

An easy all-in Printing Process for Printing Acrylic/ Wool Blended Fabrics with Reactive Dyes"

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Abstract:-

In this work acrylic/ wool fabrics is printed with one dye (Reactive dyes) in one step as an easy method. The main aim of this study is increasing the printability of acrylic fabrics towards reactive dyes which are not usually used for acrylic coloration, by using commonly available finishing agent, N-methyloldihydroxyethyleneurea (N-MDHEU), which increase the cathodicity of the acrylic fabrics surface enhancing the electrostatic attraction between the negatively charged dye molecules and protonated carbonium group of N-MDHEU. Different factors that may affect the printability of blended fabrics will be studied with respect to color strength and fastness properties. The results of the experimental work offer a new viable method for applying one class of dyes (reactive dyes) on the acrylic/ wool blended fabrics. It was found that addition of (N-MDHEU) in printing past gave good printability with reactive dyes .The effects of the addition of (N-MDHEU) in printing past are characterized by infrared spectroscopic.

Key Words:-

Acrylic/wool blended fabrics, reactive dye, crosslinking, N-methylol compound, printability, fastness properties.

Introduction:-

In our modern world, the image of wool has changed: it is seen today by the consumer as an expensive, high-value fibre with natural softness and elegance. It is tending to be increasingly blended with other fibres. There are three main reasons for this: economy, fashion and function. (1)

Of all the synthetic fibres, acrylic fibres have the most wool-like character, and knitted goods made of wool/acrylic are similar in appearance, handle and wear properties to articles made of pure wool. The strength and bulk properties of acrylic fibres are enhanced by the water-sorption and aesthetic properties of wool fibers when the two fibres are combined in an intimate blend.

Acrylic/wool blended fabrics are the most difficult blend to print, however, demanding the use of incompatible dyes: an acid dye for the wool and a basic dye for the acrylic fibre. Some studies have been reported where the material was first treated with Sandospace R. The pretreated material was then printed as if it were 100% acrylic fibre, with basic dyes chosen for good

light fastness properties; prints of acceptable wet fastness were obtained.(2)

Printing wool with Reactive dyes offer several advantages apart from the obvious one of good wet fastness properties as possess better solubility than acid dyes, and can usually sprinkled directly into the print past as solids without the use of dye solvents and they required shorter steaming times which is of obvious advantage in continuous steaming. On the other hand, printing with reactive dyes does lead to certain problems, such as a tendency to unlevelness in large blotches in some shade areas. (2)

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.(3)(4)(5)(6)

Dimethylol dihydroxy ethylene urea (DMDHEU) and modified dimethylol dihydroxy ethylene urea (modified DMDHEU) are compounds which contain N-methylol and mainly N-alkoxymethyl

groups and they are extensively used in textile industry as durable press finishers. (Figure 1)

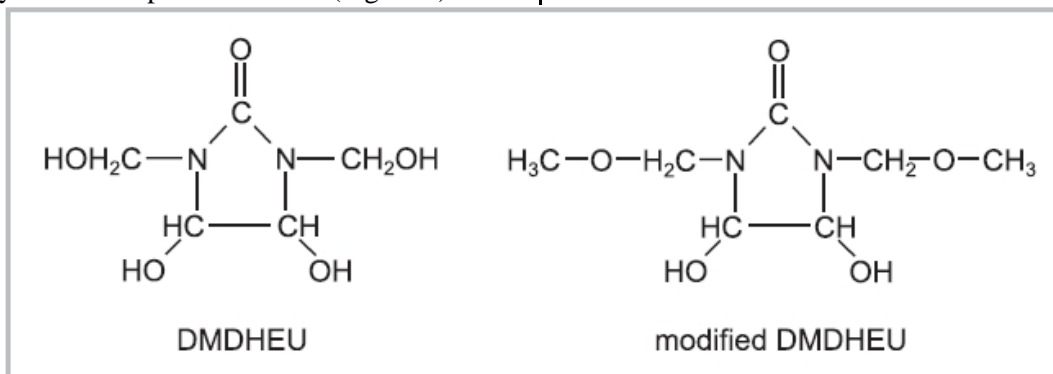


Figure 1:chemical formula of DMDHEU and modified DMDHEU

During the finishing process the N-methylol compounds can react with hydroxyl groups of cellulose, which is the most preferable reaction; they may also react with themselves or with reactive NH groups. (Figure 2) Splitting of acetalic bonds is catalytically accelerated by acids

and by the basis as well. To minimise the release of formaldehyde from the crosslinking reagents and the finished textile fibres, derivatives of N-methylol compounds have recently been used as durable press finishing reagents. (7)

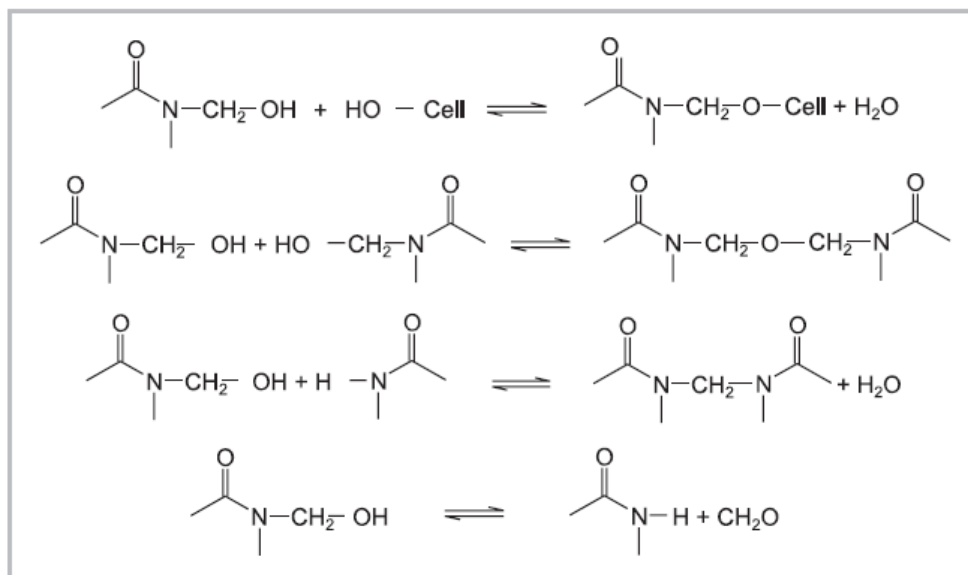


Figure 2: Equilibrium reactions of N-methylol compounds

Equilibrium reactions of N-methylol compounds with hydroxyl groups of cellulose, with themselves, with reactive NH groups and the formaldehyde release

In the interest of making acrylic fibres less hydrophobic ,anionic dyeable thus amenable for sold shad printing of acrylic /wool blended fabrics using one type of dyes(reactive dyes),it was thought that the use of commonly available finishing agent, N-methylol dihydroxyethylene urea (N-MDHEU), will increase the cationicity of

the acrylic fabrics surface enhancing the electrostatic attraction between the negatively charged dye molecules and protonated carbonium group of N-MDHEU.

In this work an easy technical printing process has been devised by using N-methylol dihydroxyethylene urea in the printing past along with reactive dyes and additives. The advantages of this process that acrylic/wool fabrics is printed

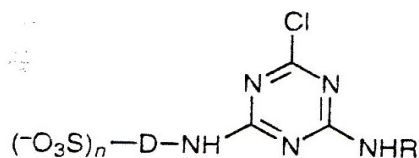
in one step with one classes dyestuffes. Different factors affecting printability and fastness properties are thoroughly investigated. The effect of cross linking agent on the crease recovery angle and tensile strength is also investigated.

METHODOLOGY

Experimental Design:

Material: A plain weave 1-1 (52 yarns/inch in warp -45 yarns/inch in weft) weighing 160 g/m² in a ratio of 70% acrylic&30 % wool provided by Misr Spinning & Weaving Co. Mehalla El Kobra, Egypt was used throughout this work.

Dyes: the reactive dyes used were **suncion scarlet H-E3G** (Suncolours®) based on MCT reactive group



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

-Magnesium chloride, Ammonium chloride, Citric acid, urea which used in this work, was commercially available.

Thickening agents: Sodium alginate, supplied by Mansanto, United Kingdom, under the commercial name Manutex M320

Detergent agents: nonionic detergent (Sera® Fast C-RD) DyStar.

Fixing agents: CIBAFIX®(Ciba Specialty Chemicals)

Measurements:-

Color strength of the prints (k/s) was measured at the wave length of the maximum absorbance using a SF600+-CT Data colors spectrophotometer. Wrinkle recovery angles

(W&F°) were measured (8) using the crease recovery apparatus type FF – 07 (Metrimpex). Fastness properties to washing, crocking and perspiration of the printed specimens were evaluated according to the AATCC test methods:

[61-1996], [18-1997] and [15-1997] (9)

Printing Method:-

There are main factors of most importance when printing acrylic/wool blended fabrics with reactive dye using the present printing method- first, effect of crosslinking agent concentrations, second, the effect of catalyst type and concentrations and third, the temperature /time of steaming that required for the dye to fix onto the fibers to achieve a satisfactory printing properties. In order to illustrate the effect of each one, the 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	Water
500	gm/kg	Thickener (sod.alginate), (10%)
50	gm/kg	urea
8	gm/kg	magnesium chloride
Y	gm/kg	Balance (between thickener or water)
1000	gm/kg	(At pH 5.5-6)

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.

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 cm²).

Fastness Testing:

The color 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.

Infrared Spectra:

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

Results and Discussion:-

1 - Effect of cross linking agent concentration on the K/S:

As for as the change in the color values i.e., "K/S" of the printed fabric samples as a function of a cross linker "modified DMDHEU" conc. in the printing past along with catalyst (8g/kg), table (1) shows that increasing Arkofix® NG-ET concentration up to 100g/kg has a positive effect on increasing K/S "color yield values" most probably due to changing the hydrophobicity/hydrophilicity ratio of acrylic due to crosslinking, i.e. high affinity for reactive dye printing. (10,11,12).

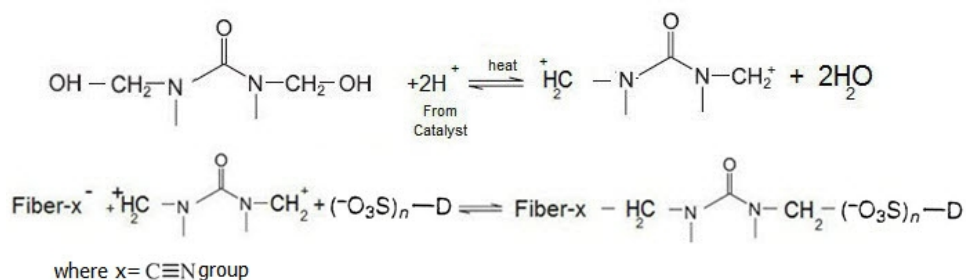
Table (1): Effect of cross linking agent concentration on the K/S

Cross linking agent conc. g/kg	K/S
0	2.21
20	2.43
40	2.75
60	3.28
80	5.78
100	8.81
120	8.97

**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.

In the case of acrylic fibres we can suggest formation of new electrostatic attraction through the presence of active material N-methylol dihydroxyethylene urea under specified reaction conditions



We can also considered the N-methylol compounds as a cationic leveling agent which form complexes with dye molecules and increase the rate of uptake and cover dyeability variations in wool (13).

Infrared Spectra

(Fig. 4) shows the infrared spectroscopic analyses of both unprinted printed without cross

liker and printed with cross linker acrylic/ wool fabrics. Blue plot for unprinted, red plot for printed without cross liker and turquoise plot printed with cross linker. The infrared spectroscopic analysis of in turquoise plot shows that disappears the pick at 2240 cm⁻¹, Also, it is observed some changes in absorption between 3200 cm⁻¹ and 3600 cm⁻¹

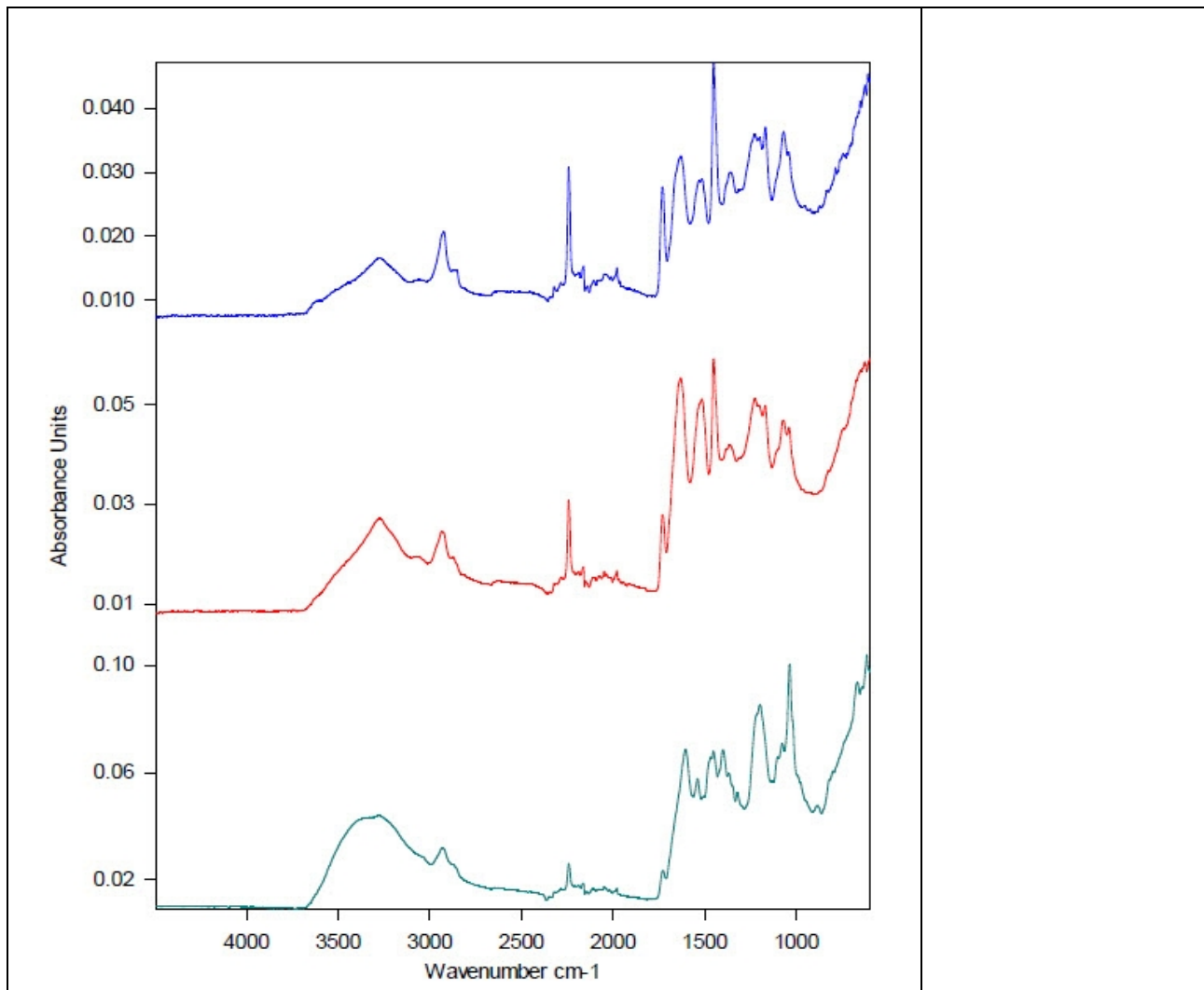


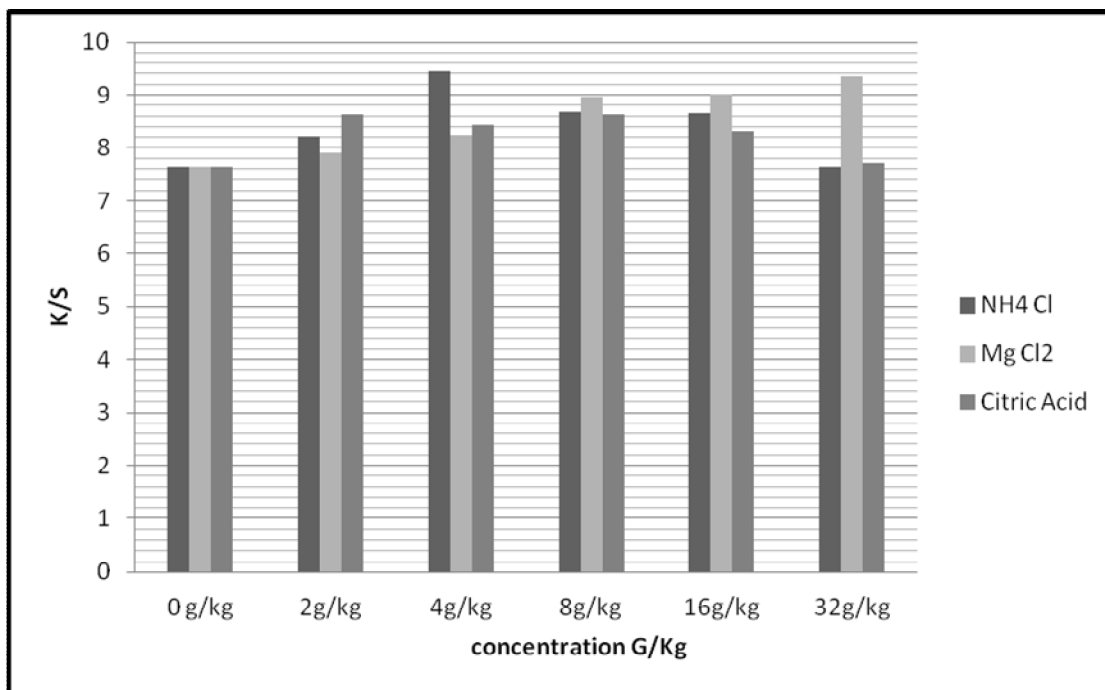
Figure (4): FTIR analysis of acrylic / wool blended fabrics

Unprinted Acrylic/wool	
printed without crosslinking agent	
printed with crosslinking agent	

It may conclude that many observed changes took place during printing process. The changes

included mainly C=C formation. In presence of cross linking agent, C≡N bonds were transformed to C=N, C=C and C=O of wool (amide I) were removed indicating that chemical bonds were formed through these bonds.

2- Effect of Catalyst types & concentration on K/S:



Figure(4): Effect of Catalyst types & concentration on K/S

**20g/kg reactive dye, 500g/kg thickener, 50 g/kg urea, 100g/kg Arkofix® NG-ET, steaming at 120° C for 25 minutes*

Figure (4) represents the effect of catalyst type and conc. on the extent of printed fabrics, within the range examined, it is clear that increasing the catalyst concentration up to 4g/kg for NH₄Cl, 8g/kg for Citric acid (1:1) and 32g/kg for Mg Cl₂ in the printing paste brings about an improvement in the K/S values regardless of the used catalyst, which could be discussed in terms of higher extent of fixation of the crosslinking agent onto the 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 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:

NH₄Cl > Mg Cl₂ > Citric acid.

3-Effect of urea concentration on K/S:

Urea is an essential ingredient in wool printing pastes-it aids solution of the dye in the printing paste, and it acts as humectants, promoting wool swelling and dye penetration during steaming (2). On the other hand the addition of urea in the dyeing of poly (acrylonitrile) fibre increases dye exhaustion because of plasticizing action of urea on acrylic fibre. (14).

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

Urea conc. g/kg	K/S
0	7.48
50	8.85
100	8.82
150	8.21
200	7.73

**20g/kg reactive dye, 500g/kg thickener, 2g/kg Amm..chloride, 100g/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.

4-Effect of Steaming Temperature on 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 125°C for 25min results in a gradual increase in the color value of the prints. Further increase in steaming temperature, i.e. beyond 125°C has practically no effect.

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

Steaming temp. ° C	K/S
No steaming	7.00
110	8.09
115	8.61
120	8.98
125	10.48
130	10.16

**20g/kg reactive dye, 500g/kg thickener, 2g/kg Amm..chloride, 100g/kg Arkofix® NG-ET, 50 g/kg urea, steaming for 25 minutes*

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

Steaming time (Min.)	K/S
No steaming	7.00
5	9.51
15	10.89
25	10.49
35	10.31
45	10.25

This enhancement in 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. (15)Furthermore, the rate 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. (16)

For a given printing conditions, it appears that steaming at 125°C for 25min. would be the proper conditions for attuning higher K/S values. Further rising in using temperature, i.e. beyond 125°C 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.

5-Effect of Steaming Time on K/S:

**20g/kg reactive dye, 500g/kg thickener, 2g/kg Amm..chloride, 100g/kg Arkofix® NG-ET, 50 g/kg urea, steaming at 125° C*

Table (4) shows the effect of steaming time on the color strength, i.e. K/S values. It's clear that prolonging the steam fixation time up to 15min. at

125oC is accompanied by an improvement in 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. Further increase in fixation time, i.e. up to 15min. at 125oC 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.

Fastness properties of acrylic /wool prints:-

Many studies have been devoted to improve the fastness properties of anionic dyes by pretreating or aftertreating the fibres with amines or reactive cationic agents. Most of these studies have used

monomeric or polymeric quaternary ammonium salts having different reactive groups.(17) Table 5 shows fastness properties of printed acrylic/ wool fabrics with different dyes.

In this work the acrylic/wool printed fabrics first 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 and then aftertreating with reactive cationic agents namely CIBAFIX®(Ciba Specialty Chemicals) by exhaustion method(1-3% at 20-30 C° at pH 6-7 for 20 min) to improve the fastness properties of

acrylic /wool prints with reactive dyes. It was found that the using fixing agent gives significant increase in washing fastness.

Applying the optimum conditions of the printing acrylic/wool blended fabrics with reactive dyes according to this work to four different reactive dyes to confirm the effect of crosslinking agent on the fastness properties the acrylic/wool blended prints were evaluated according to the ATCC test methods and the data obtained represented in Table (5).

Table (5) Fastness properties of acrylic/wool prints









Reactive Dye	Wet fastness properties								
	Washing			Perspiration				Rubbing	
	Alt.	Sta.		Acidic		Alkaline		Wet	Dry
		w	o	Alt.	Sta.	Alt	Sta.		
Suncion Scarlet H-3G	4	4/5	4/5	4	4	4	4	3/4	4
Sunfix Navy Blue MF-RD	4	4	4/5	4	3/4	4	3/4	3/4	4/5
Cibacron Yellow P.6GS C.I. Reactive yellow 95	4	4/5	4/5	4	4	4	4	3/4	4/5
Cibacron Orange P-4R C.I. Reactive Orange 35	4/5	4	4/5	4	3/4	4	3/4	3/4	4

Where: Alt: Alteration, Sta: Staining,w:wool,o:cotton.

The data in Table (5) signify that: the wash, perspiration and rubbing fastness properties of the obtained printed sample were very good to excellent (3/4 to 4/5).

A comparison between two different samples printed with optimum printing conditions that obtained in this study: (a) acrylic/wool blended fabrics printed with printing paste contained cross linking agent,(b) acrylic /wool blended fabric printed with the printing paste doesn't contained the cross linking agent were made by using SF600+-CT Data colors spectrophotometer to determined the color difference. The data represented in table (6).

Table (6) color difference of acrylic /wool blended samples printed with optimum conditions

Reactive dyes	Printed samples		Color Difference %
	With crosslinking	Without crosslinking	
Suncion Scarlet H-3G			8.219%
Sunfix Navy Blue MF-RD			5.384%
Cibacron Yellow P.6GS			1.781%
Cibacron Orange P-4R			1.761%

It is clear from table (6) that using Arkofix® NG-ET as a crosslinking agent has a positive effect on increasing K/S "color yield values i.e. high affinity for reactive dye printing.

Tensile Strength, Elongation % and crease recovery

Table 7 shows data of tensile strength and elongation % of unprinted, printed without cross linker and printed with cross linker of acrylic/ wool fabrics. The tensile strength increased with printed fabrics without cross linker especially as well as printed fabrics with cross linker.

Table (7):Effect of cross linking agent on wrinkle recovery (WRA) Tensile Strength of acrylic/wool prints

Samples	Tensile Strength g/cm ²	Elongation %	WRA	
			W°	F°
Unprinted	0.8	30	117	121
Printed without cross linking	1.12	38	118	122
Printed with cross linking	1.06	35	108.5	108.8

Where: WRA: wrinkle recovery angle, T.S: tensile strength , W°:warp, F°:weft

In the data of elongation % of both printed without cross linker and printed with cross linker fabrics increases than unprinted one. Also, it was found that the data of elongation % give little increase, this may attributed to opening up fibre structure with addition cross linker in printing peats. The wrinkle recovery of printed fabrics with cross linker has some change than unprinted and printed only.

Conclusions:-

This paper offer a new viable method for applying one class of dyes (reactive dyes) on the acrylic/ wool blended fabrics by using Arkofix® NG-ET as a crosslinking agent. increasing. The experimental work indicated that Arkofix® NG-ET concentration up to 100g/kg has a positive effect on increasing K/S "color yield values,

2g/kg for NH₄Cl in the printing paste brings about an improvement in the K/S values regardless of the used catalyst, which could be discussed in terms of higher extent of fixation of the crosslinking agent onto the fibers thereby enhancing the extent of dye uptake as well as its fixation, 50g/kg urea in the printing paste increase K/S "color yield values, The increased k/s in presence of urea is related to the dye solubility and /or plasticizing action of urea on acrylic/ wool blended. increasing the steaming temp. up to 125oC for 15min results in a gradual increase in the color value of the prints. The wash, perspiration and rubbing fastness properties of the obtained printed acrylic/ wool blended were very good to excellent.

References

1. Aspland J.R., Textile Dyeing and coloration Research Triangle Park, AATCC, 105 (1997).
2. Brody H.. Synthetic Fiber Materials, John Wiley& Sons, Inc.,605 Third Avenue ,New York ,NY 10158, p.74:87,(1994).
3. Cardanone J. M., G. Boa, A. Francis and W. N. Marmer, , Text. Chem. And Color. 29 (9), 30-36 (1997).
4. Grüner Franz, International Textile Bulletin,Vol.47, issue 2,p.73(2001).
5. Ibrahim N. A., E. M. R. El Zairy, M. R. El Zairy, H. M. Khalil, , AATCC Review, (July, August 2011).
6. Ibrahim N. A., E. M. R. El Zairy, M. R. El Zairy, H. M. Khalil, coloration technology, 126, 1 (2010).
7. Kantoush F.A. & A. Afet El-Sayed, Journal of Applied Polymer Science, 119(3),issue5, 2595-2601(2011).
8. Lewis David M, Wool Dyeing, Society of Dyers & Colourists,P.317-340(1992).
9. Subramanian M.,JTATM,Vol.5 issue 2,summer(2006)- 2009
10. Voncina Bojana, Dominika Bezek, Alenka Majcen leMarechal, FIBRES & TEXTILES in Eastern Europe July/September (2002)
11. Zohdy M. H., A.M El-Naggar, M.M Marie, Materials Chemistry and Physics, 61(11), issue3, 237-243 (1999).

12. Elshishtawy Reda M. & Nahed S. Ahmed, Coloration Technology 121(5), issue 3, 139-146(2005).
13. Elshishtawy Reda M. et al, Dyes and pigments 74, 215-222(2007).
14. Mishra S P, P George Peter RAJ, P Hemamalini & B Sivakumar, colourage ,May,p.15- 17(1992)
15. Kamat S Y and A K Prasad, Indian Textile Journal,102,11,89(1991).
16. 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).
17. Bell V A,D M Lewis, Textile Research Journal, February P.129(1983).