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# Synthesis of Reactive Auxiliaries for Dye Resist Treatment of Wool

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**Abstract:** Three reactive auxiliaries containing s-triazine-based reactive groups were synthesized and the dye resist effects achieved on wool were evaluated. The results obtained indicated that, the dye resist effect achieved with the bifunctional reactive Auxiliary ($R_2$) was exhibited the highest value. The effect of the dye bath pH, salt concentration, dyeing temperature, dyeing time, conc. of dye and conc. of auxiliaries were also studied. Good fastness properties of the dyed fabric were achieved.

**Keywords:** Reactive auxiliaries, dyeing wool, dye resist, colour strength, fastness properties

## INTRODUCTION

Auxiliary products of various types are commonly used in the dye bath during the low temperature dyeing of wool[1]. Such chemicals are used to promote dye bath exhaustion and to achieve level dyeing[2].

A resist process may be defined[3] as one which modifies a textile fiber in such away that when the resist treated fiber is subsequently dyed, it absorbs dye to a lesser extent or at a slower rate than does untreated fiber. Various treatments have been proposed for imparting dye resist effects to wool, for example, sulphonation,acetylation, glyoxylation, deposition of polymers, alkaline chlorination and treatment with formaldehyde,sulphamic acid[4,5], tannic acid /metal salts, synthetic tanning agents[6,7,8] and also colourless reactive compounds[9,10]. Among them reactive dye resist agents are preferred due to their easy handling and application[10].

A viable dye resist agent must be completely cured and bound firmly to the wool substrate in order to achieve satisfactory dye resist effects[11].

Increasing the substantivity between the substrate and the dye resist agents is one of the most important factors needed to improve dye resist effects.In order to increase this substantivity one possible effective dye resist method would be to covalently bind the dye resist agents to the wool substrate using suitable fiber reactive groups[11].

In this work we synthesized three reactive auxiliaries containing s-triazine based reactive groups which were used for treating wool. Three acid dyes containing different number of sulphonic acid groups were used for dyeing treated wool.

## MATERIALS AND METHODS

**Material and Chemicals:** Scoured and bleached wool fabric with the following characteristics was purchased from Misr for Spinning and Weaving Company, Mahalla El-Kobra, Egypt; weight 205 $gm^{-2}$, 72 ends per inch, 64 picks per inch. Before using, the fabric was treated with a solution containing 5g $L^{-1}$ non-ionic detergent (Hostapal CV, Clariant), at 50 °C for 30 min.Then, the fabric was thoroughly washed with water and air dried at room temperature. Diamino benzene sulphonic acid (95% assay), cyanuric chloride (99% assay) and sulphanilic acid (99% assay) were supplied by Aldrich.All other chemicals employed were of analytical grade. The codes, the chemical names and chemical structures of the synthesized reactive auxiliaries are given in table (1).

**Dyes:** Three acid dyes which have different numbers of sulphonate groups were used (fig1). The commercial names and color Index names for these dyes are given in table (2).

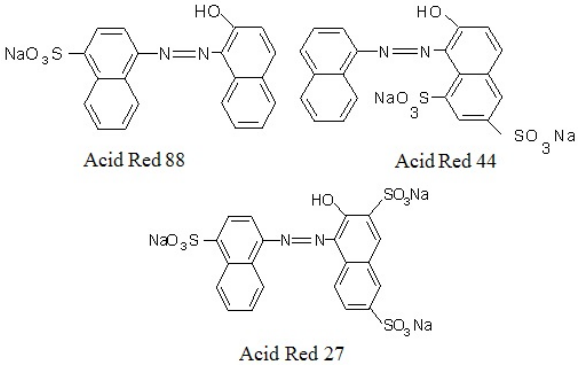


**Fig. 1:** Dye structures.

**Purification of Chemicals:**

**Cyanuric Chloride:** Cyanuric chloride[12] was crystallized from petroleum ether (b.p90-100 ºC), and dried under vacum at room temperature.

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**Table 1:** The Codes, the Chemical Name and Chemical Structures of the Synthesized Reactive Auxiliaries

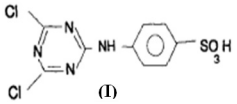
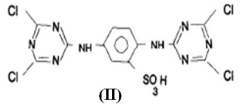
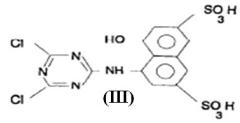
| Code | Name | Structure |
|---|---|---|
| R1 | 2, 4-Dichloro-s-triazine-6-yl-p-aminophenyl-sulphonic acid. |  (I) |
| R2 | 2, 5-Bis (2, 4-dichloro-s-triazine-6-yl)-amino phenyl-sulphonic acid. |  (II) |
| R3 | 2, 4-Dichloro-s-triazine-6-yl-amino-8-naphthol-3, 6-disulphonic acid. |  (III) |

**Table 2:** Dyestuffs Used

| Commercial name | Color index name | No. of SO- 3 groups |
|---|---|---|
| Acid Red 88 | CI Acid Red 88 | 1 |
| Crystal Scarlet | CI Acid Red 44 | 2 |
| Amaranth | CI Acid Red 27 | 3 |

**Sulphanilic Acid:** 100 gm of sulphanilic acid in about 500 ml sodium carbonate solution was boiled then filtered and made strongly acid with hydrochloric acid. The solution was then neutralized with 1N sodium carbonate. The hot solution was cooled to 0 ºC with stirring and the precipitate of sodium sulphanilate was filtered off. The crystals were dissolved in 500 ml distilled water and the solution was filtered and then acidified with concentrated hydrochloric acid. The material was then recrystalysed from hot distilled water and dried at 120 ºC overnight.

**1-amino -8 naphthol -3, 6 disulphonic acid (H acid):** Sodium carbonate (20gm) was added to a solution of 100 gm of (H acid) in 750ml of hot distilled water, followed by 5gm of activated charcoal.the suspension was stirred for 20 min and filtered by suction. H acid was precipitated by adding 50 ml of conc. HCL, then filtered by suction and washed with distilled water. The Mother H acid was dried overnight.

**Procedures:**

**Synthesis of 2,4 dichloro – s -triazine -6- yl- p-amino phenyl sulphonic acid sodium salt($R_1$)[13]:** sulphanilic acid (20 gm in 100 ml water) was added slowly to cyanuric chloride (22 gm in 200 ml acetone containing about 100 gm ice) whilst maintaining the pH of the solution at 7 by the addition of 2 N sodium carbonate.the reaction mixture was stirred for 1.5-2h the product was filtered off, washed thoroughly with acetone and then oven dried.

**Synthesis of 2, 5-Bis (2, 4 dichloro-s-triazine-6-yl) -amino phenyl sulphonic acid sodium salt ($R_2$):** cyanuric chloride (20 gm) in acetone (100ml) and ice was added to a solution of 2,5- diamino benzene sulphonic acid(10 gm) as a slurry, whilst maintaining the pH at 7 by the addition of a solution of saturated sodium carbonate. The reaction mixture was stirred for 3h and the product was filtered off, washed thoroughly with acetone and then oven dried.

**Synthesis of 2, 4- dichloro-s- triazine-6-yl-amino-8-naphthol 3, 6 disulphonic acid sodium salt ($R_3$)[14]:** 20 gm (H-acid) was dissolved in 1N sodium bicarbonate solution, the solution diluted to 250 ml and neutralized with acetic acid. this solution was dropped simultaneously into a well stirred suspension of finely divided cyanuric chloride (10 gm)in acetone and ice water (2:1)at 0ºC over 3h when pH was stable at 7 the reaction was complete,the product was filtered off and dried at room temperature.

**Characterization of Products:** Melting points were measured by a Gallankamp Melting Point Apparatus. IR Spectra were obtained (KBr discs) on Pue Unicam Spectra 1000.$^1$HNMR Spectra were measured on avarian 400 MHz Spectrometer for solutions in $(CD_3)_2$ SO using $SiMe_4$ as internal standard.Mass Spectra were performed on HP model MS-5988. Microanalyses for C, H and N were performed on Avario Elementry (table 3). Analytical data were obtained from the service laboratory center in NRC.

**Application of Reactive Auxiliaries:** The wool samples were treated with each compound at various concentrations (1, 2, 4, 8 and 16% oww) by an exhaustion process using liquor ratio of 20:1. auxiliary were added and the process was started at 40 °C and run for 20 minutes, during which pH 4 was established, salt ammonium sulphate ( 1% oww). Then the bath was raised to the boil over 30 minutes and held for 60 minutes at 100 ºC. Afterwards, samples were rinsed for 15 minutes and dried at room temperature.

**Table 3:** Characterization data of reactive auxiliaries

| Product code | Elemental composition | | | 1H NMR. (DMSO) | IR(cm-1) |
|---|---|---|---|---|---|
| | C | H | N | | |
| $R_1$ | $[E]^1$ 27.40 | 1.72 | 21.30 | 7.5(m,5H,ArH), 11.2(s,1H,-NH-) | 1180,1557, 3500 |
| | $[F]^2$ | 26.50 | 1.78 | 21.12 | |
| $R_2$ | $[E]^1$ 28.51 | 2.39 | 14.78 | 7.5-7.8(m,3H,ArH), 11.01-11.2 | 1181,1560, 3446 |
| | $[F]^2$ 27.80 | 2.10 | 13.85 | (s, respectively 1H ,-NH-) | |
| $R_3$ | $[E]^1$ 33.42 | 1.72 | 11.99 | 7.5(m,5H,1Ph) , 11.1( s,1H, -NH- ) | 1196,1560, 3445 |
| | $[F]^2$ 32.87 | 1.42 | 11.63 | | |

$[E]^1$: Expected value.
$[F]^2$: Found from elemental analysis.

**Determination of Mass Gain:** Weight gain was determined on the basis of oven dry weight, measured before and after the application of the reactive auxiliaries.

**Dyeing of Wool Fabric:** The resist effectiveness of reactive auxiliaries on wool was evaluated using the three dyes listed in table (2). Dyeing process was carried out in a dye bath containing ammonium sulphate (0.5-2.5% oww), using a liquor ratio of 20:1 at pH (3-8 ),the dye bath temperature (40- 100 ºC ) and dyeing time(20- 90 minutes) and dye conc. (1- 4 %). Afterwards, samples were rinsed for 15 minutes and dried at room temperature.

**Dye Resist Evaluation:** To evaluate dye resist effectiveness, the treated wool samples were dyed in a competition with untreated wool (differential dyeing technique,DD), we quantified the dye resist effectiveness (RE) of the different auxiliaries by calculating RE values from the reflectance values (K/S) of the dye treated and untreated wool samples.K/S values were obtained at the wavelength of maximum dye absorption:

$$\%Resist = \frac{[(K/S_{untreated}) - (K/S_{treated})]}{(K/S_{untreated})} \times 100$$

## RESULTS AND DISCUSSIONS

**Dyeing:**

**Effect of Dye Bath pH:** Figure 2 shows that the pH values of the dye bath have a considerable effect on the dyeability of wool fabrics with dye resist technique, DD process using the auxiliaries $R_1$, $R_2$ and $R_3$ and acid red 27. The effect of the dye bath pH can be attributed to the correlation between auxiliary structure and wool fabric. It can be seen from the results given in fig (2) that the $R_2$ treated wool achieves a higher dye resist at the same pH value than the $R_3$ and $R_1$ treated wool. One might be attempted to deduce that this differences arises because $R_2$ reactive resist

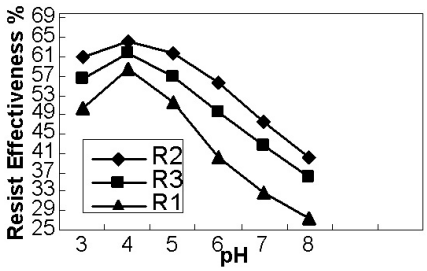



**Fig. 2:** The effect of pH on resist effectiveness of auxiliaries ($R_1$, $R_2$, $R_3$), conditions: temperature100 0 C, time 40 min., dye conc. 3%,conc. of salt 1%and conc. of auxiliaries 4%.

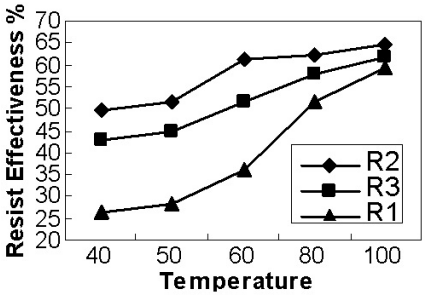



**Fig. 3:** the effect of the temperature on Resist effectiveness of auxiliaries ($R_1$,$R_2$,$R_3$), conditions : pH 4, time 40 min.dye conc. 3% ,conc. of salt 1% and conc. of auxiliaries 4%.

contains two s- triazine reactive moieties which leads to a higher degree of fixation of $R_2$ at pH 4 to the wool fiber. As clearly observed in figure (2) it was noticed from the figure that higher dyeability at pH 4 and then the dyeability decreases as the pH increases.

**Effect of Temperature:** The effect of temperature on the dyeability of wool fabrics with dye resist technique, DD process using the auxiliaries $R_1$, $R_2$ and $R_3$ and acid red 27 was conducted at different temperatures (40-100 ºC). As shown in figure (3), it is clear that the dye resist increases with increasing dyeing temperature for the three used auxiliaries $R_1$,$R_2$,$R_3$ and reaches maximum value at 100 Oc.

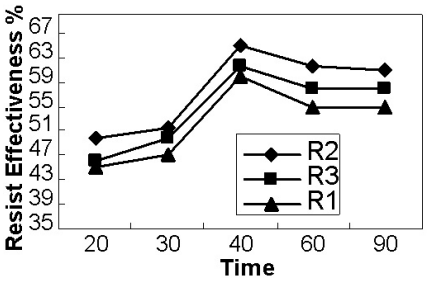



**Fig. 4:** The effect of time on Resist effectiveness of auxiliaries ($R_1$, $R_2$, $R_3$), conditions: pH 4, temperature100 0 C, dye conc. 3 %,conc. of salt 1% and conc. of auxiliaries 4%.

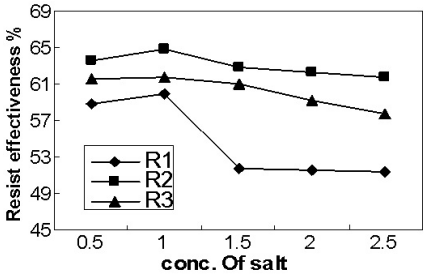



**Fig. 5:** The effect of conc.of salt on Resist effectiveness of auxiliaries ($R_1$, $R_2$, $R_3$), conditions: pH 4, temperature100 0 C, time 40 min.,dye conc. 3 %and conc.of auxiliaries 4%.

**Effect of Dyeing Time:** The effect of time on the dyeability of wool fabrics with dye resist technique, DD process using the auxiliaries $R_1$, $R_2$ and $R_3$ and acid red 27 was conducted at different temperatures (20-90 min.). As shown in fig. (4), it is clear that the dye resist increased as the dyeing time increase up to 40 min, and then it began to decrease.

**Effect of the Salt Conc.:** The effect of conc. of salt on the dyeability of wool fabrics with dye resist technique, DD process using the auxiliaries $R_1$, $R_2$ and $R_3$ and acid red 27 was conducted at different conc. (0.5-2.5% oww). As shown in figure (5), it is clear that the dye resist increases with increasing conc. of salt and reaches maximum value at 1% oww and then it began to decrease.

**Effect of the Dye Bath Conc.:** The effect of the dye bath conc. on the dyeability of wool fabrics with dye resist technique, DD process using the auxiliaries $R_1$, $R_2$ and $R_3$ was conducted at different dye bath conc. (1-4% oww) of acid red 27. As shown in figure (6), it is clear that the dye resist increase with the increasing of dyeing concentration and reaches the maximum value at 3% of dye concentration.

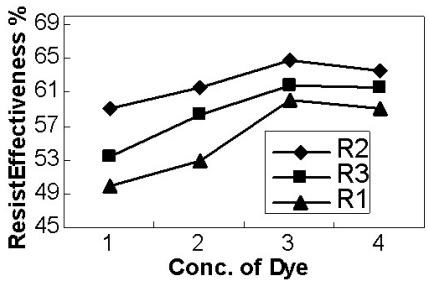



**Fig. 6:** the effect of the conc. of dye on Resist effectiveness of auxiliaries ($R_1$,$R_2$,$R_3$), conditions: pH 4 temperature100 0C, time 40min.,conc. of salt1%and conc. of auxiliaries 4%.

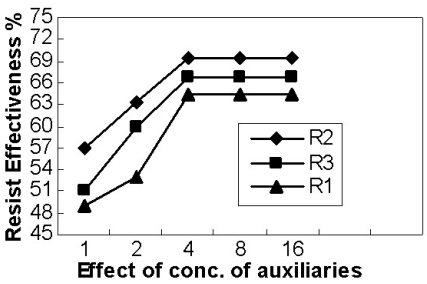



**Fig. 7:** The effects of conc. of auxiliaries on Resist effectiveness of auxiliaries ($R_1$, $R_2$, $R_3$), conditions: pH 4, time 40 min., temperature 100°C,conc. of salt 1% and dye conc.3% of acid red 27.

**Effect of the Conc. of Auxiliaries:** The effect of the conc. of auxiliaries on the dyeability of wool fabrics with dye resist technique, DD process using the auxiliaries $R_1$, $R_2$ and $R_3$ was conducted at different conc. of auxiliaries (1, 2, 4,8 and16%oww). As shown in figure (7), it is clear that the dye resist increases with the increasing of the concentration of auxiliaries and reach the maximum value at (4% oww) of auxiliary concentration.

**DD and DR techniques:** After reaching the optimum conditions for dyeing treated wool using $R_1$, R2, R3, to obtain maximum dye resist effect, we investigated the effectiveness of the auxiliaries using two different dyeing processes at the same conditions. The treated wool was dyed separately (dye resist technique, DR) to estimate the overall dye resist effect. On the other hand treated wool samples were dyed in competition with untreated wool (differential dyeing technique, DD) to estimate the differential dyeing behavior. The three acid dyes listed in table (2) were used.

The obtained results suggest that the dye resist effect achieved with the bifunctional reactive resist ($R_2$) was superior to that achieved by the monofunctional reactive resist ($R_1$).The explanation for this difference might be that there are cross links introduced by the

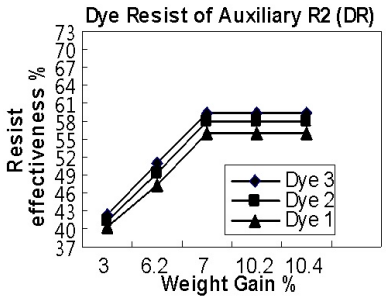
**Table4:** Fastness properties of the dyed wool using the auxiliaries ($R_1$, $R_2$, $R_3$)

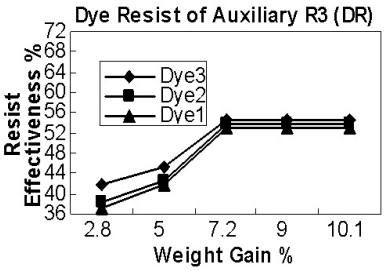
| Dye | Aux | Rubbing Fastness | | Washing fastness | | | perspiration Fastness | | | | | | Light |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Alkaline | | | Acidic | | | |
| | | Dry | Wet | Alt | Sc | Sw | Alt | Sc | Sw | Alt | Sc | Sw | |
| 1 | 0 | 3-4 | 3-4 | 3 | 3-4 | 4 | 3-4 | 3 | 3-4 | 3 | 3-4 | 3 | 6 |
| | $R_1$ | 4 | 3-4 | 3-4 | 3-4 | 4 | 3-4 | 3-4 | 3-4 | 4 | 4 | 4 | 6 |
| | $R_2$ | 4-5 | 4-5 | 5 | 4-5 | 5 | 4-5 | 4-5 | 4-5 | 5 | 5 | 5 | 7-8 |
| | $R_3$ | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4-55 | 4-5 | 4-5 | 6-7 |
| 2 | 0 | 3-4 | 3 | 3-4 | 4 | 4 | 3-4 | 4 | 4 | 3-4 | 3-4 | 4 | 5 |
| | $R_1$ | 4 | 3-4 | 3 | 3-4 | 3-4 | 3-4 | 4 | 3-4 | 3-4 | 3-4 | 4 | 5-6 |
| | $R_2$ | 5 | 4 | 4 | 5 | 4-5 | 5 | 5 | 5 | 4-5 | 4-5 | 5 | 7 |
| | $R_3$ | 4-5 | 4 | 3-4 | 4-5 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4-5 | 6 |
| 3 | 0 | 3-4 | 3-4 | 4 | 3-4 | 4 | 3-4 | 3 | 4 | 4 | 4 | 4 | 6 |
| | $R_1$ | 4 | 3-4 | 4 | 3-4 | 4 | 4 | 3-4 | 4 | 3-4 | 4 | 4 | 6-7 |
| | $R_2$ | 5 | 4-5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 4-5 | 5 | 5 | 8 |
| | $R_3$ | 4 | 4 | 4-5 | 4 | 4-5 | 4-5 | 4 | 4-5 | 4 | 4-5 | 4-5 | 7 |

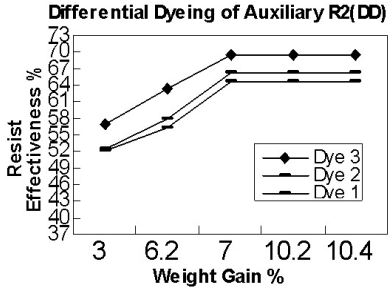
Aux:auxiliaries Alt: alteration

Sc: staining on cotton Sw: staining on wool

0: sample without treatment of auxiliaries



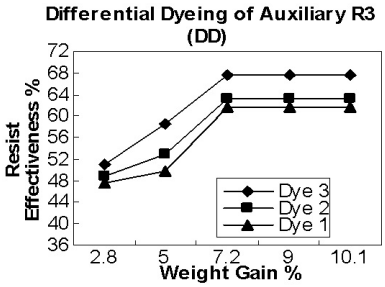




**Fig. 8 a,b:** Resist effectiveness of $R_2$ versus auxiliary uptake of the fibers

**Fig. 9a,b:** Resist effectiveness of $R_3$ versus auxiliary uptake of the fibers.

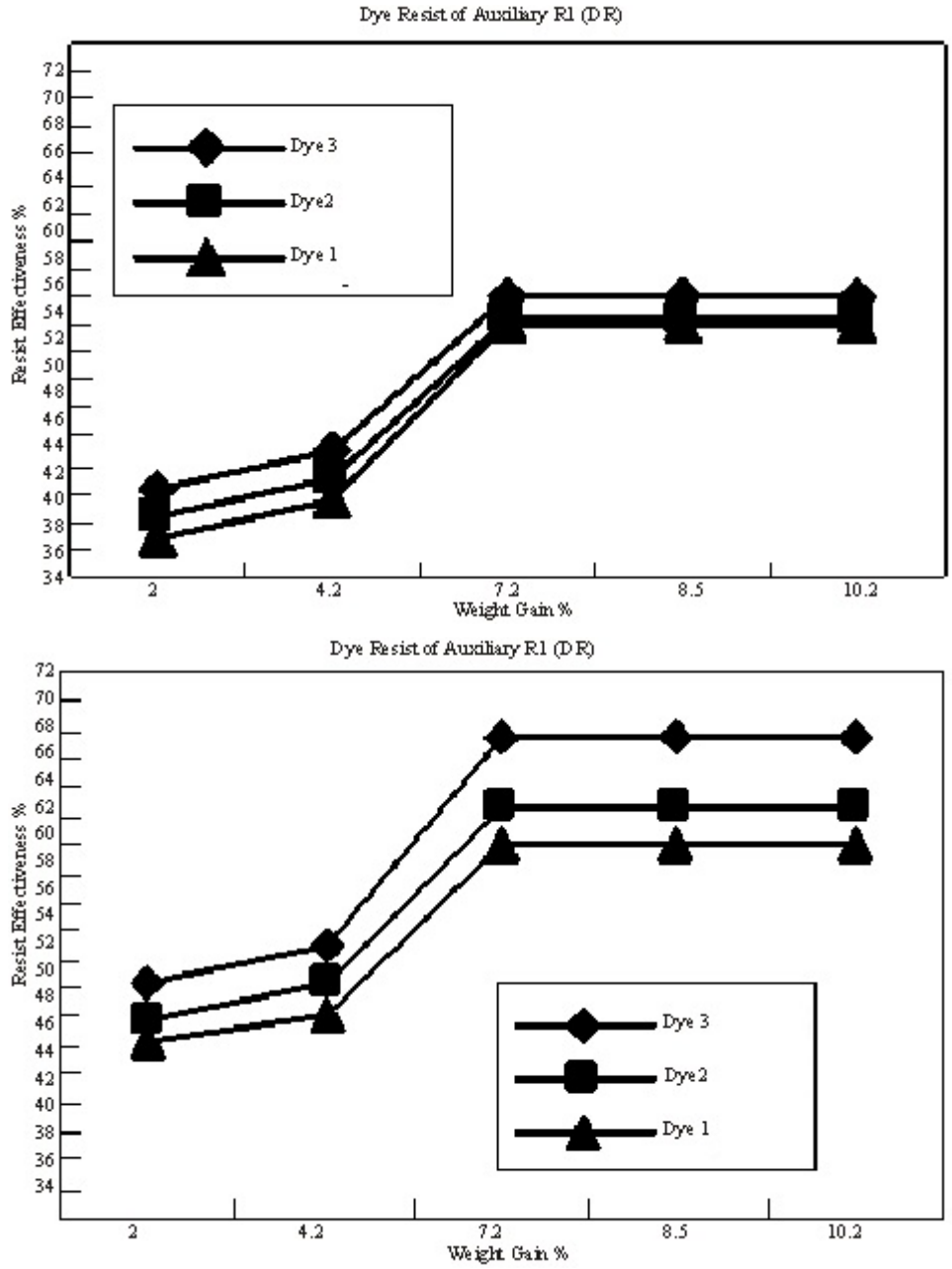



**Fig. 10a,b:** Resist effectiveness of $R_1$ versus auxiliary uptake of the fibres

bifunctional groups of ($R_2$),increasing the substantivity between the substrate and the dye resist agents which is one of the important factors needed to improve dye resist effects[15,16]. Figures (8, 9,10) show the resist effectiveness of the three auxiliaries used, depending on the amount of auxiliary fixed to the fibers. At low auxiliary uptake, the three compounds differ greatly from each other. At equal weight gain, $R_2$ shows a better resist effect than $R_3$,and $R_3$ in turn have better resist effect than $R_1$. Above an uptake of 7.2%, the resist effectiveness of the auxiliaries tends toward a limiting resist value for the three dyes used.

It must be concluded that other factors such as molecular configuration, in addition to ionic/ hydrophobic mechanism, could affect the achieved weight gains, since the inductive effect of the electron withdrawing nitrogen on the s- triazines activates the reactive centers on the carbon atoms of s-triazines more than those of other heterocycles. Morever, the electro negativity of the leaving groups adjacent to the

reactive centers also partly contributes to the increased reactivity of the reactive centers. Also molecular structures of the dyes used have an effect on the dye resist values obtained. Acid red 27 gives higher values of dye resist that is because this dye contains three sulphonic acid groups, thus strong electrostatic forces are built up between treated fibers and dye, which leads to an efficient electrostatic repulsion of the dye molecules. The dye is not absorbed quite readily and is not able to penetrate into the fibers [17].

It can be seen from the results given in fig (8, 9, 10) that the $R_2$ treated wool achieves a higher weight gain than the $R_1$ treated wool. One might be attempted to deduce that this differences arises because $R_2$ reactive resist contains two s- triazine reactive moieties which leads to a higher degree of fixation of $R_2$ to the wool fiber.

**Fastness Properties:** Fastness properties of the dyed fabrics are shown in table 4.The results indicated that treated wool with the three auxiliaries $R_1$,$R_2$,$R_3$ using the three acid dyes give good to very good results for rubbing,perspiration, light and washing fastness. $R_2$ shows better fastness properties than $R_1$and $R_3$ with the three acid dyes.

**Conclusion:** Three reactive auxiliaries containing s-triazine-based reactive groups were synthesized and the dye resist effects achieved on wool were evaluated using two different techniques DR, DD.

The obtained results suggested that the dye resist effect achieved with the bifunctional reactive resist was superior to that achieved by the monofunctional reactive resist and the DD technique gives better dye resist effect than DR one. Good fastness properties of the dyed fabric were achieved.

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