Research paper

Preparation of Novel Non-Halogen Flame-Retardant Papers

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【Summary】

Halogen-containing flame-retardant paper products have both good efficacies and cost competitiveness. However, facing increasingly stringent environmental protection and safety requirements, these products could become a liability in service. Developing effective and cost-competitive non-halogen flame retardant paper products has thus become a goal of product development by the paper industry. In this study, we investigated the application of certain papermaking functional additives, particularly minerals, to develop fire-resistant agents or flame-retardant papers that are not liable to become soggy when exposed to moisture in the atmosphere. Five inorganic pigments (calcium carbonate, kaolin clay, magnesium hydroxide, aluminum hydroxide, and sericite mica) and a swelling-type flame-retardant (a phosphor-nitrogen (P-N) organic compound) were examined. We applied the minerals either by internal addition to a pulp furnish and formation into base sheets, or by surface coating applied to commercial copy paper substrates, and finally by adding the minerals at different proportions internally to the pulp furnish and then surface coating with the P-N compound. The prepared sheets were tested for their flame-retardation performance. Service environment-simulated treatments were also conducted on the papers to observe changes in their mechanical properties, so as to find the optimal flame-retarding filler ratios and coating amount formulations. The economic efficiencies of the various formulations were also analyzed to serve as a database for research and industrial reference. In total, 5 blended formulas allowed the papers to attain a class I flame-retardation rating. After the degradation test and economic analysis, we deemed that aluminum hydroxide and magnesium hydroxide were too expensive, and were liable to lose their fire-resistance after degradation. Sericite mica-treated paper showed lower strength losses after degradation treatment; however, the fire rating decreased to class III. Calcium carbonate- and kaolin clay-based papers had reduced fire ratings to class II after degradation.

Key words: non-halogen flame-retardant paper, phosphorus flame-retardant, inorganic additives, fire-resistance, flame-retardation.

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研究報告

非鹵素抗燃紙的開發研究

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摘　要

　　鹵素系列的抗燃紙效果及成本相當有競爭力，但是面對愈來愈嚴格的環保及安全要求，如何開發具有抗燃效果及成本有競爭力的非鹵素抗燃紙，為業界企待開發的目標。本研究開發不易回潮的防火劑及防火紙，選用五種無機填料(碳酸鈣、白土、氫氧化鎂、氫氧化鋁及絹雲母)及膨脹型抗燃劑(磷氮有機化合物)，分別利用內添於紙漿中抄造原紙、表面塗佈於市售影印紙等方式確認材料之抗燃性，另外再以內添不同填料比例於紙漿中抄造原紙並於原紙表面塗佈磷氮有機化合物的方式，對於紙張基材進行抗燃性之研究，配合環境模擬處理，同時觀察紙張機械性質的變化，以期找出最適抗燃填料比例及塗佈量配方，並分析各配方之經濟效益，以作為抗燃紙學術研究資料及提供業界參考。5種比例配方耐燃紙均可達抗燃一級標準，經劣化試驗以及經濟效益分析綜合評比，氫氧化鋁、氫氧化鎂價格昂貴且經劣化處理後會失去抗燃效果，絹雲母經劣化處理紙張強度損失較少，但抗燃減至三級標準，碳酸鈣、白土經劣化處理，則減至二級標準。

關鍵詞：非鹵抗燃紙、磷系抗燃劑、無機填料、抗燃、防燄。

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INTRODUCTION

Flame-retardant papers on the market basically belong to 4 genres: chlorine-type flame retardant-based, bromine-type flame-retardant-based, phosphorus and halogen flame retardant-based, and inorganic flame-retardant-based ones (Youngs 1997). Although halogen-based chemicals endow papers with good flame-retarding efficacy and often have good cost competitiveness, a trend toward increasingly stringent environmental protection and safety regulations is certain to affect their future. Thus, developing non-halogen flame-retarding papers with good efficacy and cost benefits has become a subject eagerly awaited by a section of the industry. Traditional phosphate-based flame-retarding papers meet the requirements of non-halogen, non-toxic, and low-fume characteristics, however, papers incorporating chemicals are liable to become soggy when exposed to atmospheric moisture, leading to a hindrance of their more-widespread acceptance.

　　Special formulations of flame-retarding paper are often proprietary knowledge of commercial establishment not available to the public, and are rarely examined in the literature either. The existing literature indicates that Lan et al. (2003) used a halogen-based flame-retarding agent for internal addition, and found that with a ratio of 1: 2 of calcium chloride to sodium silicate, the CNS 7614 class I flame-retardation level was achieved. Chiou (1982) examined the internal addition of antimony oxide, tetrabromophthalic anhydride $[(C_6H_2Br_2OH)_2C(CH_3)_2$, TBPA], and incombustible asbestos fibers and glass fibers in paper and their anti-flame efficiencies. The incombustible additive should be limited to

5~8% of the fiber, otherwise, the strength properties of the paper were adversely affected (Battista 1964). Phosphate and inorganic flame-retarding agents are also used. Su et al. (1999) utilized phosphate to react with urea to produce ammonium phosphate as a flame-retardant. At a molar ratio of phosphoric acid/urea of 0.1:0.3 M, practically no flame-retardation was achieved. At a molar ratio of $\geqq$ 0.2:0.6 M, however, the resulting flame-resistant pulp could reach Japan JISA-1322 flame-retardation class II for thin construction materials. And at a phosphoric acid/urea molar ratio of $\geqq$ 0.5:1.5 M, the resulting paper conformed to the requirements of class I flame-retardant paper regardless of the residual flaming time, residual ember time, or char-length stipulations. Lo (1997) used aluminum oxide at a wet-end dosage of 10% and surface coating of 43.2% and achieved a good fire-resistant temperature.

The purpose of this study was to develop flame-retarding agents and flame-retarding paper that do not become soggy when exposed to atmospheric moisture for prolonged periods. Five inorganics (calcium carbonate, kaolin clay, magnesium hydroxide, aluminum hydroxide, and sericite mica), and a swelling-type anti-flame chemical, phosphorus-nitrogen (P-N) organic compound were examined for their anti-flame efficacies. Environmental simulation treatments were also carried out to determine the effects of degradation and moisture absorption on the mechanical strengths of the papers, in order to find the pigment proportions and coating formulations that could attain optimal flame-retarding performance. We also examined the economic efficiencies of the formulations to establish fire-retarding paper formulations that are both environmentally friendly protection and cost competitive. The information may be very useful for paper companies seeking to de-velop some specialty paper products.

MATERIALS AND METHODS

Materials

Bleached hardwood Kraft pulp (BHKP) was from Taiwan Pulp and Paper Corporation (Taipei, Taiwan).

Inorganic pigments included 1) calcium carbonate ($CaCO_3$), ground calcium carbonate (GCC), 75F (Omya Taiwan, Suao, Taiwan); 2) kaolin clay: Huberfil L (J.M. Huber Co., Atlanta, GA, USA); 3) magnesium hydroxide $Mg(OH)_2$: M-0035 (Katayama Chemicals, Osaka, Japan); 4) aluminum hydroxide $Al(OH)_3$: A-0260 (Katayama Chemicals); and 5) sericite: A grade washed sercite mica, with an average particle diameter of 10 μm (Sunshine Mica, Taitung, Taiwan).

The swelling type anti-flame agent was a P-N organic compound, AF-100, from Derfu Chemicals (Taichung, Taiwan).

Methods

Paper conversions
Surface coating

We used commercial photocopy paper with 80 g m^{-2} grammage (Double A, Advanced Agro Co., Bangkok, Thailand) as the base paper, used 20% acrylic resin as a binder, and prepared coating colors incorporating the aforementioned pigments or the swelling-type anti-flame agent, coated with a laboratory bar-coater using a coat weight on 1 side of 20, 40, 60, and 80 g m^{-2} papers.
Internal addition

In a BHKP furnish, different proportions (10, 20, 30, 40, and 50 wt%) of the inorganic pigments or the swelling-type chemical were blended. Handsheets of 80 g m^{-2} were formed in accordance with the method of TAPPI standard T205 om-88.

Internal addition + surface coating

In the pulp furnish, 10% calcium carbonate was added, then the filler type anti-flame agents were added using the test pigments at 10, 20, 30, 40, and 50 wt% charges together with other wet-end functional chemicals in order of 1% of the AKD sizing agent, 0.8% cationic starch, and 0.03% cationic retention aid polymer. Handsheets of 80 g m^{-2} were formed as described above, then a surface coating of 10, 15, 20, 25, and 30 g m^{-2} of the swelling-type anti-flame agent (P-N compound) was applied to the air-dried sheets.

Degradation treatment

In accordance with CNS 12886-1, paper specimens were placed in a 150℃ forced-draft oven for 24 h. The specimens were then removed and placed in an atmosphere of 23 $\pm$1℃, and 50$\pm$2% relative humidity for a further 24 h.

Methods of evaluation

Flame-resistance test

Test specimens of suitable sizes (70$\times$ 210 mm) were cut, weighed, and tested for their flame resistance in accordance with CNS 10760. The charring lengths of the test strips in centimeters were recorded together with the residual flaming time (s) and residual ember time (s).

Paper strength tests

Papers were tested for their tensile, bursting, and internal tearing strengths according to the standard methods of CNS 12607, 1353 and 1355, respectively.

Evaluation of economic benefits

The raw material costs of making 1 metric tonne (mt) of a specialty fire-resistant paper were tallied. A fixed cost of water and electricity was assumed, then the types of inorganic additives and their dosages to the unit production costs relationship were examined. Table 1 shows the unit costs of the raw materials. The equations of calculation were:

Dosage (kg mt^{-1}) = blend ratio (%) / solids content (%)$\times10^3$.

Mass of coating wt. (kg mt^{-1} paper) = 10^3 / grammage of the handsheet (g m^{-2})$\times$Coating wt. (g m^{-2}) = 10^3 / 80×20 = 250.

Table 1. Unit costs of flame-retardant paper raw materials

Item	Unit cost (NT$ kg^{-1})	Solids content (%)	Blend ratio (%)	Dosage (kg mt^{-1})	Material cost (NT$ mt^{-1} paper)
BHKP	17.11	84.2	80[1]	950.12	16,257
			70[2]	831.35	14,224
CaCO$_3$	1.62	99.9	10	100.10	162
Kaolin clay	7.71	99.0	10	101.01	779
Mg(OH)$_2$	860	99.5	10	100.50	86,432
Sericite	5.71	82.6	10	121.07	691
Al(OH)$_3$	1,000	90.9	30	330.03	330,033
AKD	19.81	16.1	1	62.11	1230
Cationic starch	16.8	92.5	0.8	8.65	145
Retention aid	148	86.1	0.03	0.35	52
Acrylic resin	35	39.0	20	128.21	4487
Phosphorus-nitrogen compound	85	100.0	80	200.00	17,000

In 2010, the average exchange rate was US$ 1.00≒NT$ 30.4.

[1] formulations 1-4.

[2] formulation 5.

Dosage of coating (kg mt^{-1}) = blend ratio (%) / solids content (%)$\times$250.

Material cost (NT\$ mt^{-1}) = dosage (kg mt^{-1})$\times$ unit cost (NT\$ kg^{-1}).

Production cost (NT\$ mt^{-1} paper) = the sum of material cost$\times$10^3/(10^3 + 250).

RESULTS AND DISCUSSION

Methods of conversion

First, we incorporated the 6 materials, i.e., calcium carbonate, kaolin clay, magnesium hydroxide, aluminum hydroxide, sericite mica, and a P-N organic compound into/onto the paper using internal addition and surface-coating processes. We then conducted flame-resistance tests to ascertain their performance. Surface coating

When the P-N organic compound was coated on to the base paper with a coat weight of 15 g m^{-2}, the resulting paper produced a char length of 6.1 cm. At a coat weight of 35 g m^{-2}, however, the resulting paper achieved the state prescribed by CNS 7614 as class I flame-resistant thin material (char length < 5 cm), as shown in Fig. 1. Coating the paper surface with the P-N compound caused it to form a layer of a swelling carbonized substance which separated heat and oxygen from the substrate, preventing its further combustion. When inorganics were individually coated on to base paper surfaces, only the magnesium hydroxide one achieved some flame resistance. At a coat weight of 80 g m^{-2}, the resulting paper had a char length of 5.7 cm (Fig. 2). When the paper was burning, the heated magnesium hydroxide decomposed to produce water vapor which diluted the concentration of combustible gases. The magnesium oxide that formed on the surface of the substrate was also an effective barrier separating oxygen, hence it had flame-retardation efficacy. Aluminum hydroxide, on the other
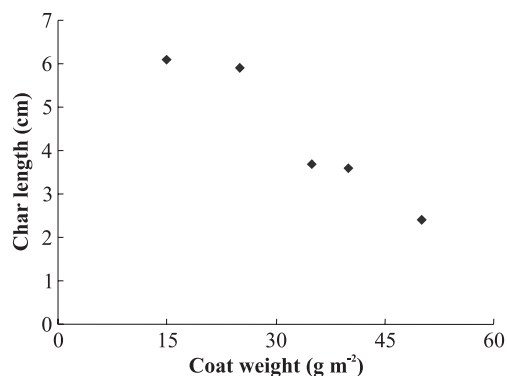

Fig. 1. Coat weight of the phosphorus-nitrogen compound vs. the char length of the resulting papers.
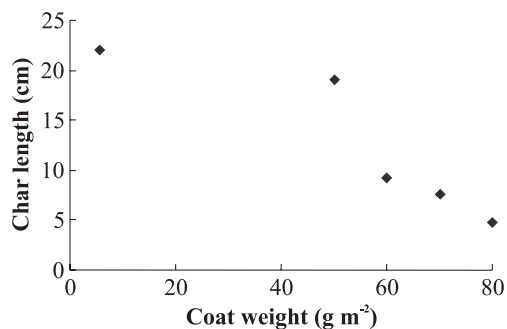

Fig. 2. Coat weight of magnesium hydroxide vs. the char length of the resulting papers.

hand, required a coat weight of 100 g m^{-2} (beyond the range of our experimental parameters) to achieve some flame resistance, with a char length of 6 cm. In the burning process, the aluminum hydroxide on the substrate underwent the same decomposition reaction to produce water vapor and aluminum oxide which exerted the same functions as in the case of magnesium hydroxide. It, however, had a residual ember time of 27 s, suggesting a poor self-extinguishing capacity. Although its flame resistance increased with the applied coat weight, the excessive coat weight caused the ensuing paper to have a very rough tactile property, and the surface and mechanical

properties of the original base sheet were adversely affected. Coating with calcium carbonate, kaolin clay, or sericite alone rendered the resulting paper incapable of apparent flame resistance (data not shown).

Internal addition

In cases where the anti-flame agent or inorganics were individually added to the paper by an internal addition route, none achieved significant flame-resistance (data not shown). These materials probably filled in among the fibers without creating any effective barrier or endowing the fiber with a flame-resistance capability. This result was in congruency with that of Lo (1997) who reported using 50% aluminum hydroxide internally added to a base paper and was still unable to obtain flame-resistance.

Internal addition + surface coating

We internally added different proportions (10, 20, 30, 40, and 50 wt%) of pigments (calcium carbonate, kaolin clay, magnesium hydroxide, aluminum hydroxide, and sericite mica) in the series. In addition, a retention aid chemical was also added to increase the retention of the pigments and other wet-end functional chemicals. Then the internally filled base sheets were further surface-coated with the P-N organic compound of different coat weights (10, 15, 20, 25, and 30 g m^{-2}) in a bid to find the optimal formulation for flame-retardation.

Figures 3~7 show the effects of 5 inorganic pigment at different loadings and different P-N compound coat weights on the resulting paper flame-retardation performance. The ash content represents the actual retention of pigments in the papers, and char length is a measure of the anti-fire effectiveness. The effects of the P-N compound coat weight suggested that for all 5 pigments, the greater the coat weight, the shorter the char length

became. There were no problems of residual flame or residual ember either. Mostly, at a surface coat weight of 10 g m^{-2}, the resulting papers attained class II flame-retardation (char length < 10 cm). Magnesium hydroxide filler, however, required a P-N surface coat weight of 20 g m^{-2} to reach class II flame-retardation.

As for the effects of dosage and retention of inorganic pigments, except for the case of aluminum hydroxide, generally, the higher the ash content, the longer the char length became, suggesting poor flame-retardation. Thus, at a 10 wt% dosage of the pigments, the optimal anti-flame effect was achieved.
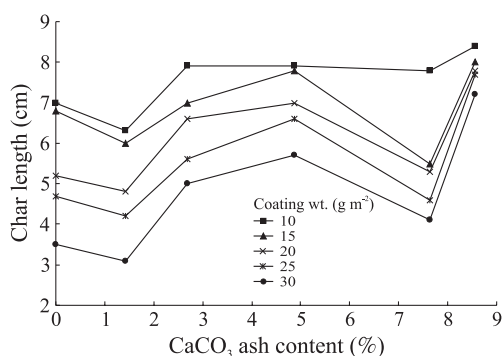
Fig. 3. Effects of the calcium carbonate ash content and phosphorus-nitrogen compound coating on the char length of the resulting papers.
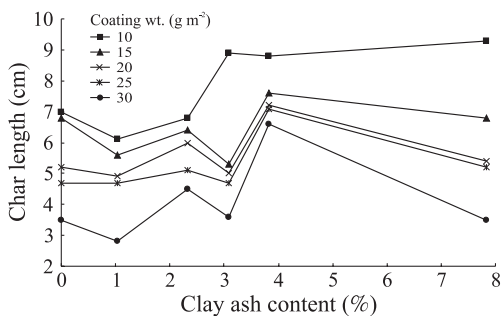
Fig. 4. Effects of the kaolin clay ash content and phosphorus-nitrogen compound coating on the char length of the resulting papers.
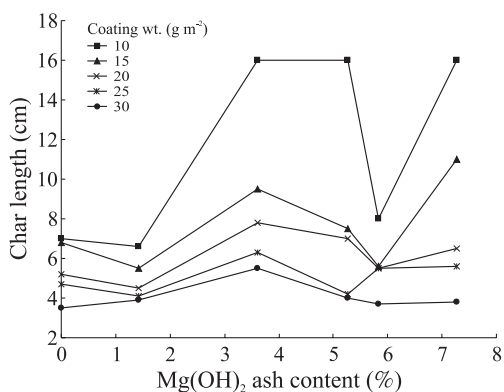
Fig. 5. Effects of the magnesium hydroxide ash content and phosphorus-nitrogen compound coating on the char length of the resulting papers.
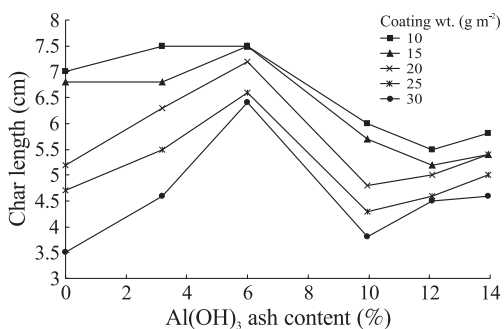

Fig. 6. Effects of the aluminum hydroxide ash content and phosphorus-nitrogen compound coating on the char length of the resulting papers.
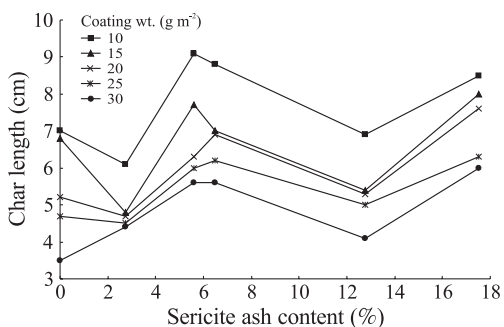

Fig. 7. Effects of the sericite mica ash content and phosphorus-nitrogen compound coating on the char length of the resulting papers.

Figure 6 shows that even at a 10% dosage, paper with aluminum hydroxide achieved class II flame-retardation; whereas at 30% loading, the best efficacy was attained. Figure 7 shows that for sericite mica, the higher the ash content, the poorer the flame-resistance became. However, at ash contents of 2.74 and 12.75%, shorter char lengths were observed. The probable cause might be that the platy pigment particles aligned themselves on the fiber surfaces to provide a better barrier or shield, allowing the P-N surface coating to exert better effects.

Overall, the flaming test evaluation results indicated that the optimal dosages of the internally added pigment were 10% each for calcium carbonate, kaolin clay, magnesium hydroxide, and sericite mica and 30% for aluminum hydroxide. The surface coating of the P-N compound was optimal at 30 g m^{-2} which produced the shortest char length; even at the 20 g m^{-2} coat weight, however, class II flame-resistance was achieved.

Degradation treatment

In order to understand the performance of the flame-retardant papers we prepared, the 5 formulations (with the internal addition of with 10% each of calcium carbonate, kaolin clay, magnesium hydroxide, and sericite mica and 30% aluminum hydroxide), all surfaces coated with 20 g m^{-2} of the P-N compound were put through an accelerated aging treatment. The post-treatment specimens were tested for their bursting, tearing, and tensile strengths and flaming evaluation. The results are shown in Figs. 8~11.

The control set indicated that the bursting strength was closely related to the interfiber capacity against the external pressure. With strong interfiber bonding and proper filling of the interstices with filler particles, a sturdy 3-dimensional network was achieved
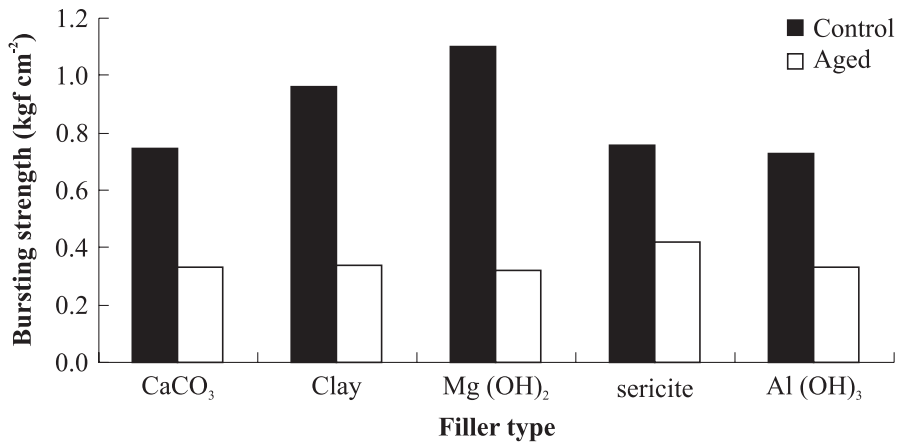
Fig. 8. Bursting strength of the post-aging fire-retardant papers filled with various fillers.
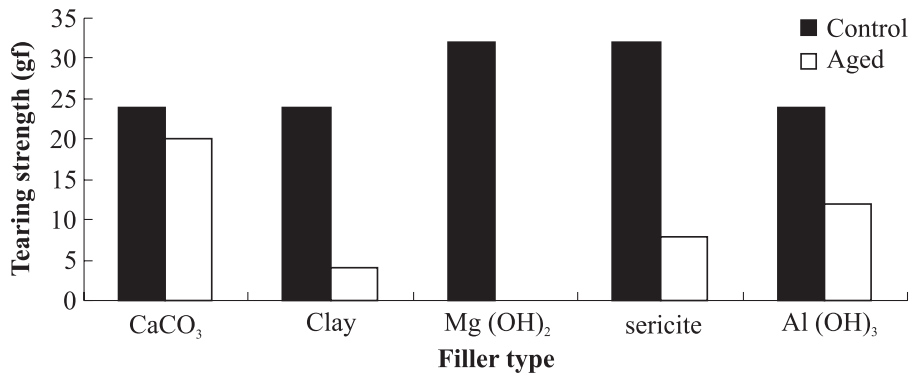

Fig. 9. Tearing strength of the post-aging fire-retardant papers filled with various fillers.
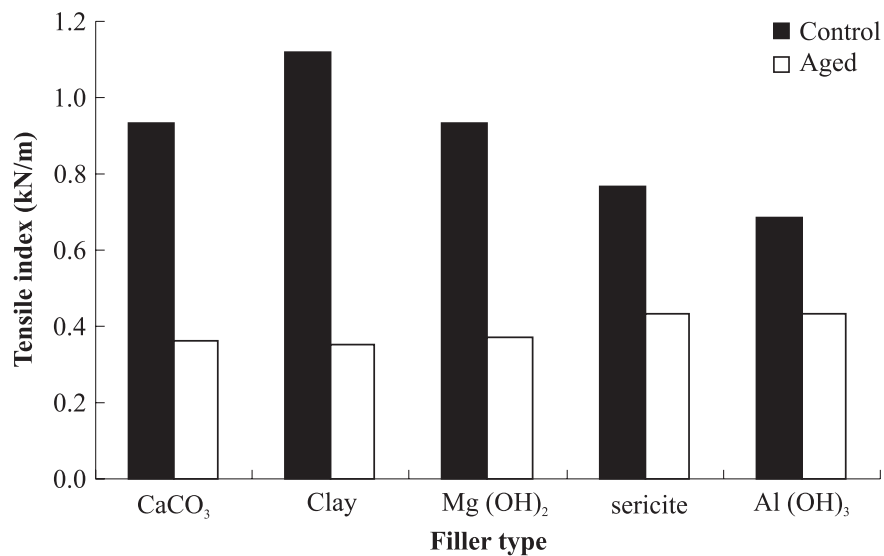

Fig. 10. Tensile index of the post-aging fire-retardant papers filled with various fillers.
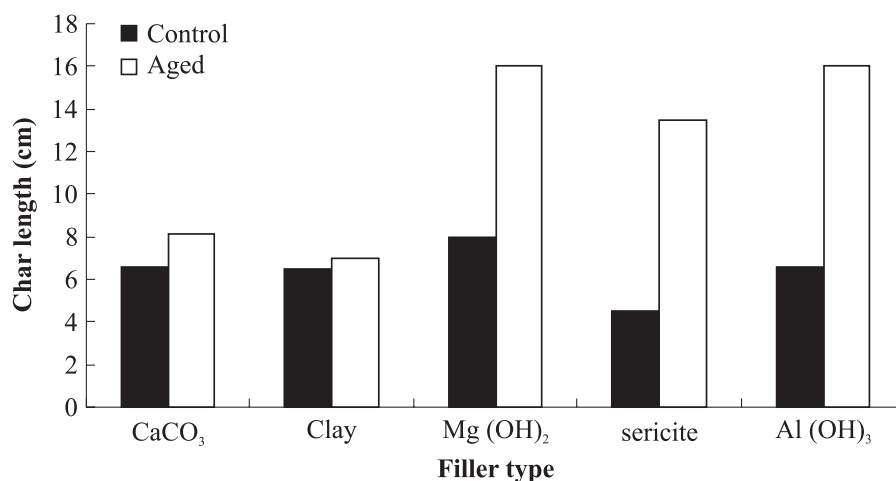
Fig. 11. Char lengths of the post-aging fire-retardant papers filled with various fillers.

and strong bursting strength exhibited. Conversely, upon high-temperature aging, the interfiber bonds degraded, causing the paper to greatly lose its bursting strength. As Fig. 8 shows, different pigments exerted differed effects on the residual bursting strength. Paper filled with magnesium hydroxide lost 70.9% of its original strength which was the greatest, followed by kaolin clay with a 64.6% decrease; while sericite mica fared the best with a decrease of 44.7% in bursting strength.

Figure 9 shows the effects of different fillers on the internal tearing strength of the flame-retardant papers. Tearing strength is known to correlate with fiber length and the capacity of the fiber network to resist shear forces along the plane of the network. Aging treated paper suffered high-temperature degradation of intrinsic fiber strength and interfiber bonding strength, lending to decreases in tearing strength. The sheets internally filled with magnesium hydroxide lost nearly all their tearing strength; those filled with calcium carbonate suffered the smallest loss of 16.7%.

The effects of accelerated aging on the tensile strength of the flame-retardant papers filled with different pigments are shown in

Fig. 10. Interfiber bonding through hydroxyl groups forming hydrogen bonds contributed to the strength of the network. Fillers generally interfere with hydrogen bonds and tend to reduce the tensile strength. In the degradation test, tensile strength was adversely affected with a notable loss of strength. The paper filled with 10% kaolin clay fared the poorest and lost 68.4% of its original tensile strength; those filled with calcium carbonate and magnesium hydroxide lost 60% of their tensile strength; whereas aluminum hydroxide-filled paper was least affected and showed a decrease of 37.1% of its original strength.

Figure 11 illustrates the char length of post-aging fire-retardant papers filled with various pigments. All papers filled with studied pigments lost some flame-retarding capacities (longer char lengths). Sericite mica-, magnesium hydroxide-, and aluminum hydroxide-filled papers all failed to retain any fire rating (with char lengths of > 16 cm). The degradation condition affected the calcium carbonate- and kaolin clay-filled papers to a much smaller degree.

Cost comparisons of flame-retardant papers

Table 2 shows the unit production costs

Table 2. Economic analysis of the optimal flame-retardant formulations

No	Wet-end formulation		Coating formulation	Production cost. (NT\$ mt^{-1} paper)
	Inorganic	Functional additive		
1.	10% CaCO$_3$ + 10% CaCO$_3$	1% AKD	Binder/pigment = 1/4	31,596
2.	10% CaCO$_3$ + 10% clay	0.8% cationic starch	Coat wt. = 20 g m^{-2}	32,090
3.	10% CaCO$_3$ + 10% Mg(OH)$_2$	0.03% retention aid		100,612
4.	10% CaCO$_3$ + 10% sericite			32,020
5.	30% Al(OH)$_3$			293,738

In 2010, the average exchange rate was US\$ 1.00 ≒ NT\$ 30.4.

of producing 1 metric tonne of a particular flame-retardant paper formulation. Based on the raw material cost, formula 5 was the costliest, entailing a unit cost of NT\$293,738 mt^{-1}; it was followed by formula 3, costing NT\$100,612 mt^{-1}; and other formulas had comparable costs of NT\$32,000 mt^{-1}. The calculation did not consider retention of the filler, and therefore the actual cost would be higher; however it can be used for making comparisons between the different formulas.

CONCLUSIONS

The internal addition experimental group results indicated that calcium carbonate, kaolin clay, magnesium hydroxide, aluminum hydroxide, sericite and the P-N compound were all unable to achieve fireproof requirements. When using the P-N compound for surface coating while internally filled with pigments, a higher the coat weight and the greater the flame-retardation were achieved, with shorter char lengths and no residual flame or ember problem exhibited. Conversely, in general, the higher the filler loading, the poorer the flame-retardation efficacies became. Even at a surface P-N compound coat weight of 10 g m^{-2}, the internal addition of aluminum hydroxide allowed the resulting paper to reach class II flame-retardation (with a char length of < 10 cm) as stipulated by CNS 7614. At an aluminum hydroxide content of 9.95%, the best fireproofing efficacy was established.

Upon accelerated degradation treatment, all papers suffered decreased ratings (lengthening of the char lengths). In particular, the sericite mica-filled paper lost 66.7% of its performance. The same was true for aluminum- and magnesium hydroxide-filled papers which also lost their flame-retardation efficacy. Calcium carbonate- and kaolin clay-filled papers suffered smaller decreases in flame-resistance, and still retained their class II ranking. All mechanical strengths also showed significant reductions after degradation treatment. For bursting strength, magnesium hydroxide-filled paper lost 70.9% of its original strength. The tearing strength loss of magnesium hydroxied-filled paper was also excessive, decreasing to nearly 0; whereas calcium carbonate-filled paper still retained 83% of its original tearing strength. As to tensile strength, kaolin clay filled paper lost 68.4% of its original strength; while aluminum hydroxide-filled paper lost the least at 37.1%. Overall, after accelerated aging, calcium carbonate filled-paper appeared to fare the best, and maintained its class II ranking.

LITERATURE CITED

Battista OA. 1964. Synthetic fiber in paper making. New York: Inter science Publishers. p 97-117.

Chiou CH. 1982. The preparation of fireproof papers. Pulp Paper Mag 4:36-8. [in Chinese].

Lan HF, Kuo LS, Hsiao YL. 2003. The flame-resistance characteristics of pigment-filled papers. Res Rep Natl Taiwan Univ. Exp For 17(4):219-30. [in Chinese].

Lo HW. 1997. Studies on the base papers for laminated composites of electronic applications [MSc thesis]. Taipei, Taiwan: Paper Division, Graduate School of Paper and Printing, Chinese Culture Univ. 101 p. [in Chinese].

Su YC, Wang IC, Chen HT. 1999. Preparation of specialty papers – flame-retardant and rustproof papers. Taiwan J For Sci 14(4):385-95. [in Chinese].

Youngs RW. 1997. Flame retardant paper and paperboard: manufacture & use. Carmel, CA: FRC Technologies. p 10-4.