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Impact of Hexaamidocyclotriphosphazene on the Flame Retardancy of Paper

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Abstract
In this paper, the flame retardancy of hexaamidocyclotriphosphazene (HACTP) in paper was studied by limiting oxygen index measurement, the vertical burning test and cone calorimetry test. Meanwhile the mechanism was discussed by the analysis of residues obtained in the cone calorimeter test. The experimental results revealed that HACTP had excellent flame retardancy in paper.

Key words: *hexaamidocyclotriphosphazene, flame retardancy, paper, flame retarded paper.*

Introduction

Paper and its products from plant fibres tend to burn quite well with a bright, quick flame, hence their uses often lead to fires. With the increasing emphasis on fire safety, the demand for paper and its products with flame retardant properties has also been increasing. Especially paper products for packaging, building decoration, electronic materials and automobile exhaust emissions must have good flame retardant properties [1]. However, many paper products would not be able to meet the minimum level of fire safety established in codes and regulations without the use of flame retardants. Adding flame retardant is the main way to reduce the combustion performance of paper products. Currently there are mainly halogen system [1, 2], phosphorous system [3 - 6], nitrogen system [4, 5] and boron system flame-retardants as well as metal compounds (such as metal hydroxide [6], oxide [7 - 9] and their silicate [10, 11], etc.) for flame retardant paper. Halogen flame retardants have high efficiency, but their application is more and more limited due to safety and environmental issues [12]. Although nitrogen and phosphorus flame retardants and metal compounds have some advantages such as low toxicity, less corrosive gases and smoke formed during combustion, the efficiency of most of them is poorer, and thus their dosage is often larger for good flame retardancy, which makes the physical properties of the paper poor. By comparison, phosphazene flame retardants have some advantages such as being halogen-free, as well as having higher efficiency, less smoke, non-toxicity and non-corrosive gas formed during combustion. Therefore it is considered the development direction of flame retardants [13]. Some literatures report that hexaamidocyclotriphosphazene (HACTP) and its derivatives have good flame retardancy in textile fiber [14, 15]. Based on the similarity between paper and textile composition, authors studied the flame retardant effect of HACTP and hexa (N-hydroxymethyl)aminocyclotriphosphazene (HHMAPT) in paper, and found that they had good flame retardancy [16]. In this study, the results of HACTP are presented.

Experimental part

Canada dolphin softwood paper with a weight of 1300 g/m^2 and thickness of 1.3 mm was provided by Qingdao Tianfeng Makepaper Co., Ltd. China. Toluene was purchased from Wuhan Youji industries Co., Ltd. China. Hexachlorocyctriphosphazene was provided by Zibo Lanyin Chemical Co., Ltd. China. Ammonia was supplied by Qingdao Pengxin Gas Manufacturing Co., Ltd. China. All materials used in this work were of technical grade and used without further purification.

Preparation of hexaamidocyclotriphosphazene (HACTP)
HACTP was prepared according to literature [17]. The process is as follows: hexachlorocyctriphosphazene (69.6 g, 0.2 mol) was placed in a 1000 ml four-necked round-bottomed flask containing 600 ml of toluene equipped with a reflux condenser, thermometer, mechanical stirrer and gas inlet tube (diagram of the apparatus is shown in ***Figure 1***). The mix-

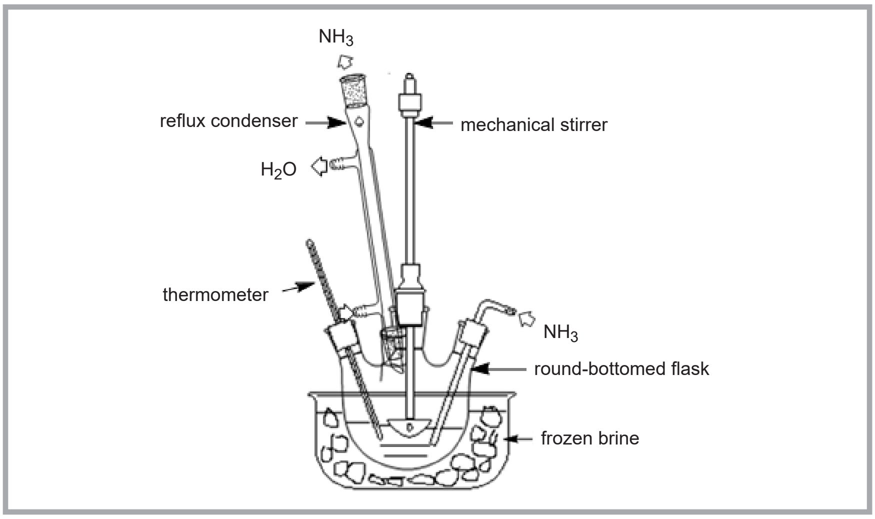

Figure 1. *Diagram of apparatus for preparation of HACTP.*

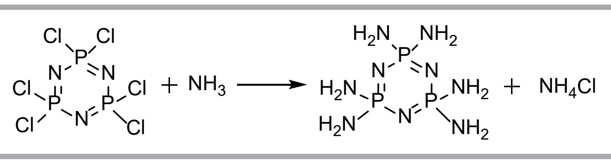
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Figure 2. *Equation of reaction 1.*

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ture was cooled to -5 - 0 °C with stirring using ice salt bath, then ammonia gas was introduced over a period of 24 hours at a temperature of -5 - 0 °C. The white powder consisted of about 42 wt.% hexaamidocyclotriphosphazene and by-product ammonium chloride was obtained by filteration and drying. The chemical reaction equation for HACTP is presented in ***Figure 2***.

Preparation of flame-retarded paper sheets

First the solution of HACTP (10 wt.% HACTP aqueous solution is colourless and has a pH of 7, a viscosity of 2.865 mPa) was sprayed evenly on the paper by a manual sprayer, and then the paper was dried in a natural environment for 1 - 2 h. During the process, HACTP was further uniformly distributed on the paper because of the permeability. Afterwards the paper containing HACTP was dried in a ZY-GZQ paper dryer (Jinan Zhongyi Instrument Co. Ltd) at about 100 °C for 1 h and at 14 - 150 °C for 10 min. The dried sheets were then cut into standard samples for flame retardant testing. The amount of HACTP can be calculated through the concentration and weight of the solution (half weight of the paper) which is sprayed onto the paper. Considering the uniformity of HACTPA in the paper, we repeated the test six times under same operator on the same apparatus, and the results were almost the same.

Flammability tests

The limiting oxygen index (LOI) was measured according to ASTM D 2863 with a JF-3 oxygen index meter (Jiangning Analytical Instrument Company, China). The specimens used for the LOI test were of dimensions 100×6.5×1.3 mm^3. The vertical burning test was carried out according to TAPPI T461 OS79 on a CZF-3 horizontal and vertical burning tester (Jiangning Analytical Instrument Company, China) with specimens of 210×70×1.3 mm^3. A cone calorimeter test was conducted with a FTT standard cone calorimeter (FTT Company, UK) in external heat fluxes of 50 KW/m^2 with specimens of 100×l00×1.3 mm^3 according to ISO 5660.

Morphology analysis of the residues

The morphology of the residues obtained in the cone calorimeter test (CCT) was observed by scanning electron microscopy (SEM, S-4800 Hitachi High-Tech Corporation, Japan).

^{31}P NMR spectra measurement

^{31}P NMR spectra were acquired with an Advance 500 spectrometer (Bruker Corporation, Germany) with D_2O as a solvent, where the sample was dissolved in 10% sodium hydroxide solution with phosphoric acid as an internal standard. ^{31}P chemical shifts were referenced to phosphoric acid (δ = 0 ppm).

Phosphorous content analysis

The content of phosphorous was measured by the gravimetric quimociac method according to ISO 6598. A 0.5000 g sample was placed in a 100 ml iodine flask containing 15 ml 10% nitric acid solution and equipped with a reflux condenser. The content was boiled for a few minutes using a heating jacket, then 35 ml of quimociao was added, which was subsequently cooled to room temperature and left to stand for 30 min for precipitation. The precipitation was followed by the procedures of filtration, drying and weighing. The content of phosphorous was calculated according to the formula presented in ISO 6598.

Results and discussion

LOI tests and UL94 classification

The effect of the dosage of HACTPA on the LOI and vertical burning property of the paper was investigated. As can be seen in ***Table 1***, the LOI of the paper increased with an increasing dosage of HACTPA, while the vertical burning property decreased. The LOI of the non flame retardant paper is 21.8%, and burns completely, but the LOI can be up to 38.0% and no burning level can be passed, where the after flame time of the vertical burning is reduced to 1.9 s, and the burning time is 0 s. Meanwhile the char length is only 6.0 mm as the dosage of HACTPA increases to 1.5 wt.%, based on the weight of paper. The LOI is equal or greater than 60.0% when the dosage of HACTPA is more than 4.0%.

Cone calorimeter analysis

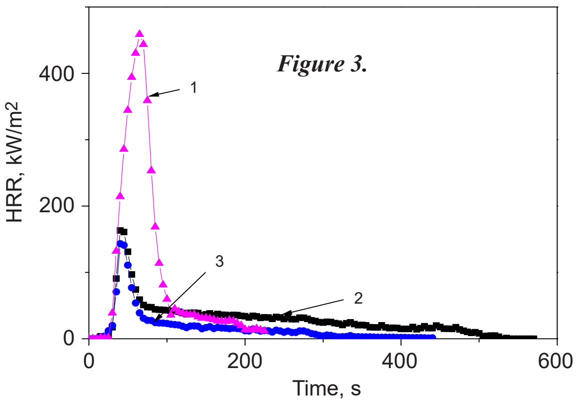
In order to further reveal the flame retardancy of HACTP in the paper, the cone calorimeter test was carried out. The heat release rate (HRR), total heat release (THR) and mass loss (ML) were analysed by th cone calorimeter test. The results are presented in ***Figure 3 - 5*** (see page 150) and some important data are listed in ***Table 2***. As can be seen from the data, the non-flame retardant paper burns very quickly after ignition, and the heat release rate increases rapidly, rising up to the maximum of 569.3 kW/m^2 in 75 s. Moreover total heat release increases rapidly and the mass decreases quickly, with the time required for complete combustion being about 235 s. However, the flame retarded paper (FR-paper) with

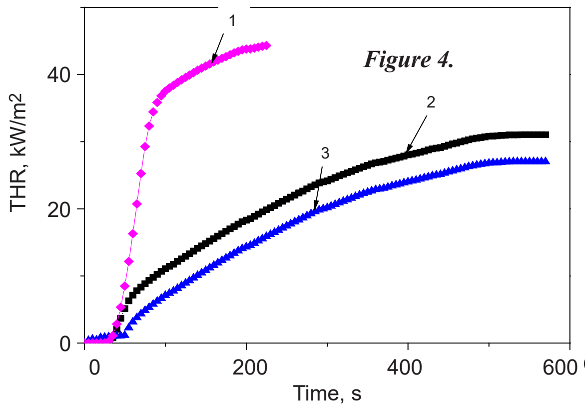
Table 1. *Influence of the dosage of HACTP on the flame retardance in paper.*

Dosage, wt.%	Vertical burning test			LOI, %
	After flame time, s	Burning time, s	Char length, mm	
0.0	125.3	422.4	-	21.8
0.5	167.6	0.0	210.0	31.6
1.0	36.7	0.0	37.0	35.3
1.5	1.9	0.0	6.0	38.0
2.0	0.7	0.0	5.0	45.0
2.5	0.6	0.0	5.0	50.0
3.0	0.7	0.0	5.0	52.0
4.0	0.5	0.0	4.0	60.0
5.0	0.4	0.0	4.0	>60.0
6.0	0.3	0.0	3.0	>60.0

Table 2. *Important cone calorimetry data.*

Term	Non-flame retardant paper	FR-paper with 3 wt.% HACTP	FR-paper with 6 wt.% HACTP
THR, kW/m^2	22.2	15.5	13.5
PHRR, kW/m^2	458.6	163.2	143.2
PHRR, Time, s	65	40	
MHRR, kW/m^2	97.0	26.5	16.7
PEHC, MJ/kg	80		
MEHC, MJ/kg	13.0	9.2	7.2
Time for ignition, s	10	15	25
Combustion time, s	170	570	565





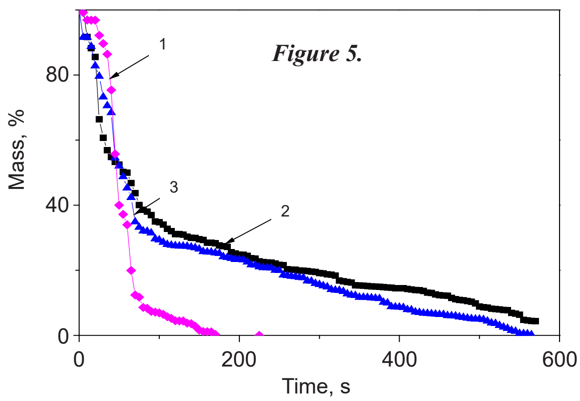


Figure 3. Heat release rate curves of paper and FR-paper with HACTP

Figure 4. Total heat release curves of paper and FR-paper with HACTP

Figure 5. Mass loss of paper and FR-paper with HACTP

1) 0% HACTP; 2) 3% HACTP; 3) 6% HACTP.

HACTP burns slowly after ignition, and the HRR increased slowly, with the mass deceasing slowly. The time required for complete combustion is prolonged. The peak heat release rate (PHRR), the mean heat release rate (MHRR), the total heat release rate, and the mean effective heat of combustion (MEHC) decreased significantly compared with the non flame retardant paper, which becomes more obvious with the increasing dosage of HACTP. The results above reveal that HACTP has good flame retardancy, which is consistent with the results of the limiting oxygen index (LOI) measurement and vertical burning test.

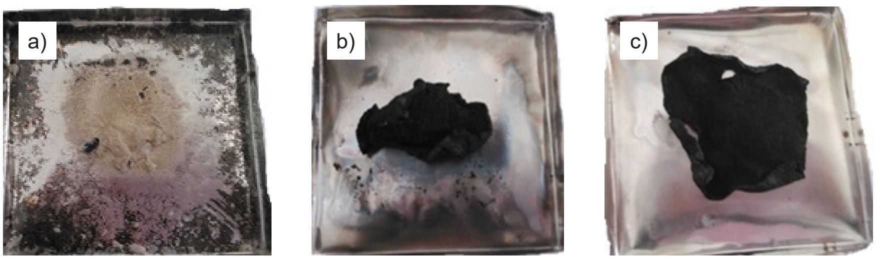


Figure 6. *Photos of residues of paper and FR-paper with HACTP a: 0% HACTP; b: 3% HACTP; c: 6% HACTP.*

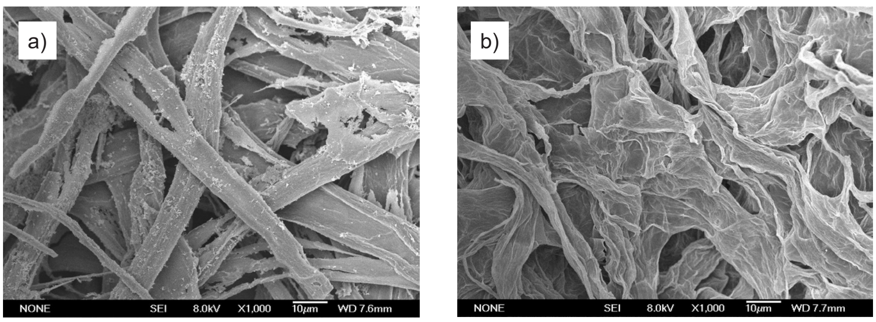


Figure 7. *SEM of residues, a) 0% HACTP; b) 6% HACTP.*

Fire retardancy mechanisms

The flame retardancy mechanism of HACTP in paper was discussed by analysis of the residue obtained in the cone calorimeter test.

As can be seen in the photos of residues shown in ***Figure 6***, that of the non flame retardant paper is hardly any, only 0.12 wt.% based on the weight of paper before burning, while the residues of the FR-paper are much more and appear intumescent, increasing with an increasing dosage of HACTP, for example, about 1.5 wt.% for FR-paper with 3 wt.% HACTP and 2.2 wt.% for FR-paper with 6 wt.% HACTP.

The SEM of the residue section presented in ***Figure 7*** shows that the residues appear to have a long sheet structure, but the residue structure of FR-paper with 6% HACTP is wider, more compact and smoother, and appears in interwoven forms, which results in better flame retardancy by means of the greater barrier effect on heat and air as well as preventing the volatilisation of the pyrolysis products of paper.

The structure of the phosphorus compound in the residue of FR-paper with HACTP (the residues were dissolved in 10 wt.% sodium hydroxide solution) was characterized by ^{31}P NMR. As can be seen in ***Figure 8***, the main chemical shift is around 5.8 ppm, which highlights that the dominant phosphorus compound is sodium phosphate (phosphoric acid compounds were converted into sodium phosphate in the presence of sodium hydroxide). The result above reveals that HACTP is converted into a phosphoric acid compound such as phosphoric acid, metaphosphoric acid and polyphosphoric acid in the process of combustion, which is consistent with the thermal degradation behavior of poly(diphenoyphosphazene) [18], presented in ***Figure 9***.

Based on the above results, it can be concluded that condensed-phase mechanisms play a major role in HACTP. In the process of combustion, HACTP is decomposed into non-volatile phosphoric acid compounds which promote the carbonisation of paper (seen equation of reaction 3 - ***Figure 9***), inert gases such as CO_2, and N_2 released from the decomposition of HACTP, as well as char foaming in the paper. The intumescent layer formed results in flame retardancy by means of the barrier effect on heat, air and decomposition products.

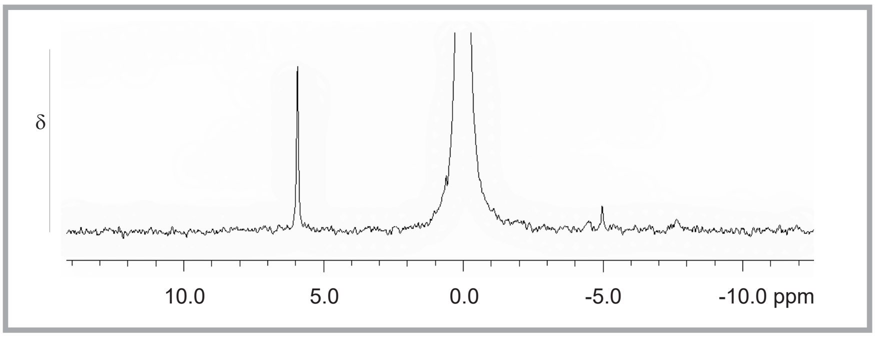


Figure 8. *^{31}P NMR of the residue of FR-paper with HACTP.*

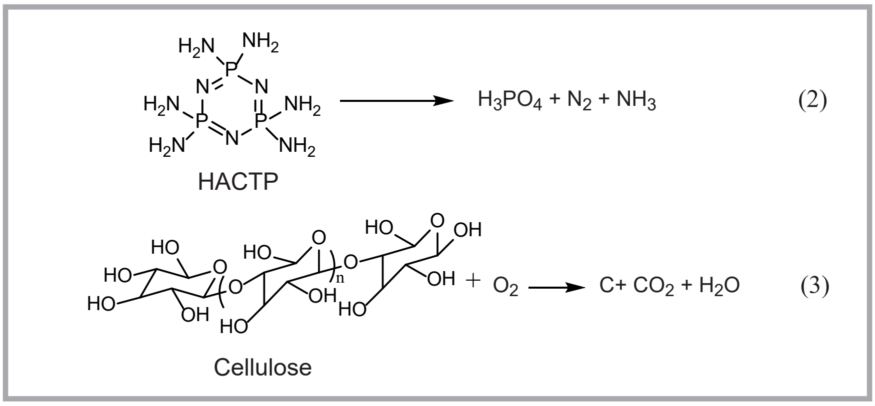


Figure 9. *Equations of reactions 2 & 3.*

Table 3. *Physical properties of papers.*

Term	Folding strength	Tearing strength, mN	Tensile strength, N·m·g^{-1}	Whiteness, %
Non- flame retardant paper	33	454	40.58	91
FR-paper with 3 wt.% HACTP	22	453	33.04	89
FR-paper with 6 wt.% HACTP	10	374	32.60	88

Physical properties of the paper

Physical properties of the papers were tested according to the standard, the results of which are shown in ***Table 3***. The data show that for FR-paper with 3 wt.% HACTP, indexes such as the folding strength, tearing strength and tensile strength are slightly reduced, but the overall strength of the papers remain stable and can meet the requirements of FR-paper application.

Conclusions

HACTP has excellent flame retardancy in paper. The LOI of the non flame retardant paper is 21.8%, and burns completely in the vertical burning test. However, when the dosage of HACTP is 1.5 wt.% based on the weight of paper, the LOI of the FR-paper can be up to 38.0%, where no burning level can be achieved; and the after flame time is reduced to 1.9 s, the burning time to 0 s, and the char length is only 6.0 mm in the vertical combustion test. The results of the cone calorimetry test reveal that the heat release rate (HRR) of FR-paper with HACTP increases slowly, with the mass loss becoming slow obviously. Moreover the peak heat release rate (PHRR), the mean heat release rate (MHRR), the mean effective heat of combustion (MEHC) and the total heat release (THR) decrease significantly, which become more obvious with an increase in the dosage of HACTP compared with the non-flame retarded paper. The residual analysis shows that HACTP played the role of flame retardancy mainly by means of the condensed phase mechanism. The HACTP was decomposed into phosphoric acid compounds in the process of combustion, which promoted the carbonisation of paper, the inertion of gases such as CO_2, N_2, NH_3 released from the thermal decomposition of HACTP, as well as char foaming in the paper. The intumescent layer formed results in flame retardancy by means of the barrier effect on heat and air as well as preventing the volatilisation of the pyrolysis products of paper.

Acknowledgments

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