Non-formaldehyde durable press finishing of dyed fabrics: evaluation of cotton-bound polycarboxylic acids

Coloration Technology
Society of Dyers and Colourists

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The polycarboxylic acids 1,2,3,4-butanetetracarboxylic acid and citric acid are used as non-formaldehyde durable press finishing agents instead of formaldehyde-releasing *N*-methylol compounds. In this study, isocratic HPLC is applied in an attempt to quantify the polycarboxylic acids that react with cellulosic material dyed with CI Reactive Red 195, CI Reactive Yellow 145 and CI Reactive Blue 221. Subsequently, the fabrics are cured with formulations containing butanetetracarboxylic acid and citric acid or a combination of both. The chromatographic determination reveals that an increase in the depth of shade results in a decrease of the amount of butanetetracarboxylic acid, except in the case when the cotton is dyed with CI Reactive Blue 221, a copper formazan complex-based dyestuff. Colour measurements indicate that the ΔE^* values decrease in the order CI Reactive Yellow 145, CI Reactive Red 195 and CI Reactive Blue 221.

Introduction

Polycarboxylic acids (PCAs), especially 1,2,3,4-butanetetracarboxylic acid (BTCA) or citric acid (CA) (Figure 1) in combination with phosphorus-containing catalysts, such as sodium hypophosphite (SHP), have proven to be the most effective substitutes for the formaldehyde-releasing crosslinking agents such as the *N*-methylol compound dimethyloldihydroxyethylene urea (DMDHEU) [1–5]. During the cure process, normally conducted at 180 °C for 90 s, the carboxy groups of the PCA form ester linkages with the hydroxymethyl groups of the cellulose chain via an anhydride intermediate. As a consequence, a crosslinking reaction takes place thus imparting durable press properties to the cotton fabric. These ester linkages are resistant to multiple alkaline home launderings.

Several scientists have studied the dyeability of PCA-treated fabrics with various dyes, applying different additives [6–12]. A number of investigations have been undertaken in order to study the effects of crosslinking on the properties of dyed fabrics. The treatment of dyed fabrics with PCA also gives rise to coloration changes that can be balanced to some extent if a single dyestuff is employed [13]. The application of CA results in higher colour difference (ΔE) values as compared to DMDHEU-finished fabrics [14]. The main cause of the shade changes in PCA finishing appears to be the SHP catalyst, which acts as a reducing agent. Addition of a second phosphono-based catalyst causes lower shade change due to the decreased influence of the strong SHP reducing agent [15]. A lower shade change is also obtained when imidazole or 2-methylimidazole are applied as catalysts instead of SHP, compared to PCA-treated fabrics [16]. The same holds for the application of trisodium citrate and the combination of sodium oxalate and sodium formate [17]. Single-step dyeing and finishing treatment of cotton has also been tested in the course of various investigations in order to minimise shade changes [18,19].

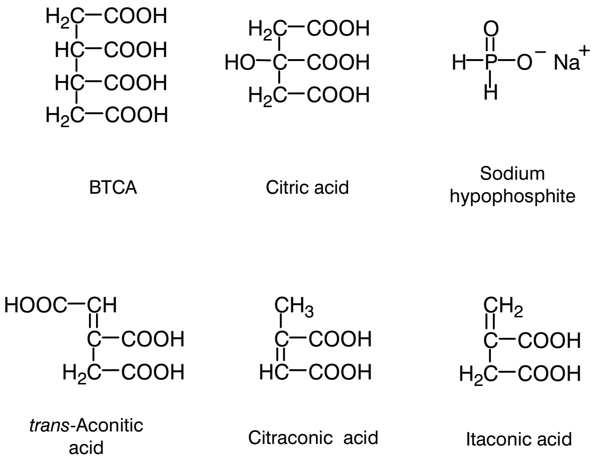

Figure 1 Structural formulae of PCAs used as crosslinking agents, the catalyst SHP and examples of unsaturated PCAs formed during the curing process of CA-treated fabrics

The quantification of cotton-bound PCA has only been applied to undyed fabrics so far [20–24]. Therefore the aim of this study was to determine the amount of BTCA and CA that reacts with cellulosic material dyed with reactive dyes.

Experimental

Materials and fabric treatment

The reactive dyes CI Reactive Yellow 145, CI Reactive Red 195 and CI Reactive Blue 221 were commercially obtained (Table 1). The auxiliaries Meropan NX (a sequestering agent), Biavin 109 (a concentrated gliding and crease

Table 1 Characteristics of the dyestuffs used in this study

Dye	Structural type	Reactive groups
CI Reactive Red 195	Azo	Monochlorotriazine, vinylsulphone
CI Reactive Yellow 145	Azo	Monochlorotriazine, vinylsulphone
CI Reactive Blue 221	Copper formazan complex	Monochlorotriazine, vinylsulphone

prevention agent) and Cotoblanc NSR (a soaping agent) were obtained from CHT, Tübingen, Germany. Sodium hypophosphite monohydrate (SHP) ($NaH_2PO_2 \bullet H_2O$) was supplied by Merck, Darmstadt, Germany. *meso*-1,2,3,4-Butanetetracarboxylic acid, citric acid, aconitic acid, citraconic acid and itaconic acid were obtained from Sigma Aldrich, Steinheim, Germany. All substances were reagent grade chemicals.

Desized, scoured, bleached and mercerised 100% cotton fabric, weighing 109 g/m^2, was used throughout the investigations.

Dyeing process

The fabrics were dyed according to the profile depicted in Figure 2. A: Meropan NX (1.0–2.0 g/l), Biavin 109 (0.3 g/l), dyestuff (0.2–4% owf); B: sodium chloride (30–80 g/l); C: sodium carbonate (5.0 g/l); D: sodium hydroxide, 38 °Bé (0.5–3 ml/l); E: acetic acid (1.0 ml/l); F: Cotoblanc NSR (0.3 g/l).

Finishing process

The pre-weighed, dyed fabric was impregnated in a treatment bath containing a crosslinking agent and a catalyst. No softener was applied. The catalyst was added to the formulation immediately before application. Subsequently, the sample (30 × 50 cm) was passed through a two-roll laboratory padder (HVL 500 Mathis AG, Niederhasli, Switzerland; air pressure 1 bar, fabric speed 3 m/min). This treatment gave a wet pick-up of about 100–109%, depending on the original weight of the fabric treated. After drying (2 min, 100 °C) the fabric was cured for a specified time at 180 °C in a laboratory dryer (Benz Dryer, Zürich, Switzerland), washed with occasional stirring (sodium carbonate 1 g/l, 10 min, 50 °C, wash liquor 1 l) and finally dried again (3 min, 80 °C).

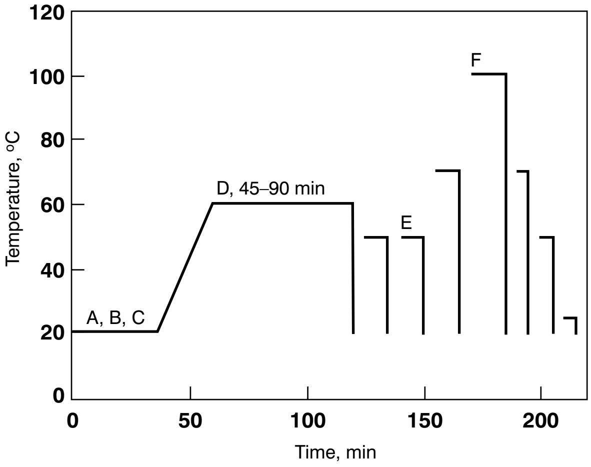

Figure 2 Dyeing profile used in this study

Analytical methods

Apparatus

HPLC measurements were performed using the following components: autosampler (Model Marathon, Spark BV, Emmen, Netherlands); injection valve 20 µl (Rheodyne, Cotati, CA, USA); pump (JASCO PU-1580, Kyoto, Japan); strong cationic exchange column, 300 × 7.8 mm ID (Aminex HPX-87-H, Bio-Rad Labs., Richmond, CA, USA); oven compartment (Shimadzu CTO-2A, Kyoto, Japan); UV-detector (Shimadzu SPD-10 AVVP, Kyoto, Japan); chromatography software (Borwin, JMBS Developments, Le Fonatnil, France). The chromatographic conditions were as follows: mobile phase, sulphuric acid (c = 0.005 mol/l); flow rate, 0.7 ml/min; column oven temperature, 80 °C; UV-detector wavelength, 210 nm.

Sample preparation

Portions of the PCA-treated fabric were cut into small pieces (1–2 g), accurately weighed and transferred to the reaction vessel. Sodium hydroxide (40 ml; c = 1 mol/l) was added. The reaction mixture was treated at 100 °C for 20 min. After hydrolysis, extraction and wash solutions were transferred to a 50 ml volumetric flask and allowed to cool. Finally, the volumetric flask was adjusted to the mark with sodium hydroxide (c = 1 mol/l). Prior to the chromatographic analysis, the solution was filtered through a polytetrafluoroethylene disposable filter unit.

Fabric whiteness and shade changes were evaluated using DataColor 3890 spectrophotometer with D65/10° illumination. Dry crease recovery angle (DCRA) was measured according to ISO 2313. Tensile strength was measured according to DIN EN ISO 13934-1.

Results and Discussion

HPLC analysis proved an excellent technique for the qualitative and quantitative determination of PCA, when applied as a non-formaldehyde crosslinking agent to undyed cellulosic material [20–24]. It was therefore of high interest to investigate the quantification of the PCAs that have reacted with the dyed cellulosic material.

A previous study demonstrated that the application of the analytical method used in the course of the current study enables the separation, and therefore the identification and quantification, of all the PCAs that are normally applied as non-formaldehyde crosslinking agents for cotton materials [24]. Figure 3 shows the chromatograms obtained when the saponification liquors of the cotton samples dyed with the three reactive dyes were analysed.

An excellent separation of all PCAs of interest was obtained. Additionally, the recovery of BTCA and CA was determined. For this purpose, 5 mg of the dyestuff and 100 mg of BTCA or CA were dissolved in 50 ml of sodium hydroxide (c = 2 mol/l) and heated at 100 °C for 15 min. The results of the chromatographic evaluation are listed in Table 2. The data obtained indicate that under the chromatographic conditions chosen the recovery of BTCA is enhanced when CI Reactive Blue 221 is present in the saponification liquor.

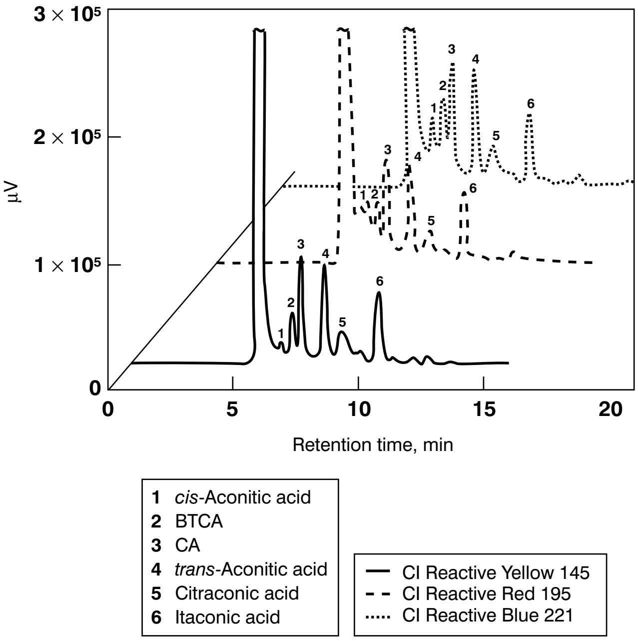

Figure 3 Chromatograms of the saponification liquors of dyed cotton fabrics treated with a formulation containing: BTCA, 15 g/l; CA, 45 g/l; and SHP, 65 g/l

Table 2 Results of the chromatographic evaluation of the recovery of BTCA and CA from cotton samples dyed with the three dyestuffs

	Recovery (%)	
Dye	BTCA	CA
CI Reactive Red 195	97.3	98.6
CI Reactive Yellow 145	97.5	98.6
CI Reactive Blue 221	106.2	91.8

The values of the cotton-bound PCA (mg PCA/g fabric) that had been determined chromatographically were not corrected using the recovery data. The corresponding standard deviation values were calculated from two runs and were in the range of ± 1.50 mg/g.

Influence of the amount of PCA

In order to determine the influence of the amount of PCA used, cotton samples were dyed with CI Reactive Red 195 (0.4 and 4.0% owf shade) and subsequently cured at 180 °C for 90 s with finishing formulations containing various amounts of BTCA or CA (40, 60, 80 and 100 g/l). The portion of cotton-bound BTCA, the DCRA values and the change of shade are shown in Table 3. As expected, an increase of the BTCA content in the formulation brings about an increase of the amount of BTCA reacting with the cotton fabric.

Except in the case when 40 g/l of BTCA was applied to the cotton fabric, the amount of cotton-bound BTCA was somewhat lower when the fabric was dyed with 4.0% owf depth of shade. Tensile strength retention value dropped dramatically as the concentration of BTCA was increased. However, a comparison of tensile strength measurements of the 0.4 and 4.0% owf dyed fabrics reveals that the fabrics with the higher depth of shade have slightly improved retention values. These two phenomena can be explained by the fact that due to the reaction of the dyestuff with the cellulosic material, the portion of the hydroxy groups that can react with the BTCA is reduced.

As expected, the DCRA value increased as the amount of PCA in the formulation increased. A remarkable difference in ΔE^* was observed as soon as the amount of BTCA in the formulation reached the value of 60 g/l.

The application of CA as a non-formaldehyde cross-linking agent resulted in the additional formation of unsaturated carboxylic acids, aconitic acid, citraconic acid

Table 3 Influence of BTCA concentration on the properties of cotton samples dyed with CI Reactive Red 195

BTCA conc. (g/l)	Dye conc. (% owf)	BTCA on fabric (mg)[a]	DCRA (w + f)[b] (°)	TSR[c] (%)	ΔE^*	ΔL^*	ΔC^*	ΔH^*
40	0.4	28.4	246	56.2	4.83	0.340	− 3.983	− 2.706
	4.0	32.0	228	60.2	4.91	− 0.263	− 2.441	− 4.247
60	0.4	47.1	256	48.9	5.36	0.689	− 4.406	− 2.969
	4.0	42.8	253	54.2	5.61	0.060	− 2.333	− 5.096
80	0.4	62.2	276	46.4	5.32	0.793	− 4.330	− 2.991
	4.0	60.0	273	53.6	5.58	0.008	− 2.333	− 4.984
100	0.4	73.3	280	43.8	5.25	0.922	− 4.196	− 3.021
	4.0	68.8	276	45.0	5.50	− 0.107	− 2.429	− 4.936
Control[d]	0.4		100	100				
	4.0		105	100				

[a] Related to 1 g fabric and 100% wet pick-up
[b] ‘w + f’ = warp and fill
[c] Tensile strength retention
[d] Dyed and unfinished

Table 4 Influence of CA concentration on the properties of cotton samples dyed with CI Reactive Red 195

		PCAs on fabric (mg)[a]									
CA conc. (g/l)	Dye conc. (% owf)	CA	Aconitic acid	Citraconic acid	Itaconic acid	DCRA (w + f)[b] (°)	TSR[c] (%)	ΔE^*	ΔL^*	ΔC^*	ΔH^*
40	0.4	26.3	0.50	0.12	0.34	202	64.9	4.56	0.539	– 3.776	– 2.490
	4.0	23.6	0.71	0.14	0.58	208	68.2	4.65	0.353	– 1.629	– 4.337
60	0.4	34.3	0.90	0.23	0.64	225	61.4	5.73	1.580	– 4.867	– 2.580
	4.0	29.7	1.04	0.26	0.78	216	62.5	5.22	0.453	– 1.625	– 4.943
80	0.4	41.3	1.33	0.34	0.91	244	56.2	5.59	1.534	– 4.894	– 2.226
	4.0	35.3	1.54	0.40	1.08	234	61.7	5.28	0.502	– 2.014	– 4.851
100	0.4	49.8	1.86	0.49	1.27	260	55.4	5.16	1.554	– 4.485	– 2.031
	4.0	46.8	2.11	0.61	1.49	253	59.9	5.44	0.522	– 2.172	– 4.956
Control[d]	0.4					100	100				
	4.0					105	100				

[a] Related to 1 g fabric and 100% wet pick-up
[b] 'w + f' = warp and fill
[c] Tensile strength retention
[d] Dyed and unfinished

Table 5 Influence of BTCA and CA concentration on the properties of cotton samples dyed with CI Reactive Yellow 145, CI Reactive Red 195 and CI Reactive Blue 221

				On fabric (mg)[a]				
Dye	Dye conc. (%)	On fabric (mg)[a] BTCA	DCRA (w + f)[b] (°)	CA	Aconitic acid	Citraconic acid	Itaconic acid	DCRA (w + f)[b] (°)
Single BTCA or CA								
CI Reactive Yellow 145	0.2	43.6	248	37.7	0.52	0.09	0.29	200
	4.0	42.4	247	35.2	0.89	0.12	0.53	198
CI Reactive Red 195	0.2	42.5	256	38.7	0.65	0.11	0.38	196
	4.0	36.8	253	34.0	0.98	0.13	0.62	226
CI Reactive Blue 221	0.2	40.4	252	39.4	1.00	0.18	0.63	204
	4.0	43.3	254	32.2	1.08	0.55	0.69	207
Control		37.6[c]	233	34.5[d]	0.87	0.06	0.54	174
Combination BTCA/CA								
CI Reactive Yellow 145	0.2	12.2		23.9	0.47	0.16	0.41	236
	4.0	12.6		23.2	0.51	0.16	0.43	230
CI Reactive Red 195	0.2	12.6		21.0	0.48	0.17	0.41	243
	4.0	8.7		21.0	0.51	0.15	0.42	232
CI Reactive Blue 221	0.2	10.7		20.5	0.42	0.17	0.36	233
	4.0	15.8		23.1	0.62	0.20	0.42	219
Control		10.6[e]		21.7	0.45	0.15	0.38	212

[a] Related to 1 g fabric and 100% wet pick-up
[b] 'w + f' = warp and fill
[c] Undyed and finished (60 g/l BTCA)
[d] Undyed and finished (60 g/l CA)
[e] Undyed and finished (15 g/l BTCA, 45 g/l CA)

and itaconic acid (see Figure 1). Generation of these acids is due to decarboxylation and dehydration reactions of CA under the curing conditions chosen (180 °C, 90 s) [21]. The results of the evaluation of the dyed CA-treated fabrics are presented in Table 4. As in the case of BTCA-treated fabrics, the amount of cotton-bound CA steadily increased with the content of CA in the formulation. Furthermore, the amount of CA reacting with the cellulose was also slightly reduced as the shade depth increased from 0.4 to 4.0% owf. This trend was not observed with cotton-bound unsaturated PCA. The DCRA values increased and the tensile strength retention decreased as the amount of CA increased in the formulation. This was observed at both 0.4 and 4.0% owf. However, the values were considerably lower in comparison to the BTCA-treated fabrics.

Influence of the dyestuff

To investigate the influence of the dyestuff applied, cotton samples were dyed with different concentrations of each of the reactive dyes (0.2 and 4.0% owf). Subsequently, these specimens were cured with formulations containing 60 g/l BTCA or 60 g/l CA and 65 g/l SHP added in each case. The samples were washed and subjected to a chromatographic analysis as described in the Experimental section. The PCA on the fabric and the DCRA values are shown in Table 5.

The influence of the depth of shade on the amount of bound PCA was more pronounced when CA was applied in the finishing formulation. The amount of BTCA reacting with the cellulose was slightly lowered, in the case of CI Reactive Yellow 145, when the depth of shade was increased to 4.0%. The value for BTCA decreased more significantly on going from the lower to the higher depth of shade when the fabric was dyed with CI Reactive Red 195.

Figure 4 shows the evaluation of colour change. At a 0.2% owf depth of shade, the ΔE^* values of the CA-treated fabrics were approximately the same, whereas the colour change of the fabrics finished with BTCA decreased in the order: CI Reactive Yellow 145 > CI Reactive Red 195 > CI Reactive Blue 221.

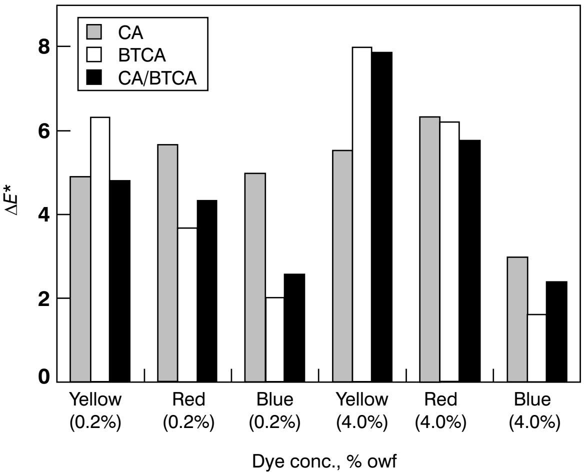

Figure 4 Colour difference (ΔE^*) of the cotton fabric treated with non-formaldehyde crosslinking agents based on PCA

Combination of BTCA and CA

Table 5 depicts the results obtained with a formulation composed of 45 g/l CA, 15 g/l BTCA and 65 g/l SHP. This formulation was selected because BTCA is too expensive to be used in technical scale operations, and its content in the formulation should be reduced.

As expected, the reduction of BTCA concentration in the formulation from 60 to 15 g/l resulted in a decrease in bound BTCA regardless of which type of dyestuff had been applied.

When the fabric was dyed with CI Reactive Red 195 an increase in shade change from 0.2 to 4.0% owf resulted in a decrease in cotton-bound PCA.

In contrast to these findings the amount of cotton-bound BTCA increased as the depth of shade of the CI Reactive Blue 221-dyed fabric was raised from 0.2 to 4.0% owf. This observation can be explained by the fact that the recovery of BTCA was found to be 106.2% under the chromatographic conditions chosen.

The controls (single BTCA or CA) were undyed and treated with either 60 g/l BTCA or 60 g/l CA. The controls of the combination of BTCA and CA were also undyed and finished with 45 g/l CA and 15 g/l BTCA. The corresponding values of the cotton-bound PCA were lower compared to the dyed fabrics. This unexpected tendency may be explained as follows. At a depth of shade of 0.2% owf it can be assumed that the PCA reacts with the cellulosic material to the same extent as the undyed control. However, an additional interaction of the PCA with the dyestuff can be taken into consideration. Consequently, the amount of the chromatographically detected PCA is enhanced. An increase in the depth of shade from 0.2 to 4.0% owf may result in a reduction of the accessibility of the PCA to the cellulose and therefore the amount of cotton-bound PCA decreases. The greater depth of shade should also result in an increase of the portion of PCA that interacts with the cotton-bound dyestuff. According to the results obtained it can be assumed that the PCA-dyestuff interaction is not so effective.

These data indicate that the dyestuff influences the amount of cotton-bound PCA. Since these investigations had been performed on three dyestuffs further detailed studies must be undertaken with more different types of dyes in order to confirm these phenomena.

The DCRA of the BTCA/CA-treated fabrics were lower in comparison to the BTCA-finished samples. However, the values were higher than those of the CA-treated fabrics. The results of the colour measurements revealed that the application of the BTCA/CA formulation offers similar results in comparison to the BTCA-treated fabrics (Figure 4).

Conclusions

Cotton samples dyed with CI Reactive Red 195, CI Reactive Yellow 145 and CI Reactive Blue 221 were finished with various formulations containing BTCA or CA, or a combination of BTCA/CA in a 1:3 ratio. The chromatographic determination of the PCAs that have reacted with the cellulose clearly demonstrates that the analytical technique applied enables the quantification of the PCAs that have reacted with dyed cotton samples. An increase in the depth of shade results in a decrease in the amount of PCAs, confirmed with the DCRA determination, except when cotton samples are dyed with CI Reactive Blue 221, a copper formazan complex-based dyestuff. The dyestuffs react with the hydroxy groups of the cellulose and consequently fewer hydroxy groups are available for the esterification reaction with polycarboxylic acids. This phenomenon is confirmed by the fact that the application of higher depths of shade results in a decrease in the amount of cotton-bound PCA, except with CI Reactive Blue 221, since the recovery of this dye was > 106% under the chromatographic conditions used.

Azo dyes showed a greater sensitivity towards SHP, presumably because of its tendency to behave as a reducing agent. The evaluation of the colour measurements indicates that the ΔE^* values decrease in the order of CI Reactive Yellow 145, CI Reactive Red 195, CI Reactive Blue 221.

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Web ref: 20020507