Research on flame-retardant paper prepared by the method of in-pulp addition of ammonium polyphosphate

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ABSTRACT: At present, the production of flame-retardant paper usually uses the impregnation method of phosphorus-nitrogen flame retardants in paper. There are few reports on the application of an in-pulp addition method. In this paper, the solubility of ammonium polyphosphate (APP) and its effect on flame-retardant paper were investigated for use in an in-pulp addition method.

It was found that APP particles were square, with an average particle size of 21.88 μm. The particle size decreased significantly after immersion in water at 25°C for 24 h. Furthermore, most of the APPs were dissolved after immersion in water at 90°C for 0.5 h, and the residuals agglomerated and their shape turned into an amorphous form. The APP possessed strong electronegativity and could partially ionize in water. The solubility of APP was 0.18 g/100 mL water at 25°C and increased quickly when the temperature was higher than 30°C. Therefore, APP should be added to the pulp at temperatures below 30°C. The tensile strength of the paper initially increased with the addition of APP, and it reached the maximum value when the APP content was 10% and then gradually decreased. The limiting oxygen index (LOI) value of the paper was 28.7% when the added amount of APP was 30% and cationic polyacrylamide (CPAM) was 0.08%, reaching the flame-retardant level.

Application: This study investigated the solubility of APP at different temperatures. This can provide a reference for production of flame-retardant paper by an in-pulp addition method at a paper mill.

Paper is considered an important cellulose-based material [1,2], and it has been universally used in construction, agriculture, packaging, printing, and other applications due to its advantages of biodegradability, renewability, and low expense [3-5]. However, the chief weakness of cellulose paper is that it is combustible, which could cause personal injury and property loss in some cases [6]. Consequently, flame-retardant paper has gained increasing attention. A variety of modification methods have been substantially researched, which can be classified as impregnation, coating, and in-pulp addition of flame retardants.

At present, impregnation and coating processes are common methods for improving the flame retardancy of cellulose-based paper. Impregnation generally employs water-soluble flame retardants to deliver flame retardancy for paper [7-9]. Chen et al. [10] synthesized modified phytic acid as a flame retardant to prepare a flame-retardant paper with a limiting oxygen index (LOI) of 41.5% using the impregnation method. Other water-soluble flame retardants like diammonium phosphate [11,12], guanidine phosphate (GP) [13], and guanidine sulfamate (GS) [14] have also been used with the impregnation method. However, in practical applications, the water-soluble flame retardant usually decreases water resistance, mechanical properties, and flame-retardant durability of the paper [15,16]. The coating process is also an effective method for preparing flame-retardant paper [17-19]. Priegert et al. [20] used polymethylene phosphine (PMP) or polymethylene phosphine oxide (PMP-O) to form a coating film that improved the LOI value of the paper to about 25%, and efforts have been made to further research the processing flexibility of PMP and PMP-O. Wang et al. [21] developed a coating layer consisting of ammonium polyphosphate (APP)/pentaerythritol and silicon dioxide (SiO_2) nanoparticles that could reduce the burning speed and keep the fibrous structure of paper after combustion. This coating could resist a small fire for a short time. However, the flame retardant was only distributed on the surface of the paper [22-24].

Many researchers utilized in-pulp addition technology to implant flame retardant into the pulp or fabrics. Wang et al. [25] synthesized magnesium-aluminum-carbon trioxide layered double hydroxide (Mg-Al-CO_3 LDH) with high positive charge density as filler, and the LOI value of the paper was above 25% and the whiteness of the flame-retardant paper increased to 82.1% at the dosage of 20 wt%. Xiao et al. [26] proposed a composite of aluminum hydroxide and decabromine diphenyl oxide that could inhibit thermal decomposition. However, inorganic flame retardants are generally not only low-efficiency, but they also decrease the mechanical properties of the material [27,28]. Ammonium polyphosphate (APP) as an effective flame retardant

had been investigated by some researchers with an in-pulp addition method to prepare flame-resistant papers [29]. It was found that APP-diatomite (DE) composites could decrease the rate of the smoke release peak value and the production of carbon monoxide (CO) or carbon dioxide (CO_2) [30]. The APP-DE composite fillers had a lower peak heat release rate and total heat release as well [31]. Also, the char layer formed by APP composite flame-retardants could protect the framework stability of paper in a flame, which reduced the mass loss of the system [32]. Yang et al. [33] prepared a flame-resistant paper with synthesized APP-melamine cyanurate (MCA) core-shell fillers. The APP/MCA played a role in improving the thermal stability of the paper, and the LOI value of the paper reached 29.3% with the addition of 30% APP.

Ammonium polyphosphate has been proven to be an effective flame retardant for cellulose-based paper [34]. However, APP particles possess the property of partial dissolution in water, which would decrease the retention of APP in paper [35,36]. Until now, there has been no research report on the influence of the solubility of APP on the flame-retardant property of paper in the papermaking process. In this paper, the solubility of APP and its effect on the paper flame retardance were investigated for use with an in-pulp addition method.

MATERIALS AND METHODS

Materials

Bleached softwood kraft pulp (BSKP) and ground calcium carbonate (GCC) were supplied by Zhejiang Jinchang Specialty Paper Co. Ltd. (Zhejiang province, China). The APP was obtained from Zhejiang Xiongxiong Technology Co. Ltd. (Zhejiang province, China). Cationic polyacrylamide (CPAM) was purchased from SNF China Flocculant Co. Ltd. (Jiangsu province, China).

Preparation of flame-retardant paper

Researchers added to and stirred APP or GCC as fillers for softwood bleached kraft pulp with a beating degree of 38.3°SR, and CPAM was added as a retention and drainage agent. Then, handsheets were formed in a handsheet former.

Characterization

To determine the particle size, conductivity, zeta potential, and particle charge density, 100 mL of distilled water containing 1.0 g of APP was stirred in a beaker, followed by ultrasonic dispersion for 20 min. Then, it was measured with a laser particle size analyzer (Mastersizer 2000, Malvern Panalytical; Malvern, UK), zeta potential meter (Zetasizer Nano ZS90, Malvern Panalytical), and charge density meter (PCD-03, BTG-Mütek; Herrsching, Germany), respectively.

The LOI value of the paper was tested with an oxygen index tester (ZR-01, Qingdao Ruixinjie Instrument Co. Ltd.; Shandong province, China) according to ASTM D2863-2000 "Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics."

The solubility of APP was measured according to HG/T 2770-2020 "Industrial ammonium polyphosphate." Then, 10 g of APP powder was dispersed in 100 mL distilled water and oscillated for 20 min at temperatures ranging from 10°C to 75°C, and 20 mL of the supernatant was centrifuged at 2000 rpm for 20 min and transferred to a beaker. The beaker containing the supernatant was dried to a constant weight at 160°C. The solubility (ϱ) of APP was calculated according to Eq. 1:

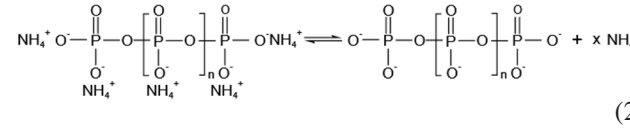
$$\varrho = (m_1 - m_2)/V \times 100 \quad (1)$$

where m_1 represents the weight of the supernatant and beaker, m_2 represents the weight of the beaker, and V is the volume of the supernatant.

RESULTS AND DISCUSSION

Electrochemical performance and morphology of APP

The ionization equation of APP in water is shown in Eq. 2 [37]. Due to the electron attraction of the double bond of P=O in the APP molecule, APP owns a strong polarity and ammonium ion NH_4^+ is easy to ionize, so APP particles possess strong electronegativity in water. Its zeta potential was -64.10 mv (measured with the Zetasizer Nano ZS90), the charge density was -9.24 meq/g (measured with the PCD-03 meter), and the conductivity was 208 us/cm (tested with the Zetasizer Nano ZS90), indicating that APP was able to partially ionize in water. In addition, as shown in Eq. 3 [38], APP is also able to be hydrolyzed in water with the P-O-P bonds breaking to form phosphoric acids, which will cause a change in the morphology and the particle size of APP.



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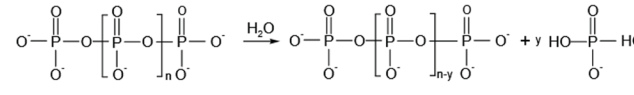
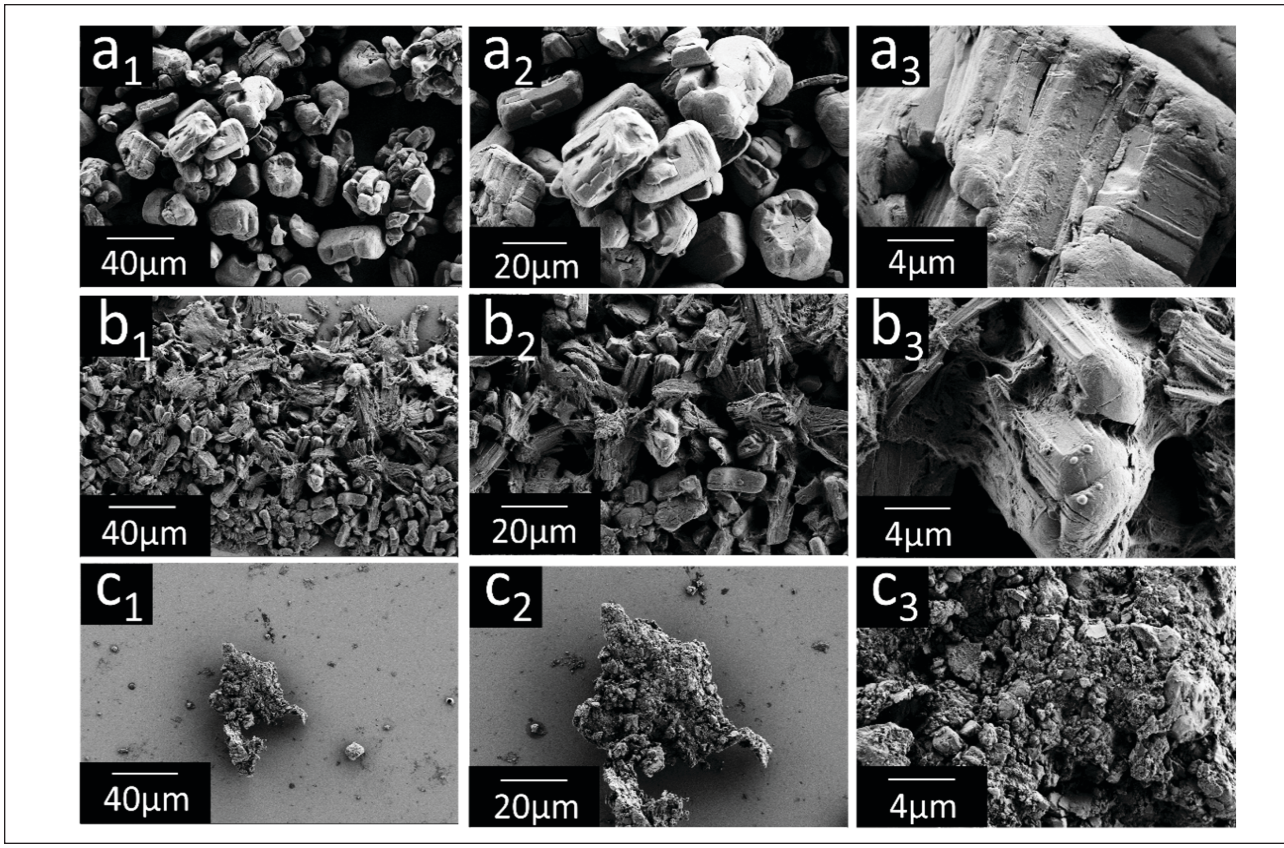
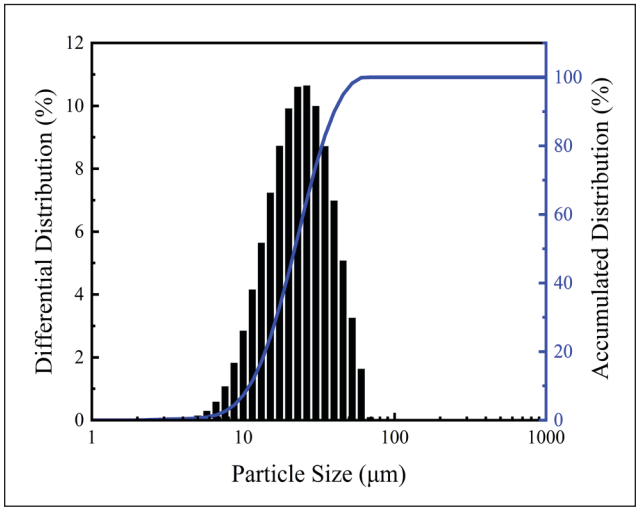


(3)

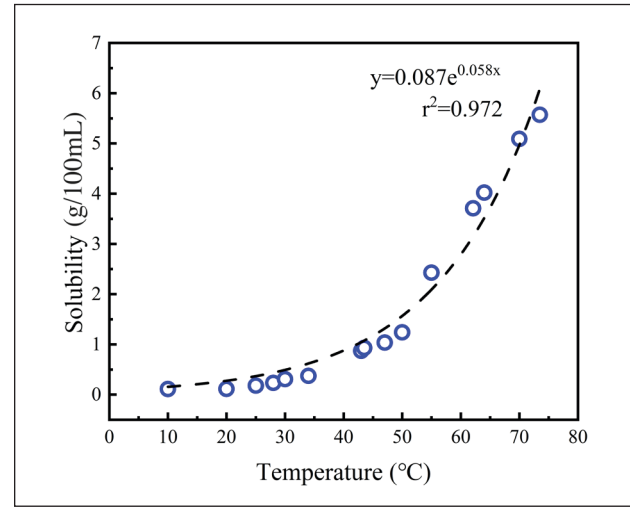
Three APP powders treated in different conditions in water were prepared, and their scanning electron microscope (SEM) images are shown in **Fig. 1**. The original APP powder was square with no significant agglomeration between particles (Fig. 1a), the size distribution was narrow (**Fig. 2**), and the average particle size was 21.88 μm. Compared with Fig. 1a, the particle size clearly decreased when they were



1. Scanning electron microscope (SEM) images of the ammonium polyphosphate (APP) powders: (a) the original APP powder; (b) the APP powder immersed in water at 25°C for 24 h; and (c) the APP powder immersed in water at 90°C for 0.5 h.



2. The APP particle size distribution.

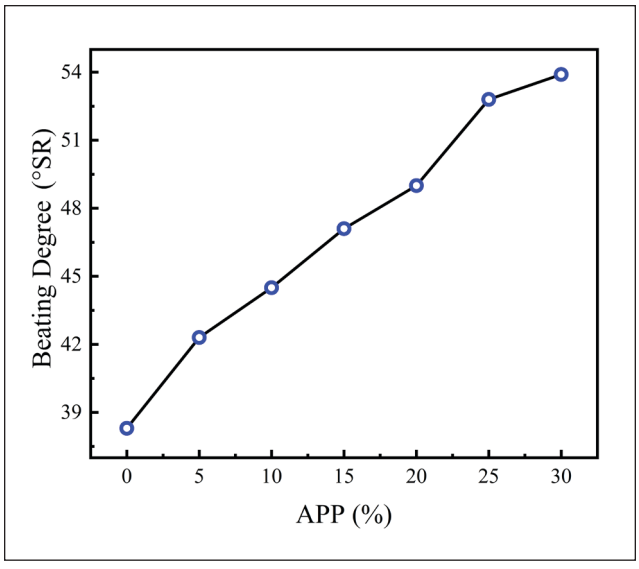


3. The APP solubility curve.

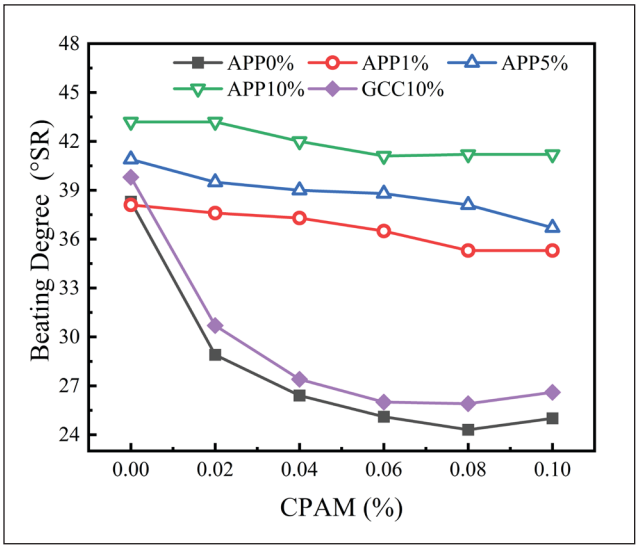
dried after being immersed in water at 25°C for 24 h (Fig. 1b). However, it retained the original morphology. When the treatment condition changed to 90°C for 0.5 h in water, most of the APP was dissolved, the residuals agglomerated, and the square shape disappeared and turned into amorphous form (Fig. 1c). As shown in Eq. 2 and Eq. 3, APP hydrolyzes and ionizes in water to form NH_4^+ and phosphoric acids, and the rates of the hydrolysis and ionization increase rapidly with the increase of water temperature [39]. Hence, the water temperature had a great impact on the morphology of APP.

Solubility of APP

The relationship between the temperature and solubility of APP in water is shown in **Fig. 3**. The solubility gradually increased as the temperature increased. When the



4. Effect of APP on the beating degree.

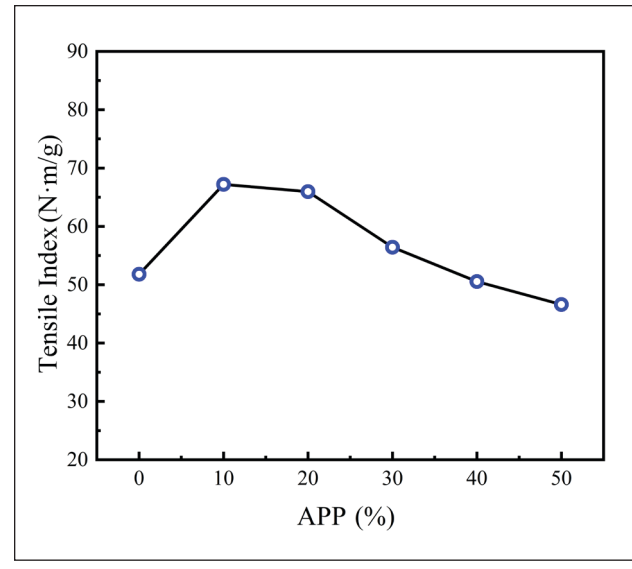


5. Effect of cationic polyacrylamide (CPAM) on the beating degree.

temperature was increased from 10°C to 30°C, the solubility slowly increased. The solubility was 0.11 and 0.18 g/100 mL water at 10°C and 25°C, respectively. When the temperature was 30°C, the solubility was 0.31 g/100 mL water, which was a 200% increase compared to when the temperature was 10°C. When the temperature was increased from 30°C to 50°C, the solubility noticeably increased. The solubility at 50°C was 1.24 g/100 mL water, which was a 588.9% increase compared to when the temperature was 25°C. Also, the solubility sharply increased when the temperature was more than 50°C. Therefore, APP should be added to the pulp at temperatures below 30°C to avoid serious dissolution.

Influence of APP on drainage of the pulp

As shown in **Fig. 4**, the beating degree of the pulp gradually increased with the increase of APP content. When CPAM was used, as shown in **Fig. 5**, the beating degree dropped with the increase of the CPAM content. When the added amount of APP was 0% and CPAM increased from 0% to 0.08%, the beating degree of the pulp decreased from 38.3°SR to 25.1°SR and then kept stable. When 10% of GCC was added to the pulp, similar to the addition of APP at 0%, the beating degree decreased quickly with the increase of the CPAM content. However, when the added amount of APP was 1%, 5%, and 10%, respectively, the beating degree of the pulp gradually decreased with the increase of CPAM, but the decreasing range was narrow.



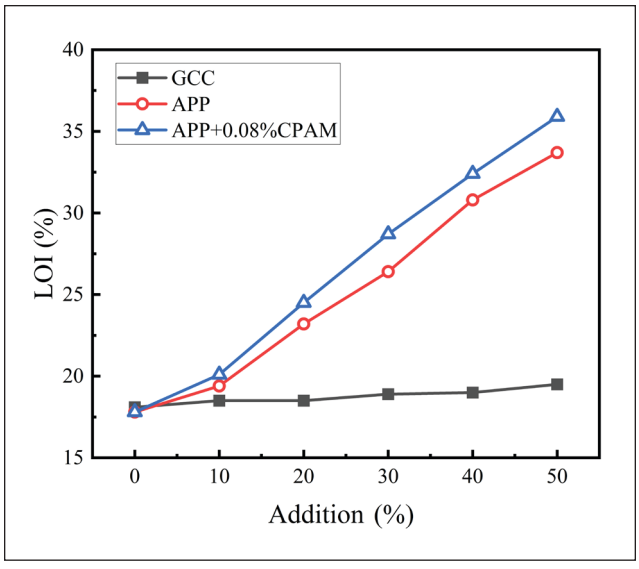
6. Effect of APP on the tensile strength.

Effect of APP on the tensile strength of paper

As shown in **Fig. 6**, with the increase of APP content, the tensile strength of the paper initially increased, and then began to decrease after reaching the maximum value. When the added amount of APP was 10%, the tensile index reached the maximum value of 67.2 N·m/g. When the added amount was 40%, the tensile index was 50.5 N·m/g, which was lower than that of paper with no APP. This was probably because some of the APP ionized in water, which formed R-O$^-$ (polyphosphate ion) and NH_4^+. When the added amount of APP in pulp was moderate, R-O$^-$ combined with the hydroxyl groups on the fiber surface to form hydrogen bonds, and NH_4^+ on the APP surface also could form hydrogen bonds with cellulose; therefore, the paper tensile strength improved. While the added amount of APP increased more, the hydroxyl groups on the fiber surface were not able to balance with the R-O$^-$ and NH_4^+ on the APP surface, and most of the APP filled in the gaps between the fibers as filler; therefore, the tensile strength decreased.

Effect of APP on the flame retardant

Ammonium polyphosphate is an intumescent flame retardant that plays a flame-retardant role through condensed phase



7. Effect of APP on the flame retardant (LOI = limiting oxygen index).

and gas phase. When the temperature is higher than 225°C, APP will decompose and release steam (H_2O) and ammonia (NH_3) to dilute O_2 concentration, playing the role of gas phase flame retardant. When the temperature is higher than 280°C, APP will further decompose and release H_2O and NH_3, and at the same time, generate polyphosphoric acid and polymetaphosphoric acid with strong dehydration, so that the surface of the organic materials, such as fibers, will be rapidly dehydrated and carbonized, and viscous carbonized matter with heat insulation and oxygen isolation will be generated. When the temperature is over 420°C, the main chain of APP is broken and forms a variety of phosphoric acid azeotropes and lots of double bonds to create a three-dimensional network structure with the organic materials, playing the role of condensed phase flame retardant [40,41]. As shown in **Fig. 7**, with the increase of GCC content, the LOI value of the paper was almost unchanged, meaning that the paper had no flame-retardant property. By contrast, the LOI value of the paper modified with the increase of APP, and the LOI value further increased while adding 0.08% of CPAM. When the added amount of APP was 30% and CPAM was 0.08%, the LOI value of the paper was 28.7%, reaching the flame-retardant level.

CONCLUSIONS

In the present article, it was shown that:

1. The morphology of the APP particles was square, with an average particle size of 21.88 µm. After being immersed in water at 25°C for 24 h, the particle size decreased significantly. After being immersed in water at 90°C for 0.5 h, most of the APP particles dissolved, the residuals agglomerated, and the square shape disappeared and turned into amorphous form.
2. The APP owns strong electronegativity and could partially ionize in water.
3. The solubility of APP was 0.18 g/100 mL water at 25°C, and the solubility increased significantly when the temperature was over 30°C. Therefore, APP should be added in pulp at temperatures below 30°C to avoid its serious dissolution.
4. The tensile strength of the paper initially increased with the APP addition, reached the maximum when the APP content was 10%, and then gradually decreased.
5. The beating degree of the pulp gradually increased with the increase of the added amount of APP. When the addition of APP was 30% and CPAM was 0.08%, the LOI value of the paper was 28.7%, reaching the flame-retardant level. **TJ**

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ABOUT THE AUTHORS

We chose to study this topic because ammonium polyphosphate (APP) is usually applied through the impregnation or coating method when producing flame-retardant paper. There are few reports on application with an in-pulp addition method.

This study investigated the solubility of APP and its effect on flame-retardant paper with in-pulp addition. The most difficult aspect of the research was obtaining basic performance information for APP.

We discovered that APP possesses strong electronegativity and can partially ionize in water. Our most surprising finding was that APP must be added into pulp at low temperature, which is one of our key technologies in this research.

From this study, mills may get new ideas on how to improve the flame retardancy of paper and reduce the solubility of APP. One next step is to modify APP to increase its flame-retardant effect on paper.

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