

Nonformaldehyde-Nonphosphorus Durable Press Finishing of Cotton with Carbodiimide and Butanetetracarboxylic Acid

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카보다이마이드와 부탄테트라카르복실산을 이용한 면의
무포름알데히드-무인 방추 가공

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Abstract

부탄테트라카르복실 산을 이용한 면직물의 DP 가공에서 가장 효과적인 촉매로 알려진 sodium hypophosphite(SHP)를 대체하기 위하여 carbodiimide 촉매의 효과를 알아보았다. Carbodiimide 촉매로는 cyanamide(CY), dicyandiamide(DCY)와 disodium cyanamide(DSC)를 사용하였다. DCY와 DSC가 일반적으로 CY보다 좋은 방추도와 방추속도를 보였고 또한 독성이 낮고 저장시 안정도 등이 우수하므로 산업적인 응용이 가능하다. 필요한 방추도와 물리적성질의 균형을 위해서 가공액의 pH 조절이 가장 중요한 인자로 나타났다. 촉매존재시에 면과 부탄테트라카르복실산의 에스터화 가교 반응 메커니즘을 제안하였다. 또한 황화 염료로 염색된 염색포에 대한 가공 효과 분석시 carbodiimide 촉매가 SHP보다 대체로 작은 색상 변화를 유발시켰다. 이러한 연구 결과는 부양화와 여러 염료의 색상 변화를 유발시키는 SHP를 사용하지 않고 부탄테트라카르복실산과 carbodiimide 촉매를 이용한 무포름알데히드, 무인 가공제의 면직물 DP 가공의 가능성을 보여 주고 있다.

Key words: carbodiimide, cotton, DP finishing, non-phosphorus catalyst, environmentally-friendly process; 카보다이마이드, 면, 방추가공, 무인 촉매, 환경 친화 가공

I. INTRODUCTION

Catalysts employed during durable press (DP)

treatment of cotton with polycarboxylic acids have been mainly phosphinic or phosphonic acid derivatives¹⁻⁴. Although, these catalysts minimized degradation of cotton during curing process, eutrophication of these phosphorus-containing compounds to water source is well known⁵. In addition,

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sodium hypophosphite, which was the most efficient catalyst among these phosphorus-containing compounds, resulted in considerable shade changes to sulfur and some reactive dyed fabrics, due to its reductive nature^{6,7}.

To substitute these phosphorus-containing catalysts in the esterification reaction of polycarboxylic acid and cellulose, various compounds have been recently examined. These include imidazole and its derivatives⁸, salts of α -hydroxy acids such as malonic acid, citric acid, tartaric acid⁹, and lactic acid¹⁰, mono- and disodium salts of unsaturated dicarboxylic acids such as fumaric, maleic, and itaconic acids¹¹. Although the effectiveness was not as great as other types of catalysts, partial salts of saturated acids such as succinic acid could be used as catalysts for the similar esterification reaction¹².

Previous study revealed that carbodiimides have been used in promoting reactions between cellulose and compounds containing phosphonated and carboxylated reactive groups such as reactive dyes and flame retardant finishes¹³⁻¹⁵. However, a little information is available in the application of these carbodiimides in the DP finishing treatment of cotton with polycarboxylic acid except a recent patent literature¹⁶.

Therefore, in this study we investigated the role of carbodiimide catalysts in the nonformaldehyde DP finishing treatment of cotton in the presence of polycarboxylic acids, especially BTCA.

II. EXPERIMENTAL

Desized, scoured, and bleached 100% cotton print cloth (weight 107 g/m²) obtained from Test Fabrics (#400) was used throughout the study. Polycarboxylic acids such as citric acid, maleic acid, malonic acid, and ethylenediamine tetraacetic acid disodium salts were purchased from Aldrich Chemicals. Catalysts including sodium hypophosphite monohydrate (NaH₂PO₂ · H₂O) and carbodiimides

such as cyanamide (50% solution in water, CY), disodium cyanamide (95% purity, DSC), and dicyandiamide (DCY) were also obtained from the Aldrich. 1, 2, 3, 4-Butanetetracarboxylic acid (BTCA) was supplied from Tokyo Kasei Chemicals. Triton X-100 and Cyanalube TSI from Aldrich Chemicals and American Cyanamide were used as a wetting agent and softener, respectively. All chemicals were reagent grade and used without further purification.

A conventional pad-dry-cure process (two dips and nips) was used throughout the study. The fabric was impregnated in a finishing bath containing 6.5% or 8% on the weight of bath (owb) BTCA, carbodiimide catalyst, 1% owb Cyanalube TSI, and 0.1% owb Triton X-100. A padding pressure of 2 psi produced the fabric with a wet pick-up of about 90-100%. Drying was carried out at 85C for 5 minutes and curing was at 180C for 2 minutes. The fabric was then washed for 30 minutes in the running tap water (process-washing) to remove unreacted acids and catalysts, and finally dried again in the laboratory oven for 5 minutes at 85C. As a comparison purpose, the fabric was also treated with BTCA and SHP. Control fabric was also process-washed and dried as above.

Three different methods were used to estimate performance properties of the treated fabrics: durable press (DP) rating (AATCC 124-1992), dimensional change (AATCC 135-1992), and conditioned wrinkle recovery angle (WRA, AATCC 66-1990) methods. Mechanical properties of the treated fabrics were determined by using the following test methods: Elmendorf tearing test (ASTM D-1424-82), strip breaking strength (ASTM -1682-64), Stoll flex abrasion resistance (ASTM -1175-55T). All the mechanical tests were carried out in warp direction.

Whiteness index was measured by Hunter Ultrascan Sphere Spectrocolorimeter according to ASTM E313-67. BTCA was also applied to the

Table 1. Performance properties of cotton fabrics treated with 6.5% BTCA and carbodiimide catalysts.*

catalyst (mole ratio vs. BTCA)	% add-on	DP rating	DC(%) ^b		CWRA (w+f) ^b	T.S. ^b (%)	B.S. ^b (%)	S.F.A. ^b (%)	WI ^b	Bath pH
			warp	filling						
control	0.0	1.3	-5.21	-4.69	169	100.0	100.0	100.0	80.9	-
SHP 0.5:1	7.2	4.0	-0.39	0.0	278	69.9	46.6	20.5	82.2	2.1
SHP 1:1	4.4	4.0	-0.26	0.0	280	73.5	40.7	11.4	72.4	2.2
CY 0.5:1	6.0	3.0	-0.78	-0.39	254	87.6	76.4	86.8	71.8	1.9
CY 1:1	6.4	3.3	-0.39	-0.39	259	80.9	64.3	82.4	70.0	1.9
DSC 0.25:1	6.8	3.3	-0.39	0.0	276	77.2	60.9	49.5	79.5	3.2
DSC 0.5:1	6.4	3.0	-0.39	-0.39	269	77.2	62.7	65.2	83.4	3.7
DSC 0.75:1	5.9	3.8	-0.39	-0.39	256	85.7	73.6	75.8	83.4	4.2
DSC 1:1	4.2	3.3	-0.26	-0.13	248	85.3	70.0	56.8	77.7	4.5
DCY 0.5:1	6.7	3.4	-0.39	-0.39	262	89.4	64.3	53.1	75.7	2.0
DCY 1:1	6.8	3.8	-0.39	-0.13	272	83.2	64.9	52.0	73.3	1.9

* All treating bath contained 1% softener and 0.1% Triton X-100. The fabric was dried at 85C for 5 minutes and cured at 180C for 2 minutes. ^b Dimensional change, conditioned wrinkle recovery, retentions of tearing strength, breaking load, and Stoll flex abrasion resistance, and whiteness index. All measured after one laundering except whiteness index measured after process washing.

dyed fabrics in the presence of carbodiimide catalysts to examine effects of DP finishing on shade changes of the dyed fabrics. The shade change was evaluated by AATCC Gray scale method for visible shade changes, ΔE and reflectance measurements by the Hunter Spectrocolorimeter. The K/S value was calculated by the Kubelka-Munk equation as follows:

$$K/S = (1-R)^2/2R$$

where R was the reflectance of the sample at the wavelength of maximum absorption⁷.

III. RESULTS AND DISCUSSION

As shown in Table 1, treatment of cotton cellulose by BTCA and carbodiimide catalysts considerably improved fiber resilience of the treated fabrics indicated by substantial increase in DP rating,

dimensional change, and conditioned WRA. All three factors were measured after one home laundering and negative dimensional change values indicated the fabric shrinkage after laundering.

In general, CY was less effective than SHP in improving DP rating and WRA of the treated fabrics at the same molar ratio versus BTCA. The CY treatment also caused more dimensional changes after laundering. On the other hand, at 1:1 ratio of DCY versus BTCA and at 0.25:1 mole ratio of DSC vs. BTCA at least two of three factors (DP rating, dimensional change, and WRA) were comparable to those of the fabric treated by BTCA and SHP.

In addition, the carbodiimide-treated fabrics showed considerably higher retentions of mechanical properties (Table 1), compared with those of SHP-treated fabric. Especially, at similar dimen-

sional changes increase in retention of Stoll flex abrasion (SFA) resistance was substantial. For example, retention of SFA resistance was 11.4% at 1:1 mole ratio of SHP vs. BTCA, while at 1:1 mole ratio of DCY or 0.25:1 ratio of DSC vs. BTCA, retention of SFA resistance increased to 52.0% and 49.5%, respectively.

DSC was also applied to cotton fabrics at different concentrations in the presence of 6.5% of BTCA. As shown in Table 1, values in dimensional change were relatively consistent with varying DSC concentration. On the other hand, conditioned WRAs were continuously decreased with increase in DSC concentration. At the same time, retentions of mechanical properties were increased up to 0.75 mole ratio of DSC vs. BTCA and leveled off or decreased. The decrease in wrinkle recovery angle and increase in mechanical properties can be mainly due to pH changes occurred by increase of DSC concentration in the bath.

Whiteness index was measured before home laundering, but after process-washing. The fabrics treated with BTCA and DSC showed high whiteness indices (close to 80), as shown in Table 1, comparable to that of the fabrics treated by BTCA and SHP. We believe that the high whiteness index of the BTCA and DSC treated sample was also mainly due to the high pH of the treating bath. On

the other hand, SHP is a reductive in nature and has a bleaching effect on the treated fabric resulting in whiter fabric. However, a further increase in SHP concentration decreased whiteness index of the treated fabric. The different whiteness indices by varying SHP concentration have been also observed in our previous study¹⁷⁾. Overall, the treated cotton fabrics showed excellent whiteness indices after the DP finishing treatment by BTCA and carbodiimide catalysts.

These results clearly show that these carbodiimide compounds can be used as nonphosphorus catalysts in DP finishing treatment of cotton fabrics with BTCA. However, cyanamide is a primary skin irritant and its stability during the storage is low. Commercial samples are either solid or 50% aqueous solution which requires cool and dry condition to store¹⁸⁾. Therefore, the use of DCY and DSC is much preferred over CY in practical applications.

It has been claimed that the addition of ammonium ion in the treating bath enhanced the fixation of phosphorus-containing reactive dyes toward cellulose molecules¹⁹⁾. We, therefore, also examined the effects of ammonium ions during the reaction of BTCA and carbodiimides with cellulose. As seen in Table 2, the fabrics are treated by 8% BTCA and DCY in the presence of added aqueous ammonia.

Table 2. Effect of ammonia in the performance properties of cotton treated with BTCA and dicyandiamide.^a

NH ₃ (mole ratio vs. DCY)	% add-on	DP rating	DC(%) ^b warp filling		CWRA ^b (w+f)	T.S. ^b (%)	B.S. ^b (%)	S.F.A ^b (%)	Bath pH
control	0.0	1.3	-5.21	-4.69	169	100.0	100.0	100.0	-
0	7.2	3.5	0.0	0.0	289	85.3	53.6	39.2	1.9
0.25	7.2	3.8	0.0	0.0	275	89.7	63.6	54.9	2.8
0.5	6.4	3.5	0.0	0.0	275	88.2	61.4	76.6	3.1
1.0	5.4	3.3	-0.78	-0.78	262	95.6	64.3	138.5	3.5

^a All treating bath contained 8% BTCA, DCY (1:1 mole ratio vs. BTCA), 1% softener, and 0.1% Triton X-100. The fabric was dried at 85C for 5 minutes and cured at 180C for 2 minutes. ^b All abbreviations are the same as Table 1.

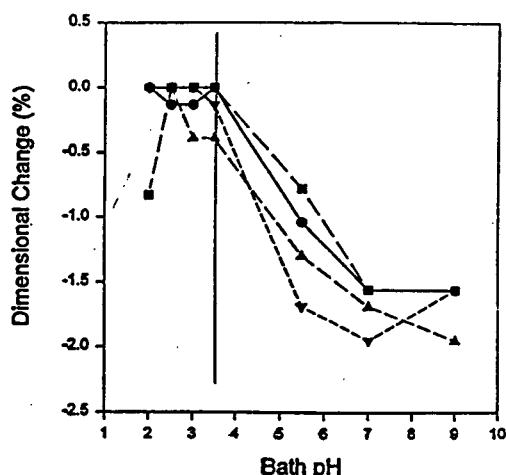


Fig. 1. Dimensional changes of the DP finished cotton fabrics treated by 6.5% BTCA and CY or DCY (1: 1 mole ratio vs. BTCA) at different pH values.

● CY-warp, ■ CY-filling,
▲ DCY-warp, ▼ DCY-filling.

Some properties increased while some decreased. Most significant increase was observed in retention of SFA resistance. Retentions of other mechanical

properties were also improved but the increase was not as great as that of SFA resistance. However, at the same time decrease in WRA and increase in dimensional change at high ammonia concentration indicated the effect of high pH on the esterification reaction of BTCA and cellulose molecules.

In order to confirm the pH effect in DP finishing of cotton with BTCA in the presence of carbodiimide catalysts, we treated cotton fabrics with BTCA and CY or DCY at different levels of bath pH. The pH of the bath was controlled by addition of 50% sodium hydroxide buffer solution. As shown in Fig. 1, the pH was an important factor in determining dimensional change. Up to pH 3.5 dimensional change was relatively consistent, and then started to decrease sharply. Wrinkle recovery angle values showed a similar trend (not shown).

In addition to BTCA, we also examined other polycarboxylic acid systems such as EDTA, citric acid, maleic acid, and malonic acid to treat cotton cellulose in the presence of DCY. Dicarboxylic

Table 3. Performance properties of cotton fabrics treated with various polycarboxylic acids and dicyandiamide.^a

DCY(mole ratio vs. PCA)	PCA ^b	% add-on	DP rating	DC(%)		WI ^c	
				warp	filling	before	after
control	0.0	1.3	-5.21	-4.69	80.9	97.1	
0.5	EDTA	0.6	2.3	-1.04	-1.82	77.8	95.2
	CA	5.7	3.0	-0.78	-0.78	40.8	48.6
	MA	4.1	3.0	-1.04	-0.78	38.1	42.7
	MOA	3.6	3.3	-0.52	-0.78	24.8	48.3
1.0	EDTA	1.1	2.0	-1.56	-1.56	77.3	93.7
	CA	6.0	3.3	-0.39	-0.78	40.4	40.0
	MA	3.4	2.8	-0.91	-0.91	30.3	42.4
	MOA	4.1	3.0	-1.04	-0.78	16.7	38.7

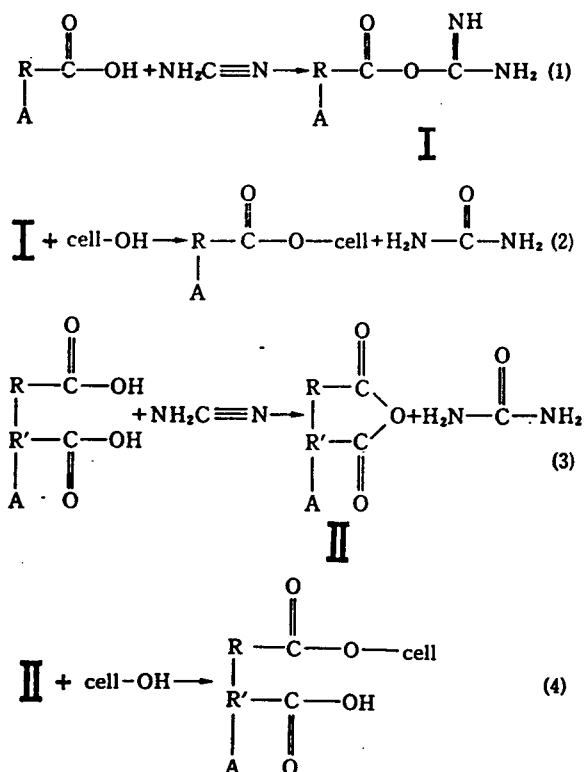
^a All treating bath contained 8% polycarboxylic acid(PCA), DCY, 1% softener, and 0.1% Triton X-100. The fabric was dried at 85C for 5 minutes and cured at 180C for 2 minutes.

^b PCA: ethylenediamine tetraacetic acid disodium salts(EDTA), citric acid(CA), maleic acid(MA), and malonic acid(MOA).

^c Before laundering(after processing-washing) and after one laundering.

acids were also included to examine if they can form crosslinking with cellulose, rather than one-side reaction (anchoring) in the presence of carbodiimide catalysts. However, these acids did not show sufficient levels of smooth drying appearance as shown in Table 3. In addition, except EDTA-treated fabrics the treatment with PCA and DCY caused considerable yellowing of the treated fabrics. The fabric whiteness was not recovered by home launderings. This is believed due to the formation of considerable amounts of urea, which might have been sorbed into the cotton cellulose. Substantial increases of the whiteness indices in the untreated control fabric and EDTA-treated samples were due to the sorption of fluorescent whitening agent from the AATCC detergent 124.

We believe that the tautomeric carbodiimide



[Scheme 1] Carbodiimide catalyst in cellulose esterification with BTCA (A is the moiety of BTCA)

catalysts could facilitate the esterification of polycarboxylic acid and cellulose in two ways as shown in Scheme 1. Both reactions involve the formation of urea. In equations (1) and (2), carbodiimide facilitated a direct esterification between cellulose and BTCA, where as the carbodiimide enhanced the formation of an anhydride intermediate that was a precursor for the esterification between BTCA and cellulose in equations (3) and (4). Therefore, low effectiveness in improving DP rating and dimensional change of the treated cotton with other PCAs such as maleic acid tended to suggest that the anhydride formation in equations (3) and (4) was more important in carbodiimide catalysis than the direct esterification mechanism. At least three carboxylic groups in the molecule are needed to induce esterification cross-linking on cellulose when the reaction proceeds through the anhydride formation⁸. Furthermore, the formation of urea by hydrolysis of carbodiimide can also easily occur at elevated temperature and

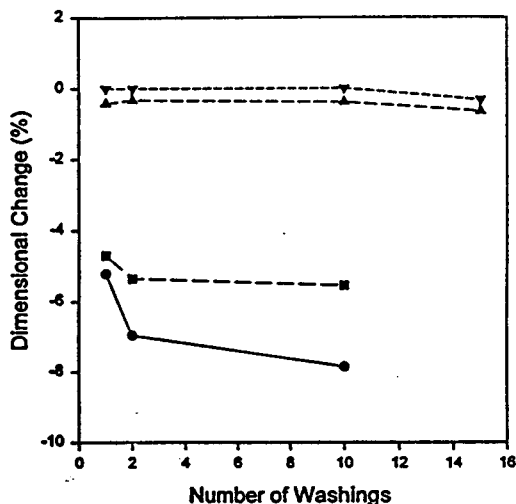


Fig. 2. Durability of the DP finished cotton fabrics treated by 8% BTCA and DCY (1: 1 mole ratio vs. BTCA). All values are average of two samples.

● control-warp, ■ control-filling,
▲ DCY-warp, ▼ DCY-filling.

Table 4. Color changes of the dyed fabrics treated by BTCA and various catalysts.^a

Dyes ^b	Gray Scales				ΔE^c				Relative K/S value ^c			
	CY	DSC	DCY	SHP	CY	DSC	DCY	SHP	CY	DSC	DCY	SHP
1	3	2~3	3	4	0.64	2.28	1.41	0.59	106.1	102.8	100.2	99.6
2	4~5	5	4~5	2~3	0.59	0.74	0.85	1.60	103.0	103.0	98.5	92.4
3	3~4	3	3	2	1.84	3.37	3.30	4.17	85.7	82.0	85.2	72.5
4	4~5	5	4~5	2~3	0.52	0.66	1.05	2.31	96.2	93.1	89.1	87.7
5	4	4~5	4	2~3	0.13	0.23	0.30	1.67	98.1	97.1	101.5	93.3

^a All treating bath contained 8% BTCA, catalyst (1:1mole ratio vs. BTCA), 1% softener and 0.1% Triton X-100. The fabric was dried at 85°C for 5 minutes and cured at 180°C for 2 minutes. ^b Dyes: 1 (C.I. Leuco Sulfur Yellow 1), 2 (Leuco Sulfur Blue 20), 3 (Leuco Sulfur Green 2), 4 (Leuco Sulfur Brown 96), and 5 (Leuco Sulfur Black 2). ^c ΔE was measured against the dyed, untreated cotton fabrics. Relative K/S values were calculated as follows: Relative K/S = [(K/S)_{sample} / (K/S)_{dyed unfinished}] × 100

acidic conditions, as in the finishing conditions used in the present study¹⁸. Therefore, we presume that different catalytic activity of the three carbodiimides in esterification could be related to the hydrolysis rate of the individual compound.

A repeated home laundering can be a good estimation of the durability of the finishes. As shown in Fig. 2, the untreated control and the fabric treated by BTCA and DCY were washed up to 15 times in a washing machine and their dimensional changes were measured. In both warp and filling directions, dimensional change for the DCY-treated fabric was only slightly varied indicating the durability of the finishes.

It has been known that SHP caused considerable shade changes in sulfur dyed samples^{6,7}. In this study, five different leuco sulfur dyes were selected to dye cotton fabrics prior to finishing treatment by the methods described elsewhere^{19,20}. After the DP finishing of the dyed samples, color changes were measured by three methods, as shown in Table 4. Relative K/S was calculated based on the ratio between the dyed and finished samples and the dyed and unfinished samples. Therefore, the value close to 100% represents that no or little color change has occurred by the finishing treatment. In general,

sodium hypophosphite showed the most significant shade changes except the fabric dyed with C.I. Leuco Sulfur Yellow 1. For some cases, certain levels of shade changes were observed from the fabrics treated with carbodiimide catalysts and BTCA. The most substantial color change occurred with the fabrics dyed with C.I. Leuco Sulfur Green 2 which changed its shade from green to bluish

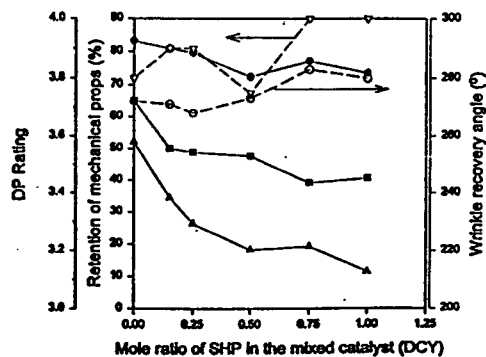


Fig. 3. Performance properties of the DP finished cotton fabrics treated by 6.5% BTCA and a mixed system of DCY and SHP. Total mole ratio of two compounds vs. BTCA was 1: 1.

● retention of tearing strength, ■ retention of breaking load, ▲ retention of Stoll flex abrasion, ○ CWRA, ▽ DP rating.

green. For an individual dye, all three factors (Gray scale, ΔE and relative K/S) were in good agreement in terms of differentiating shade changes.

We also examined mixed catalyst systems of SHP and carbodiimide. The fabrics were treated by 6.5% BTCA in the presence of mixture of SHP and DCY, as shown in Fig. 3. With increasing amounts of SHP concentration in the mixed systems WRAs and DP ratings were slightly improved. On the other hand, retention of SFA resistance decreased continuously between 52% and 11.4%, while retentions of breaking load and tearing strength were only marginally decreased. The same trend was observed with other nonphosphorus catalysts such as imidazole and mono or disodium salts of dicarboxylic acids^{8,11,12}.

IV. CONCLUSIONS

Carbodiimide compounds such as cyanamide, dicyandiamide, and disodium cyanamide have been examined in the DP finishing of cotton with polycarboxylic acid. Cyanamide was tended to be slightly less effective than two other compounds. In addition, DCY and DSC are also preferred catalysts due to toxicity and storage problems of CY. Addition of small amounts of ammonia can enhance retention of SFA resistance of the treated fabrics, probably due to the pH effect. The bath pH must be controlled precisely to obtain desirable smooth drying appearance as well as retentions of mechanical strength and whiteness of the treated fabrics. These carbodiimides generally caused less shade changes for the fabrics dyed by selective sulfur dyes. The treated fabric showed durability of the finishes when washed by home laundering process.

The use of these carbodiimides in the presence of BTCA can produce smooth drying cotton fabrics by "environmentally-friendly" nonformaldehyde-nonphosphorus DP finishing treatment.

REFERENCES

- 1) Welch, C. M., Tetracarboxylic Acids as Formaldehyde Free Durable Press Finishing Agents, *Textile Res. J.* 58(8), 480-486 (1988).
- 2) Welch, C. M. and B. A. K. Andrews, Ester Cross-links: A Route to High Performance Non-formaldehyde Finishing of Cotton, *Textile Chem. Color.* 21(2), 13-17 (1989).
- 3) Choi, H., Nonformaldehyde Polymerization-Cross-linking Treatment of Cotton Fabrics for Improved Strength Retention, *Textile Res. J.*, 62(10), 614-618 (1992).
- 4) Choi, H. and C. M. Welch, Unsaturated Dicarboxylic Acids in Nonformaldehyde DP Finishing of Cotton, Book of Papers, AATCC International Conference & Exhibition, Atlanta, GA, October 4-7, 1992, pp. 287-293.
- 5) Hudson, R. B. and M. J. Dolan, Phosphoric Acids and Phosphates, in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., vol. 17, M. Grayson, Ed., John Wiley & Sons, NY, 1980, p. 471.
- 6) Brodman, G. L., Performance of Nonformaldehyde Cellulose Reactants, *Textile Chem. Color.* 22(11), 13-16 (1990).
- 7) Choi, H., Li, J. D., Goodin, R. D., and T. D. Pratt, Shade Changes in Dyed Cotton Treated with Nonformaldehyde-Nonphosphorus Durable Press Finishes, *Amer. Dyestuff Rept.* 83(2), 38-43 (1994).
- 8) Choi, H., Welch, C. M., and N. M. Morris, Nonphosphorus Catalysts for Formaldehyde-Free DP Finishing of Cotton with 1, 2, 3, 4-Butanetetracarboxylic Acid, Part I: Aromatic N-Heterocyclic Compounds, *Textile Res. J.* 63(11), 650-657 (1993).
- 9) Welch, C. M. and J. G. Peters, Curing Agents Having Low or Zero Phosphorus Content for Formaldehyde Free DP Finishing with Polycarboxylic Acids, *Textile Chem. Color.*, 25(10), 25-29 (1993).
- 10) Park, J. L., Lee, E. S., and S. W. Ko, Durable Press Finish of Cotton Fabrics with 1, 2, 3, 4-Butanetetracarboxylic Acid, *J. of the Korean Fiber Society*, 33(5), 429-435 (1996).
- 11) Choi, H., Welch, C. M., and N. M. Morris, Nonphosphorus Catalysts for Formaldehyde-Free

- DP Finishing of Cotton with 1, 2, 3, 4-Butanetetracarboxylic Acid. Part II: Sodium Salts of Fumaric, Maleic, and Itaconic Acids. *Textile Res. J.* 64(9), 501-507 (1994).
- 12) Choi, H. and C. M. Welch, Saturated and Unsaturated Carboxylic Acid Salts as Curing Additives for Butanetetracarboxylic Acid Treatment of Cotton, *Textile Chem. Color.* 26(6), 23-27 (1994).
 - 13) Nkeonye, P. O., Reactive Dyes Containing Phosphonic and Carboxylic Acid Reactive Groupings and Their Reactions with Cellulose, *J. of the Society Dyers and Colour.*, 102(12), 384-391 (1986).
 - 14) American Cyanamide Co., Jpn. Kokai Tokkyo Koho JP 82 47,973, Creaseproofing of Cellulosic Fibers and Their Blends, 1982, cited in Chemical Abstracts 97: 7779x, 1982.
 - 15) American Cyanamide Co., Jpn. Kokai Tokkyo Koho JP 82 47,974, Creaseproofing of Textiles, 1982, cited in Chemical Abstracts 97: 40278f, 1982.
 - 16) Hansen, J. H. and P. H. Riggins, Formaldehyde-Free Textile Finish, U.S. Patent 5, 205, 836, April 27, 1993.
 - 17) Choi, H., Nonionic and Cationic Curing Additives Which Improve the Whiteness of Citric Acid Treated Cotton, *Textile Chem. Color.* 25(5), 19-23 (1993).
 - 18) May, D. R., Cyanamides, Kirk-Othmer Encyclopedia of Chemical Technology, Edited by H. F. Mark et al., 3rd ed., Vol.7, John Wiley & Sons, NY, 1979, p. 291.
 - 19) Colour Index, 3rd edition, The Society of Dyers and Colourists, Yorkshire, England, American Association of Textile Chemists and Colorists, North Carolina, U.S.A., 1971.
 - 20) Giles, C. H., A Laboratory Course in Dyeing, 3rd ed., The Society of Dyers and Colourists, England, 1974, p. 69.