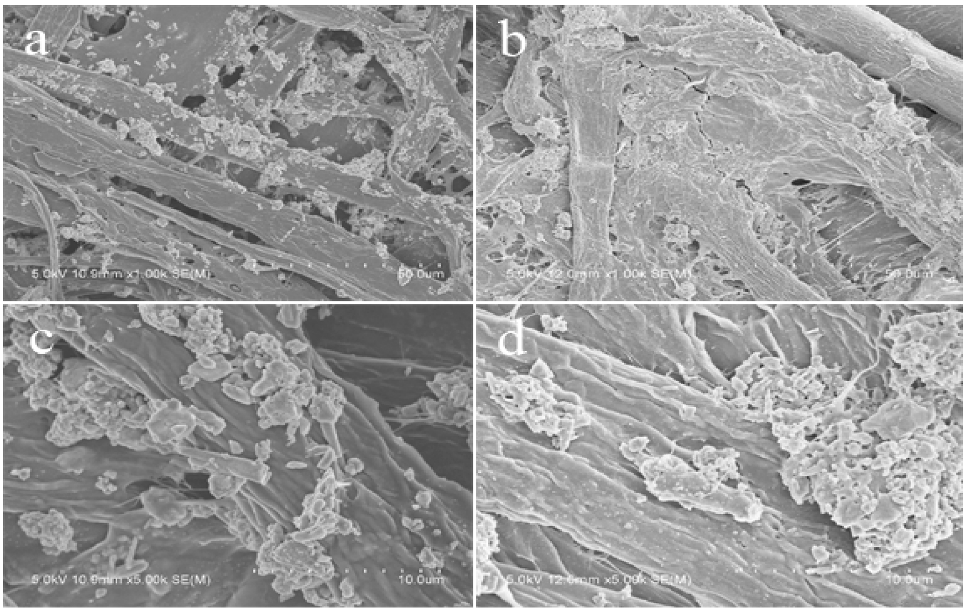

Figure 7. Morphology of the char residues of treated Xuan papera after VFT at low magnification (×1000): (a) X-AP6, (b) X-AP10 and high magnification (×5000): (c) X-AP6, (d) X-AP10.

treatment of Xuan paper promoted the formation of stable char. Therefore, the spray-coating flame-retardant treatment of Xuan paper with AP changed the thermal decomposition process to promote the formation of stable char.

2.5. TG-FTIR Spectroscopy. TG-FTIR analysis provides useful information about the gas products during the pyrolysis process at different temperatures.[33] To investigate the gas-phase flame-retardant action, the flame-retardant-treated Xuan paper was analyzed by TG-FTIR spectroscopy. Figure 6 shows the 3D diagram and FTIR spectra of volatiles of treated Xuan paper at different temperatures.

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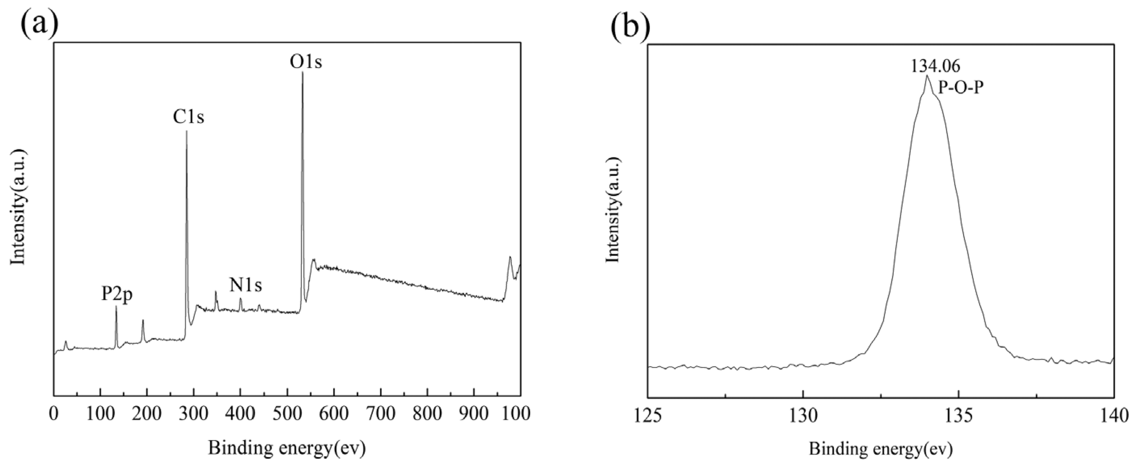

Figure 8. XPS spectra of the X-AP10 char residue after VFT: (a) full survey spectrum and (b) P 2p spectrum.

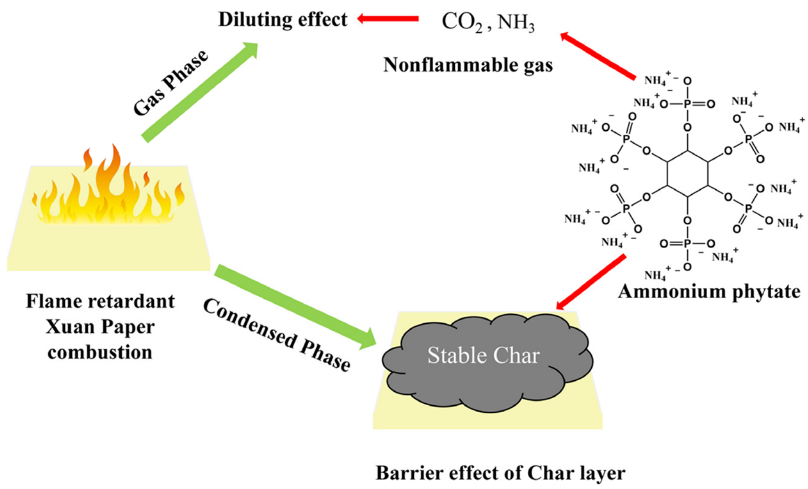

Figure 9. Schematic of flame-retardant mechanism.

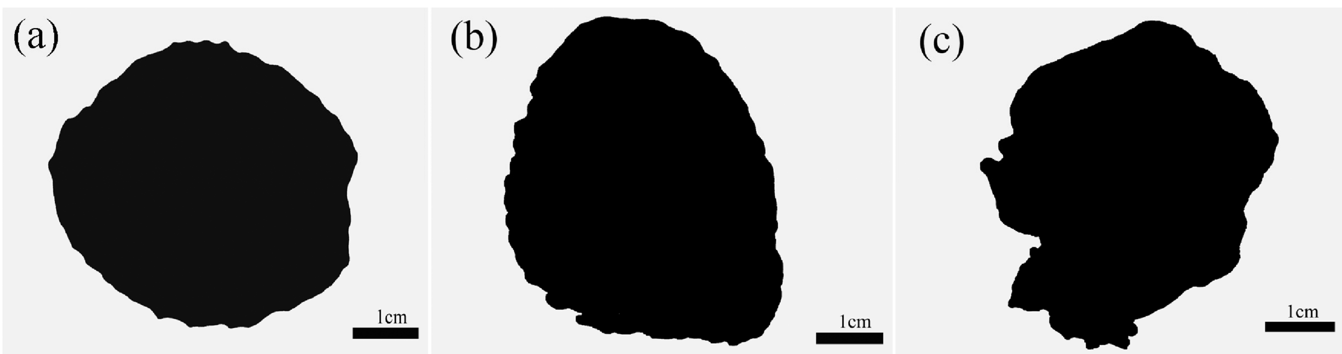

Figure 10. Photographs of ink dispersion of Xuan papers: (a) untreated, (b) X-AP6, and (c) X-AP10.

The absorption peaks exist at 930 and 962 cm^{-1}, which are attributed to NH_3 at the temperature of 200 °C. This may have arisen from the decomposition of AP. CO_2 (2400−2200 cm^{-1}) can be found in the spectra from 250 to 280 °C.[34] The peaks at 1170, 1110, and 1020 cm^{-1} at the temperature of 280 °C are ascribed to the absorption peaks of P=O and P−O−C belonging to AP. There are also peaks at 1725 and 1510 cm^{-1} belonging to the characteristic absorption peaks of C=O and aromatic rings in the spectra of 280 °C. When a flame-retardant Xuan paper was combusted, AP decomposes to form ammonia gas (NH_3) and phosphate. Phosphate decomposes to form phosphorus acid which promotes the dehydration and carbonification of Xuan paper in the condensed phase. Therefore, these results revealed that the flame-retardant-treated Xuan paper acts through the condensed phase action by promoting the char formation and the gas-phase action by releasing the inert species (NH_3 and CO_2) to dilute the fuel load.

2.6. Morphology and XPS of the Char Residues. The surface morphology of the char residues of treated Xuan papers is shown in Figure 7, and the XPS spectra of the char residue are shown in Figure 8.

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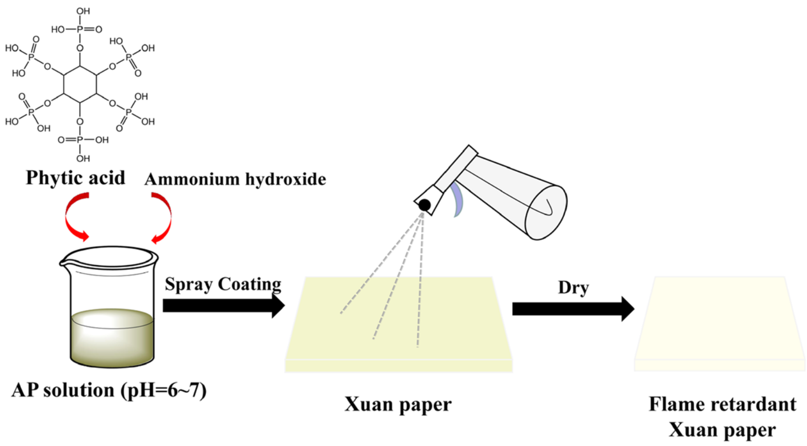

Figure 11. Schematic representation of spray coating of Xuan paper.

As can be seen from Figure 7, the treated Xuan paper formed char residue after VFT, and the paper fiber shape was kept intact. It was also found that the char layer existed on the paper fiber surface. As shown in the SEM images of the char residues, AP formed a thin glassy coating on the pulp fibers which excluded the oxygen of combustion. Therefore, the flame-retardant treatment of Xuan paper promoted the formation of stable char and glassy coatings which are beneficial for reducing the flammability of Xuan paper.

XPS was used to study the chemical composition of char residue. As can be seen from Figure 8, carbon, oxygen, nitrogen, and phosphorus elements exist in the char residue. One peak appears at 134.06 eV, corresponding to the P−O−P bond in the P 2p spectrum,[35] which is generated from the decomposition of AP. These results revealed that flame-retardant-treated Xuan paper mainly acts through the condensed phase.

Therefore, the treated Xuan papers act through both gas-phase and condensed phase flame-retardant action, while the main flame-retardant mode of action is the condensed phase. The schematic of the flame-retardant mode of action is shown in Figure 9.

2.7. Ink-Wetting Property of Treated Xuan Papers. The ink-wetting property is one of the most important properties of Xuan paper. Figure 10 shows the ink dispersion photographs of Xuan papers before and after treatment.

The ink spread on the untreated Xuan paper easily shows good ink-wetting property, and the ink also spreads on the treated Xuan papers easily. The ink-spreading area of the treated Xuan papers has not been influenced after the treatment. Even when the Xuan paper was treated by 10 wt % AP solution, the spreading area was almost the same with that of the untreated one. Therefore, the spray coating of AP solution on Xuan papers slightly influenced the ink-wetting property.

3. EXPERIMENTAL SECTION

3.1. Materials and Chemicals. Xuan paper (38 g/m^2) which was made from the pulp of blue sandalwood bark and rice straws was purchased from Anhui Yuchen Paper Co., Ltd. (Anhui, China). Phytic acid (PA) solution (70%) and ammonium hydroxide solution (AR, 25∼28%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Ink was purchased from Beijing Yidege Ink Co., Ltd.

3.2. Flame-Retardant Treatment of Xuan Paper by Spray Coating. PA solutions of different mass concentrations were prepared by diluting the original PA solution in deionized water. Then, the pH values of the solutions were adjusted to 6∼7 using ammonium hydroxide solution to prepare different concentrations of AP solutions.

Xuan paper was flame-retardant-treated with different concentrations of AP solutions by spray coating on both sides, and the wet pick-up of all papers was kept at 100% ± 10%. Then, the treated papers were dried at 70 °C for 2 h in an oven. The treated Xuan papers named X-AP2, X-AP4, X-AP6, X-AP8, and X-AP10, representing the papers, were treated by 2, 4, 6, 8, and 10 wt % AP solutions, respectively. The spray-coating process of Xuan paper is shown in Figure 11.

Further, the add-on of Xuan paper after spray coating with different concentrations of AP solutions was calculated as follows

$$\text{add-on (\%)} = \frac{m - m_0}{m_0} \times 100\%$$

where m_0 is the mass of the untreated paper, and m is the mass of Xuan paper after spray coating by different concentrations of AP solutions.

3.3. Characterization. A Thermo Nicolet Avatar 6700 Fourier transform infrared (FTIR) spectrometer (Thermo Electron, USA) was used to determine the FTIR spectra of Xuan papers before and after treatment.

The flame retardancy of Xuan papers was determined by LOI, VFT, and CCT. The LOI value was determined on a JF-3 oxygen index instrument (Jiangning Analysis Instrument, China) at room temperature according to the ASTM D2863 standard testing procedure. VFT was proceeded on a YG(B)-815D-I flame-retardant performance tester (Wenzhou Darong, China) according to the ASTM D6413 standard testing procedure. CCT was proceeded on an FTT0007 cone calorimetry instrument (FTT, UK), with the incident radiant flux of 35 kW/m^2, according to the ISO 5660 standard.

The thermal stability of Xuan papers before and after treatment was performed on a DTG-60H thermal analyzer (Shimadzu, Japan) in the range of room temperature to 800 °C, with the heating rate of 10 °C/min, both under nitrogen and air atmosphere. TG-FTIR analysis was conducted on a TENSOR 27 FTIR spectrometer (Bruker, Germany), which was connected with a TG 209 F3 thermal analyzer in the range of room temperature to 800 °C.

The morphology of Xuan papers before and after treatment and that of char residues after VFT were viewed by a Hitachi S-4800 scanning electron microscope. X-ray photoelectron

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spectroscopy (XPS) of the char residue of treated Xuan papers was performed by an ESCALAB 250Xi spectrometer (Thermo Fischer, USA).

The dispersal behaviors of ink droplets of the same volume (50 μL) which were dropped onto the Xuan paper from the same height of 1 cm were recorded by a digital camera to evaluate the ink-wetting property of Xuan paper.

4. CONCLUSIONS

In this study, Xuan paper was flame-retardant-treated through the spray coating of AP solution. The flammability of the treated Xuan paper was greatly reduced, with the LOI value higher than 30%, when it was treated with higher than 6 wt % AP solution. Further, the LOI value continued to increase to higher than 40% when it was treated with 10 wt % AP solution. The char length greatly reduced to less than 10 cm. The THR, pHRR, and FGR values of the cone calorimetry test of the treated Xuan paper were much lower than those of the untreated one, revealing that the flammability of the treated Xuan paper was greatly reduced. TGA results showed that the spray coating of flame-retardant-treated Xuan paper by AP changed the thermal decomposition process to promote the formation of stable char. The flame-retardant mode of action of treated Xuan papers is both through gas phase and condensed phase. The TG-FTIR results revealed that the flame-retardant-treated Xuan paper released inert species (NH_3 and CO_2) to dilute the fuel load, confirming the gas-phase flame-retardant action. The SEM results showed that the flame-retardant-treated Xuan paper promotes the formation of stable char. The XPS spectra of the char residue revealed the phosphorus-containing components existing in the condensed phase, which confirmed the condensed phase flame-retardant action. The ink-wetting property of treated Xuan paper was slightly influenced. This research provides the experimental basis for the development of flame-retardant Xuan paper using ecofriendly flame retardants through simple and convenient spray coating for safety and preservation.

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Notes

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