Effects of Plasma Treatment and Metal-Ion Chelation on Lightfastness of Dyed Polyester/Cotton Fabric

C. J. JAHAGIRDAR, YASMIN SRIVASTAVA

Applied Physics Division, Department of Chemical Technology, University of Mumbai, Matunga, Mumbai, 400 019, India

Received 3 June 2000; accepted 21 August 2000

ABSTRACT: Polyester/cotton blend fabric was dyed with Chemistron dye—a mixture of reactive/disperse dyes. Dyed fabrics were subjected to radiofrequency (RF) plasma treatment of different duration and were subsequently treated with metal salts. The effect of surface modification by plasma and dye–metal complex on colorfastness to light is discussed. Evaluation of the improvement in lightfastness was made using the CIE system of color measurement with a standard illuminant D65 and 10° standard observer. The color parameters and color deviations were obtained by Data flash–100 color measurement spectrophotometer with chroma QC 3.0 color quality control software. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 292–299, 2001

Key words: lightfastness; color deviation; plasma; chelation; metal–salt

INTRODUCTION

The action of light on dyes and textile materials involves a complex series of processes. Although much work has been done on the light induced fading of dyes, photodegradation of synthetic dyes continues to be a commercially important problem and the subject of considerable research. The success of the next generation of lightfast dyes will depend on the development of colorants that take into account the results of photofading mechanisms.

Improvements in the properties of dyeing, by chelate formation with metal ions, are as old as dyeing itself. The most common metal is chromium,[1] followed by copper, cobalt, nickel. In application, the metal and dyes may be applied separately with dye–metal bonding taking place within the textile (mordant dyeing) or the dye–metal bonding may be carried out by the manufacturer, the resulting metal–complex dyes then being regarded as acid dyes. Improvements in fastness to light were claimed for direct dyes after treatment with salts of nickel, zinc, and especially copper.[2] Treatment with metal salts apparently produces chelates[3] with improved lightfastness.

Plasma treatment has been employed to modify surface of textile substrates and to improve the textile properties. Wakida et al.[4] treated several natural and regenerated cellulose fibers with low-temperature plasma. The relative free radical intensity of the plasma-treated fibers was measured by electron-spin resonance (ESR) spectroscopy. Ohta et al.[5] showed that dyed fabrics can be plasma treated without color change. In dyeing polyester fibers, colorfastness was improved by drying the dyed fabric without washing the fibers with a reducing agent, and then treating the fibers with low-temperature plasma of a gaseous oxidizing or reducing agent. This gave the colored fabric excellent fastness to washing and fading.[6]

A U.S. patent on increasing the color density and improving colorfastness of dyed fabrics has

Correspondence to: C. J. Jahagirdar (cjjahagirdar@hotmail.com).

Contract grant sponsor: All India Council for Technical Education (AICTE), New Delhi.

Journal of Applied Polymer Science, Vol. 82, 292–299 (2001)

been reported,[7] where a dyed fabric was treated in an amino-modified organopolysiloxane and then exposed to low-temperature plasma. Earlier work in this laboratory has been carried out for imparting soil resistance by plasma treatment.[8]

The action of plasma is confined only to the surface regions without penetrating the bulk[9,10]; hence in the present investigation, an attempt was made to study the effect of plasma modification and chelation of dye with metal ions on the lightfastness.

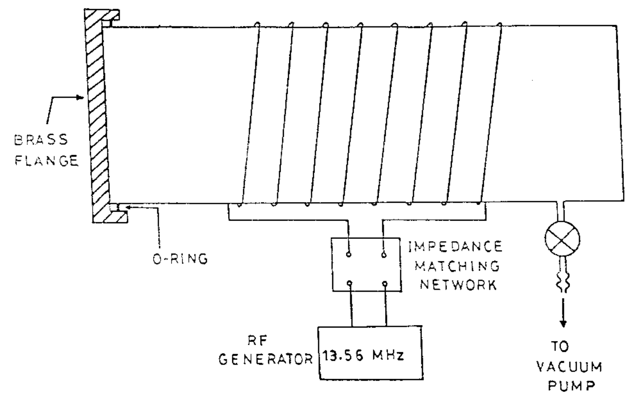

Figure 1 Experimental setup for plasma treatment.

MATERIALS

Bleached mercerized polyester/cotton shirting with a blend composition of 67% polyester and 33% cotton was supplied by Morarjee Gokuldas Spinning and Weaving Mills, Mumbai. Chemistron Brilliant blue 4R dye, a mixture of neutral dyeable reactive dye and a disperse component, which gives good brilliancy and color depth without acidic pH, were supplied by Chemiequip Limited, Mumbai, India. Forosol Brill Red PC dye was supplied by Clariant Ltd. (Mumbai, India), a mixture of disperse and direct dye for one-bath, one-stage dyeing of polyester/cotton blends. Nickel (II) sulfate hexahydrate ($NiSO_4$-$6H_2O$) and cobalt (II) sulfate heptahydrate ($CoSO_4$-$7H_2O$) were supplied by Thomas Baker (Chemicals) Limited., Mumbai, India.

EXPERIMENTAL

Single-Bath Dyeing of Polyester/Cotton Blend With Chemistron Dye

The sample (polyester/cotton blend) was entered in a dye bath (material to liquor ratio 1:50) containing dye for a 2% shade. We added 30 g/L Na_2SO_4 and then started raising the temperature from 40–50°C to 80°C, dye at 80°C for 10 min and then raised the temperature to 130°C and dyed at 130°C for about 30 min. The dye bath was cooled to 80°C and the liquor discharged, followed by neutral soaping and washing.

Single Bath Dyeing of Polyester/Cotton Blend With Forosol Dye

The dyeing method was the same as that described above, except that Na_2SO_4 was 10 g/L, and dyeing pH was kept at 4.5–5 throughout the dyeing process. Sandacid PBI was used for this purpose.

Metal–Salt Treatment

Metal complexes were formed on all dyed fabrics by aftertreating the dyed substrates with solutions of nickel (II) and cobalt (II) sulfates under slightly alkaline conditions for 30 min at 100°C. These samples were then dried and measured for their fastness using the CIE system of color measurement.

Plasma Treatment

A Pyrex glass tube of 4.5-cm internal diameter and 32.5-cm length was designed for treatment. One end of the tube was sealed, while the other end was closed with a removable brass flange. Neoprene rubber O-rings were used inside the flanges to provide a vacuum seal. Radiofrequency (RF) power was applied through a 13.56-MHz RF generator (1.5-kW capacity) supplied by Universal R.F. Equipment (Mumbai, India). The generator was inductively coupled to the plasma tube through an impedance matching network. The experimental arrangement is shown in Figure 1.

A fabric sample of about 0.5 g was kept in the center (perpendicular to the electrode) of the plasma tube. The tube was then closed and evacuated down to 0.1 Torr with a rotary vacuum pump. Evacuation was carried out for another 10 min. The RF supply was then switched on and the plate current increased until glow discharge was initiated. The glow discharge was maintained at the required plate current. The treatment was carried out for the required durations, after which it was switched off and the sample was allowed to

Table I Fading (ΔE) of Metal–Salt-Treated and -Untreated Chemistron-Dyed Polyester/Cotton Blend

	Fading (ΔE)			
Sample	8 h	16 h	24 h	32 h
A	5.26	7.55	9.43	10.22
B	1.87	3.14	4.16	5.28
C	1.56	2.36	3.98	4.47

be in vacuum for another 10 min; the vacuum pump was then turned off, the tube was purged with air, and the sample was removed for study.

Electron Spin Resonance Measurement

Electron spin resonance (ESR) experiments were carried out on a Varian E-112 E-line century series ESR spectrometer, which uses 100-kHz field modulation. Tetracyanoethylene (TCNE; $g = 2.00277$) was used as a standard for g-factor measurements. The scan range has been selected to record only the lines in the vicinity of free-electron resonance.

Measurement of Color Parameters and Color Deviation

Color parameters for untreated and treated dyed fabrics were taken over the visible range of 400–700 nm, using a Dataflash-100 Color measurement spectrophotometer[11] supplied by Data Color International. Untreated and treated samples were kept in Fade-o-meter (Suntest CPS). Color deviations were measured for the interval of 8 h using AATCC gray scale color change.

Table III Lightfastness Rating of Metal–Salt-Treated and -Untreated Chemistron-Dyed Polyester/Cotton Blend

Sample	Lightfastness
A	2–3
B	4
C	4
D	4–5

A, 2% dyed, untreated; B, 2% dyed, $NiSO_4$ treated; C, 2% dyed, $CoSO_4$ treated; D, 2% dyed, plasma treated for different times, treated with $NiSO_4$.

RESULTS AND DISCUSSION

Tables I and II show the fading behavior of untreated and treated fabrics. It is clear from Table I that treatment with metal salt alone, without any prior treatment with plasma, drastically reduces the fading as compared to untreated dyed fabric. This finding indicates that the metal complex formation strengthens the bond between the dye and the reactive sites on fibers, thereby improving the fastness to the rating of 4 (with color deviation $\Delta E \approx 1.87$), as compared with 2–3 (with color deviation $\Delta E \approx 5.26$) for untreated fabric (Table III).

Surface modification brought about by plasma plays a vital role in improving the lightfastness. Dyed fabrics were exposed to RF plasma treatment, for various durations of ≤ 25 min, and were then subsequently treated with solutions of metal sulfates. Dyed fabrics, subjected to plasma treatment before treating with metal–salt, demonstrated further enhancement in fastness to the rating 4–5 ($\Delta E \approx 1$) (Tables II, III). This enhancement in fastness can be attributed to plasma

Table II Fading (ΔE) of Chemistron-Dyed Polyester Cotton Blend, Plasma Treated for Various Durations and Then Treated with $NiSO_4$

	Plasma	Fading (ΔE)			
Sample	Exp. Time (min)	8 h	16 h	24 h	32 h
D	0.5	1.27	2.00	2.80	3.80
	1	1.20	1.83	2.67	3.50
	2	1.17	1.62	2.42	3.53
	5	1.11	1.50	2.41	3.25
	10	0.97	1.66	2.12	3.15
	25	1.01	1.50	2.08	3.01

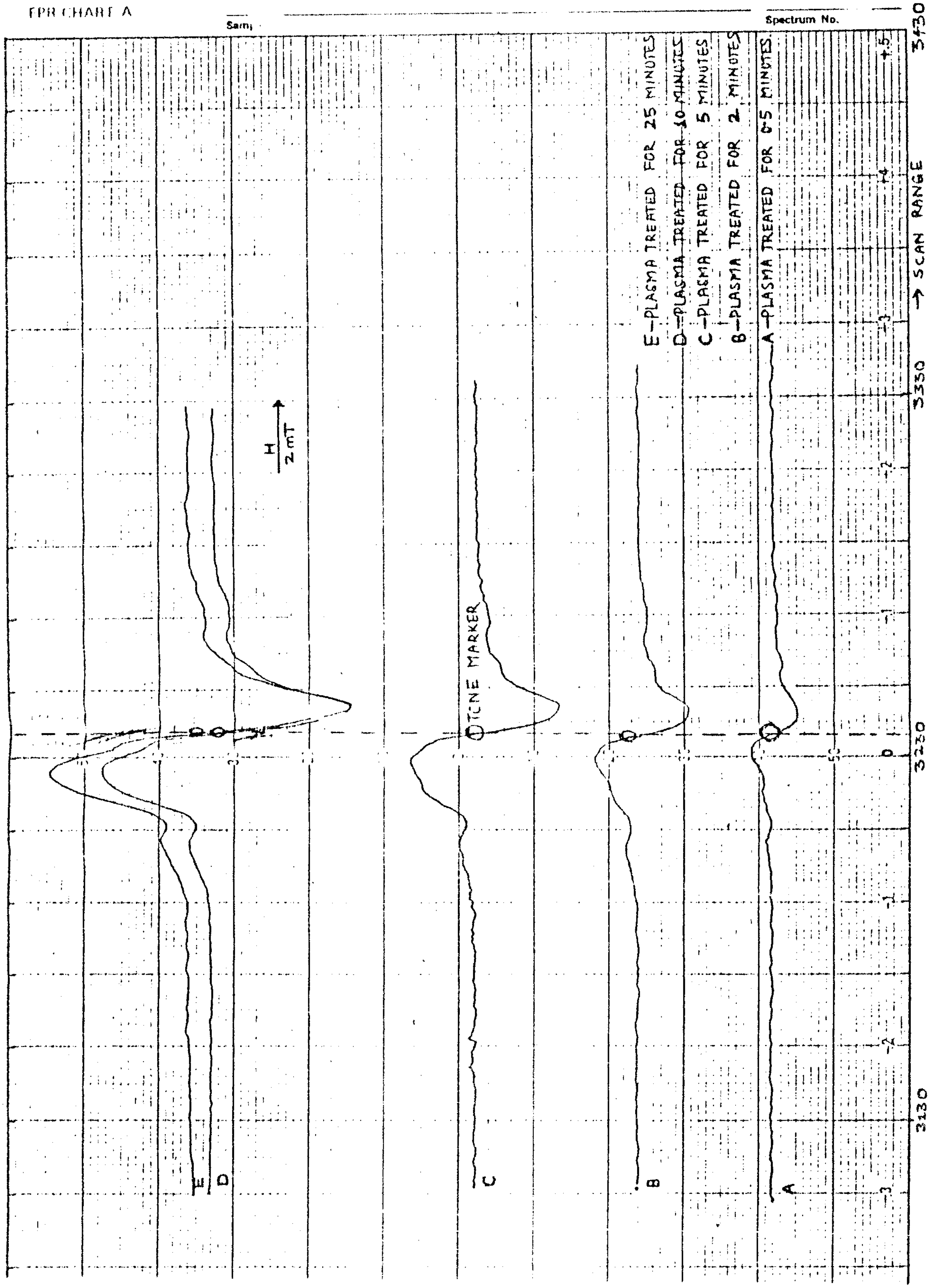

Figure 2 ESR spectra of Chemistron-dyed polyester/cotton blend plasma-treated for various durations.

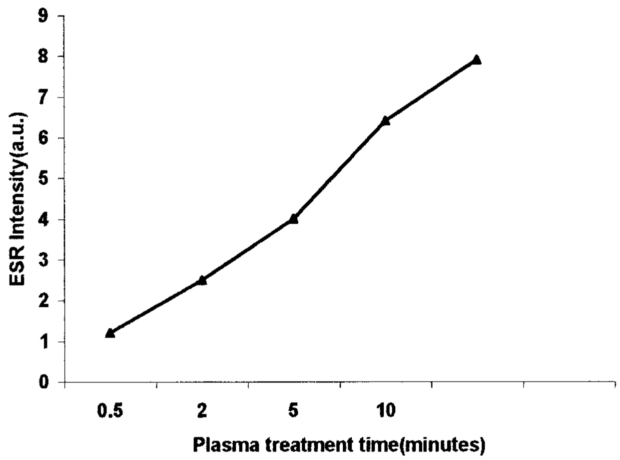

Figure 3 ESR intensity vs plasma treatment time (Chemistron dyed).

Table V Mechanical Properties of Plasma-Treated 2% Dyed Polyester/Cotton Blend

Sample	Plasma Treatment Time (min)	Load at Break (g)	Tensile Strength Retained (%)	Elongation at Break (%)
A	Control	310	100	33.2
	0.5	305	98.3	32.5
	1.0	302	97.5	30.4
	2.0	295	95.1	30.3
	5.0	285	91.9	28.7
	10.0	280	90.3	27.5
B	25.0	260	83.8	25.8
C	—	330	106.4	30.0

A, untreated sample; B, 2% dyed and plasma treated for various durations; C, 2% dyed and treated with $NiSO_4$.

treatment, which improves the surface reactivity of the dyed fabric by creating more radical sites. These radical sites help in the formation of a better complex with metal ion, further improving the fastness. The presence of free radicals was substantiated by ESR measurements. The ESR spectra of plasma-treated samples (Fig. 2) show the formation of free radicals near the free electron resonance region. As the plasma treatment time increases, the number of free radicals generated increases (Fig. 3). Table II demonstrates that as plasma exposure time increases, fading decreases, but long exposures of 25 min gave rise to etching, whereas small duration of plasma treatment (e.g., 1–2 min) gave significant improvement in lightfastness, retaining the original color, strength, and other textile properties of the fabrics, as shown in Tables IV and V. Hence, it was observed that a plasma exposure time of 1–2 min was the optimum time of treatment for improving the lightfastness without disturbing other textile properties.

In the present investigation, it was of interest to analyze whether the poor fastness of Chemistron dye (a mixture of disperse and reactive dyes) was caused by the degradation of disperse or the reactive component of the dye. From the results of Table VI, it is clear that 100% cotton dyed with the reactive component showed poor fastness (rating 2), whereas 100% polyester dyed from the disperse component showed comparatively good fastness (rating of 4). This finding indicates that the poor fastness of Chemistron dye is mainly due to photodegradation of the reactive component, and not the disperse. It is also observed from Table VI that metal salt treatment significantly improves the

Table IV Color Parameters of Plasma–Treated 2% Dyed Polyester/Cotton Blend

Sample	Plasma Treatment Time (min)	Color Parameters				
		*L**	*a**	*b**	*C*	*h*
A	Control	39.3	1.6	−27.7	27.8	273.3
B	0.5	39.5	1.5	−27.7	27.8	273.2
	1.0	40.0	1.5	−27.7	27.7	273.2
	2.0	40.1	1.0	−27.1	27.1	272.2
	5.0	40.5	0.8	−26.6	26.6	271.8
	10.0	41.4	0.5	−25.1	25.1	271.2
	25.0	41.7	0.1	−23.6	23.6	270.3

A, 2% dyed, untreated sample; B, 2% dyed, plasma treated for various durations.

Table VI Light and Washfastness Rating of Dyed Cotton, Polyester, and Polyester/Cotton Blend

Sample	Lightfastness
Cotton	
Untreated	2
$NiSO_4$ treated	3
Polyester	
Untreated	4
$NiSO_4$ treated	4
Polyester/cotton	
Untreated	2–3
$NiSO_4$ treated	4

lightfastness of dyed 100% cotton (to a rating of 3, as compared with 2 for untreated), whereas the lightfastness of dyed 100% polyester remains unchanged with treatment with metal salt (i.e., 4). The significant improvement in fastness of dyed 100% cotton is mainly attributable to the formation of metal complex with the dye molecule and the reactive sites on the fibers. It can be concluded that only the reactive dye molecules participate in the formation of complex with the metal ion, whereas the disperse component, which is more stable to light, remains inert to the metal salt treatment and does not participate in the formation of the complex with metal ion. Also to check the generality of the treatment with other dyes, the above method of metal–salt and plasma treatment was given to Forosol-dyed polyester/cotton blend for improved lightfastness.

As shown in Table VII, metal–salt treatment alone, without any prior plasma treatment, does not show any improvement in lightfastness of Forosol-dyed polyester/cotton blend. This observation can be attributed to the fact that Forosol dye, being a mixture of direct and disperse dye, has no reactive functional groups available for the formation of complex with metal ions, hence no improvement in fastness. Dyed samples subjected to plasma treatment before treating with metal salt showed improved lightfastness to the rating of 4—5 ($\Delta E \approx 1.07$), as compared with untreated, with a rating of 4 ($\Delta E \approx 2.25$), as shown in Tables VIII and IX.

This result clearly indicates that plasma treatment of the dyed substrate gives rise to the formation of radical sites, substantiated by ESR (Figs. 4, 5). These radical sites help in the formation of a complex with metal ion, thereby improving the lightfastness.

Thus, the plasma technique is a very efficient process, with the following advantages: (1) it has a short duration of treatment; (2) it is a dry-state process, hence no effluent disposal problem; (3) only surface properties can be changed without significantly altering bulk properties; and (4) it is environment friendly. Large-scale feasibility of the process was not studied. The present experiments were carried out only on the laboratory scale.

The authors are thankful to Chemiequip Ltd., Clariant (India) Ltd. for supplying us with Chemistron and Forosol dyes, respectively, and to Morarji Gokuldas Spinning and Weaving Co. for supplying us with and poly-

Table VII Fading (ΔE) of Metal–Salt-Treated and -Untreated Forosol-Dyed Polyester/Cotton Blend

	Fading (ΔE)			
Sample	8 h	16 h	24 h	32 h
A	2.2	2.6	2.8	4.3
B	2.3	2.8	3.0	4.2

Table VIII Fading (ΔE) of Forosol-Dyed Polyester Cotton Blend, Plasma Treated for Various Durations and Then Treated with $NiSO_4$

		Fading (ΔE)			
Sample	Plasma Exp. Time (min)	8 h	16 h	24 h	32 h
C	0.5	1.7	2.3	2.4	2.8
	2	1.6	2.1	2.4	2.6
	5	1.3	1.5	2.1	2.4
	10	1.0	1.3	1.9	2.0

Table IX Lightfastness Rating of Treated and Untreated Forosol-Dyed Polyester/Cotton Blend

Sample	Lightfastness
A	4
B	4
C	4–5

A, 2% dyed, untreated; B, 2% dyed, $NiSO_4$ treated; C, 2% dyed, plasma treated for different times, treated with $NiSO_4$.

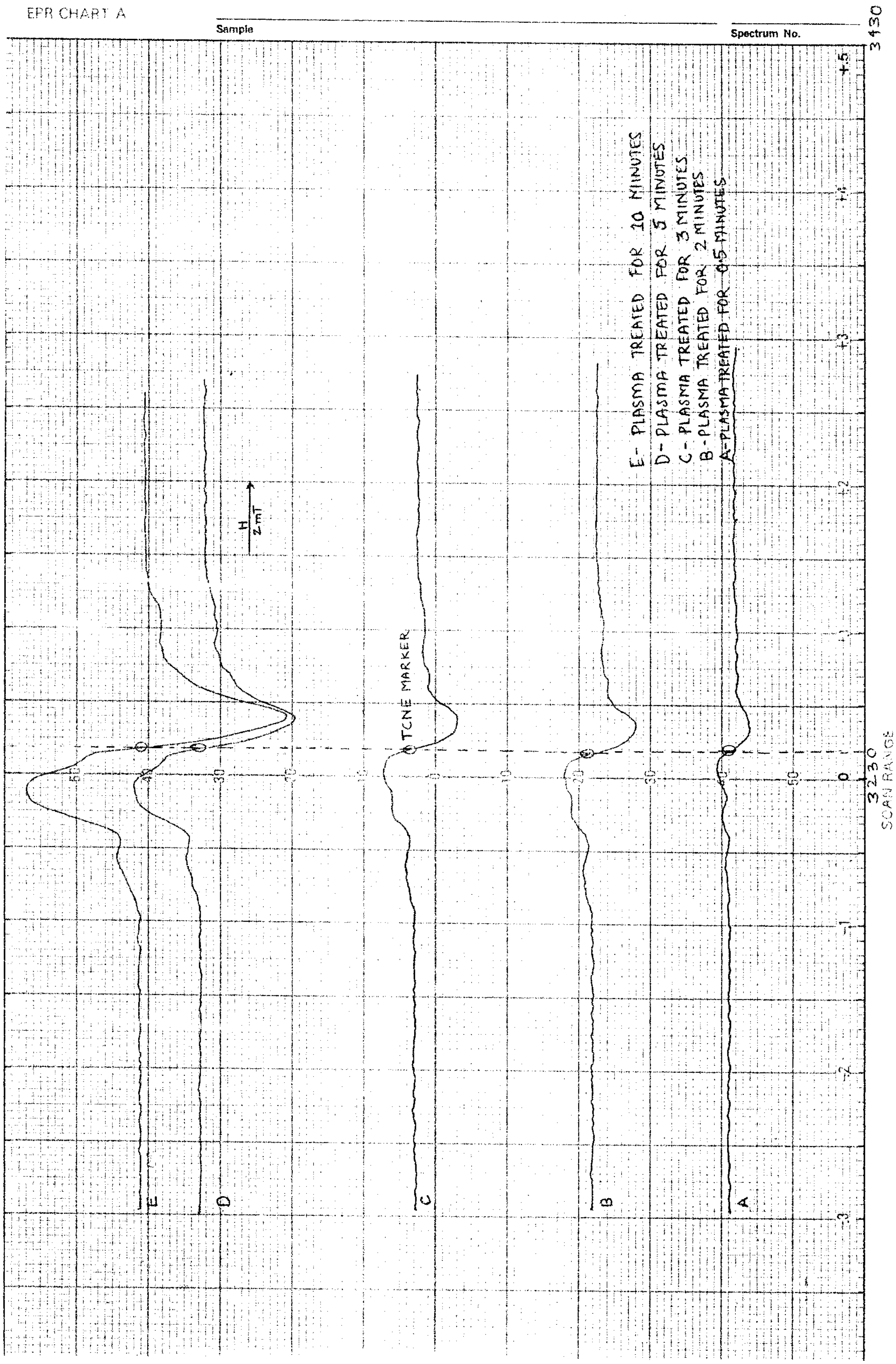

Figure 4 ESR spectra of Forosol-dyed polyester/cotton blend plasma treated for various durations.

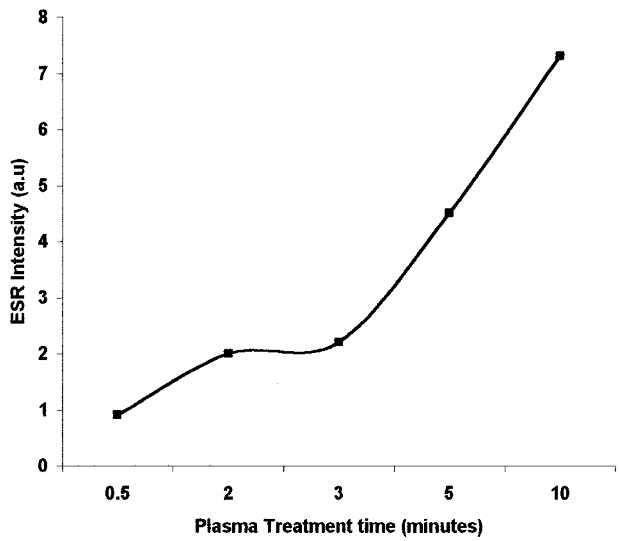

Figure 5 ESR intensity vs plasma treatment time (Forosol dyed).

ester/cotton blend fabric. We are also thankful to Dr. Gundurao, Principal Research Scientist, of R.S.I.C., I.I.T., Mumbai, India, for helpful discussions during the progress of this work.

REFERENCES

1. Johnson, A. The Theory of Coloration of Textiles, 2nd ed.; Society of Dyers and Colourists: Bradford, UK, 1989.
2. SCI, BP 531470 (1941); SCI, BP 532329 (1941); Diserens, Teintex 18, 683, 769 (1953); Wegmann, Teintex 17, 275 (1952).
3. Moustafa, M. M. JSDC 1995, 111, 349.
4. Wakida, T.; Takeda, K.; Tanaka, I.; Takagashi, T. Text Res J 1989, 59, 49.
5. Ohta, K. K.; Takahasi, K.; Sacki, M.; Kadota, K. J Text Mach Soc Jpn 1989, 42, 556.
6. Unitaka Ltd. Jap. Pat. 58, 115, 187, Vide C. A. 1984, 101, 8420.
7. Ueno, S.; Nomura, H.; Hashizume, S. Nishide, T. Shin-Etsu Chemical Co. Ltd., Tokyo; Emori and Co. Ltd., Nikka Chemical Ind. Co. Ltd.; USP 4, 619, 667 (28 Oct. 1986).
8. Jahagirdar, C. J.; Venkatakrishnan, S. J Appl Polym Sci 1990, 41, 117.
9. Ward, T. L.; Jung, H. Z.; Hinojosa, O; Benerito, R. R. Surf Sci 1978, 76, 257.
10. Ward, T. L.; Hinojosa, O.; Benerito, R. R. Polym Photochem 1982, 2, 109.
11. Jahagirdar, C. J.; Venkatakrishnan, S.; Srivastava, Y. J Text Assoc 1998, 59, 27.