

STUDIES ON THE FLAME RETARDANCY OF NITROGEN-RICH TEXTILES

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STUDIES ON THE FLAME RETARDANCY OF NITROGEN-RICH TEXTILES

by

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Dedicated to my respectful parents and supervisors without whose constant support this thesis was not possible. They always inspire me. At the same time, my thanks also go to my friends whose advice really worked for this thesis

CERTIFICATE

This is to certify that the thesis entitled “**Studies on the Flame Retardancy of Nitrogen-rich Textiles**” being submitted by **Mr. Prasun Mathur**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Department of Textile and Fibre Engineering, is a record of bonafide research work carried out by him. Mr. Mathur has worked under my guidance and supervision and fulfilled all the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.



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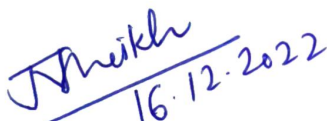
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ABSTRACT

Fire is a worldwide issue that claims lives and causes significant damages to the properties. Due to the stricter fire regulations, the fire hazards have been reduced. This substantiates that flame retardancy is very important. The addition of flame retardants into the materials causes the delaying or extinguishing of flame growth and decreasing the flame spread time. Their inclusion can prevent the loss of life and destruction of properties. It has been observed that flame retardants made of phosphorus and halogens are very effective.

The use of non-halogen based flame retardants in textile products is becoming more important because of the close contact that textiles have with humans and the potential risks connected with halogen-based flame retardants. Due to worries about eco-toxicity and associated regulatory pressures, the development of novel flame retardants is gaining interest. In recent years, it has become clear that phosphorus-based flame retardants are an effective alternative to halogen-based flame retardants. The numerous studies have shown that the combination of nitrogen and phosphorus-based compounds enhances the flame retardancy of cellulosic textiles. The wool, silk, nylon 6, and acrylic are among the fibres that are rich in nitrogen. The nylon 6 and acrylic are synthetic fibres, while wool and silk are natural fibres made of proteins. Although these fibres are rich in nitrogen but burn quickly. Interestingly, among these four fibres, wool is considerably more flame retardant. The disulphide linkages between molecules are present in the wool. However, there are few reports on the use of sulphate-based flame retardants to textiles. This makes it interesting to investigate and conduct research on the mechanisms applicable in the flame retardant finishing of such nitrogen-rich textile fabrics and studying their burning behaviour particularly after finishing with sulphur and phosphorus-based chemicals. This research work is divided into four parts.

The first part of the research covers the flame retardant finishing of wool fabric. The limiting oxygen index (LOI) of wool is 25. In the vertical flammability test, it ignites and burns entirely. The efficacy of the phosphorus and sulphur-based flame chemicals was investigated in this study. The impact of concentration of phosphorus and sulphur-based chemicals on flame retardancy was also assessed. It was discovered that at around 20 percent w/v concentration in the pad bath, limiting oxygen index of 30 or higher could be obtained. To test the durability of compounds after drying and curing, the treated samples

were washed. Wool responded well to phytic acid, phosphoric acid, sulphamic acid, ammonium sulphate, and ammonium peroxydisulphate. Wool has not shown good efficiency with aluminium sulphate. The limiting oxygen index of wool was not significantly impacted by thiourea. The sulphamic acid and 1,2,3,4-butane tetracarboxylic acid (BTCA) were used in the development of the durable flame-retardant wool.

The second part of the research presents the outcomes of treating a silk cloth with various phosphorus and sulphur-based chemicals. Studies have been done on the impact of concentration. At the appropriate concentration, a limiting oxygen index of 30 or higher was attained. The analysis of the effect of washing on the limiting oxygen index of dried and cured samples has been reported. A potential method for flame retardancy has been developed. Aluminium sulphate and thiourea were ineffective even on silk. The chemicals that showed the promise were phosphoric acid, ammonium sulphate, aluminium peroxadisulphate, and sulphamic acid. The sulphamic acid and BTCA were used to develop the flame retardant silk.

The third part of the research presents studies on the flame retardancy of nylon 6 fabric. Upon burning, the untreated fibre melts and drips. The chemicals based on phosphorus and sulphur were applied. The LOI of at least 30 was obtained. The nylon 6 stopped dripping. The phosphate salts showed good results. With the exception of aluminium sulphate, the sulphate salts were similarly found to be quite effective. Thiourea that was shown to be ineffective in earlier on wool and silk, however, thiourea worked nice on nylon 6. Thiourea was used in the development of the durable flame retardant nylon 6. It is challenging to conduct the test successfully in order to evaluate the effectiveness of different chemicals because nylon 6 drips during bottom burning. A top burning method was investigated as an alternative, which produces more reliable results because the fabric does not drip. This chapter also explored in depth the flame retardancy mechanism of the thiourea. According to the findings, thiourea dispersed and became confined into nylon 6 while it predominately existing on the surface of wool and silk. Thiourea degrades first and is unable to give wool and silk flame retardancy because flame retardancy is a bulk property.

This fourth part of the research presents the results of experiments performed for the flame retardancy of acrylic fabric. The chemical diffusion is difficult in acrylic fibre and T_g is significantly high than that of nylon 6. The diffusion of chemicals was analysed using the

exhaust method and combined two-step procedures. The different amines were used to perform the amination. This was followed by phosphoric acid, phytic acid, and sulphamic acid. It was found that the cationization process utilising amines was inefficient in terms of flame retardancy. The modification of acrylic by amino oximation, followed by treatments with phosphoric acid, phytic acid and sulphamic acid was however successful, and greatly improved flame retardancy. This treated acrylic fabric was durable to wash as well.

सार

आग एक विश्वव्यापी मुद्दा है जो जीवन का दावा करता है और संपत्तियों को महत्वपूर्ण नुकसान पहुंचाता है। आग के कड़े नियमों के कारण आग के खतरों को कम किया गया है। यह इस बात की पुष्टि करता है कि ज्वाला मंदता बहुत महत्वपूर्ण है। सामग्री में ज्वाला मंदक को जोड़ने से लौ के विकास में देरी या बुझ जाती है और लौ के फैलने का समय कम हो जाता है। इनके शामिल होने से जानमाल की हानि और संपत्तियों के विनाश को रोका जा सकता है। यह देखा गया है कि फॉस्फोरस और हैलोजन से बने ज्वाला मंदक बहुत प्रभावी होते हैं।

कपड़ा उत्पादों में गैर-हलोजन आधारित ज्वाला मंदक का उपयोग अधिक महत्वपूर्ण होता जा रहा है क्योंकि वस्त्रों का मनुष्यों के साथ घनिष्ठ संपर्क है और हैलोजन-आधारित ज्वाला मंदक से जुड़े संभावित जोखिम हैं। पर्यावरण-विषाक्तता और संबंधित नियामक दबावों के बारे में चिंताओं के कारण, नवीन ज्वाला मंदक का विकास रुचि प्राप्त कर रहा है। हाल के वर्षों में, यह स्पष्ट हो गया है कि फॉस्फोरस-आधारित ज्वाला मंदक हलोजन-आधारित ज्वाला मंदक का एक प्रभावी विकल्प है। कई अध्ययनों से पता चला है कि नाइट्रोजन और फास्फोरस-आधारित यौगिकों का संयोजन सेल्यूलोसिक वस्त्रों की ज्वाला मंदता को बढ़ाता है। ऊन, रेशम, नायलॉन 6, और ऐक्रेलिक उन रेशों में से हैं जिनमें नाइट्रोजन की मात्रा भरपूर होती है। नायलॉन 6 और ऐक्रेलिक सिंथेटिक फाइबर हैं, जबकि ऊन और रेशम प्रोटीन से बने प्राकृतिक फाइबर हैं। हालांकि ये फाइबर नाइट्रोजन से भरपूर होते हैं लेकिन जल्दी जल जाते हैं। दिलचस्प बात यह है कि इन चार रेशों में ऊन काफी अधिक ज्वाला मंदक है। ऊन में अणुओं के बीच डाइसल्फ़ाइड संबंध मौजूद होते हैं। हालांकि, वस्त्रों के लिए सल्फेट-आधारित ज्वाला मंदक के उपयोग पर कुछ रिपोर्टें हैं। यह ऐसे नाइट्रोजन युक्त वस्त्रों के ज्वाला मंदक परिष्करण में लागू तंत्रों की जांच और अनुसंधान करना दिलचस्प बनाता है और विशेष रूप से सल्फर और फास्फोरस-आधारित रसायनों के साथ खत्म होने के बाद उनके जलने के व्यवहार का अध्ययन करता है। इस शोध कार्य को चार भागों में बांटा गया है।

शोध के पहले भाग में ऊनी कपड़े की ज्वाला मंदक फिनिशिंग शामिल है। ऊन का सीमित ऑक्सीजन सूचकांक (एलओआई) 25 है। ऊर्ध्वाधर ज्वलनशीलता परीक्षण में, यह पूरी तरह से प्रज्वलित और जलता है। इस अध्ययन में फॉस्फोरस और सल्फर आधारित ज्वाला रसायनों की प्रभावकारिता की जांच की गई। ज्वाला मंदता पर फास्फोरस और सल्फर-आधारित रसायनों की एकाग्रता के प्रभाव का भी आकलन किया गया था। यह पाया गया कि पैड बाथ में लगभग 20 प्रतिशत w/v सांद्रता पर, 30 या उससे अधिक का सीमित ऑक्सीजन सूचकांक (LOI) प्राप्त किया जा सकता है। सुखाने और उच्च तापमान पर सुखाने

(curing) के बाद यौगिकों के स्थायित्व का परीक्षण करने के लिए, उपचारित नमूनों को धोया गया। फाइटिक एसिड, फॉस्फोरिक एसिड, सल्फामिक एसिड, अमोनियम सल्फेट और अमोनियम पेरॉक्सीडिसल्फेट के लिए ऊन ने अच्छी प्रतिक्रिया दी। एल्युमिनियम सल्फेट के साथ ऊन ने अच्छी दक्षता नहीं दिखाई है। ऊन का सीमित ऑक्सीजन सूचकांक (LOI) थायोयूरिया से महत्वपूर्ण रूप से प्रभावित नहीं था। टिकाऊ लौ-मंदक ऊन के विकास में सल्फामिक एसिड और 1,2,3,4-ब्यूटेन टेट्राकार्बोक्सिलिक एसिड (बीटीसीए) का उपयोग किया गया था।

शोध का दूसरा भाग रेशम के कपड़े को विभिन्न फास्फोरस और सल्फर-आधारित रसायनों के साथ इलाज के परिणामों को प्रस्तुत करता है। एकाग्रता के प्रभाव पर अध्ययन किए गए हैं। उपयुक्त एकाग्रता पर, 30 या उच्चतर का सीमित ऑक्सीजन सूचकांक प्राप्त किया गया था। सूखे और ठीक किए गए नमूनों के सीमित ऑक्सीजन सूचकांक पर धुलाई के प्रभाव का विश्लेषण बताया गया है। ज्वाला मंदता के लिए एक संभावित विधि विकसित की गई है। रेशम पर भी एल्युमिनियम सल्फेट और थियोरिया अप्रभावी थे। जिन रसायनों ने वादा दिखाया था, वे थे फॉस्फोरिक एसिड, अमोनियम सल्फेट, एल्युमिनियम पेरॉक्साडिसल्फेट और सल्फामिक एसिड। ज्वाला मंदक रेशम को विकसित करने के लिए सल्फामिक एसिड और बीटीसीए (BTCA) का उपयोग किया गया था।

शोध का तीसरा भाग नायलॉन 6 कपड़े की ज्वाला मंदता पर अध्ययन प्रस्तुत करता है। जलने पर, अनुपचारित फाइबर पिघल जाता है और टपकता है। फास्फोरस और सल्फर-पर आधारित रसायनों को लागू किया गया था। कम से कम 30 का सीमित ऑक्सीजन सूचकांक (LOI) प्राप्त किया गया था। नायलॉन 6 टपकना बंद हो गया। फॉस्फेट लवणों ने अच्छे परिणाम दिखाए थे। एल्युमिनियम सल्फेट के अपवाद के साथ, सल्फेट लवण समान रूप से काफी प्रभावी पाए गए। थायोयूरिया जो पहले ऊन और रेशम पर अप्रभावी दिखाया गया था, हालांकि, थायोयूरिया ने नायलॉन 6 पर अच्छा काम किया। थायोयूरिया का उपयोग टिकाऊ ज्वाला मंदक नायलॉन के विकास में किया गया था। नायलॉन 6 का मूल्यांकन करने के लिए सफलतापूर्वक परीक्षण करना चुनौतीपूर्ण है। विभिन्न रसायनों की प्रभावशीलता क्योंकि नीचे जलने के दौरान नायलॉन 6 टपकता है। एक विकल्प के रूप में एक शीर्ष जलने की विधि की जांच की गई, जो अधिक विश्वसनीय परिणाम उत्पन्न करती है क्योंकि कपड़ा टपकता नहीं है। इस अध्याय में थायोयूरिया की ज्वाला मंदता तंत्र की गहराई से खोज की गई है। निष्कर्षों के अनुसार, थायोयूरिया फैल गया और नायलॉन 6 में सीमित हो गया, जबकि यह मुख्य रूप से ऊन और रेशम की सतह पर मौजूद था। थायोयूरिया का पहले

अवक्रमण हो जाता है और ऊन और रेशम की ज्वाला मंदता देने में असमर्थ होता है क्योंकि ज्वाला मंदता एक थोक संपत्ति है।

शोध का यह चौथा भाग ऐक्रेलिक कपड़े की ज्वाला मंदता के लिए किए गए प्रयोगों के परिणाम प्रस्तुत करता है। ऐक्रेलिक फाइबर में रासायनिक प्रसार मुश्किल है और कांच पारगमन तापमान (T_g) नायलॉन 6 की तुलना में काफी अधिक है। निकास विधि और संयुक्त दो-चरण प्रक्रियाओं का उपयोग करके रसायनों के प्रसार का विश्लेषण किया गया था। एमिनेशन करने के लिए अलग-अलग एमाइन का इस्तेमाल किया गया था। इसके बाद फॉस्फोरिक एसिड, फाइटिक एसिड और सल्फामिक एसिड आया। यह पाया गया कि ज्वाला मंदता के संदर्भ में अमाइन का उपयोग करने वाली धनायनीकरण प्रक्रिया अक्षम थी। अमीनो ऑक्सीमेशन द्वारा ऐक्रेलिक का संशोधन, इसके बाद पीए, पीवाईए और एसए के साथ उपचार सफल रहा, और लौ मंदता में काफी सुधार हुआ। यह विकसित ऐक्रेलिक कपड़ा धोने के लिए भी टिकाऊ था।

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LIST OF ABBREVIATIONS

Abbreviation	Full form
DAP	Dihydrogen ammonium phosphate
DHP	Diammonium hydrogen phosphate
PA	Phosphoric acid
PYA	Phytic acid
AS	Ammonium sulphate
ALS	Aluminium sulphate
APDS	Ammonium peroxydisulphate
SA	Sulphamic acid
TH	Thiourea
W	Wool
S	Silk
N	Nylon
A	Acrylic
HCl	Hydrochloric acid
E	Ethylenediamine
D	Diethylenetriamine
T	Triethylenetetramine
HH	Hydroxylamine hydrochloride
SH	Sodium Hydroxide
MLR	Material to Liquor Ratio
FTIR	Fourier Transform Infra-Red
EDX	Energy Dispersive X-Ray
CHNS	Carbon, Hydrogen, Nitrogen, Sulphur
SEM	Scanning Electron Microscopy
VFT	Vertical Flammability Test
LOI	Limiting Oxygen Index
CRA	Crease Recovery Angle
TGA	Thermogravimetric Analysis
AA	Aminoximated acrylic
AAPA	Aminoximated acrylic treated with phosphoric acid
AAPYA	Aminoximated acrylic treated with phytic acid
AASA	Aminoximated acrylic treated with sulphamic acid
BEL	Burnt Entire Length