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Concurrent Dyeing and Finishing: V. One-bath Dyeing and Easy-care Finishing of Cotton Fabrics with Acid Dyestuffs and *N*-Methylol Compounds Using Different Catalytic Systems

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SUMMARY

A number of catalysts have been used for effecting concurrent dyeing and easy-care finishing of cotton fabric with acid dyes and N-methylol finishing agents. Factors affecting the process, such as the nature and concentration of catalyst, the finishing agent, the additive and the dye as well as curing temperature, were investigated. Evaluation of the simultaneously dyed and finished fabric was made with respect to colour strength, wrinkle recovery and fastness properties. The results obtained indicate that, of the eleven catalysts used, ammonium persulphate is the best for effecting concurrent dyeing and finishing of cotton fabric using acid dye and dimethyloldihydroxyethylene urea (DMDHEU).

INTRODUCTION

Numerous reports from this division[1–13] as well as from other laboratories[14–21] have discussed the feasibility of concurrent dyeing and easy-care finishing of cotton-containing fabrics, but less information[22–27] is available on the simultaneous dyeing and finishing of cotton fabrics with acid dyes and *N*-methylol crosslinking agents.

Bearing this in mind, an approach was attempted in the present work to establish a single-step process for dyeing and easy-care finishing of cotton

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fabrics with acid dyes and *N*-methylol compounds under various conditions to attain optimization as well as to evaluate the process.

EXPERIMENTAL

Fabric

Mill-scoured and bleached plain weave (23 picks × 23 ends/cm) cotton fabric (poplin, Kafr El-Dawar, Alexandria) was used.

Reagents

Ammonium persulphate ($(NH_4)_2S_2O_8$), potassium persulphate ($K_2S_2O_8$), sodium persulphate ($Na_2S_2O_8$), potassium pyrosulphate ($K_2S_2O_5$), sodium thiosulphate ($Na_2S_2O_3 . 5H_2O$), thiourea ($H_2N . CS . NH_2$), glucose, ammonium chloride (NH_4Cl), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), magnesium chloride hexahydrate ($MgCl_2 . 6H_2O$), ammonium sulphate ($(NH_4)_2SO_4$), acrylamide and urea were of reagent grade.

The finishing agents used were Arkofix NG and Cassurit HML, which are based on dimethyloldihydroxyethylene urea (DMDHEU) and highly etherified methylolmelamine respectively. These finishing agents, with about 50% solid content, were supplied by Farbwerke Hoechst, West Germany. Non-ionic wetting agent (Sunaptol DB) was supplied by Francolor, France.

Acid dyes Kiton Scarlet 4R, Polar Red RS, and Tectilon Red 2B KWL were supplied by Ciba–Geigy.

Combined dyeing and finishing

Unless otherwise indicated, the combined dyeing and finishing process involved padding the fabric twice in a solution containing the acid dye (7·5 g/litre), finishing agent (100 g/litre), $(NH_4)_2S_2O_8$ (0·025 mol/litre) and non-ionic wetting agent (2 g/litre). After being dried at 80 °C for 5 min, the fabric was cured at 160 °C for 3 min, washed thoroughly, soaped, rinsed and finally dried.

Testing

The treated fabric samples were evaluated for colour strength, expressed as K/S (where K is the absorption coefficient and S is the scattering coefficient). The latter was calculated from the reflectance measurements using Hunter Lab Colorimeter Model D25-M-2 and the Kubelka–Munk equation.[28]

Dry wrinkle recovery angles were measured using the crease recovery apparatus, type FF-07 Metrimpex.

Evaluation of washing, rubbing and perspiration fastness properties were performed according to methods described elsewhere.[29]

RESULTS AND DISCUSSION

Effect of using different redox catalysts

Table 1 shows the effect of the nature and concentration of the redox catalyst on the colour strength, expressed as K/S, and the dry wrinkle recovery of the simultaneously dyed and finished cotton fabrics. It is seen that increasing the concentration of the redox catalyst, containing equal amounts of oxidant and reductant, from 0 to 0·025 mol/litre, is accompanied by a significant increase in the colour strength. This is observed regardless of the kind of redox catalyst used. The enhancement in colour strength could be attributed to one or more of the following factors: (a) dye fixation through chemical reaction with the finishing agent during the curing step; (b) physical entrapment by the resin in the accessible regions;[22,27] and (c) through an interaction between free radicals supposed to be formed in both the fibre and the dye in the presence of free-radical generating species, i.e. redox catalysts.[30] With respect to the redox catalyst, the colour strength follows the order:

$$(NH_4)_2S_2O_8/K_2S_2O_5 \geq (NH_4)_2S_2O_8/\text{ thiourea} > (NH_4)_2S_2O_8/\text{glucose} > (NH_4)_2S_2O_8/Na_2S_2O_3$$

The same holds true for dry wrinkle recovery; increasing the redox catalyst concentration is accompanied by a substantial enhancement in the wrinkle recovery angles, irrespective of the catalyst used. This is a direct consequence of increasing the extent of crosslinking. Further increase in concentration of redox catalyst, i.e. beyond 0·02 mol/litre,

TABLE 1

Effect of Nature and Concentration of Redox Catalyst

[DMDHEU (100 g/litre); redox catalyst (0·00 to 0·025 mol/litre each), Kiton Scarlet 4R (7·5 g/litre), non-ionic wetting agent (2 g/litre), drying at 80°C for 5 min, curing at 160°C for 3 min.]

Redox catalyst concentration	$(NH_4)_2S_2O_8/K_2S_2O_5$		$(NH_4)_2S_2O_8/Na_2S_2O_3$		$(NH_4)_2S_2O_8$/*glucose*		$(NH_4)_2S_2O_8$/*thiourea*	
	Colour strength K/S	*DWRA*[a] *(W + F) (deg.)*	*Colour strength K/S*	*DWRA (W + F) (deg.)*	*Colour strength K/S*	*DWRA (W + F) (deg.)*	*Colour strength K/S*	*DWRA*[a] *(W + F) (deg.)*
0·000	0·060	140	0·060	140	0·060	140	0·060	140
0·010	0·440	194	0·098	152	0·348	190	0·166	196
0·015	1·565	245	0·412	192	1·125	222	1·530	228
0·020	2·340	270	1·542	212	2·100	249	2·303	256
0 025	2·590	276	1·713	225	2·320	258	2·502	265

[a] DWRA, dry wrinkle recovery angle of the warp (W) and weft (F) directions.

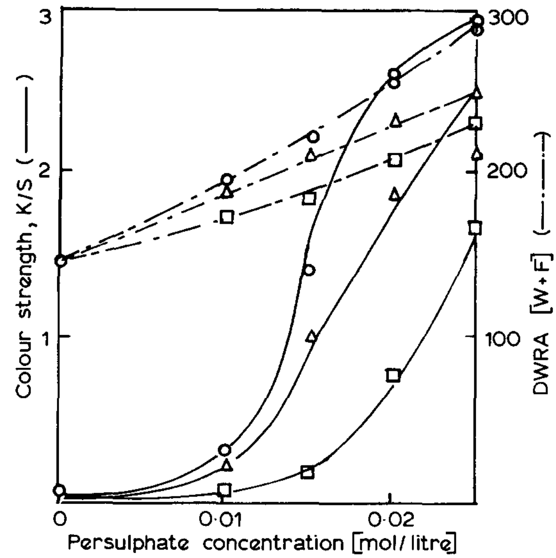

Fig. 1. Effect of persulphate concentration on the colour strength (*K/S*) and dry wrinkle recovery angle (DWRA) of simultaneously dyed and finished cotton fabric. ○, $(NH_4)_2S_2O_8$; △, $K_2S_2O_8$; □, $Na_2S_2O_8$.

causes no significant changes in the wrinkle recovery angles of the simultaneously dyed and finished cotton fabrics.

Effect of using different persulphate catalysts

Figure 1 illustrates the effect of $(NH_4)_2S_2O_8$, $K_2S_2O_8$ and $Na_2S_2O_8$ when independently used at different concentrations from 0 to 0·025 mol/litre, together with DMDHEU (100 g/litre), Kiton Scarlet 4R (7·5 g/litre) and a non-ionic wetting agent (2 g/litre) in the dyeing–finishing bath on the colour strength and dry wrinkle recovery of the simultaneously dyed and finished cotton fabrics. It is seen that increasing the concentration of persulphate salt causes considerable increase in colour strength as well as in wrinkle recovery angles. On the other hand, a comparison between the maximum colour strengths and wrinkle recovery angles obtained with the three persulphate salts indicates the following order of efficiency:

$$(NH_4)_2S_2O_8 > K_2S_2O_8 > Na_2S_2O_8$$

This order signifies differences between these catalysts in rate of dissociation and/or decomposition as well as in the initial pH of the dyeing–finishing bath.

Comparison of different catalysts

A number of conventional catalysts were used to assess in particular the efficiency of the persulphate catalysts in inducing reaction of the acid dye with cotton cellulose in presence of DMDHEU. Catalysts included: NH_4Cl, $NH_4H_2PO_4$, $(NH_4)_2SO_4$ and $MgCl_2 . 6H_2O$ in comparison with $(NH_4)_2S_2O_8/K_2S_2O_5$ and $(NH_4)_2S_2O_8$. The results obtained together with the conditions employed are given in Table 2.

It is clear that the colour strength varies significantly when using different catalytic systems. For a given set of conditions, the colour strength follows the order:

$$(NH_4)_2S_2O_8 > NH_4H_2PO_4 \geq MgCl_2 . 6H_2O > (NH_4)_2S_2O_8/K_2S_2O_5 > (NH_4)_2SO_4 > NH_4Cl > \text{Blank (without catalyst)}$$

Table 2 further indicates that the dry wrinkle recovery of the simultaneously dyed and finished cotton fabric follows the order:

$$(NH_4)_2S_2O_8 > (NH_4)_2S_2O_8/K_2S_2O_5 \geq MgCl_2 . 6H_2O \geq (NH_4)_2SO_4 > NH_4Cl > NH_4H_2PO_4 > \text{Blank (without catalyst)}$$

Thus, the type and nature of catalyst must affect reaction between

TABLE 2
Comparison of the Effect of Different Catalysts
[DMDHEU (100 g/litre), Kiton Scarlet 4R (7·5 g/litre), non-ionic wetting agent (2 g/litre), drying at 80 °C for 5 min.]

Catalyst	*Curing conditions (°C/min)*	*Colour strength K/S*	*DWRA*[a] *(W + F) (deg.)*
$(NH_4)_2S_2O_8/K_2S_2O_5$, 0·025 mol/litre	160/3	2·59	276
$(NH_4)_2S_2O_8$, 0·025 mol/litre	160/3	2·99	287
NH_4Cl, 5 g/litre	140/5	2·04	258
$NH_4H_2PO_4$, 5 g/litre	140/5	2·85	245
$(NH_4)_2SO_4$, 5 g/litre	140/5	2·22	270
$MgCl_2 . 6H_2O$, 12 g/litre	160/3	2·81	273
Blank	—	0·06	140

[a] DWRA, dry wrinkle recovery angle.

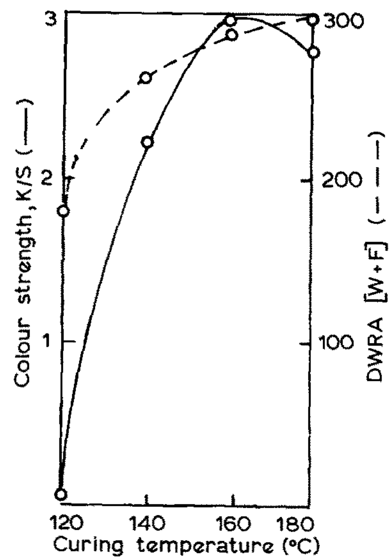

Fig. 2. Effect of curing temperature on the colour strength (K/S) and dry wrinkle recovery angle (DWRA) of simultaneously dyed and finished cotton fabric. DMDHEU (100 g/litre), $(NH_4)_2S_2O_8$ (0·025 mol/litre), dye (7·5 g/litre), non-ionic wetting agent (2 g/litre), drying at 80 °C for 5 min and curing at 160 °C for 3 min.

DMDHEU and the cellulose hydroxyl groups as well as interaction with the acid dye.

Effect of curing temperature

It has been shown above that of the six catalysts used, $(NH_4)_2S_2O_8$ is the best for effecting concurrent dyeing and finishing of cotton fabric. It appears, therefore, of interest to investigate the effect of cure temperature on both the colour strength and dry wrinkle recovery angle using 0·025 mol $(NH_4)_2S_2O_8$/litre as catalyst (Fig. 2). Evidently, raising the curing temperature from 120 to 160 °C brings about significant enhancement in colour strength as well as in wrinkle recovery angle. This could be associated with the favourable effect of temperature on the decomposition of $(NH_4)_2S_2O_8$, and with the extent of crosslinking reaction of *N*-methylol groups of DMDHEU with cellulose hydroxyl groups, as well as with interaction with the dye molecules. Above 160 °C, the effect of curing temperature is to bring about substantial decrease in colour strength without necessarily causing significant improvement in dry wrinkle recovery of the simultaneously dyed and finished cotton fabric.

Effect of type and concentration of *N*-methylol finishing agent

Two *N*-methylol finishing agents in common use were examined to find the most suitable combination for concurrent dyeing and easy-care finishing of cotton fabric. These finishing agents are Arkofix NG (DMDHEU) and Cassurit HML (highly etherified methylolmelamine). The dyeing–finishing treatment was carried out using $(NH_4)_2S_2O_8$ catalyst under conditions specified in Table 3. It shows the effect of complete and partial replacement of Cassurit HML by Arkofix NG on the colour strength and dry wrinkle recovery of cotton fabric. Evidently the nature of the finishing agent exerts a considerable influence on the colour strength as well as on the wrinkle recovery angle. Within the range studied, pure Arkofix NG represents the best finishing agent, whilst pure Cassurit HML is the worst.

Using mixtures of Arkofix NG/Cassurit HML at different ratios brings about finished products with intermediate colour strengths and wrinkle recovery angles, but both the colour strength and wrinkle recovery angle are higher, the higher the proportions of Arkofix NG in the mixtures. This indicates that Arkofix NG is much better than Cassurit HML in the concurrent dyeing and finishing of cotton fabric.

TABLE 3

Effect of Type and Concentration of *N*-Methylol Finishing Agent [$(NH_4)_2S_2O_8$ (0·025 mol/litre), non-ionic wetting agent (2 g/litre), dye (7·5 g/litre) drying at 80 °C for 5 min, curing at 160 °C for 3 min.]

Finishing agent concentration (g/litre)		*Colour strength K/S*	*DWRA*[a] *(W + F) (deg.)*
Arkofix NG	*Cassurit HML*		
100	0	2·99	287
75	25	2·65	280
50	50	2·42	271
25	75	2·30	266
0	100	2·14	256
0	0	0·121	140

[a] DWRA, dry wrinkle recovery angle.

Differences in the properties of simultaneously dyed and finished cotton fabric samples treated with the *N*-methylol finishing agents under investigation could be associated with differences in (a) reactivity of the finishing agent, (b) molecular size and structure of the finishing agent, (c) amount of finishing agent polymerized within the fibre, i.e. self-condensed, rather than reacted with cellulose via crosslinking, (d) length of crosslinks,[31] and (e) compatibility of the finishing agent with the padding bath ingredients as well as its ability to react with the dye.

Effect of additives

Table 4 shows the effect of acrylamide and urea, when independently used at different concentrations (0–30 g/litre) in the dyeing–finishing bath, on the colour strength and dry wrinkle recovery of the simultaneously dyed and finished cotton fabrics. It is clear that increasing acrylamide concentration in the padding bath is accompanied by an increase in colour strength within the range studied. The opposite holds true in the case of addition of urea. This suggests that the presence of acrylamide renders the dye more soluble, gives a more open fibre structure which enables dye molecules to enter more easily and provides dyeing sites for ionic dyes.[32]

Table 4 also shows the effect of different additives on the dry wrinkle recovery of the simultaneously dyed and finished cotton fabric. Evidently, increasing acrylamide or urea concentration from 0 to 30 g/litre is accompanied by a decrease in the dry wrinkle recovery angles. This

TABLE 4

Effect of Adding Acrylamide and Urea Independently to the Dyeing–Finishing Bath [DMDHEU (100 g/litre), $(NH_4)_2S_2O_8$ (0·025 mol/litre), Kiton Scarlet 4R (7·5 g/litre), non-ionic wetting agent (2 g/litre), drying at 80 °C for 5 min, curing at 160 °C for 3 min.]

Additive concentration (g/litre)	*Acrylamide*		*Urea*	
	Colour strength K/S	*DWRA (W + F) (deg.)*	*Colour strength K/S*	*DWRA (W + F) (deg.)*
00	2·99	287	2·99	287
10	3·06	274	2·88	281
20	3·14	266	2·70	271
30	3·22	259	2·55	262

TABLE 5
Effect of Dye Nature
[DMDHEU (100 g/litre), dye (10 g/litre), $(NH_4)_2S_2O_8$ (0·025 mol/litre), non-ionic wetting agent (2 g/litre), drying at 80 °C for 5 min, curing at 160 °C for 3 min.]

Dyestuff	*DWRA (W + F) (deg.)*	*Colour strength K/S*		*Rubbing*		*Washing*[a]		*Perspiration*[a]			
								Acidic		*Alkaline*	
		After soaping	*After DMF*	*Dry*	*Wet*	*C*	*S*	*C*	*S*	*C*	*S*
Kiton Scarlet 4R (C.I. 16255)	292	3·43	1·44	3	2–3	3–4	3	2	2	2	2
Polar Red RS (C.I. 23635)	296	1·22	0·33	3	2	2	3	4	3	3–4	2
Tectilon Red 2B KWL	285	0·49	0·30	2–3	2	4	4	4	4	3–4	4

[a] C, colour change; S, cotton stain.

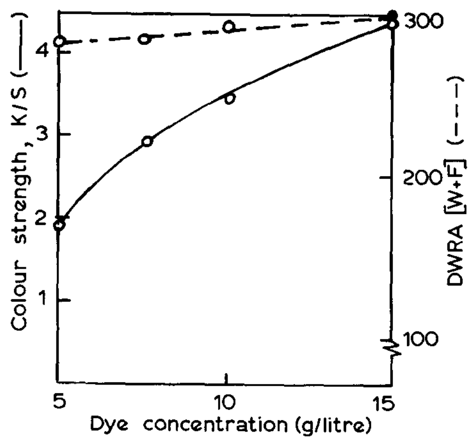

Fig. 3. Effect of dye concentration on the colour strength (K/S) and dry wrinkle recovery angle (DWRA) of simultaneously dyed and finished cotton fabric. DMDHEU (100 g/litre), $(NH_4)_2S_2O_8$ (0·025 mol/litre), dye (5–15 g/litre), non-ionic wetting agent (2 g/litre), drying at 80 °C for 5 min, and curing at 160 °C for 3 min.

reflects the buffering effect of both acrylamide and urea on the ammonium persulphate catalyst.

Effect of dye concentration

Figure 3 shows that the colour strength of the simultaneously dyed and finished cotton fabrics is increased by increasing the dye concentration from 5 to 15 g/litre. On the other hand, increasing the dye concentration is accompanied by a substantial increase in the dry wrinkle recovery angle from 280 to 300°.

Nature of the dye

The ability of $(NH_4)_2S_2O_8$ to catalyze concurrent dyeing and finishing of cotton fabrics with various acid dyestuffs and the fastness properties of the dyeings are shown in Table 5. $(NH_4)_2S_2O_8$ is an adequate catalyst for effecting dyeing and finishing of cotton fabrics, as evidenced by the colour strength, expressed as K/S, and improved wrinkle recovery. The colour strength of the simultaneously dyed and finished cotton fabric after extracting with DMF is due to chemical linkage between cotton cellulose and dyestuff via the pendant methylol groups of the finishing agent in addition to the dyestuff entrapped inside the crosslinked network that cannot be extracted with DMF.[27,28] On the other hand, the data indicate that the nature of dye, i.e. its molecular size, configuration, substituents, etc., does influence the colour strength as well as fastness properties of the simultaneously dyed and finished cotton fabric. It is also seen that there are no significant differences in dry wrinkle recovery of the simultaneously dyed and finished fabrics upon using these acid dyes.

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