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## **A Novel Method for the Crease-Resist Finishing and Dyeing of Cotton Fabrics using Phenolic-Formaldehyde Resins and Diazonium Salts**

**Part I: A Preliminary Investigation**

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# A NOVEL METHOD FOR THE CREASE-RESIST FINISHING AND DYEING OF COTTON FABRICS USING PHENOLIC-FORMALDEHYDE RESINS AND DIAZONIUM SALTS

## PART I : A PRELIMINARY INVESTIGATION

BY R.E. HORN

### ABSTRACT

*A method is described by which cotton fabric is treated with phenolic-formaldehyde resins and then dyed by immersion in solutions of stabilised diazonium salts which couple to the resins. The treated fabrics have satisfactory crease-resist and tensile properties together with a good handle. The colours vary from yellow to red and the fabrics have excellent properties of fastness to washing and dry rubbing.*

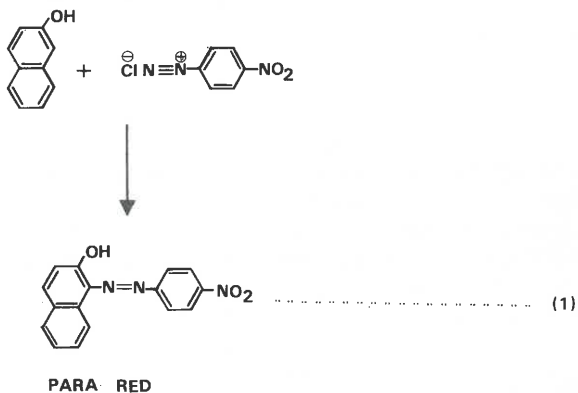
### INTRODUCTION

In 1918 Marsh and his co-workers at Tootal Broadhurst Lee embarked on a study "to give vegetable fibres those properties of resilience and crease recovery naturally possessed by animal fibres"<sup>1</sup>. They studied many substances and eventually found that *phenolic-formaldehyde* and *urea-formaldehyde* resins gave useful results. Because urea-formaldehyde could be readily hydrolysed with alkali and hence by washing, much of their early work was concerned with the former type. In 1928 patents<sup>2,3,4</sup> were granted and in 1930, crease-resist textiles, using phenol-formaldehyde, were produced on a commercial scale in Italy and France. Unfortunately the great disadvantage of using phenolic-formaldehyde resins was found to be that they were discoloured, and this discolouration intensified under the influence of light. Although much effort was made to overcome this difficulty the problem was not solved.

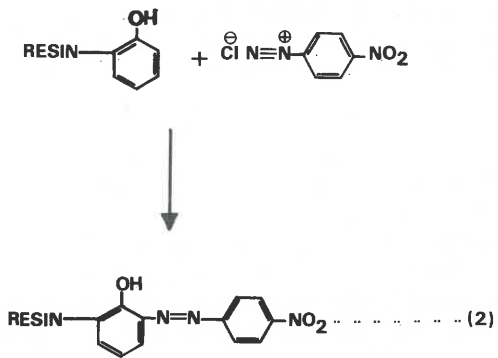
Emphasis was then shifted to amino-aldehyde resins and with great success. In 1932 the TBL crease-resist process was announced and by 1939, to quote Marsh<sup>1</sup> "the process was practised by hundreds of firms in no fewer than 19 countries." During the post-war years a large number of new colourless resins, most with superior properties to urea-formaldehyde, were developed<sup>8,9</sup> and some, such as DMDHEU (dimethylol-4, 5-dihydroxyethylene urea), became widely applied. Nevertheless urea-formaldehyde is still used extensively today and Smith<sup>6</sup> recently roughly estimated that "the distribution of products for creaseproof and related finishes in the U.K. would be urea-formaldehyde 55 per cent, melamine formaldehyde 10 per cent, DMDHEU 30 per cent and other products 5 per cent". It is little wonder, therefore, that with the search for good

colourless resins the use of the discoloured phenolic-formaldehydes for crease-resist finishing should be almost forgotten. In fact the only fairly recent investigation undertaken was in 1959 by Chance, Perkerson and McMillan<sup>7</sup> who were interested in using a phenolic-formaldehyde as a crease-resist and rot-proofing agent.

It seemed reasonable, however, to consider whether a phenolic-formaldehyde resin could be used in other ways; *firstly* to impart a crease-resist finish to cotton and then *secondly* to colour the fabric by acting as a *coupling component for a diazonium salt*. In this manner the colour of the resin could be changed to a more attractive colour, depending on the type of phenol or diazonium salt used. To explain the principle more simply the formation inside the cotton fibre of Para Red, an insoluble azo pigment, will serve as an example. The fabric is soaked first in an alkaline solution of  $\beta$ -naphthol, dried and then immersed in a solution containing *p*-nitrobenzenediazonium chloride. The red azo dye is formed according to equation (1).



By substituting a phenol-formaldehyde resin for  $\beta$ -naphthol, equation (1) now becomes



Thus, by first applying a phenolic-formaldehyde resin to a cotton fabric (using the usual pad-dry-cure method) and then immersing the treated fabric in a solution containing a diazonium salt, an attractively coloured, crease-resistant fabric should be obtained. By varying the type of phenol or diazonium salt used a useful range of colours could be developed.

The object of this investigation, therefore, was to prepare a number of different phenolic-formaldehyde resins and apply them to cotton fabric. A series of diazonium salts were then coupled to the resins and the properties of the resulting crease-resist finished and dyed fabrics were assessed.

## EXPERIMENTAL

A plain weave, bleached, all-cotton poplin fabric of the following specifications was used throughout this study: The fabric density was 131 g/m<sup>2</sup> with a sett of 33,5 ends and 22,8 picks per cm. The yarn linear densities were warp 17,7 tex Z879 and weft 24,5 tex Z859. Samples of fabric 30 cm x 30 cm were used for each treatment.

The phenolic-formaldehyde resins were prepared by the following methods:

### *m*-Cresol-formaldehyde

*m*-Cresol (27 g, 0,25 mole), 40 per cent formaldehyde solution (20 g, 0,25 mole) and 20 per cent NaOH solution (4 g) were charged to a flask and diluted to 60 g with water. The flask was sealed and after standing at room temperature for 16 h, ethanol (8 g) was added and the whole made up to 100 g with water.

### Phenol-formaldehyde

Phenol (25 g, 0,27 mole), 40 per cent formaldehyde solution (22 g, 0,27 mole) and 20 per cent NaOH solution (4 g) were boiled, under reflux, for 15 min. The solution was allowed to cool to room temperature after which it was diluted to 90 g with water.

### *o*-Chlorophenol-formaldehyde

*o*-Chlorophenol (40 g, 0,31 mole), 40 per cent formaldehyde solution (100 g, 1,23 mole) and 20 per cent NaOH solution (5,6 g) were boiled under reflux for 15 min, then rapidly cooled to room temperature.

Each of the prepared solutions was padded (3 dips, 3 nips) at 100 per cent expression, onto samples of cotton fabric by means of a Benz pad mangle, dried

for 3 min at 100°C and cured for 5 min at 150°C. The samples were then soaped at the boil for 30 min in a solution containing 0,2 *per cent* ®Ultravon HD and 0,2 *per cent* Na<sub>2</sub>CO<sub>3</sub>, after which they were rinsed and dried.

The fabrics next were immersed for 30 sec in an alkaline bath (A) at room temperature, passed through a pair of squeeze rollers and into a diazo bath (B) also at room temperature. After a storage time of 1 min the samples were passed through a final pair of squeeze rollers and soaped for 10 min at 60°C in a solution containing 0,2 *per cent* ®Ultravon HD and 0,2 *per cent* Na<sub>2</sub>CO<sub>3</sub>. The compositions of the two baths are set out below:

BATH A:	3 <i>per cent</i>	}	NaOH
	or 1 <i>per cent</i>		
	or 0,5 <i>per cent</i>		
	0,2 <i>per cent</i> :		®Nonidet P40
BATH B:	0,6 <i>per cent</i> :		C.I. Azoic Diazo Component (Fast Salt)
	1 <i>per cent</i> :		Glacial Acetic Acid
	0,2 <i>per cent</i> :		®Nonidet P40

The C.I. Azoic Diazo Components used were stabilised diazo compounds (Fast Salts). After the soaping the fabrics were rinsed in cold water and dried.

For the purpose of comparison a length of cotton fabric (160 g) was dyed on a small laboratory winch with 2 *per cent* C.I. Reactive Orange 4. The liquor-to-goods ratio was 60:1 and dyeing was commenced at 30°C. After 10 min. NaCl (250 g) was added over 10 min followed by Na<sub>2</sub>CO<sub>3</sub> (20 g in 100 ml water) after a further 30 min. The fabric was run for 60 min, at 30°C, and then rinsed clear.

Samples (30 cm x 30 cm) of the cotton fabrics dyed with C.I. Reactive Orange 4 were treated with the crease-resist resins shown in Table I. Each solution of resin was padded (3 dips, 3 nips) at 100 *per cent* expression, onto the fabric by means of a Benz pad mangle. The samples were then dried at 100°C for 3 min, cured at the temperature shown, and finally soaped at the boil for 15 min in a solution of 0,2 *per cent* ®Ultravon HD and 0,2 *per cent* Na<sub>2</sub>CO<sub>3</sub>.

**TABLE I**  
**CREASE-RESIST RESINS APPLIED TO SAMPLES OF DYED COTTON FABRIC**

Crease-Resist Resin	Commercial Name	% Resin (omf)	% <sup>Ⓜ</sup> Matexil WA-PP (omf)	% Catalyst (omf)	Cure Time (min)	Cure Temp. (°C)
Urea-Formaldehyde	ⓂKnittex ASL	9	0,5	2% TEA-HCl 0,3% NH <sub>4</sub> NO <sub>3</sub>	5	150
Melamine-Formaldehyde	ⓂAerotex M3	10	0,5	2% TEA-HCl 0,3% NH <sub>4</sub> NO <sub>3</sub>	5	150
Dimethylol-4, 5-dihydroxyethylene urea (DMDHEU)	ⓂFixapret CP	10	0,5	2% TEA-HCl 0,3% NH <sub>4</sub> NO <sub>3</sub>	5	160

TEA-HCl = Triethanolamine.HCl;

ⓂMatexil WA-PP = Wetting agent;

omf = on mass of fabric.

All treated fabrics were then subjected to the following tests:

### **Test Methods:**

The crease recovery angle of the fabrics was measured, at 65% RH and 20°C, on a Monsanto Wrinkle Recovery Tester. The flexural rigidity was determined by the cantilever method. The tear strength was measured on an Elmendorf Tear Strength Tester and the bursting strength on a Mullen Tester. The resistance of the fabrics to flex abrasion was determined on a Stoll Abrasion Tester.

In addition to the physical properties the colour of each of the phenolic-formaldehyde resin-treated fabrics was measured on a Harrison-Shirley Digital Colorimeter. From the tristimulus values, XYZ, the dominant wavelength ( $\lambda_D$ ) and excitation purity ( $P_e$ ) were calculated.

The fastness of the dyeings to washing (ISO 4), dry rubbing (ISO/R105-1959E) and light (ISO 105/VII - 1972E Pt 4, using a Xenotester 450), were also determined.

Finally, the durability of the treatments to domestic laundering was evaluated by washing the fabrics at 60°C in an automatic washing machine, using @LSD64 as detergent, for up to 15 washing cycles. Between each 30 min wash cycle the fabrics were tumble-dried for 30 min at 60°C.

## **RESULTS AND DISCUSSION**

### **Physical Properties:**

During some preliminary experiments it was found that in order to couple certain diazonium salts to the resins high concentrations of NaOH in bath A were required. C.I. Azoic Diazo Component 36, for example, could not be coupled to the resin unless 3 per cent NaOH in bath A was used, while for C.I. Azoic Diazo Component 3, 0,5 per cent was sufficient. As a consequence it was felt that this variation in NaOH concentration might have a variable hydrolysing effect on the resin and hence affect the properties of the treated cottons. This was studied by applying to *m*-cresol-, phenol- and *o*-chlorophenol-, formaldehyde resin treated samples C.I. Azoic Diazo Component 36 at 3 per cent NaOH in bath A, C.I. Azoic Diazo Component 4 at 1 per cent NaOH in bath A and C.I. Azoic Diazo Component 3 at 0,5 per cent NaOH in bath A. Some physical properties of the fabrics were then determined and the results obtained are shown in Table II. These results were subjected to a statistical analysis of variance and it was found that the concentration of NaOH in bath A had had no significant effect on any of the physical properties. The mean value for each physical property of each resin-treated sample, irrespective of diazo component



TABLE II

PHYSICAL PROPERTIES OF PHENOLIC RESIN-TREATED COTTON SAMPLES

Fast Salt	Resin	% Add-on (omf)	Monsanto Crease Recovery Angle (W+F)°	Bursting Strength $\frac{\text{kg}}{\text{cm}^2}$	Tear Strength (Mean W+F) N	Bending Length cm	Stoll Flex Abrasion (Mean W+F) cycles to rupture
Untreated	—	0	167	696	7,8	1,91	1030
C.I. Azoic Diazo Component 36 (Bath A, 3% NaOH)	<i>m</i> -Cresol Phenol	15,6	252	593	6,9	1,94	156
	<i>o</i> -Chloro-phenol	16,6	240	618	7,5	1,76	220
		10,8	225	667	8,0	1,78	219
C.I. Azoic Diazo Component 4 (Bath A, 1% NaOH)	<i>m</i> -Cresol Phenol	15,7	251	618	6,7	1,81	191
	<i>o</i> -Chloro-phenol	16,4	243	618	7,5	1,83	261
		10,9	226	652	8,5	1,74	203
C.I. Azoic Diazo Component 3 (Bath A, 0,5% NaOH)	<i>m</i> -Cresol Phenol	15,8	254	599	6,5	1,84	156
	<i>o</i> -Chloro-phenol	16,6	236	616	7,1	1,84	177
		10,7	224	647	8,1	1,75	250

used, was therefore calculated and the results are presented in Table III together with, for the purpose of comparison, the properties of samples dyed and resin-finished with commercially available products.

It can be seen that the highest crease recovery angle of the phenolic resins was 252° obtained with *m*-cresol, phenol was next with 240° and *o*-chlorophenol the lowest (225°). As would be expected the other properties followed a similar pattern with *m*-cresol giving the lowest values for bursting strength, tear strength and flex abrasion and *o*-chlorophenol the highest. The bending length also showed the same trend with the highest being *m*-cresol and the lowest *o*-chlorophenol. Although the *o*-chlorophenol treatment produced a sample with only 10.8 per cent resin on the fabric it was not possible to increase the crease recovery angle by the application of more resin as the fabric became stiff and rigid and the crease recovery angle decreased. This was also found with the other two resins, in fact the crease recovery angles given in Table III were the maximum attainable as addition to the fabrics of more resin reduced the values.

When the physical properties of the phenolic and commercial resin treated fabrics are compared, a few interesting features arise. Firstly the crease recovery angles obtained with the phenolic resins were lower than the angles found with the commercial resins although *m*-cresol was very close to the value of 254° obtained with urea-formaldehyde. This would appear to rule out the use of phenolic resins for permanent press treatments which require a crease recovery angle of at least 280°<sup>10,11</sup>. However, this is no disadvantage as urea-formaldehyde does not reach this requirement and yet is used extensively<sup>6</sup>. Veldsman and Hanekom<sup>12</sup> have suggested the following crease recovery angles for certain types of resin finish, "Pure Finish = 160°, Crease-Resist = 230°, Wash and Wear = 260° and Durable Press = 300°". Clearly by their definition, therefore, the phenolic resins are approximately around the categories Crease-Resist and Wash and Wear.

The second point to come out of Table III is that the tensile properties of the phenolic resins were different to those found with the commercial resins. As can be seen both the bursting strengths and tear strengths were higher for the former group, in fact in the case of *o*-chlorophenol, for example, these values were almost double those obtained with DMDHEU. The bending length results also were satisfactory being far lower for the phenolic resins than for urea-formaldehyde or melamine-formaldehyde although DMDHEU was found to be even lower. In fact, the samples treated with phenolic resins had a very soft handle which is perhaps surprising when the large amount of resin that was on the fabric is considered. A comparison of the respective flex abrasion results shows that the phenolic resins may have performed slightly better, although there was only a very small difference between the two groups.

**TABLE III**  
**MEAN PHYSICAL PROPERTIES OF RESIN-TREATED SAMPLES**

Resin	Add-on % on Mass of Fabric	Monsanto Crease Recovery Angle (W+F)°	Bursting Strength kNm <sup>-2</sup>	Tear Strength (Mean W+F) N	Bending Length cm	Stoll Flex Abrasion (Mean W+F) cycles to rupture
Untreated	0	167	645	7,8	1,91	1030
<i>m</i> -Cresol	15,7	252	603	6,9	1,86	167
Phenol	16,5	240	617	7,4	1,81	219
<i>o</i> -Chlorophenol	10,8	225	655	8,2	1,76	224
Urea-formaldehyde	5,7	254	482	5,7	3,53	147
Melamine-formaldehyde	5,4	262	446	5,6	2,07	134
DMDHEU	6,1	281	387	4,6	1,54	60

## Fastness of the Fabrics to Home Laundering:

In order to assess the durability of the resin-treated cotton samples the fabrics were washed for up to 15 cycles in an automatic washing machine and tumble-dried between each cycle. The crease recovery angle, tear strength and the effect on the shade (estimated against the grey scales) of each fabric were determined after 5 and 15 cycles. The results are shown in Table IV.

As can be seen there was no large decrease in the crease recovery angles of the phenolic resins after 15 wash cycles. Although the crease recovery angle for *m*-cresol was down by 11° (mean) compared to the unwashed sample, phenol was only 8° lower and with *o*-chlorophenol there was a negligible change. Approximately the same losses in crease recovery angle were found with the commercial resins, urea-formaldehyde negligible change, melamine-formaldehyde, 7° lower and DMDHEU 5° lower. A common feature, however, with the phenolic resins was a gradual, though small, decrease in the tear strength during washing. This was not found to the same extent with urea-formaldehyde or melamine-formaldehyde although with DMDHEU the tear strength was down by a similar amount to the phenolic resins after 15 cycles. Machine washing had a negligible effect on the shade of the phenolic resins, whereas C.I. Reactive Orange 4 with the commercial resins showed quite a loss in depth of shade after only five washes. However, other reactive dyes may have given better fastness properties.

## Some Properties of the Colours Produced:

In order to assess the range of colours which might be attainable with this process a series of stabilised diazo salts (Fast Salts) of C.I. Azoic Diazo Components, selected from the groups anthraquinone, diphenyl, monoazo and phenyl, were applied to phenolic resin-finished samples. The colours produced were defined in terms of *excitation purity* ( $P_e$ ), *dominant wavelength* ( $\lambda_d$ ), and *brightness* (Y) which were calculated from the respective tristimulus values X, Y, Z. The results are tabulated in Table V.

As can be seen the majority of the colours produced had dominant wavelengths which lay between 578 nm and 611 nm, that is the yellow to orange-red region. Only two, namely C.I. Azoic Diazo Component 38 applied to both phenol and *o*-chlorophenol were outside these limits, in fact both were purple and as their values for  $\lambda_d$  fell on the straight line joining the extremities of the spectrum locus, the complementary dominant wavelengths have been given for each.

The values obtained for the excitation purities ( $P_e$ ) of all the colours lay between 0,59 and 0,11, although for the majority these limits could be reduced to between 0,50 and 0,22 whilst the values for the brightness (Y) were between 38,0

PROPERTIES OF RESIN-TREATED SAMPLES AFTER MACHINE WASHING

Resin	C.I. Azoic Diazo Component	NaOH (%) Bath A	Crease Recovery Angle (W + F) <sup>o</sup>			Tear Strength (N)			Effect on Shade		
			0 wash	5 washes	15 washes	0 wash	5 washes	15 washes	0 wash	5 washes	15 washes
Untreated	—	—	167	157	160	7,8	7,6	8,4	—	—	—
<i>m</i> -Cresol	36	3	252	250	241	7,0	6,5	5,8	5	5	4-5
<i>m</i> -Cresol	4	1	251	248	240	6,8	6,3	6,1	5	4	4
<i>m</i> -Cresol	3	0,5	254	254	242	6,6	6,6	6,2	5	4-5	4-5
<i>m</i> -Cresol	Mean		252	251	241	6,8	6,5	6,0			
Phenol	36	3	240	235	238	7,6	7,1	6,9	5	4-5	4-5
Phenol	4	1	243	236	227	7,7	7,1	6,9	5	4-5	4-5
Phenol	3	0,5	236	238	232	7,3	6,8	6,9	5	4D	4-5
Phenol	Mean		240	236	232	7,5	7,0	6,9			
<i>o</i> -Chlorophenol	36	3	225	221	231	8,2	7,7	7,3	5	4-5	4-5
<i>o</i> -Chlorophenol	4	1	226	234	219	8,6	7,8	7,3	5	4-5D	4-5D
<i>o</i> -Chlorophenol	3	0,5	224	219	223	7,3	7,3	7,1	5	4-5D	4-5
<i>o</i> -Chlorophenol	Mean		225	225	224	8,0	7,6	7,1			
Urea- formaldehyde	C.I. Reactive Orange 4		254	258	253	4,5	4,9	4,7	5	3D	3D
Melamine- formaldehyde	C.I. Reactive Orange 4		262	259	255	5,7	5,7	5,5	5	3D	3D
DMDHEU	C.I. Reactive Orange 4		281	270	276	4,7	4,2	4,2	5	3-4	3-4D

TABLE V

## SPECIFICATIONS OF CHROMATICITY AND SOME FASTNESS PROPERTIES OF TREATED SAMPLES

	% NaOH Bath A	Excitation Purity P <sub>e</sub>	Dominant wavelength $\lambda_d$ (nm)	Brightness $\gamma$	Wash Fastness (ISO 4)			Fastness to dry Rubbing	Fastness to Light
					Effect on Shade	Staining Cotton	Staining Viscose		
<b>ANTHRAQUINONE</b>									
<b>C.I. Azoic Diazo</b>									
<b>Component 36:</b>									
<i>m</i> -Cresol	3	0,36	598	21,6	4-5D	5	5	4	3-4
Phenol	3	0,28	611	17,4	4-5D	5	5	4	3
<i>o</i> -Chlorophenol	3	0,31	611	14,5	5D	5	5	4-5	2-3
<b>DIPHENYL</b>									
<b>C.I. Azoic Diazo</b>									
<b>Component 35:</b>									
<i>m</i> -Cresol	3	0,53	583	27,6	4	4-5	5	4	4
<i>m</i> -Cresol	0,5	0,36	578	38,0	4G	5	5	5	5-6
Phenol	3	0,47	588	21,9	4R	5	5	4-5	4-5
Phenol	0,5	0,22	591	27,6	3-4R	4-5	5	5	4
<i>o</i> -Chlorophenol	3	0,33	596	16,1	4	5	5	4	2-3
<i>o</i> -Chlorophenol	0,5	0,22	599	16,5	5	4-5	5	5	3
<b>C.I. Azoic Diazo</b>									
<b>Component 41:</b>									
<i>m</i> -Cresol	3	0,47	581	32,7	4	4-5	5	4-5	4-5
Phenol	3	0,29	587	29,1	3-4D	5	5	5	4-5
<i>o</i> -Chlorophenol	3	0,30	595	18,6	5	5	5	5	3
<b>MONOAZO</b>									
<b>C.I. Azoic Diazo</b>									
<b>Component 4:</b>									
<i>m</i> -Cresol	1	0,50	586	26,2	4-5	4-5	5	4	4
Phenol	1	0,44	591	22,5	4-5D	5	5	4-5	3
<i>o</i> -Chlorophenol	1	0,47	595	15,2	4-5	5	5	4-5	2-3
<b>C.I. Azoic Diazo</b>									
<b>Component 38:</b>									
<i>m</i> -Cresol	0,5	0,22	582	23,5	5R	5	5	5	3
Phenol	0,5	0,11	-494	19,5	5	5	5	4-5	3
<i>o</i> -Chlorophenol	0,5	0,14	-494	13,4	5	5	5	4-5	2-3
<b>PHENYL</b>									
<b>C.I. Azoic Diazo</b>									
<b>Component 3:</b>									
<i>m</i> -Cresol	0,5	0,53	583	32,2	4G	5	5	4	4-5
Phenol	0,5	0,47	584	26,7	5D	5	5	4	3-4
<i>o</i> -Chlorophenol	0,5	0,50	588	17,5	4-5D	5	5	4	2-3
<b>C.I. Azoic Diazo</b>									
<b>Component 5:</b>									
<i>m</i> -Cresol	1	0,29	587	24,8	4D	5	5	5	3
Phenol	1	0,25	601	21,1	4-5	5	5	4-5	3
<i>o</i> -Chlorophenol	1	0,19	602	15,8	4-5	4-5	5	5	2-3
<b>C.I. Azoic Diazo</b>									
<b>Component 8:</b>									
<i>m</i> -Cresol	1	0,39	584	33,2	4D	5	5	4	3-4
Phenol	1	0,33	590	26,4	4	5	5	4-5	3-4
<i>o</i> -Chlorophenol	1	0,28	601	18,5	5	5	5	4-5	2-3
<b>C.I. Azoic Diazo</b>									
<b>Component 13:</b>									
<i>m</i> -Cresol	3	0,59	586	26,7	4-5	4-5	5	4-5	4
<i>m</i> -Cresol	1	0,44	584	33,4	4D	4-5	4-5	4	4-5
Phenol	3	0,55	588	22,7	4R	5	5	4	3-4
Phenol	1	0,42	586	27,5	4-5	5	5	4	4-5
<i>o</i> -Chlorophenol	3	0,50	588	17,5	5	5	5	4	3
<i>o</i> -Chlorophenol	1	0,36	591	19,4	4D	4-5	4-5	4-5	2-3
<b>C.I. Azoic Diazo</b>									
<b>Component 16:</b>									
<i>m</i> -Cresol	3	0,50	586	31,2	3-4Y	5	5	4	4
<i>m</i> -Cresol	0,5	0,39	584	34,9	3-4D	5	5	5	4-5
Phenol	3	0,44	587	25,9	4B	5	5	4	4
Phenol	0,5	0,31	590	27,9	4	5	5	4	4
<i>o</i> -Chlorophenol	3	0,44	591	17,9	3-4	5	5	4-5	3
<i>o</i> -Chlorophenol	0,5	0,30	595	18,9	4	4-5	5	4	3
<b>C.I. Azoic Diazo</b>									
<b>Component 40:</b>									
<i>m</i> -Cresol	1	0,33	590	30,0	4-5	5	5	5	4
Phenol	1	0,33	590	25,3	3-4R	5	5	5	4
<i>o</i> -Chlorophenol	1	0,25	601	15,8	4-5	4-5	5	4-5	3
<b>C.I. Azoic Diazo</b>									
<b>Component 49:</b>									
<i>m</i> -Cresol	3	0,42	586	23,4	4	5	5	5	4
Phenol	3	0,47	588	22,9	3-4	4-5	5	4	3-4
<i>o</i> -Chlorophenol	3	0,42	594	15,4	4-5	5	5	5	2-3
<b>C.I. Reactive Orange 4:</b>									
Urea-formaldehyde					4D	4	4-5	3	3-4
Melamine Formaldehyde					4-5	4-5	5	3-4	3-4
DMDHEU					4-5R	4-5	5	2-3	3-4

and 13,4. This data seems to indicate that a rather limited range of colours was produced and in fact when the chromaticity co-ordinates of each colour were plotted on the CIE chromaticity chart a circle could be drawn around all the points whose centre had the co-ordinates 0,40 0,36 and whose radius was only 0,07 chromaticity units.

When Table V is examined in greater detail a number of not unexpected trends become evident. For any stabilised diazo salt *m*-cresol always gave the lowest value for  $\lambda_d$ , and the highest for Y, while *o*-chlorophenol gave the highest value for  $\lambda_d$  and the lowest for Y with the values for phenol between the two. This showed that *m*-cresol tended to yield colours which were yellower and brighter than phenol and *o*-chlorophenol while the *o*-chlorophenol colours were redder and duller. Thus the type of phenolic resin used had an effect on the final colour of the fabric. In all cases also *m*-cresol gave higher values for  $P_e$  than the other two resins which were nearly always close to one another.

As only a small number of stabilised diazo salts were studied it is difficult to draw any definite conclusions from the relationship between the colours produced and the different salts used. The monoazo, diphenyl and phenyl salts did seem to span approximately the same range of values for  $\lambda_d$ ,  $P_e$  and Y while the anthraquinone salt, as might be expected, gave slightly higher values for  $\lambda_d$  and hence dyeings which were more red.

It was also found that by changing the concentration of NaOH in bath A it was possible to vary the depth of shade of the fabric produced. This was shown with C.I. Azoic Diazo Components 13, 35 and 16. As can be seen (Table V) when the concentration of NaOH was reduced the values for Y increased while  $P_e$  decreased, hence showing a loss in depth of shade. Thus the higher the NaOH concentration in bath A, the deeper the shade.

The fastness of the colours to washing (ISO 4), dry rubbing and light were assessed next and the results are also shown in Table V. As can be seen the fastness of the colours to washing was excellent, the majority having ratings above four with the staining of cotton and viscose almost negligible. The fastness to dry rubbing was also satisfactory while the light fastness of the colours was not quite so good, the majority having ratings which were in the region of 3 to 4. *o*-Chlorophenol consistently gave, irrespective of stabilised diazo salt used, lower values for light fastness than both *m*-cresol and phenol which were approximately the same.

Further studies are being undertaken in order to find ways of increasing the colour range and also shortening the process. The results of these experiments will be reported in Part II, together with certain estimates of the costs involved in this technique.

## SUMMARY

A novel method has been devised for the crease-resist finishing and dyeing of cotton fabric. In this process some *phenolic-formaldehyde resins* are prepared and applied by the pad-dry-cure method to cotton fabrics. After soaping, rinsing and drying, the fabrics enter, for 30 sec, a bath containing NaOH at a concentration of 3 per cent or 1 per cent or 0,5 per cent, depending upon the depth of shade required, and then immersed, for 1 min, in a solution of a *stabilised diazonium salt*. In this bath the diazonium salt is coupled to the phenolic-formaldehyde resin on the cotton and when the fabric enters an alkaline soap solution, the colour is fully developed.

Fabrics treated in this way were found to have satisfactory crease-resist and tensile properties together with a soft handle. The colours produced were in the range yellow to orange-red and had excellent fastness properties to washing and dry rubbing although light fastness was not quite as good.

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## THE USE OF PROPRIETARY NAMES

Products marked ® are registered trade names. The fact that chemicals with proprietary names have been mentioned in this investigation in no way implies that SAWTRI recommends them or that there are not others of equal or greater merit.

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