

# **STUDIES IN DEVELOPMENT OF NOVEL FUNCTIONAL DYES FOR TEXTILES**

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**DEPARTMENT OF TEXTILE AND FIBRE ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
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# **STUDIES IN DEVELOPMENT OF NOVEL FUNCTIONAL DYES FOR TEXTILES**

by

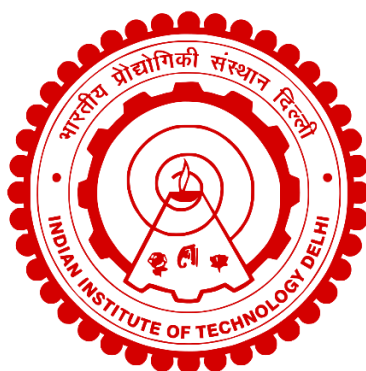
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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

*to the*



**Department of Textile and Fibre Engineering**

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**August 2023**

*Dedicated to “My Family, Teachers and Friends”*

## **Certificate**

This is to certify that the thesis titled ‘**Studies in Development of Novel functional Dyes for Textiles**’, being submitted by **Mr. Ankit Kumar Singh, Entry No. 2020TTZ8015** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. He has worked under my guidance and supervision and fulfilled the requirements for submission of the thesis, which has attained the standard required for a PhD degree at this institute.

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

**Date:** 02/08/2023

**Place:** New Delhi

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## Abstract

Development of functional textiles (mosquito repellent, antibacterial, UV-protective, and flame retardant) using novel routes is highly demanded. Mosquito-borne diseases are a great concern for human health, and an increment in urbanisation is causing a rise in the population of mosquitoes. Efficient methods and products for preventing mosquito bites are the urgent need of the hour. To protect against mosquitoes, mosquito-repellent textile is an attractive option. Dyes provide an attractive appearance to a textile substrate, and functional dyes can impart functional properties to textile substrates, thereby eliminating textile finishing process. The present work explores the synthesis and application of novel functional dyes for imparting functional properties, such as mosquito repellency, antibacterial activity, UV protection, and flame retardancy to textile materials.

In the first part of this research, the preparation of a mosquito repellent-cum-UV-protective nylon using a novel reactive dye was attempted. The synthesis of dye involves the reaction of cyanuric chloride with H-acid (4-Amino-5-hydroxy-2,7-naphthalenedisulfonic acid) to generate cyanuric-H-acid, which was further reacted with diazotised 4-amino-N, N-diethyl-3-methylbenzamide (DEET-NH<sub>2</sub>) to synthesise a novel cold brand reactive dye. Functional properties (mosquito repellency and UV protection) of dyed nylon and its durability against the laundering treatments were evaluated. An outstanding mosquito repellency (100%) and a good UV protection were achieved on dyed nylon.

In the second part of this research, a novel disperse dye based on diazotised sulfadiazine, and 4-hydroxy coumarin was developed. The dyeing of polyester with the synthesised disperse dye was performed. The exhaustion (%), fixation (%), and colouration properties (L\*, a\*, b\*, K/S) were studied. The disperse dye imparted excellent UV protection, good antibacterial activity (>68%), and outstanding mosquito repellency (100%).

In the third part of this research, the synthesis of a new acid dye to develop mosquito-repellent and UV-protective nylon was attempted. The acid dye was synthesised by reacting a diazotised derivative of ethyl anthranilate with H-acid. The acid dye was utilised for the dyeing of nylon, and dyeing characteristics (exhaustion and fixation)

were examined. The dyed fabrics were imparted with 100% mosquito repellency and excellent UV protection.

In the fourth part of this research, a cationic (basic) dye was developed. The reaction of mosquito repellent (diazotized ethyl anthranilate) with imidazole generated an azo dye, which was further quaternised to make a cationic dye. Acrylic fibre dyed with the synthesised dye was evaluated for fastness and functional properties. The dye's colouration properties, such as exhaustion and fixation, were also determined. The dyed fabric showed multifunctional properties (mosquito repellency of 100% and excellent UV protection), which were retained to a significant extent even after laundering treatments.

In the fifth part of this research, an aromatic amine (4,4'-(1,4-phenylenebis(1,3,4-oxadiazole-5,2-diyl)) dianiline) was prepared from the polyester bottle waste. A new acid dye was developed on wool using the *in-situ* dyeing method by the reaction of the diazotised amine with H-acid. The evaluation of colouration and fastness properties of dyed wool was performed. The dyed wool was also studied for antibacterial and UV protection effects. An antibacterial activity of more than 70% and excellent UV protection were displayed by dyed wool.

In the sixth part of this research, an acid dye was developed to provide wash-durable flame-retardant protection to wool. A phosphorus and nitrogen-based compound containing multiple amino groups was synthesised. The amine was diazotised and reacted with H-acid to synthesise acid dye *in-situ* on wool fabric. The flame retardancy provided by dyed wool was determined using the limiting oxygen index (LOI), vertical flammability, and cone calorimetry analysis. The colour appearance, colour values, and fastness properties of dyed wool were evaluated to check the dyeing properties of the acid dye on wool fibre. The newly developed acid dye provided wash-durable colouration and flame-retardant effects to wool. A maximum LOI value of 35.5 was obtained, and the dyed wool displayed efficient flame retardancy.

## सार

नवीन मार्गों का उपयोग करके कार्यात्मक वस्तुओं (मच्छर विकर्षक, जीवाणुरोधी, पराबैंगनी सुरक्षात्मक और ज्वाला मंदक) के विकास की अत्यधिक मांग है। मच्छर जनित बीमारियाँ मानव स्वास्थ्य के लिए एक बड़ी चिंता का विषय हैं, और शहरीकरण में वृद्धि से मच्छरों की आबादी में वृद्धि हो रही है। मच्छरों के काटने को रोकने के लिए प्रभावी तरीके और उत्पाद समय की तत्काल आवश्यकता है। मच्छरों से बचाव के लिए मच्छर भगाने वाला कपड़ा एक आकर्षक विकल्प है। रंजक एक कपड़ा सबस्ट्रेट को एक आकर्षक रूप प्रदान करते हैं, और कार्यात्मक रंग कपड़ा सबस्ट्रेट को कार्यात्मक गुण प्रदान कर सकते हैं, जिससे कपड़ा परिष्करण प्रक्रिया समाप्त हो जाती है। वर्तमान कार्य कार्यात्मक गुण प्रदान करने के लिए नवीन कार्यात्मक रंगों के संश्लेषण और अनुप्रयोग की पड़ताल करता है, जैसे कि मच्छर विकर्षक, जीवाणुरोधी गतिविधि, पराबैंगनी संरक्षण, और कपड़ा सामग्री को ज्वाला मंदता।

इस शोध के पहले भाग में, एक नए प्रतिक्रियाशील रंजक का उपयोग करके एक मच्छर विकर्षक-सह-पराबैंगनी सुरक्षात्मक नायलॉन तैयार करने का प्रयास किया गया था। रंजक के संश्लेषण में सायन्यूरिक-एच-एसिड उत्पन्न करने के लिए एच-एसिड (४-एमिनो-५-हाइड्रॉक्सी-२,७-नेफ़थलेनडिसल्फ़ोनिक एसिड) के साथ सायन्यूरिक क्लोराइड की प्रतिक्रिया शामिल है, जिसे आगे डायज़ोटाइज़्ड ४-एमिनो-एन, एन-डायथाइल-३-मिथाइलबेनज़ामाइड के साथ प्रतिक्रिया दी गई थी। एन-डायथाइल-३-मिथाइलबेनज़ामाइड (डीईईटी-एनएच<sub>२</sub>) एक नए कोल्ड ब्रांड प्रतिक्रियाशील रंजक को संश्लेषित करने के लिए। रंगीन नायलॉन के कार्यात्मक गुणों (मच्छर विकर्षक और पराबैंगनी संरक्षण) और लॉन्ड्रिंग उपचार के खिलाफ इसकी स्थायित्व का मूल्यांकन किया गया। रंगीन नायलॉन पर एक उत्कृष्ट मच्छर विकर्षक (१००%) और एक अच्छा पराबैंगनी संरक्षण प्राप्त किया गया।

इस शोध के दूसरे भाग में, डायज़ोटाइज़्ड सल्फ़ाडियाज़ाइन और ४-हाइड्रॉक्सी कुमारिन पर आधारित एक नवीन डिस्पर्स रंजक विकसित की गई थी। संश्लेषित डिस्पर्स रंजक के साथ पॉलिएस्टर की रंगाई का प्रदर्शन किया गया। एग्ज़हौस्ट (%), फिक्सेशन (%), और कोलोरेशन गुण का अध्ययन किया गया। डिस्पर्स रंजक ने उत्कृष्ट पराबैंगनी संरक्षण, अच्छी जीवाणुरोधी गतिविधि (>६८%), और उत्कृष्ट मच्छर विकर्षक (१००%) प्रदान किया।

इस शोध के तीसरे भाग में, मच्छर-विकर्षक और पराबैंगनी-सुरक्षात्मक नायलॉन विकसित करने के लिए एक नए एसिड रंजक के संश्लेषण का प्रयास किया गया था। एच-एसिड के साथ एथिल एंथ्रानिलेट के डायज़ोटाइज़्ड डेरिवेटिव पर प्रतिक्रिया करके एसिड रंजक को संश्लेषित किया

गया था। नायलॉन की रंगाई के लिए एसिड रंजक का उपयोग किया गया था, और रंगाई विशेषताओं (एक्सहोस्टिव (%), फिक्सेशन (%)) की जांच की गई थी। रंगे हुए कपड़ों को १००% मच्छर विकर्षक और उत्कृष्ट पराबैंगनी संरक्षण प्रदान किया गया।

इस शोध के चौथे भाग में एक बेसिक रंजक विकसित की गई। इमिडाज़ोल के साथ मच्छर विकर्षक (डायज़ोटाइज़्ड एथिल एंथ्रानिलेट) की प्रतिक्रिया से एक एज़ो रंजक उत्पन्न हुई, जिसे बाद में एक धनायनित रंजक बनाने के लिए क्वार्ट टीनाइसेशन किया गया। संश्लेषित रंजक के साथ रंगे हुए ऐक्रेलिक फाइबर का मूल्यांकन स्थिरता और कार्यात्मक गुणों के लिए किया गया था। रंजक के रंग गुण, जैसे एक्सहोस्टिव (%), फिक्सेशन (%), भी निर्धारित किए गए थे। रंगे हुए कपड़े में बहुक्रियाशील गुण (१००% मच्छर विकर्षकता और उत्कृष्ट पराबैंगनी सुरक्षा) दिखाई देते हैं, जिन्हें लॉन्ड्रिंग उपचार के बाद भी काफी हद तक बनाए रखा गया था।

इस शोध के पांचवें भाग में पॉलिएस्टर बोतल के कचरे से एक एरोमैटिक एमाइन (४, ४'-(१, ४-फेनिलीनबीस(१, ३, ४-ऑक्साडियाज़ोल-५-, २-डायल)) डायनिलिन) तैयार किया गया था। एच-एसिड के साथ डायज़ोटाइज़्ड अमाइन की प्रतिक्रिया से इन-सीटू रंगाई विधि का उपयोग करके ऊन पर एक नया एसिड डाई विकसित किया गया था। रंगे हुए ऊन के रंग और स्थिरता गुणों का मूल्यांकन किया गया था। जीवाणुरोधी और यूवी संरक्षण प्रभावों के लिए रंगे हुए ऊन का भी अध्ययन किया गया था। ७०% से अधिक की एक जीवाणुरोधी गतिविधि और रंगे हुए ऊन द्वारा उत्कृष्ट पराबैंगनी संरक्षण प्रदर्शित किया गया।

इस शोध के छठे भाग में, ऊन को धोने-टिकाऊ लौ-प्रतिरोधी सुरक्षा प्रदान करने के लिए एक एसिड रंजक विकसित की गई थी। एक फास्फोरस और नाइट्रोजन-आधारित यौगिक जिसमें कई अमीनो समूह होते हैं, को संश्लेषित किया गया था। ऊन के कपड़े पर इन-सीटू में एसिड रंजक को संश्लेषित करने के लिए अमीन को डायज़ोटाइज़ किया गया और एच-एसिड के साथ प्रतिक्रिया की गई। रंगे हुए ऊन द्वारा प्रदान की जाने वाली ज्वाला मंदता को सीमित ऑक्सीजन सूचकांक (एलओआई), ऊर्ध्वधर ज्वलनशीलता और कोन कैलोरीमेट्री विश्लेषण का उपयोग करके निर्धारित किया गया था। ऊन फाइबर पर एसिड रंजक के रंगाई गुणों की जांच करने के लिए रंगीन ऊन के रंग रूप, रंग मूल्यों और स्थिरता गुणों का मूल्यांकन किया गया था। नव विकसित एसिड रंजक ने ऊन को धोने योग्य रंग और लौ-मंदक प्रभाव प्रदान किया। ३५.५ का अधिकतम एलओआई मूल्य प्राप्त किया गया था, और रंगे हुए ऊन ने कुशल ज्वाला मंदता प्रदर्शित की।

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