APPLYING A NOVEL PROCEDURE FOR PRINTING ACRYLIC FABRICS WITH ANIONIC DYES

A.I. FATHALLAH[1] and L. K. EL-GABRY[2]

1-Textile Printing, Dyeing and Finishing Division, Faculty of Applied Arts, Helwan University,
Cairo, Egypt. 2- National Research Centre, Textile Division, Dokki, Cairo, Egypt
** Corresponding author:* Lamiaa Kamal El-Gabry *E-mail: lamiaa_gabry@yahoo.com*

Abstract

Acrylic fabrics are printed with anionic dyes i.e reactive dyes using finishing agent, N-methylol dihydroxyethylene urea (N-MDHEU) as a cross linker. Different factors that affecting on each of dye fixation as well as color yield are studied. Tensile strength and elongation % are investigated. The theoretical and applied aspects of fixing coloration of acrylic fabrics colored with reactive dyes by using new cross linking agent in the form of n-methylol compound are studied. The printed fabrics were evaluated for color yield and fastness properties. It was found that addition of (N-MDHEU) in printing past gave good printability with reactive dyes after using faxing agent (CIBAFIX). The tensile strength and elongation of printed fabrics have been improved. The effects of the addition of (N-MDHEU) in printing past are characterized by infrared spectroscopic.

Key Words: *Acrylic fabrics, reactive dye, N-methylol compound and fastness properties, FTIR, tensile strength and elongation %.*

1. Introduction

The colouration of acrylic fibers has been one of the most intensively studied of dyeing and printing problem during the past few years. Indeed the great majority of dyes applied by the usual printing methods have little or no affinity for them. But as these fibers possess very attractive and interesting properties, it was necessary to look for new methods and techniques of printing in order to ensure their future development. It is considered that widening the scope of acrylic coloration using different class of dyes would facilities the technical production of different colors of the fiber alone or its blendes with other natural fibers.

Anionic dyes namely reactive, acid and direct dyes are not usually used for acrylic coloration as these dyes suffer from the repulsive effects that occur between the anionic groups present in the fibers and those present in the dye molecules.

Many attempts have been made to coloring the acrylic with anionic dyes. Reda M. Elshishtawy et al, have been rendered the surface of acrylic fibers with amino and-or quaternary amino groups so as not only to produce antimicrobial fibers but also to enhance its anionic dyeability (1). A previous work also presented an efficient and mild pretreatment of acrylic fiber that rendered the fabric anionic dyeable with acid dyes using hydroxylamine hydrochloride in the presence of acetate salt. the pretreated fabrics were gave improved dyeability over untreated fabrics due to the ion-ion interactions between the sulphonic groups present in the dye molecules and the protonated amino groups present in the fibers(2) .M.H. zohdy et al, have been investigated the effect of Cu (Π) hydroxylanine mixture on the dyeability of acrylic fabrics towards direct dyes(3). F. A. Kantoush & A. Atef El-sayed have been obtained an acid dyeable acrylic fabrics by the pretreatment with cationic aqueous polyurethane, containing different amount of quaternary nitrogen .cationic polyurethane has the ability to interact with the carboxylic groups in the acrylic fabrics ,as well as providing basic sites suitable for acid dyeing(4). The acrylic and polyester fabrics were treated with chitosan, by pad-dry method in presence and absence of binder. The pretreated fabrics were printed with acid dye. The colour strength of the prints in presence of binder was three times higher than in its absence. The enhancement in colour strength was relied mainly on nitrogen content % of chitosan. (5)

The modified acrylic fibres with hydrazine hydrate host active basic groups, which can enable the availability of acid and reactive dye interactions, proportional to the amount of hydrazine hydrate fixed on the fibres. (6, 7). Treatment acrylic fabric with aqueous hydrazine solution led to enhanced retention of dye and firmness of colour. Pre-treatment of acrylic/wool blends with hydrazine solution followed by dyeing with acid or reactive dyes also resulted in improved colour. (8)

The enzyme used was a nitrile hydratase, a member of the class of nitrile converting enzymes. The newly formed amide groups were then able to react with the acid dyes typically used to stain natural fibres, conferring the colouring properties to the otherwise inert polymer surface. (9) Nitrile groups on the surface of acrylic fibres were selectively hydrolyzed to the corresponding amidic groups by nitrile hydratase from Arthrobacter. The dyeability with acid dyes on the enzymatically modified acrylic fibre was enhanced. The modified acrylic fibres became more hydrophilic. [(10)] The acrylonitrile was known to be a very good substrate for both nitrilases and nitrile hydratases from this organism. The dyeing efficienc was increased by enzyme treatment for both acid and cationic dyestuffs. (11)

The present communication discusses an attempt made to study the suitability of printing acrylic fabrics with Reactive dyes. The purpose is also an easy technical printing process has been devised by using commonly available cross linking agent, N-methylol dihydroxyethylene urea, which increase the cationicity of the surface enhancing the electrostatic attraction between the negatively charged dye molecules and protonated carbonium group of N-MDHEU.

The printed fabrics were evaluated for color yield and fastness properties.

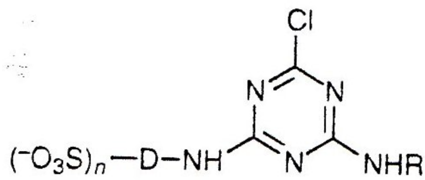
2. Experimental

2.1. Material

Acrylic fabric was used supplied by Masr El Mahalla Company. A plain woven acrylic fabric weighing is 175 g/m^2. The fabric was washed in 2g/l nonionic detergent solution at 60 °C for 45 minute, thoroughly rinsed and air dried at room temperature.

2.2. Dyes

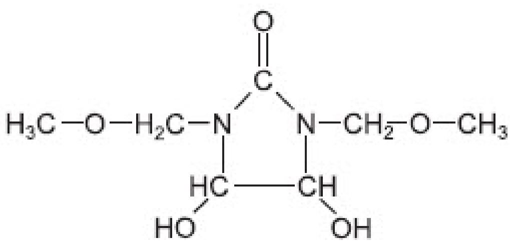
The reactive dyes used were based on the monochlorotriazine strcture (1)



1

2.3. Chemicals

Arkofix® NG-ET (clariant) the crease recovery finishing agent based on N-methylol dihydroxyethylene urea **(2)**



modified DMDHEU

(2)

Magnesium chloride, Ammonium chloride, Citric acid, urea of these studies have used nonnumeric or polymeric quaternary ammonium salts

Thickening agents

Sodium alginate, supplied by Mansanto, United Kingdom, under the comercial name Manutex M320

Fixing agent: cationic agents namely CIBAFIX®(Ciba Specialty Chemicals) is used.

2.4. Printing Method

There are main factors of most importance when printing acrylic fabrics with reactive dye using the present printing method-firstly, effect of crosslinking agent concentrations, secondly, the effect of catalyst type and concentrations and thirdly, the temperature /time of steaming that required for the dye to fix onto acrylic fibers to achieve a satisfactory printing properties. In order to illustrate the effect of each one, the acrylic fabric was printed by the manual flat silk screen technique with reactive dye, and the guide formulation for the used printing paste is given below:-

Preliminary printing recipe contents

20	gm/kg	Reactive dye (suncion scarlet H-E3G)
X	gm/kg	Cross Linking agent
500	gm/kg	Thickener (sod. alginate), (10%)
50	gm/kg	urea
8	gm/kg	magnesium chloride or (catalyst)
Y	gm/kg	Balance (between thickener or water)
1000	gm/kg	(at pH5.5-6)

A hygroscopic agent should be added to the print paste to ensure the enough amount of water, in the form of moisture, that necessary to acquire the fiber surface of PAN negative charges during fixation the prints in saturated steam at high temperature. Thus, 50 g/kg urea is enough for this purpose.

Printing-Drying at temperature of not more than 100° C to avoid yellowing of the fiber-steaming was carried out to fix the prints in moist steam at 120° C for 25 minutes- rinsing in cold water soaping in a bath containing 4g\L nonionic detergent **(Sera® Fast C-RD**) DyStar, L.R. 1: 30 at 60° C for 30 minutes- rinsing again and finally drying.

2.5. Measurements

2.5.1 Colour intensity (K/S)

Colour intensity of the prints (k/s) was measured at the wave length of the maximum absorbance using a SF600+-CT Data colors spectrophotometer.

2.5.2 Tensile Strength and Elongation %

The tensile strength and elongation of fabric before and after treatment were evaluated using a Instron Tensile Tester (USA) according to ASTM D 76 Standard Specification for Textile Testing Machines. The average was taken for 10 samples (5x 20 cm^2).

2.5.3. Fastness Testing

The colour fastness to washing was determined in accordance to ISO standard methods. The specific standard tests were: ISO 106-CO2 (1993) for wash fastness and ISO 105-EO4 (1989) for fastness perspiration.

2.5.4. Infrared Spectra

Infrared spectra were recorded on FT-IR Nicolet 5 DX Spectrophotometer. The samples were examined as 1.5% K Br pellets.

2.5.5. Crease recovery

Wrinkle recovery angles (W+Fo) were measured (13) using the crease recovery apparatus type FF – 07 (Metrimpex).The crease recoveries of acrylic fabric before and after treatment were evaluated.

3. Results and Discussion

3.1. Colour intensity

3.1.1. Effect of cross linking agent concentration on the colour intensity (K/S)

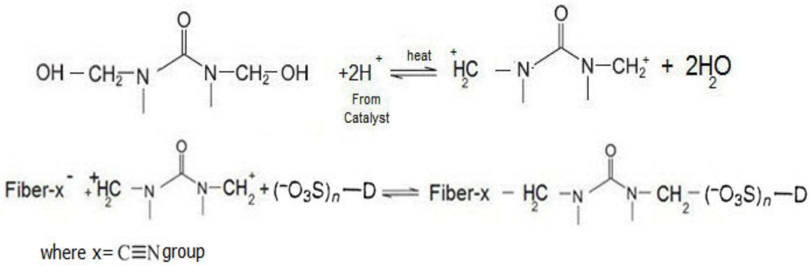
The colour intensity K/S of the printed fabric samples with different concentration of a cross linker "modified DMDHEU" are shown in table 1, in the printing past along with catalyst magnesium chloride (8g/kg). Table (1) data shows that the increase in cross linker (Arkofix® NG-ET) concentration up to 80g/kg has a positive effect on colour intensity K/S yield values most probably due to changing the hydrophopicity/ hydrophilicity ratio due to crosslinking, i.e. high affinity for reactive dye printing.(15-17). We can suggest formation of new electrostatic attraction through the presence of active material N-methylol dihydroxyethylene urea under specified reaction conditions as follow:

Table (1): Cross linking agent concentration on the Colour intensity (K/S) on printed acrylic fabric

Cross linking agent conc. g/kg	Colour intensity K/S
0	0.17
20	0.32
40	1.16
60	4.12
80	7.73
100	6.68
120	6.63

**20g/kg reactive dye, 500g/kg thickener, 50 g/kg urea,8g/kg magnesium chloride, steaming at 120° C for 25 minutes*

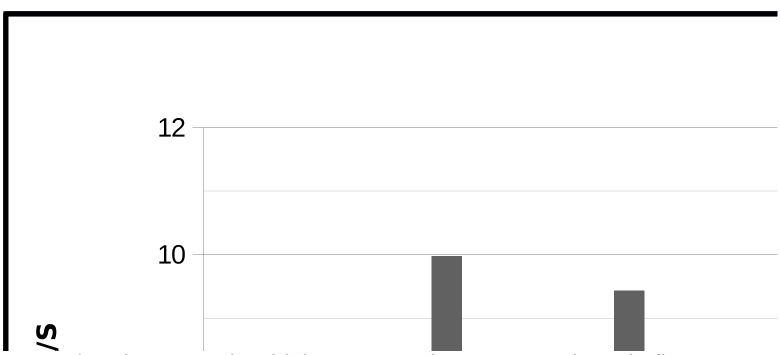
On the other hand, further increase in the used cross linking agent DMDHEU derivative concentration up to 120g/kg results in a slight decrease in the K/S values of the printed sample which could be discussed in terms of higher extent of cross linking side interactions with the reactive dye functional groups, and reduction in the number of accessible cationic sites thereby giving rise to lower depth of shades.



3.1.2. Effect of Catalyst types & concentration on the colour intensity (K/S)

Figure (1) represents the effect of catalyst type and concentrations on the extent of printed fabrics, within the range examined, it is clear that increasing the catalyst concentration up to 8g/kg for (Mg Cl_2)Magnesium chloride and Citric acid (1:1) and 2g/kg for Ammonium chloride (NH_4Cl) in the printing paste brings about an improvement in the colour intensity K/S values, which could be discussed in terms of higher extent of fixation of the crosslinking agent onto the polyacrylic fibers thereby enhancing the extent of dye uptake as well as its fixation, further increase in the catalyst concentration, has practically a marginal decreasing effect on the colour intensity K/S values of the printed fabrics which may be attributed to the oxidative effect of the used catalyst during steaming. The extent of printing is determined by the nature (or the type) the catalyst and follows the order:

NH_4Cl > Citric acid > Mg Cl_2.



**20g/kg reactive dye, 500g/kg thickener, 50 g/kg urea, 80g/kg Arkofix® NG-ET, steaming at 120° C for 25 minutes*

Figure (1): Effect of Catalyst types and concentration on the colour strength

3.1.3. Effect of urea concentration on colour intensity (K/S)

The action of urea in case of cotton fiber processing to improve dye fixation has been attributed to several factors such as swelling of cellulose, disaggregation of dye, improved dye diffusion, lowering the rate of evaporation of water on the dye, catalyst to accelerate reaction between dye and cellulose and possibility of reaction between reactive dye and urea (18). The addition of urea in the dyeing of acrylic fibre increases dye exhaustion, urea may be made the same action with reactive dyes and acrylic fabrics. The acceleration depends upon the dye and the fibre used (19).

Table (2) Effect of urea concentration on the colour intensity (K/S)

Urea conc. g/kg	Colour intensity K/S
0	7.62
50	9.98
100	7.14
150	7.56
200	5.53

**20g/kg reactive dye, 500g/kg thickener, 2g/kg Amm..chloride, 80g/kg Arkofix® NG-ET, steaming at 120° C for 25 minutes*

It is clear from Table (2) that increasing urea concentration in the printing paste is accompanied by increasing the extent of dye fixation, reaching a maximum at 50 g/Kg, then decreases by further increase in concentration up to 200g/kg. The increased k/s in presence of urea is related to the dye solubility and /or plasticizing action of urea on acrylic fibre. The decreases in the dye fixation at high concentrations of urea (100-200) may be due to higher dye solubility.

3.1.4. Effect of Steaming Temperature on the colour intensity (K/S)

Table (3) reflects the effect of steaming temperature on the depth of the printed fabric samples, the results showed that increasing the steaming temp. up to 125ºC for 25 min results in a gradual increase in the color value of the prints. Further increase in steaming temperature, i.e. beyond 125ºC has practically no effect.

This enhancement in colour intensity K/S values is a direct consequence of; facilitating the dye release from the thickener film and availability of its active sites thereby providing more possibilities for adsorption, accommodation and fixation of reactive dye molecules (21). Furthermore, the rat of dyeing depends on the speed of dye diffusion which starts above the glass transition temperature, (Tg) of the fiber, where fiber molecules acquire enough energy to move. This means the fiber softens, and the dye is allowed to diffuse. For a given printing conditions, it appears that steaming at 125ºC for 25min. would be the proper conditions for attaining higher colour intensity K/S. Further rising in using temperature, i.e. beyond 125ºC for 25min., has a negative effect on the aforementioned properties which may be attributed to the enhancement of side interactions and/or partial hydrolysis of substrate crosslinking agent / dye bonds.

Table (3): Effect of Steaming Temperature on the colour intensity K/S

Steaming temperature ºC	colour intensity K/S
110	4.97
115	9.62
120	10.32
125	**12.24**
130	11.59

**20g/kg reactive dye, 500g/kg thickener, 2g/kg Amm..chloride, 80g/kg Arkofix® NG-ET, 50 g/kg urea, steaming for 25 minutes*

3.1.5. Effect of Steaming Time on the colour intensity (K/S)

Table (4) shows the effect of steaming time on the color strength K/S values. It's clear that prolonging the steam fixation time up to 15 min. at 125°C is accompanied by an improvement in color strength K/S values of obtained prints, most probably due to the enhancement in the extent of dye release, adsorption, diffusion and retention of dye molecules onto the substrate thereby enabling more dye fixation. It could be attributed also to the plasticizing action of the urea used which facilitate diffusion of large amounts of the dye inside the substrate, thereby, dye uptake may be increased (21). Further increase in fixation time, i.e. up to 15 min. at 130°C has practically a slight negative impact on the color depth of the obtained prints that because of adversely affecting the thickener film properties and the substrate surface thereby reducing the extent of coloration.

Table (4): Effect of Steaming Time on the colour intensity K/S

Steaming time min.	colour intensity K/S
5	11.21
15	**12.83**
25	12.79
35	12.48
45	12.24

**20g/kg reactive dye, 500g/kg thickener, 2g/kg Amm..chloride, 80g/kg Arkofix® NG-ET, 50 g/kg urea, steaming at125° C*

3.2. Fastness properties of printed acrylic

Appling the optimum conditions of the printing acrylic fabrics with different reactive dyes according to this work to four different reactive dyes, first without crosslinking agent and second with crosslinking agent N-methylol dihydroxyethylene urea (N-MDHEU). (Arkofix® NG-ET) to confirm the effect of crosslinking agent to the fastness properties of acrylic prints. Table (5) shows colour difference of acrylic fabrics printed without and with cross linker at optimum conditions. It was found that colour different between printed fabrics with cross linker and without cross linker achieves to 144.5 %.

Table (5) colour difference of acrylic samples printed with optimum conditions

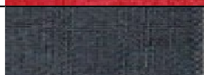
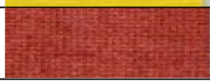
Reactive dyes	Printed samples: With crosslinking	Printed samples: Without crosslinking	Colour Difference %
Suncion Scarlet H-3G			**144.46%**
Sunfix Navy Blue MF-RD			**106.32%**
Cibacron Yellow P.6GS			**133.56%**
Cibacron Orange P-4R			**136.94%**

Table (6) clears the fastness properties of printed acrylic fabrics with and without cross linker agent. It is clear that the prints display good perspiration fastness properties ranging from 3-4 irrespective of the fabric used. And little increase in case rubbing fastens with used cross linker. The data of washing fastness clears excellent ranging from 4-5 irrespective of the fabric used after using fixing agent.

Table (6) Fastness properties of acrylic prints

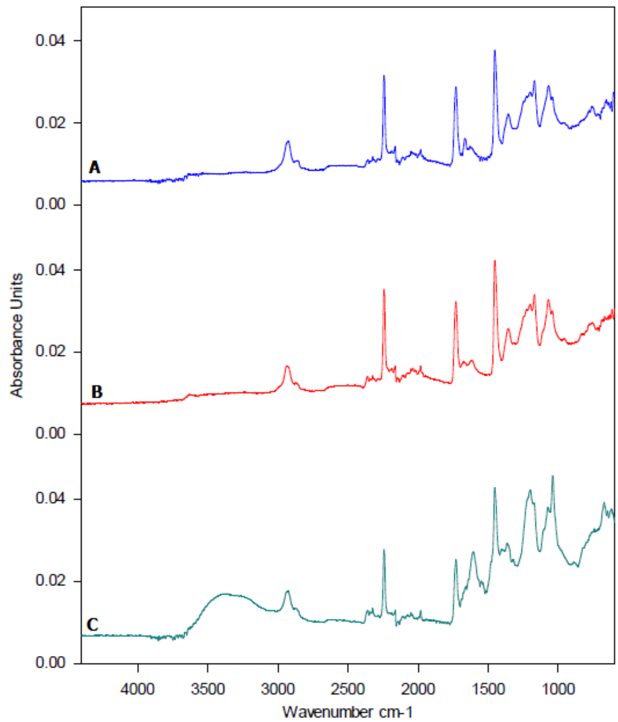
Reactive Dye	Perspiration fastness						Wash fastness						Rubbing	
	Acidic			Alkaline			Before Fixing			After Fixing				
	Alt	St_w	St_c	Alt	St_w	St_c	Alt	St_w	St_c	Alt	St_w	St_c	wet	dry
Suncion Scarlet H-E3G Without ((N-MDHEU) With ((N-MDHEU)	4 4	4 4	3 4	4 4	3/4 4	4 4/5	1 2	3 2	4 2/3	2/3 4	3 4/5	3 4/5	2/3 3	3 4
Sunfix Navy Blue MFRD Without ((N-MDHEU) With ((N-MDHEU)	4 4	3/4 ¾	3 3/4	4 4	3 3/4	3 4	1 2	2 2	2/3 2	3 4	3/4 4	3 4/5	3 4	4 4/5
Cibacron Yellow P.6GS C.I. Reactive yellow 95 Without ((N-MDHEU) With ((N-MDHEU)	4 4	3/4 4	3/4 3/4	4 4	3/4 4	3/4 4	1 2	3/4 3/4	3/4 3/4	2 4	3/4 4/5	3/4 4/5	3 4	3/4 4
Cibacron Orange P-4R C.I. Reactive Orange 35 Without ((N-MDHEU) With ((N-MDHEU)	4 4	3/4 4	3/4 3/4	4 4	3/4 4	3/4 4	1 3	3 3/4	3 3/4	3/4 4/5	4 4	4 4/5	3 4	3/4 4

Fixing agent: CIBA fix product was used as a dye-fixing agent, Alt: Alteration, **St_w**: Staining

3.3. Infrared spectroscopy

3.3. Infrared spectroscopy

Confirmation of this has been provided by the use of infra-red spectroscopy. FTIR analysis were carried out via Nicolet 380 spectrophotometer, spectral rang 4000-400cm^{-1}, resolution 4cm^{-1}, number of scans 32 and smart per former ATR. Unprinted is blue colour, printed without cross-linking is red colour and printed with cross-linking is green colour as showen in figure 2. In green beck shows big browed in range 3620 cm^{-1} - 3000 cm^{-1} also, the intensity of CN-group at 2244 cm^{-1} is decreased. Also, the intensity of COOH group at 1730 cm^{-1} is decreased this may be main the cross linker was linked with this group. It is appears new pick at1660 cm^{-1} of imide group.



(A)	**Unprinte d Acrylic**	
(B)	**printed without crosslinki ng agent**	
(C)	**printed with crosslinki ng agent**	

Figure 2: Infrared spectra of unprinted and printed of acrylic fabric

3.4. Tensile Strength and Elongation

The data of tensile strength and elongation % of the unprinted, printed and printed with cross linker of acrylic fabrics are given in table 7. The tensile strength and elongation % are improved for fabrics printed with cross linker than both unprinted and printed one.

Also, table 7 present the results of wrinkle recovery of the unprinted, printed and printed with cross linker of acrylic fabrics. It was found little change in the data of wrinkle recovery this may be main that the cross linker don't act as crosslinking agent

Table (7):Effect of cross linking agent on wrinkle recovery and tensile strength of acrylic/wool prints

Samples	Tensile Strength g/cm^2	Elongation %	Wrinkle recovery	
			W°	F°
Unprinted	1.46	36	117	121
Printed without cross linking	1.48	43	118	122
Printed with cross linking	1.56	43	108.5	108.8

W°:warp F°:weft

4. Conclusions

Acrylic fabrics have ability to reactive dyestuff when add crosslinking agent [N-methylol dihydroxyethylene urea (N-MDHEU], (Arkofix® NG-ET) in the printing past. It was found that colour difference between printed fabrics with cross linker and without cross linker achieves to 144.5 %.

It was found that the wash fastness gives excellent grades ranging from 4-5 irrespective of the fabric used after using fixing agent.

The tensile strength and elongation % are improved for fabrics printed with cross linker than both unprinted and printed one.

References

1. R. M. Elshishtawy et al, *Dyes and pigments* **74**, 215-222(2007).
2. R. M. Elshishtawy and N. S. Ahmed, *Coloration Technology* **121**(5), issue 3, 139-146(2005).
3. M. H. Zohdy, A.M El-Naggar, M.M Marie, *Materials Chemistry and Physics*, **61**(11), issue3, 237-243 (1999).
4. F.A. Kantoush and A. Afet El-Sayed, *Journal of Applied Polymer Science*, **119**(3),issue5, 2595-2601(2011).
5. O.A. Hakeim,; L. K. El-Gabry, and A. Abou-Okeil, , Accepted for publication in J. *Applied Polymer Science*(2007).
6. A.; Bendak, A.Kantouch,; and L .El-Gabry,*Am. Dyestuff Rep*., **84** (6)34 (1995).
7. L.El-Gabry, *Master Thesis*, Helwan University,Egypt(1994)
8. A.; Bendak, A.Kantouch,; and L .El-Gabry, *Tinctoria*,**91**(8),29-33 (1994).

9. E. Battistel,; M. Morra,; and M. Marinetti, *Applied Surface Science*, **177**(1-2), 32-41 (2001). Chem. Abst., 135, 154002v (2001).

10. N. Yin xu,; D. Lu,; and J Xu, *AATCC* ,Review **4** (9)28-30(2004).

11. M .Tauber, and G. Gubitz,; *AATCC* Review 1,(9) 17-10(2001).

12. B. Voncina, D. Bezek, A. M. leMarechal; *FIBRES & TEXTILES in Eastern Europe* July/September (2002).

13. J. R. Aspland; *Textile Dyeing and coloration Research Triangle Park*, AATCC, 105 (1997).

14. Technical Manual of the American Association of Textile Chemist and Colorists (AATCC), **74**, po Box 12215, Research Triangle park, Nc 27709, U.S.A, (1999).

15. J. M. Cardanone, G. Boa, A. Francis and W. N. Marmer, ,*Text. Chem. And Color.* **29** (9), 30-36 (1997).

16. N. A. Ibrahim, E. M. R. El Zairy, M. R. El Zairy, H. M. Khalil, , *AATCC Review*, (July, August 2011).

17. N. A. Ibrahim, E. M. R. El Zairy, M. R. El Zairy, H. M. Khalil, *coloration technology*, **126**, 1 (2010).

18. S Y Kamat and A K Prasad, Ind Text J, 102,11,98(1991).

19. F. Uddin., M.Lomas.; *FIBRES & TEXTILES in Eastern Europe* , , Vol. 18, No. 4 (81) 56-60(2010).

20. S P Mishra, P George Peter RAJ, P Hemamalini &B Sivakumar, *colourage* ,MAY,p.17(1992)

21. H. Brody. *Synthetic Fiber Materials*, John Wiley& Sons, Inc.,605 Third Avenue ,New York ,NY 10158, p.74:87,(1994).

22. W.A. Abdallah, E.M. R. El-Zairy, A.I. Fathallah, W. M. R. El-Zairy , Seventh International Scientific Conference, Faculty of Science, Al-Azher University, 22-24 March(2010).