PART: II

ECONOMICAL DYEING OF P/C BLENDS WITH MULTIFUNCTIONAL PROPERTY

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This paper deals with different energy conservation processes and multifunctional Auxiliaries. To meet the objectiveness, the dyeing of P/C blends is done by using high boiling swelling agent, as compared with conventional processes. Hence use of different swelling agents, results in the generation of COD and BOD low values, anti soiling etc. Finally results in economic process, which can dye both portion of blend in a single stage with disperse dye.

Key words: *Disperse dye, Economic process, P/C blend, Swelling agent.*

INTRODUCTION

Normal dyeing of P/C blends involves the elaborated process by using appropriated class of dyes for PET and Cotton portion. The proposed work aims to use Cyclodextrin (CD) and poly ethylene glycol(PEG) as a Pre-treatment to dye both polyester and cotton portion by only disperse dyes in the single stage process. Nevertheless, CD can cause some Multi functional property on the dyed fabric like hydrophilicity, anti soiling etc and the generation of COD and BOD also will be low compared with sodium alginate in the conventional process[31] And use of high boiling swelling agent like PEG is desirable in P/C dyeing to develop an economical process which can dye both the portions of the blend in a single stage with disperse dyes so that it can conserve time, energy, man power etc.[1,34] As on today commercially, the blends of P/C are successively dyed by two bath process using disperse dyes and cellulosic dyes respectively. Even though one bath processes have been tried using various combinations of cellulosic dyes along with disperse dyes, none of the processes were not successful and are not practical commercially.

The successful application of disperse dyes on P/C Blend with the help of PEG and CD bring out numerous advantages such as a) Dyeing of P/C Blend in a single stage Process by using Disperse dyes only b) Saving of water, energy, time (due to single stage process) c) Replacing of conventional surfactants and thickeners by CD. (It will give low BOD and COD Value than Conventional one) d) Enhancement of functional property of the P/C fabric by means of CD e)Minimizing of the effluent problem due to shortening processes, re-placing of more polluting surfactants etc. f) An Economical process etc.

Poly-ethylene Glycol (PEG) and Cyclodextrin (CD) can be effectively used to dye P/C blends using disperse dyes only. Which can alter the nature of polyester and cellulosic fibres contained in the P/C Blends and making it viable to dye cellulosic fibre with disperse dyes along with hydrophobic PET.

EXPERIMENTAL

Materials

Fabric: 67:33 Polyester: Cotton Knitted Sample.

Yarn: 67:33 and 50:50 Polyester: Cotton Blended Samples.

Dye stuff: Yellow C4G H/C
N.Blue 3G 200%
Scarlet BR

Special Auxiliaries:
ß-Cyclodextrin
Polyethylene glycol with m.w 400
BTCA
Sodium Hypophosphite
And all other chemicals are in laboratory reagent grade

Methods

Scouring and Bleaching

The samples were scoured and bleached by the Combined Process at 80 ºC for 45 min., with a solution containing 2 gpl Non-Ionic Detergent, 2 % Hydrogen Peroxide and 2 % sodium carbonate etc., washed with hot water, cold water, squeezed and air dried.

Chemical Treatments

Table - 1 : Various Chemical Treatments Prior to Dyeing

Methods	Treatment
U	Untreated
A	Samples Treated with PEG then steaming at 160°C for 2 min. Finally the samples were thoroughly washed with tap water and air dried.
B	Samples Treated with a mixture of PEG and Sodium hydroxide solution (95.5% / 4.5% w/w) to wet pick-up of 100 % expression then steaming at 160°C for 2 min. Finally the samples were thoroughly washed with tap water and air dried.
C	Samples Treated with a mixture of PEG and Sodium hydroxide solution (95.5%/4.5% w/w) to wet pick-up of 100 % expression then steaming at 160°C for 2 min then the samples were thoroughly washed with tap water and air dried; treated with CD in different concentration (10, 15, 20, 30,35gpl) along with BTCA-0.6%, Catalyst-SHPI-0.6% etc then Curing at 170°C for 2 min. Finally the samples were thoroughly washed with cold water and hot water, air dried.

With the influence of above chemicals treatment on dyeing property in Part-I, let us see the various surface modifications of substrate and their related property in this section.

RESULTS AND DISCUSSIONS

Surface Topography

The Surface of untreated and treated samples was studied using SEM analysis technique. Photo-micrographs corresponding to different investigated samples are depicted in the following figures.

The untreated sample has a smooth surface (Fig. 1). When these samples were treated with PEG and steam the surface

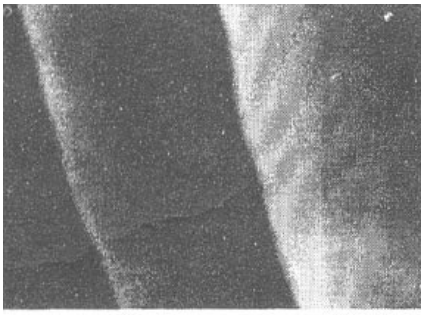


Fig. 1. SEM for the surfaces of untreated sample

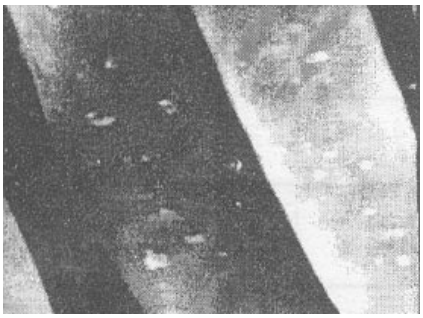


Fig. 2. SEM for the surfaces of Samples Treated with PEG then steaming.

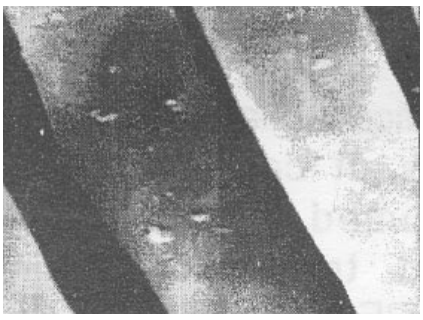


Fig. 3. SEM for the surface of Samples Treated with a mixture of PEG and Sodium hydroxide solution (95.5%/4.5% w/w) to wet pick-up of 100% expression then steaming.

becomes less coarse (Fig.1). On the other hand the surface of sample treated with sodium hydroxide and subjected to steam have changed very unevenly, the fabric becomes coarser with pits and pores as shown in (Fig. 3). After treatment

Fig. 4. SEM for the surface of Samples Treated with a mixture of PEG and Sodium hydroxide solution (95.5%/4.5% w/w) to wet pick-up of 100% expression then steaming at 160°C for 2 min; treated with CD then curing at 170°C for 2 min.

with the alkaline PEG, CD the surface of the sample becomes much coarser compared with other samples (Fig. 4). This indicates that sensitive presumably amorphous areas are susceptible to attack. The above mentioned surface observation is in full agreement with the results listed in table of Colour strength analysis.

Fastness Properties

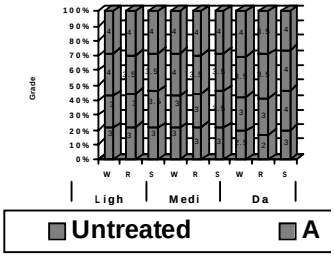
Fastness properties of treated and untreated samples are shown in Table - 2. It is clear that the present treatments improve the sublimation fastness property with high level rather than light and washing fastness since the water loving groups like hydroxyl, Carboxyl group etc will enhance the sublimation fastness property in the dyed material. Nevertheless, the fastness property of the given dyed material is mainly depend upon the percent blend proportion that means the given treatment produce good fastness property if the PET portion is more. The washing and Rubbing fastness get minimized if the depth of shade gets increased.

Table - 2 : Fastness Properties of Treated and Untreated Samples Dyed with Disperse dyes

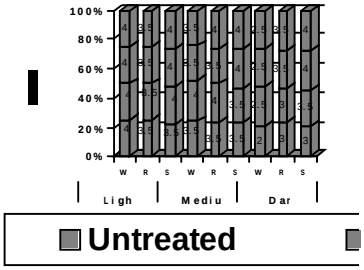
S*	Fastness Grades For																	
	67:33 Blends									50:50 Blends								
	Light			Medium			Dark			Light			Medium			Dark		
	W	R	S	W	R	S	W	R	S	W	R	S	W	R	S	W	R	S
U	3	3	3	3	3	3	3/2	2	3	4	4/3	4/3	4/3	4/3	4/3	2	3	3
A	3	3	4/3	3	3	4/3	3	3	4	4	4/3	4	4	4	4/3	3/2	3	4/3
B	4	4/3	4/3	4	4/3	4/3	4/3	4/3	4	4	4/3	4	4/3	4/3	4	3/2	4/3	4
C	4	4	4	4	4	4	4	4/3	4	4	4/3	4	4/3	4/3	4	3/2	4/3	4

*Samples (U-Untreated; A, B and C Treated)

Where, W- Wash fastness; R-Rubbing fastness; S-Sublimation fastness; U-Untreated sample



Graph 1. Fastness Grade for 67:33 P/C Blends



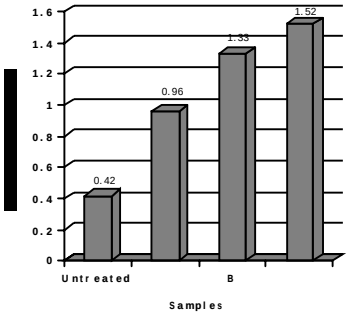
Graph 2. Fastness Grade for 50:50 P/C Blends

Moisture Regain

The moisture regain of treated and untreated samples was determined. It was found that treatments under investigation are accompanied by an increase in the moisture regain. The most pronounced effect is obtained in case of treatment C and D.This could be due to the outstanding increase in carboxylic contents and hydroxyl groups after such treatment and out of which sample D has more moisture regain than others due to carboxylic content and free hydroxyl group present in the CD Structure.

Table - 3 : Moisture Regain of Treated and Un-treated sample

Samples	Moisture Regain (%)
Untreated	**0.42**
A	0.96
B	1.33
C	1.52



Graph 3. Moisture Regain of Treated and Un-treated sample

X-Ray Investigation

The X-Ray diffraction patterns for treated and untreated samples are shown in Fig. 5.

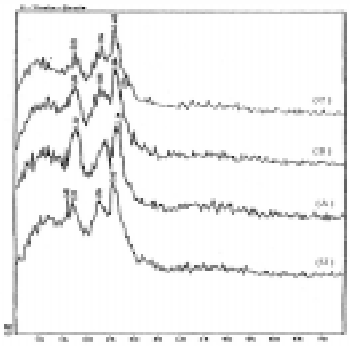
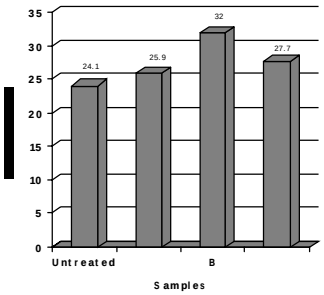


Fig. 5. X-ray Diffraction Patterns.

It is seen that all patterns have the same three peaks at 20 of 17.8°, 23.2° and 26.5° respectively. These three peaks correspond to the 010,110,100 spacing. This indicates that all such samples have the same triclinic unit cell with interplaner spacing, very close to that previously reported@.[36]

Table - 4 : D Spacing and Crystallinity of treated and untreated samples.

Samples	D-spacing			Crystallinity
	010	110	100	(%)
Untreated	5.11	3.989	3.52	24.1
A	5.257	-	3.39	25.9
B	5.10	3.93	3.54	32
C	5.133	3.9	3.50	27.7



Graph 5. D-spacing and Crystallinity of treated and untreated samples

Table - 4 indicates the measured interplaner spacing for all the samples, where minor changes in these values were observed. These values fluctuate depending on the type of treatment. It was found that the untreated sample contains 24.1% crystalline area. The treated samples with PEG with alkaline solution and CD contain 25.9 and 27.7 % respectively, crystalline area. So, structurally, i.e., in terms of the total crystalline area, there is no much significant change. Thus, it can be assumed that, upon treatment with PEG and with its alkaline solution before CD treatment, the overall crystalline areas remain the same. It seems that the treatment with treatment with PEG and sodium hyadroxide increases the degree of crystallinity; a point that contradicts with dyeing properties and MR of modified samples. As the crystallinity increases, the dye uptake also increases. Such contradiction would not happen if we consider the crystallite size. Increase of the colour strength with increasing the crystallinity confirms that a change in the crystallite size has occurred under the present treatment condition[13]. Correspond-ingly the amorphous regions accessible to the dye molecules increases due to the decrease of crystallite parts.

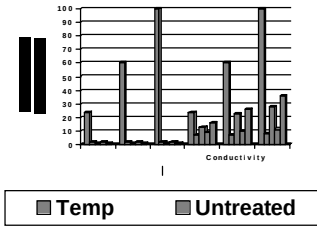
Electrical Properties

The electrical resistance R(w) and a.c.conductivity sa.c(w cm) power-1 for all the samples were measured in temperature 24-100°C and at one frequency (20 K Hz) . Variation of the R and sa.c values with change in the type of treatment is given in Table - 5.

Table - 5. Electrical resistance R (w) and a.c Conductivity s a.c (w cm) power-1 of the treated and untreated samples.

Property**	Temp.	Untreated	A	B	C
Rx10 ^{8}	24	1.7	0.9	1.8	0.8
w	60	1.7	0.6	1.6	0.6
	100	1.6	0.4	1.3	0.4
S a.cx10 $^{-10}$	24	7.2	13	9	16
(W cm) $^{-1}$	60	7	23	9.4	26
	100	7.7	28	11.2	36

** Measuring was carried out at one frequency (20 KHz)



Graph 6. Electrical resistance R (w) and a.c Conductivity s a.c (w cm) power-1 of the treated and untreated samples.

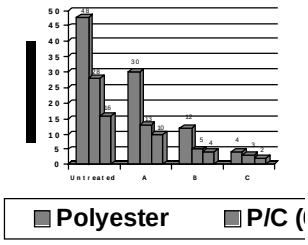
Based on the obtained data, one could conclude the following: a) a slight decrease in R and a little increase in s a.c values takes place after treatment with NaOH solution in spite of the significant increase in moisture regain of the sample b) Changes in the values of both R and s a.c are more pronounced in the case of sample C.Such treatments significantly decrease R (2-4 times) and markedly increases s a.c (2-5 times) values, as compared with those for untreated samples, and illustrates the positive effect of treatments with PEG on the electrical properties of Sample. This result postulates the amount of MR increasing after treatment with PEG and CD through resistance and conductivity changes phenomenon.

Wettability

Wettability of sample was measured by noting the time of sinking for a 5x5 cm piece under constant weight in distilled water[21]. The Table-6 shows the different wetting time for different type of treatments. Here, the water absorbing groups like carboxylic, hydroxyl etc increase the wettability of the samples rather than untreated one. Both PEG and CD having hydroxyl groups in their structure and these groups cause more hydro-philicity. However, the wettability and hydro-philicity is also depends on the percent proportion of cotton portion. Generally, the water absorbing groups increases the wettability of the material, it was known by comparing the different sinking time for the different treated samples. If the sinking time is low the wettability will be more and so on.

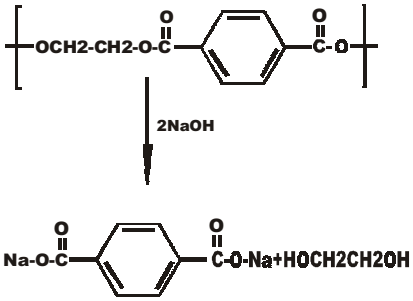
Table - 6 : Wettability of treated and untreated samples

Samples	Wetting Time(Sec)		
	Polyester	P/C	
		67:33	50:50
Untreated	48	28	16
A	30	13	10
B	12	5	4
C	4	3	2



Graph 7. Wettability of treated and untreated samples

The effect of caustic treatment on both PET and cotton is positive in nature with respect to wettability. The reaction of caustic on PET is takes in place in the following manner according to specific time, temperature, concentration etc.



Sodium Terephthalate Ethylene Glycol32

Fig. 6. Effect of Caustic on Polyester

Soil Release Testing

The polyester fabrics show a higher extent of soiling than P/C samples. However, in both cases alkali treatment and PEG treatment leads to improvement in soil removal characteristics. When the sample is treated with PEG and NaOH, dried and baked, some ester interchange between teraphthalate sodium polyglycol oxide takes place and hydrophilic grafts-COO (CH2CH2O) n H-are formed on the fibre. The treatment shows an improvement in soil release and re-deposition properties as well as a drop in static charges even after treating with CD27,18. And When CD bound chemically with fibres, it provides enhanced hydrophilicity, it performs easy removal of sweat and sweat degradation Products from the textiles, since the CD will not allow the degraded compounds in to the core of the fibre[16]. However, the soiling also depends on static charge generation property and the percent proportion of hydrophilic fibre present in the blended fabric.

Table - 7 : Soil Release Property of treated and untreated samples

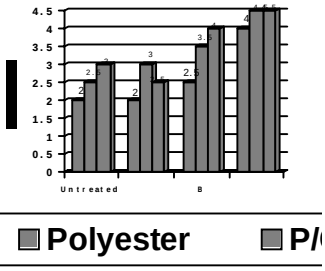
Samples	Soil Removal (Grade)		
	Polyester	P/C	
		67:33	50:50
Untreated	C	B	B
A	B	A-B	B
B	A-B	A	A-B
C	A	A	A

Pilling Tendency

Synthetic fibres are easily brought to surface of the fabric than cellulosics, because of their smooth surface and circular cross-section. Due to their higher mechanical strength and abrasion resistance, the pills remain for a longer time[21]. The Pilling tendency depends on the type of fibre in the fabric (Appendix 3). The treatment with the caustic soda solution weakens the polyester fibres resulting reduction in the pilling tendency.

In the caustic treatment, the polyester is hydrolyzed to produce water soluble sodium terephthalate and ethylene glycol (Fig. 6) resulting decrease in tenacity will takes place and it produce low pilling tendency formation.

Although, pilling may be de-aggravated by reducing electrostatic pick up of tint, dirt, or other foreign matter due to making the fibre as more moisture regain and hydrophilicity.



Graph 8. Pilling Grade of treated and untreated samples

CONCLUSION AND SUGGESTIONS

Disperse dyes do not posses any affinity for the cotton component of the P/C Blend when applied using conventional dyeing techniques. Further, tone-in-tone effect on such blends can not be achieved by using only one dye in a single dye bath application. This can be readily done by treating with PEG, NaOH, and CD etc. Nevertheless; CD improves the other functional properties like Soil release, hydrophlicity, Crease recovery also (since the BTCA is used in CD Treatment, Which is non-formaldehyde cross linking agent). These compounds improves the dye ability of disperse dyes on P/C Blended fabric. The fastness properties are also slightly improved due to the presence of PEG and CD.

Table - 8 : Pilling Grade of treated and untreated samples

Samples	Pilling Grade		
	Polyester	P/C	
		67:33	50:50
Untreated	2	3-2	3
A	2	3	3-2
B	2-3	4-3	4
C	4	5-4	5-4

The successful application of disperse dyes on P/C Blend with the help of PEG & CD bring out numerous advantages such as,

- Dyeing of P/C in a single stage process by using Disperse dyes only
- Saving of water, energy, time (due to single stage process)
- Replacing of conventional surfactants & thickeners by CD (It will give low BOD & COD Value than conventional one)
- Enhancement of functional property of the P/C fabric by means of CD
- Minimizing of the effluent problem due to shortening processes, re-placing of Surfactants etc
- Which is an Economical process since it saves time, cost etc CYCLODEXTRIN might play a significant role in the dyeing of P/C blends and might be used
  - Substitute for conventional Surfactants in P/C processing;
  - When bound chemically with fibres, it provides enhanced hydrophilicity
  - It perform easy removal of sweat and sweat degradation Products from the textiles

Appendix 1

Composition of Artificial soil[18]

Ingredients	Amount %
Peat moss	38
Cement	17
Kaolin clay	17
Silica	17
Carbon Black	1.75
Red iron-oxide pigment	0.5
Mineral oil	8.75

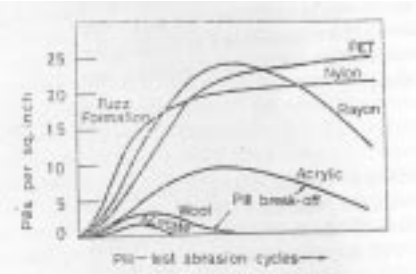
Appendix 2

	Pilling Grades*	
Rating	Description	Points have been considered
5	No Change	No visual change
4	Slight Change	Slight surface fuzzing
3	Moderate Change	Isolated fully formed pills
2	Significant Change	Distinct fuzzing
1	Sever Change	Dense fuzzing

* (Physical Testing of Textile by B.P.Saville, published by Textile Institute, 2000, pp 191

Appendix 3

Typical pill curves for common textile fibres[18]



REFERENCES

1 Agarwal.B.J and Patel B.H & Vaidya.A.A., May-June (2002)., Studies on single - bath application of dyes on polyester/Cotton Blends,, *The Textile Industry & Trade Journal,* pp.77.

2 Billmeyer Jr., F.W., and Ssltman,M., (1981)., *Principles of Colour Technology 2nd edition* : John Wiley & sons: New York; pp.140.

3 Blaeser., Hoechst-Colanese-Corp., *E.J.U.S. Patent* 4975233).

4 Bojana voncina and Alenka Majcen le Marechal, Proceedings of the Textile Institute 83rd World conference May 23-27, 2004., *ß-CD in medical & Hygienic Textiles.*

5 Booth., J.E., Principle of Textile Testing, pp.332., *CBS Publishers,* New Delhi.

6 Bureau of Indian Standards., (2001)., Handbook of Textile Testing, Part 4 Identification and Testing of Dyestuffs and Their Colour Fastness on Textile Materials(First Revision), Published by Bureau of Indian Standards, New Delhi 110002 (July 2002), (Washing: IS: 687-1979 pp.137-138), (Rubbing: IS: 766 - 1988 pp. 193-194), (Sublimation: IS: 975-1988 pp.203-204).

7 Datye, K.V., *Colurage.,* 24 (4) (1977), pp. 27.

8 Datye, K.V., Pitkar, S.C. and Rjendiran, R., *Indian J.Tech.,* pp. 5 (1966), 101;8 (19700,6).

9 Datye, K.V., Pitkar, S.C and Rjendiran, R., *Indian J.Tech.,* pp. 4 (1966),101;8 (19700,6).

10 Daul, G; Reinhyardt, R.K and Reid, J.D., (1953).,*Textile Research Journal,* pp. 23,719

11 Daul, G; Reinhyardt, R.K and Reid, J.D., (1953)., *Textile Research Journal,* 23,719

12 Han, L., Wakiada,T and Takagishi, T., (1987). *Textile Research Journal,* 57, (9), 519

13 Han. L., Wakiada, T. and Takagishi., T., (1987) *Textile Research Journal*, pp. 57, 519.

14 Hebeish, A., Shalaby, S.E. and Bayazeed,A.M., (1981) Journal of Applied Polymer Science 22, 1359(1978) & Hebeish, A., Shalaby, S.E., and Bayazeed, A.M., *Journal of Applied Polymer Science,* 26,3253.

15 Jozsef Szejtli, (2003) Cyclodextrins in the Textile Industry,, CYCLOLAB Research and Development Laboratory Ltd., Budapest, Hungary. ©2003 WILEY-VCH VERLAG GmbH & Co.KGaA,Weinheim., Starch/Starke 55 pp.191-196.

16 Jozsef Szejtli., (2003) Cyclodextrins in the Textile Industry, Starch/Starke 55(2003) pp 191-196, , CYCLOLAB Research and Development Laboratory Ltd., Budapest, Hungary. ©2003 WILEY-VCH VERLAG GmbH & Co.KGaA, Weinheim.

17 Kartaschoff, V, *Helv. Chem. Acta,* pp. 8 (1925), 928.

18 Keshav V. Datye and Vaidya., (1984) - "Chemical processing of synthetic fibres and blends", pp. 183-190.

19 Knittel. D., Buschmann H.J., Schollmeyer E. (1992): Taylor-made properties, B+W/B+M (Bekleieidung + Textile), pp. 12, 34-40).

20 Krichevskii, G.E., (1984) Textile Technology 37, (4),168 (1984) vide, Chemical abstract, 101, 112302

21 Kulrajani., M.L Polyester Textiles,. (1980) - Finishing of polyester and polyester blend fabric by Achwal., W.B., pp 264, Published by Textile Association, India

22 McGregor, R., and Peters., R.H., *JSDC*, pp. 81 (1965), 393; 429.

23 Myung. Hak. Lee, Kee Jong, Sohk-Won Ko (2000) Grafting onto Cotton fibre with Acrylamidomethylated beta cyclodextrin and its application, *Journal of Applied Polymer Science*, Vol. 78, pp. 1986-1991.

24 Savarino, P., Viscardi, G., Quagliotto. P, Montoneri, E., Barni. E, (1990): Reactivity and effects of CD in textile dyeing ; *Dyes Pigm.,* 42(2), pp. 143-147.

25 Schnider, E.F., ADR, 52 (1963), 370.

26 Shalimova, G ., Shulepova, O.I., Krutovskaya, I. V and Goncharaova, K.M., (1980) U.S.S.R Pat. 763500, Sept. 30 (1980); *Chemical abstract,* pp. 84, 32112,

27 Sheard , D. R., (1966), *Rev. Textile Progress,* 17466.

28 Shenai.V.A and Nayak, N.K., Textile Dyer and Printer, 14(23), 25 (1981), & Gawish, S.M; Ambroise, G., *American Dyestuff Reporter,* 80 (4), 22 (1991)

29 Shukla, S.R., HEDA, O.O. and Sligram, A.N., (1992)., *American Dyestuff Reporter,* pp. 81 (3), 37.

30 Sibusawa, T., (1994) Effect of dispersants on the sorption isothems of non-ionic dyes on polymers from *Water. Sen'I Gakkaishi,* 50 (120 pp. 605-607.

31 Ten Breteler, M.R. Nierstrasz., V.A. and Warmoeskerken,. M.M.C.G. Textile., December (2002) Slow-Release systems with Medical Applications, *AUTEX Research Journal,* Vol. 2, No. 4, ©AUTEX

32 Timmis, J.B., (1976). *Dyer Inter,* pp.156

33 Vaidya, A.A., (1988)., Production of Synthetic fibres, Prentice-Hall of India Pvt. Ltd.,

34 Vaidya.A.A.,*The Textile Industry & Trade Journal,* pp. 77., May-June 2002'

35 Wellman Inc. and Branum, *J.B.EP Patent,* 1248871, (2002), & Xin,L., Rultao, L., Lixia and G., *Jouranal Applied Polymer Science,* 89,(6),1996 (2003).

36 You-Lo, H and Zhishen, M., (1987) *Journal of Applied Polymer Science,* pp. 33,1479. ■