

**SOME QUANTITATIVE STUDIES IN DYEING OF
TEXTILE MATERIALS AND PHOTOSTABILITY
OF DYES AND DYEINGS**

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**A thesis submitted to the
Indian Institute of Technology, Delhi
for the award of the degree of
DOCTOR OF PHILOSOPHY**

**DEPARTMENT OF TEXTILE TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
AUGUST, 1983**

CERTIFICATE

I certify that Shri D.K. Jain has pursued the prescribed course of research. I am satisfied that the thesis presented by him is worthy of consideration for the award of the degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under my guidance and supervision and that the results contained in it have not been submitted in part or full to any other university or Institute for award of any degree/diploma.



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ACKNOWLEDGMENT

The author wishes to express his gratitude and sincere thanks to Prof. C.D. Shah for his help and guidance throughout the course of this work. It was under his tireless and continuous direction and supervision that this research was developed into a dissertation.

Appreciation is also expressed to Prof. N.M. Swani, Director of the Institute, Prof. O.P. Jain, Ex-Director, Prof. (Miss) P. Bajaj, Head, and Prof. D.S. Varma, Prof. V.B. Gupta and Prof. C.D. Shah, Ex-Heads of the Department of Textile Technology for their interest and for supplying facilities for the work.

It is acknowledged that Dr. D.N. Sharma was joint supervisor for ~~two~~ two years and four and a half months (i.e., 16-3-79 to 31-7-81). *Dr. Jain (D.K. Jain)*
The author is indebted to Dr. C.H. Giles, for arranging the gift of numerous transparent polymer films (used in this work) from industries in Britain.

Thanks are also due to the graduate students and the members of the staff of the Textile Technology Department for their cooperation.

PUBLICATIONS

The work described in this thesis has been included in the following papers.

1. Paper already published :

- (i) Dyeing of Modified Polypropylene:Cationic Dyes on Chlorinated Polypropylene.
C.D. Shah and D.K. Jain,
Text. Res. J., 53, 274 (1983).

2. Papers accepted for publication :

- (ii) Lightfastness of Lanasol (Acid Reactive) Dyes on Drawn and Undrawn Nylons.
C.D. Shah and D.K. Jain,
Text. Res. J., (In Press)
- (iii) Some Studies on n-Butanol Assisted Dyeing of Lanasol (Acid Reactive) Dyes on Nylon 66.
C.D. Shah and D.K. Jain,
Text. Res. J., (In Press).
- (iv) Some Quantitative Studies on Light Fading of Solubilised Vat Dyes on Nylon 66 Aftertreated with Hydroquinone.
C.D. Shah and D.K. Jain,
Text. Res. J., (In Press).

- (v) Mechanism of Light-Fading of Azo Dyes on Polyvinyl Chloride and Poly(ethylene-terephthalate).

C.D. Shah and D.K. Jain,
Text. Res. J., (In Press).

3. Papers already submitted to Journals for Publication :

- (vi) The Effect of Light on Nylon 6 Dyed with Procynyl (Disperse Reactive) Dyes.

C.D. Shah and D.K. Jain.

- (vii) Effect of Hydroquinone on Light-Induced Degradation of Nylon 6 Dyed with Solubilised Vat Dyes.

C.D. Shah and D.K. Jain.

- (viii) Effect of Sulphonic Acid Groups in the Monoazo Acid Dyes upon their Lightfastness on Nylon 66.

C.D. Shah and D.K. Jain.

- (ix) Dyeing of Chemically Modified Polypropylene : Cationic Dyes on Brominated Polypropylene.

C.D. Shah and D.K. Jain.

4. Papers in preparation :

- (x) Some Studies on n-Butanol Assisted Dyeing of Acid Dyes on Nylon 66.

C.D. Shah and D.K. Jain.

- (xi) Activation Energies of Light Fading of Dyes in Textile Substrates.

C.D. Shah and D.K. Jain.

- (xii) Some Studies on Solvent (Perchloroethylene) Dyeing of Disperse Dyes on Polyester.

C.D. Shah and D.K. Jain.

ABSTRACT

The thesis describes a variety of types of experiments to elucidate some dyeing processes of textile materials and to investigate some physical and chemical factors which influence photostability of dyes on textile fibres and also of dyed fibres.

The subject matter is divided into following parts and sections :

PART I DYEING OF CHEMICALLY MODIFIED POLYPROPYLENE :

Section 1. Cationic Dyes on Chlorinated Polypropylene

Polypropylene fibre has been chlorinated by the action of sodium hypochlorite under specific conditions. On chlorination, the moisture content of the fibre increases, but there is no effect on the fibre's mechanical properties.

On chlorination, marked affinity is created in the fibre for cationic dyes from alkaline medium. Eight different cationic dyes have been used on the chlorinated product under different dyebath pH conditions. Dyeings tend to show that the mechanism of application of cationic dyes on chlorinated polypropylene is a reactive type, i.e., through the formation of a covalent bond between the fibre and the dye.

Of the eight cationic dyes, seven are found to possess poor to moderate lightfastness, only Methylene Blue (C.I. Basic Blue 9) gives very good lightfastness. In all the eight dyeings, other fastness properties such as fastness to washing, bleach, sea-water and soda-boil are good. All the eight dyeings have been after-treated with iodine which increase lightfastness.

Section 2. Cationic Dyes on Brominated Polypropylene

Polypropylene fibre has been photobrominated by the action of bromine under specific conditions. On bromination, the moisture content of the fibre increases, but there is no effect on the fibre's mechanical properties.

On bromination, marked affinity is created in the fibre for cationic dyes from alkaline medium. Eight different cationic dyes have been used on the brominated product under different dyebath pH conditions. Dyeings tend to show that the mechanism of application of cationic dyes on brominated polypropylene is a reactive type, i.e., through the formation of a covalent bond between the fibre and the dye.

Of the eight cationic dyes, seven are found to possess poor to moderate lightfastness, only Methylene Blue (C.I. Basic Blue 9) gives very good lightfastness. In all the eight dyeings, other fastness properties such as fastness

to washing, bleach, sea-water and soda boil are good. All the eight dyeings have been aftertreated with iodine which increase lightfastness.

PART II INFLUENCE OF PHYSICAL FACTORS ON THE PHOTO-
STABILITY OF DYES :

Section 1. Lightfastness of Lanazol (Acid Reactive
Dyes on Drawn and Undrawn Nylons

Four Lanazol (acid reactive) dyes applied on drawn and undrawn samples of nylon in both the fixed and unfixed state have been examined for their lightfastness on the Fade-Ometer. Higher lightfastness observed on drawn nylon can be attributed to the "diffusion-restriction" (DR) effect; and also this higher lightfastness shows that these dyes are probably in a state of very low aggregation. The fixed dyeings are not found to be faster than the unfixed ones, this tends to show that the dye-fibre bond obtained in reactive type of dyeing does not seem to contribute to higher lightfastness.

Section 2. Some Studies on n-Butanol Assisted Dyeing of
Lanazol (Acid Reactive) Dyes on Nylon 66

Four Lanazol (acid reactive) dyes have been applied on nylon 66 from aqueous and also from n-butanol assisted aqueous dyebath. The effect of n-butanol is studied: n-butanol did not change the hue of the shades in solution or on the substrate to any noticeable extent, n-butanol is found to cause

disaggregation of the dyes in solution and also on the substrate, its presence in the dyebath is found to increase diffusion rate of the dyes in the substrate, and also the lightfastness of the dyeings. The increase in lightfastness can be explained as due to greater penetration of the dyes in the substrate.

Section 3. Lightfastness of Acid and Metal Complex
Dyes on Drawn and Undrawn Nylons.

Six acid, four 1:1 metal complex, and four 1:2 metal complex dyes applied on drawn and undrawn samples of nylon have been examined for their lightfastness on the Light Fastness Tester. Higher lightfastness on drawn nylon shows that these dyes are probably in a state of very low aggregation, and also this higher lightfastness can be attributed to the "diffusion restriction" (DR) effect.

Section 4. Some Studies on n-Butanol Assisted Dyeing
of Acid Dyes on Nylon 66.

Seven acid dyes have been applied on nylon 66 from aqueous and also from n-butanol assisted aqueous dyebath. n-Butanol did not change the hue of the shades in solution or on the substrate to any noticeable extent, n-butanol is found to cause disaggregation of the dyes in solution and also on the substrate, its presence in the dyebath is found

to increase diffusion rate of the dyes in the substrate, and also the lightfastness of the dyeings. The increase in lightfastness can be explained as due to greater penetration of the dyes in the substrate.

Section 5. Some Studies on Solvent (Perchloroethylene)
Dyeing of Disperse Dyes on Polyester.

Three disperse dyes have been applied on polyester from aqueous and perchloroethylene dyebaths. The effect of perchloroethylene has been studied: it did not change the hue of the shades in the substrate to any noticeable extent. It is found to depress the glass transition temperature (T_g) of the polyester film from 85°C to 56°C. Dyes applied from aqueous medium are found to be more aggregated than those applied from perchloroethylene.

The retained perchloroethylene is found to decrease lightfastness of the dyeings. It is found for each of the dye studied that higher the amount of solvent retained, lower is the lightfastness.

PART III EFFECT OF CHEMICAL FACTORS ON LIGHT FADING OF DYES :

Section 1. Some Quantitative Studies on Light Fading of
Solubilised Vat Dyes on Nylon 66 After-Treated
with Hydroquinone.

Quantitative measurements of increase in lightfastness of Solubilised Vat dyes on nylon 66 on aftertreatment with

hydroquinone have been carried out. It is found that the increase is due to anti-oxidant action of hydroquinone, and not due to ultraviolet absorption by this aftertreatment agent. Effect of aggregation is also studied. Study of relative effect of both these factors on increase in lightfastness has revealed that in case of two of the five dyes investigated, aggregation does not play any role in improving lightfastness, it is due to anti-oxidant action of hydroquinone only; while in the case of other three dyes, both the factors are found to contribute in improving lightfastness. Aftertreatment with hydroquinone is found to cause changes in particle size distribution of these dyes on nylon 66.

Section 2. Mechanism of Light-Fading of Azo Dyes on Polyvinyl Chloride and Poly(Ethylene-Terephthalate).

A series of monoazo compounds based on phenyl azo- β -naphthol and phenyl azo-8-hydroxyquinoline have been applied to polyvinyl chloride and poly(ethylene terephthalate) respectively. From the relation between the electron-attracting or withdrawing properties of the substituents in the benzene nucleus and relative fading rates, it is concluded that the fading reaction in both the dye-fibre systems is probably oxidative type. This conclusion agrees with that from earlier analysis of fading products of

anthraquinone disperse dyes on polyester. It is therefore clear that both polyvinyl chloride and poly(ethylene terephthalate) confirm with the general observation that fading on any nonprotein ^{substrate} is oxidative type, provided that oxygen has access to the dye.

Section 3. Effect of Sulphonic Acid Groups in the Monoazo Acid Dyes upon Their Lightfastness on Nylon 66.

Quantitative measurement of increase in lightfastness of monoazo acid dyes on nylon 66 with the increase in the number of sulphonic acid groups in the dye molecules has been carried out. It is inferred that the increase may be attributed to lowering of surface activity of molecules of the dye with the increase in number of sulphonic acid groups, and also to the increased possibility of ionic dye-fibre links resulting in increase in strength of dye-fibre bonding.

Section 4. Activation Energies of Light Fading of Dyes in Textile Substrates.

Activation energies of fading of four different dye-fibre systems have been measured by fading at different temperatures :

- (i) three acid dyes on gelatin film,
- (ii) three basic dyes on gelatin film,

(iii) four disperse dyes on polyester,
and (iv) two disperse dyes on polypropylene.
Activation energies of fading range between 1.4 and 9.0
k.cal/mole and depend on the nature of the substrate and the
class of the dye. This conclusion agrees with that from
earlier measurements of activation energies of same or
different dye-fibre systems.

PART IV PHOTOSTABILITY OF FIBRES IN PRESENCE OF DYES :

Section 1. The Effect of Light on Nylon 6 Dyed with Procynyl (Disperse Reactive) Dyes.

Photostability of nylon 6 has been studied in
presence of four Procynyl (disperse reactive) dyes in the
Light Fastness Tester with an MBTF lamp. The loss in
mechanical and chemical properties of the dyed material is
found to be less than that of the mock dyed material exposed
under the identical conditions. This shows that these
Procynyl dyes confer photoprotective action to nylon 6. The
extent of photoprotective action varies from dye to dye.
A dye exhibiting maximum lightfastness confers maximum
photoprotective action, and a dye possessing minimum
lightfastness shows least photoprotective action.

These results tend to confirm the previous observations that the dye which form covalent bond on dyeing also confers protective action to the dyed fibre against photochemical degradation.

Section 2. Effect of Hydroquinone on Light-Induced Degradation of Nylon 6 Dyed with Solubilised Vat Dyes.

Photostability of nylon 6 has been studied in presence of four solubilised vat dyes in the Light Fastness Tester with an MBTF lamp. Two of the four dyes exhibit catalytic activity to enhance the actinic degradation of nylon 6 whereas other two dyes are photochemically inactive and confer photoprotective action to the fibre. Photochemically inactive dyes possess better lightfastness as compared to active dyes.

Light-induced degradation of nylon 6 in presence of solubilised vat dyes is retarded by an aftertreatment with hydroquinone. It is found that this retarding action is due to anti-oxidant action of hydroquinone, and not due to ultra-violet absorption by this aftertreatment agent.

Section 3(1) : The Effect of Light on Chlorinated Polypropylene Dyed with Cationic Dyes.

All the eight dyeings as described in Section 1, Part I have been studied for their photostability in the Light Fastness Tester with an MBTF lamp.

Of the eight cationic dyes, four are found to give photodegrading action to the fibre whereas the other four afford photoprotection. The dye possessing very good lightfastness on chlorinated polypropylene, i.e., Methylene Blue (C.I. Basic Blue 9) confers maximum photoprotective action to the fibre.

Section 3(ii). The Effect of Light on Brominated Polypropylene Dyed with Cationic Dyes :

The studies in the effect of light on all the eight dyeings as described in the Section 2, Part I show that three of them give photodegrading action on the fibre whereas other five dyes have been found to afford photoprotection. Here again, the dye possessing very good lightfastness on brominated polypropylene, i.e., Methylene Blue (C.I. Basic Blue 9) confers maximum protective action on the fibre against its photodegradation.

INDEX

Page No.

ACKNOWLEDGEMENTS

PUBLICATIONS

ABSTRACTS

GENERAL INTRODUCTION

1

GENERAL EXPERIMENTAL

The source of irradiation

15

Fade-Ometer

15

Light Fastness Tester

17

Substrates used

19

Transparent films used

19

PART I

DYEING OF CHEMICALLY MODIFIED POLYPROPYLENE

SECTION 1. Cationic Dyes on Chlorinated
Polypropylene

20

INTRODUCTION

Polypropylene and its dyeability

20

Modifying polypropylene for better
dyeability

21

Effect of chlorination on properties of
polypropylene

22

Present work

23

EXPERIMENTAL

Materials and methods	24
Fibres	24
Dyes	24
Chlorination	26
Degree of chlorination	26
Moisture content	26
Dyeing	26
Mechanical properties	27
Reflectance curves	27
Aftertreatment with iodine	27
Fastness properties	27

RESULTS AND DISCUSSION

Chlorination of polypropylene	28
Moisture content	29
Mechanical properties of fibres	29
Dyeability with basic dyes	30
Mechanical properties of dyeings	31
Fastness properties	32
Wash fastness	32
Lightfastness	32
Fastness to some other agencies	33
Methylene Blue on chlorinated polypropylene	33

CONCLUSIONS

<u>SECTION 2.</u>	<u>Cationic Dyes on Brominated Polypropylene</u>	35
-------------------	--	----

INTRODUCTION

Polypropylene and its dyeability	35
Effect of bromination on properties of polypropylene	35
Present work	36

EXPERIMENTAL

Materials and methods	37
Fibre	37
Dyes	37
Bromination	37
Moisture content	38
Dyeing	38
Mechanical properties	39
Reflectance curves	39
After-treatment with iodine	39
Fastness properties	39

RESULTS AND DISCUSSION

Bromination of polypropylene	40
Moisture content	41
Mechanical properties of fibres	41
Dyeability with basic dyes	42
Mechanical properties of dyeings	43
Fastness properties	43

Wash fastness	43
Lightfastness	44
Fastness to some other agencies	44
Methylene Blue on brominated polypropylene	45
<u>CONCLUSIONS</u>	45
 <u>PART II</u>	
<u>INFLUENCE OF PHYSICAL FACTORS ON THE PHOTOSTABILITY OF DYES</u>	
 <u>SECTION 1. <u>Lightfastness of Lanasol (Acid Reactive) Dyes on Drawn and Undrawn Nylons</u></u>	
<u>INTRODUCTION</u>	46
<u>EXPERIMENTAL</u>	48
Dyes	48
Substrate	48
Fading	49
<u>RESULTS AND DISCUSSION</u>	49
Diffusion restriction effect	49
Effect of dye-substrate bonds on lightfastness	51
<u>CONCLUSIONS</u>	51
 <u>SECTION 2. <u>Some Studies on n-Butanol Assisted Dyeing of Lanasol (Acid Reactive) Dyes on Nylon 66.</u></u>	
<u>INTRODUCTION</u>	53
<u>EXPERIMENTAL</u>	
Dyes	55
Substrate	56
Dyeing	56
Dyeing by film roll technique	57
Fading and measuring procedure	57

<u>RESULTS AND DISCUSSION</u>	58
Absorption spectra of dyes	58
Effect of addition of n-butanol to the dyebath on the physical state of the dye in the solution and on the substrate.	59
Effect of addition of n-butanol to the dyebath on the diffusion of Lanasol dyes in nylon 66	61
Lightfastness of Lanasol dyes applied on nylon 66 from aqueous medium and from n-butanol assisted aqueous medium.	62
<u>CONCLUSIONS</u>	63
<u>SECTION 3. <u>Lightfastness of Acid and Metal-Complex Dyes on Drawn and Undrawn Nylons.</u></u>	
<u>INTRODUCTION</u>	65
<u>EXPERIMENTAL</u>	
Dyes	66
Substrates	69
Dyeing	69
Fading	70
<u>RESULTS AND DISCUSSIONS</u>	70
<u>CONCLUSIONS</u>	71
<u>SECTION 4. <u>Some Studies on n-Butanol Assisted Dyeing of Acid Dyes on Nylon 66.</u></u>	
<u>INTRODUCTION</u>	72
Solvent-assisted dyeing of nylon	72

<u>EXPERIMENTAL</u>	74
Dyes	74
Substrate	76
Dyeing	76
Dyeing by film roll technique	77
Fading and measuring procedure	77
<u>RESULTS AND DISCUSSION</u>	78
Absorption spectra of dyes	78
Effect of addition of n-butanol to the dyebath on the physical state of the dye in the solution and on the substrate.	79
Effect of addition of n-butanol to the dyebath on the diffusion of acid dyes in Nylon 66	80
Lightfastness of acid dyes applied on nylon 66 from aqueous medium and from n-butanol assisted aqueous medium.	81
<u>CONCLUSIONS</u>	83
<u>SECTION 5. Some Studies on Solvent (Perchloroethylene) Dyeing of Disperse Dyes on Polyester.</u>	
<u>INTRODUCTION</u>	85
<u>EXPERIMENTAL</u>	
Dyes	87
Substrate	88
Solvent (perchloroethylene) dyeing of polyester	88
Aqueous dyeing of polyester	88
Heat treatment to control various solvent retentions	89
Estimation of solvent retained by polyester	89
Fading and measuring procedure	89
Determination of glass transition temperature	90

RESULTS AND DISCUSSION

Retention of perchloroethylene in polyester	90
Effect of perchloroethylene treatment on the glass transition temperature (T_g) of the substrate	91
Absorption spectra of dyes	91
Physical state of the dye in the substrate	92
Effect of retained perchloroethylene on lightfastness of disperse dyes on polyester	92

<u>CONCLUSIONS</u>	95
--------------------	----

PART IIIEFFECT OF CHEMICAL FACTORS ON LIGHTFADING OF DYES

SECTION 1. Some Quantitative Studies on Light Fading of Solubilised Vat Dyes on Nylon 66 After-Treated with Hydroquinone.

<u>INTRODUCTION</u>	96
---------------------	----

EXPERIMENTAL

Dyes	98
Substrate	99
Dyeing	99
Aftertreatment	99
Ultra-violet absorption spectra of hydroquinone in nylon 66 film	100
Determination of amount of hydroquinone absorbed by nylon 66 film	100
Fading and measuring procedure	100

RESULTS AND DISCUSSION

Hydroquinone as an after-treatment agent	101
Absorption of hydroquinone and its effect on lightfastness	101
Mode of action of hydroquinone	101
Physical state of the dye in the fibre	103
Factors contributing to the higher lightfastness	104

Relative effect of both these factors on increase in lightfastness	105
Particle size distribution of the dyes in the substrate	106
<u>CONCLUSIONS</u>	107
SECTION 2. Mechanism of Light-Fading of Azo Dyes on Polyvinylchloride and Poly(ethylene terephthalate)	108
<u>INTRODUCTION</u>	108
<u>METHODS AND MATERIALS</u>	111
Dyes for polyvinyl chloride	111
Dyes for poly(ethylene terephthalate)	112
Substrate	112
Dyeing	112
Dyeing of polyvinyl chloride	112
Dyeing of poly(ethylene terephthalate)	113
Fading and measuring procedure	113
<u>RESULTS AND DISCUSSION</u>	114
Characteristic fading curves	116
<u>CONCLUSIONS</u>	117
SECTION 3. <u>Effect of Sulphonic Acid Groups in the Monoazo Acid Dyes upon their Lightfast- ness on Nylon 66.</u>	
<u>INTRODUCTION</u>	119
<u>EXPERIMENTAL</u>	122
Dyes	122
Substrate	124
Dyeing	124
Fading and measuring procedure	124
Measurement of surface tension	125

RESULTS AND DISCUSSION

Effect of sulphonic acid groups in acid dyes upon their lightfastness on nylon 66	125
Factors contributing to increase in lightfastness of acid dyes on nylon 66 with increase in number of sulphonic acid groups in dye molecule.	127
(a) Surface activity of dyes	128
(b) Dye-fibre bond strength	129

CONCLUSIONS 129

SECTION 4. Activation Energies of Light Fading of Dyes in Textile Substrates.

INTRODUCTION 131

EXPERIMENTAL 134

Dyes	134
Substrates	136
Purification of dyes	136
Dyeing	137
Acid and basic dyes on gelatin	137
Disperse dyes on polyester	137
Disperse dyes on polypropylene	138
Temperature control device	138

RESULTS AND DISCUSSION 139

Activation energies of acid and basic dyes on gelatin	140
Disperse dyes on polyester	140
Disperse dyes on polypropylene	140

CONCLUSIONS 141

PART IV

PHOTOSTABILITY OF FIBRES IN PRESENCE OF DYES.

SECTION 1. The Effect of Light on Nylon 6 Dyed with Procionyl (Disperse Reactive) Dyes

<u>INTRODUCTION</u>	142
Photostability of fibres dyed with fibre-reactive dyes	143
<u>EXPERIMENTAL</u>	
Dyes	144
Substrate	145
Dyeing	145
Determination of lightfastness	145
Photodegradation	146
Measurement of tensile properties	146
Measurement of relative viscosity	146
<u>RESULTS AND DISCUSSION</u>	146
Mode of photodegradation of nylon 6 using MBTF lamp as the source of irradiation	146
Photostability of nylon 6 dyed with Procynyl (disperse reactive) dyes	147
Tensile properties	148
Relative viscosity	149
Tensile properties and relative viscosity	151
<u>CONCLUSIONS</u>	151
<u>SECTION 2. Effect of Hydroquinone on Light-Induced Degradation of Nylon 6 Dyed with Solubilised Vat Dyes.</u>	
<u>INTRODUCTION</u>	152
Mechanism of degradation of nylon in presence of certain vat dyes.	153
<u>EXPERIMENTAL</u>	154
Dyes	154
Substrate	155
Dyeing	155
Aftertreatment	155

Ultraviolet absorption spectra of hydroquinone in nylon 6 film	156
Determination of amount of hydroquinone absorbed by nylon 6 yarn	156
Determination of lightfastness	156
Photodegradation	157
Measurement of tensile properties	157
Measurement of relative viscosity	157
<u>RESULTS AND DISCUSSION</u>	157
Hydroquinone as an aftertreatment agent	157
Mode of photodegradation of nylon using MBTF lamp as the source of irradiation	158
Photostability of nylon 6 dyed with vat dyes and of that dyed and aftertreated with hydroquinone	158
Tensile properties	159
Relative viscosity	161
Tensile properties and relative viscosity	162
Mode of action of hydroquinone	163
<u>CONCLUSIONS</u>	165
<u>SECTION 3(i)</u> <u>The Effect of Light on Chlorinated Polypropylene Dyed with Cationic Dyes</u>	
<u>INTRODUCTION</u>	166
<u>EXPERIMENTAL</u>	167
Dyes	167
Substrate	169
Dyeing	169
Photodegradation	169
Measurement of tensile properties	169

<u>RESULTS AND DISCUSSION</u>	170
-------------------------------	-----

Photostability of chlorinated polypropylene dyed with cationic dyes	170
--	-----

<u>CONCLUSIONS</u>	172
--------------------	-----

<u>SECTION 3(ii)</u>	<u>The Effect of Light on Brominated Polypropylene Dyed with Cationic Dyes</u>
----------------------	--

<u>INTRODUCTION</u>	173
---------------------	-----

<u>EXPERIMENTAL</u>	174
---------------------	-----

<u>RESULTS AND DISCUSSION</u>	174
-------------------------------	-----

Photostability of brominated polypropylene dyed with cationic dyes	174
---	-----

<u>CONCLUSIONS</u>	176
--------------------	-----

REFERENCES

TABLES	1 to 40
--------	---------

FIGURES	1 to 105
---------	----------