Research Article

Development of a Process to Prevent Back Contamination Caused by Cationization After Cationic Digital Reactive Printing on Cotton Knitted Fabrics

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Received: 19 May 2025
Revised: 26 July 2025
2nd Revised: 18 October 2025
Accepted: 24 November 2025
Published: 27 November 2025

Reference: Malatyalı, D., Baloğlu, S. İ., & Alpaslan, S. E. (2025). Development of a process to prevent back contamination caused by cationization after cationic digital reactive printing on cotton knitted fabrics. *The European Journal of Research and Development, 5*(1), 263–275.

Abstract

Due to the restricted fixation and hydrolysis of reactive dyes, digital inkjet printing on cotton materials presents difficulties with low color output and substantial wastewater formation. Cotton can be cationically modified to improve color strength, decrease salt requirements, and boost dye absorption and fixation. However, conventional two-stage cationization methods are time-consuming and water-intensive, and they frequently result in back staining when the cloth is washed, with unfixed colors discoloring the white (unprinted) portions. By adopting a rotary printing process to directly put cationic printing primer onto cotton knitted fabrics, this study explores a novel one-step method to address these problems. We created three distinct pretreatment formulations: two with varying quantities of sodium hydroxide and 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) and a reference with no cationic ingredients. These formulations were applied to fabric, then digitally printed, air dried and steamed. In order to assess how well the printed fabrics prevented back-contamination, they were subsequently put through two distinct post-washing techniques; rope washing and open-width washing. The primary *objective was to determine whether a combined cationization and printing process could simplify workflow and significantly reduce water and chemical consumption while ensuring print quality. The level of back contamination was assessed qualitatively by visually assessing the contamination of white areas after each washing process. The results from this study will provide important insights into the discussion on the industrial applicability of cationic cotton, particularly by addressing the issue of persistent contamination and exploring more sustainable, one-step processing solutions. The results obtained from this study contribute to the development of more efficient and environmentally friendly digital printing processes for cotton fabrics by providing important insights into the discussions on the industrial applicability of cationic cotton fabric, particularly by addressing the issue of persistent contamination in cationization and investigating more sustainable, one-step process solutions.*

Keywords: *Digital Printing, Reactive Printing, Cationization, CHPTAC, Cotton, Knitted Fabric*

1. Introduction

The conventional method of dyeing cotton generally uses besides the dyes, the following chemical inputs: sulfate or sodium chloride, sodium hydroxide, sodium carbonate, acetic acid, surfactant, and chelating agent. Anionic dyes are often used for conventional cotton dyeing. This process, however, has a moderate affinity and it is estimated that less than 70% of the dye interacts with the cotton fiber (Correia et al., 2020).

Cationization is an alternative chemical process used in the pre-treatment of cotton fabrics, which provides cationic sites to cellulose fibers. After treatment, the fiber becomes positively charged, thus improving the interaction between reactive dyes and the substrate. The cationic agent 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) has low toxicity to humans and the environment and is widely used in the cationization of cotton fabrics. Most importantly, CHPTAC is a small-sized cationic modifier and does not cause the precipitation of reactive dyes (Rainert et al., 2024).

Ink-jet printing of textiles has developed rapidly in recent years because of its rapid response to fashion patterns and satisfactory printing effects. This modern printing is suitable for small-scale production to meet personal demand. In the future, it is largely possible that conventional flat rotary screen or roll printing techniques will be replaced by ink-jet printing. Unlike in conventional printing, cotton fabrics need to be pretreated in ink-jet printing with a pretreatment formulation containing a thickener, alkali, and urea, and then dried to remove water prior to ink-jet printing (Ma et al., 2017).

When it comes to all over printing with cellulosic substrates, reactive dyes are the preferred choice due to their bright shades, excellent uniformity properties, and exceptional fastness properties. However, reactive dyes have a low affinity for cotton fabrics (Rainert et al., 2024) same as conventional cotton dyeing method.

Due to limited reactivity and hydrolysis of the reactive groups during dye fixation step, reactive dyes only have a fixation of 50–80%, resulting in producing a large amount of dye wastewater. Moreover, monochloro-s-triazine dyes with low reactivity are commonly used in ink formulation to meet the requirement for stability, resulting in even low color yield of the prints. Therefore, one of the key problems for ink-jet printing of reactive dyes is the unsatisfactory color yield, which restricts the application of reactive ink-jet printing in producing deep colors (Ma et al., 2017).

Also, reactive dye is much easy to hydrolyze during steaming so the dye fixation rate and color strength are low and hydrolysed reactive dyes in the waste water may pose an environmental hazard. The cotton fabrics were modified by cationic compound, greatly enhancing the adsorption of reactive dyes. In addition to increasing color strength and dye fixation rate, cationic modification decreases the steam time by increasing the combination of the dye with the fibers. However, there are two disadvantages in using cationization method for inkjet printing. First, it is a two-step method that time consuming and high water consuming: the cotton has been treated with CHPTAC and sodium hydroxide through exhaust or pad-cure, acid washing and drying process; then the treated cotton is sized with sodium bicarbonate, urea and thickener, following dried, printed with reactive dyes and steamed. Second, due to that the cotton was all cationic the printed fabric was easily stained on the white areas by the unfixed dye contamination during washing process. If cationization and fixation are conducted at one step, the process will be simpler and significant time and water saving. CHPTAC is used as cationic agent in the one-step inkjet pretreatment technology and it is relatively nontoxic, is not an irritant or skin sensitizer (Farrell, 2012), and is widely used in cationic modification of cotton (Wang et al., 2018).

However, cationic cotton has still not seen a considerable industrial recognition aside from niche markets. This happens because of the concerns about the safety of cationic agents, cost of cationic agents and cationization process, lack of results in large scale procedures and lack of methodology to transition from a conventional to a cationic cotton dyeing. Also, the unpleasant smell that persists in the cationic fabric following treatment is a major worry with industrial cationization (Wolela AD et al., 2022). Trimethyl amine (TMA) is released when alkali and CHPTAC are combined to create reactive epoxypropyl trimethylammonium chloride (EPTAC) and to help cellulose and EPTAC interact. Because it smells like dead fish, the volatile TMA is extremely repulsive and may be easily found in the methods used to cationize cotton (Farrell et al., 2015).

In this study, we aimed to bring benefits such as increasing dye fixation, reducing water consumption, time saving and printing patterns clearer and more durable. On the other side, the technique may help to reduce dye wasting and other chemicals. So, makes the process more sustainable.

2. Materials and Methods

%100 cotton bleached three thread fabric, ludigol (BASF), sodium bicarbonate, urea (Ozan Boya ve Kimyevi Maddeler Tarım İnş. San. Ve Tic. A.Ş), alginate (CHT), sodium hydroxide (Ak-Kim Kimya San. Ve Tic. A.Ş.), CHPTAC (Sigma Aldrich).

Rotary printing machine (Stork), digital printing machine (Atexco), steam fixation machine, Wet fabric opening machine (Corino macchine), rope washing machine (Pulivia), open width washing machine (Corino machine).

2.1. Method

2.1.1. Cationic Printing Primer Application

Unlike traditional methods, digital printing paste reformulated for rotary printing and this paste was applied to the fabric using rotary printing technique instead of priming by padding technique.

A total of three formulations (paste-1-2-3) were applied individually, one without CHPTAC to be used as a reference and the others with two formulations containing varying amounts of CHPTAC.

Also, paste-0 was applied by conventional padding method for comparing back staining performance between two primer application methods.

Table 1. Digital reactive printing pre-treatment paste-0 (Reference)

Chemical Name	Amount of Chemical (g/kg)
Water (40-50 ^{o}C)	692
Sodium bicarbonate	30
Synthetic thickener	120
Ludigol	20
Urea	100

CHPTAC	10
Sodium hydroxide	28

Table 2. Digital reactive printing pre-treatment paste-1 (Reference)

Chemical Name	Amount of Chemical (g/kg)
Water (40-50 ^{o}C)	775
Sodium bicarbonate	30
Alginate	75
Ludigol	20
Urea	100

Table 3. Cationic digital reactive printing pre-treatment paste -2

Chemical Name	Amount of Chemical (g/kg)
Water (40-50 ^{o}C)	737
Sodium bicarbonate	30
Alginate	75
Ludigol	20
Urea	100
CHPTAC	10
Sodium hydroxide	28

Table 4. Cationic digital reactive printing pre-treatment paste -3

Chemical Name	Amount of Chemical (g/kg)
Water (40-50 ^{o}C)	699
Sodium bicarbonate	30

Alginate	75
Ludigol	20
Urea	100
CHPTAC	20
Sodium hydroxide	56

2.1.2. Digital Printing Process of Fabric

The printing processes were performed on a Atexco ink jet printer with a pass number of 4 and resolutions of 360 and 720 dpi. All prints were air dried and fixated on a steamer at 105 °C.

2.1.3. Washing Methods for Digital Printed Fabric

The fabric, which had been treated with cationic paste using the rotary printing technique, was washed in various washing machines. Among the washing methods we have at our facility and are believed to reduce back-contamination, the selected methods are; rope washing and open-width washing. Color measurements were used to monitor the extent of color contamination caused by different washing methods and washing performance was compared.

2.1.3.1. Washing With Rope washing machine:

Fabric that is processed in rope (tubular/looped) form rather than spread open in a batch or continuous washing machine. Widely used for cleaning in dyehouses following bleaching, scouring or dyeing. More flexible and compact than open-width washing, but if not managed, it could result in creases.

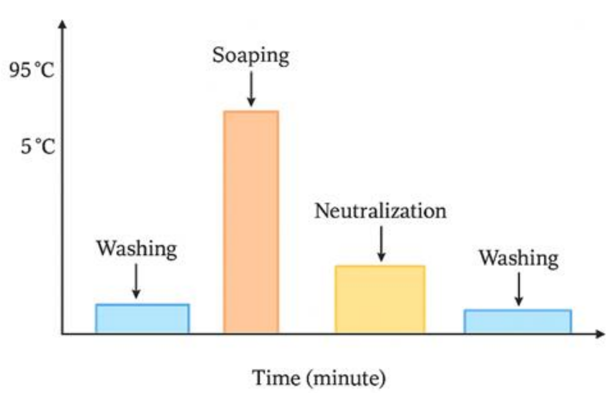

Figure 1: Graphic of rope washing process.

2.1.3.2. Washing With Open Width Fabric Washing Machine:

Instead of washing fabrics in tube or rope shape, this machine is made to wash them continuously in an open, unrolled, or flat state. Frequently seen in facilities that finish knitted and woven textiles. Prevents the uneven washing, wrinkles, and rope marks that can happen with rope washing machines. Guarantees consistent washing, which is crucial for sensitive, expensive or premium textiles. Overflow washing through 2 bath was applied to cationic printed fabric (Biancalani & Toccafondi, 2021). Process parameters are; 30 oC temperature and fabric passinig speed 10 m/min.

3. Results

Cationic printing pastes, both conventional pad-dry and rotary printing, and printing pastes containing no cationic agents were applied to 100% cotton fabrics. Fastness tests were conducted on ready-to-sew fabrics that had been subjected to digital printing, steam fixation, washing and finishing processes.

3.1. Fastness Tests Results

Perspiration acid and perspiration alkali fastness tests were performed according to the ISO 105-E 04 standard and the results are listed in Table 5.

Table 5. List of perspiration acid and alkaline fastness test results according to ISO 105-E 04 test standard.

Pre-treatment Paste No.	Washing process	Perspiration Acid Fastness			Perspiration Alkaline Fastness		
		Cotton	Nylon 6.6	Polyester	Cotton	Nylon 6.6	Polyester
0	Rope washing	3	3/4	4/5	3	4/5	4/5
1	Rope washing	4/5	4/5	4/5	4/5	4/5	4/5
2	Rope washing	4/5	4/5	4/5	4/5	4/5	4/5
3	Rope washing	4	4/5	4/5	4	4/5	4/5
1	Open width fabric washing	2	2/3	4	2	2/3	4
2	Open width fabric washing	2	2/3	4	2	4	4/5

3	Open width fabric washing	2	3	4	2	3/4	3

When the results are examined, it is seen that if rope washing is applied, the contamination in cotton, nylon and polyester products is low as a result of perspiration fastness tests, but only polyester contamination is relatively low as a result of open width washing.

Water and washing fastness results according to ISO 105-E01 and ISO 105-C06 standards are as shown in Table 6.

Table 6. List of water (ISO 105-E 01) and wash fastness test results (ISO 105-C 06).

Pre-treatment Paste No.	**Washing process**	**Water Fastness**			**Wash Fastness**		
		Cotton	**Nylon 6.6**	**Polyester**	**Cotton**	**Nylon 6.6**	**Polyester**
0	Rope washing	4/5	4/5	4/5	4/5	3	4/5
1	Rope washing	4/5	4/5	4/5	4/5	3	4/5
2	Rope washing	4/5	4/5	4/5	4	2	4/5
3	Rope washing	4/5	4/5	4/5	4/5	2	4/5
1	Open width fabric washing	3	4	4/5	4/5	4/5	4/5
2	Open width fabric washing	2	4	4	4	4/5	4/5
3	Open width fabric washing	2	2	3	4	4/5	4/5

According to the results in Table 6, it is clearly seen that the water fastness of open width washed fabrics is low and that reactive dyes that have an affinity for cotton contaminate the cotton too much, because of unbound dyes cannot be removed successfully by open width washing method. Additionally, the washing fastness after the rope wash is generally successful, and nylon contamination increases only as the amount of cationic agent increases.

Colour change after washing according to the ISO 105-C 06 standard, rubbing fastness according to the AATCC 8 standard and light fastness tests according to the ISO 105-B02 standard were evaluated and the results are given in Table 7.

Table 7. List of physical (ISO 105-C 06, AATCC 8) and light fastness (ISO 105-B02) test results.

Pre-treatment Paste No.	Washing process	Color Change After Washing	Rubbing Fastness		Light Fastness	Acid Light Fastness	Alkaline Light Fastness
			Wet	Dry			
0	Rope washing	4/5	2	3	4/5	4/5	4/5
1	Rope washing	4/5	3	4/5	4/5	4	4
2	Rope washing	4/5	2	4	4/5	4/5	4/5
3	Rope washing	4/5	2	3/4	4	4/5	4/5
1	Open width fabric washing	4/5	2	4/5	4/5	4/5	4/5
2	Open width fabric washing	4/5	2	4/5	4/5	4/5	4/5
3	Open width fabric washing	4/5	2	4	4/5	4/5	4/5

When the results in Table 7 are examined, it can be said that the cationization process has no effect on the post-wash appearance, rubbing fastness and light fastness tests.

Visuals of the fabrics which were pre-treated by pad-dry system are shown at Figure 2. Figure 2 shows the results at the end of washing with rope washing machine and open width washing machine after digital printing and fixation.

Also, the qualitative evaluation of the open width washing and rope washing results after digital printing of printing pastes containing and not containing cationic agents applied to fabric with rotary printing is as shown in the Figure 3.

Figure 2: a) Visual evaluation of fabric which were pre-treated with paste 0 by pad-dry system and rope washed after digital printing, b) Visual evaluation of fabric which were pre-treated with paste 0 by pad-dry system and open width washed after digital printing.

As can be seen in the image above, the cationic paste application by pad-dry technique causes back contamination in both washing methods, and open-width washing is less effective in removing unbound dyes.

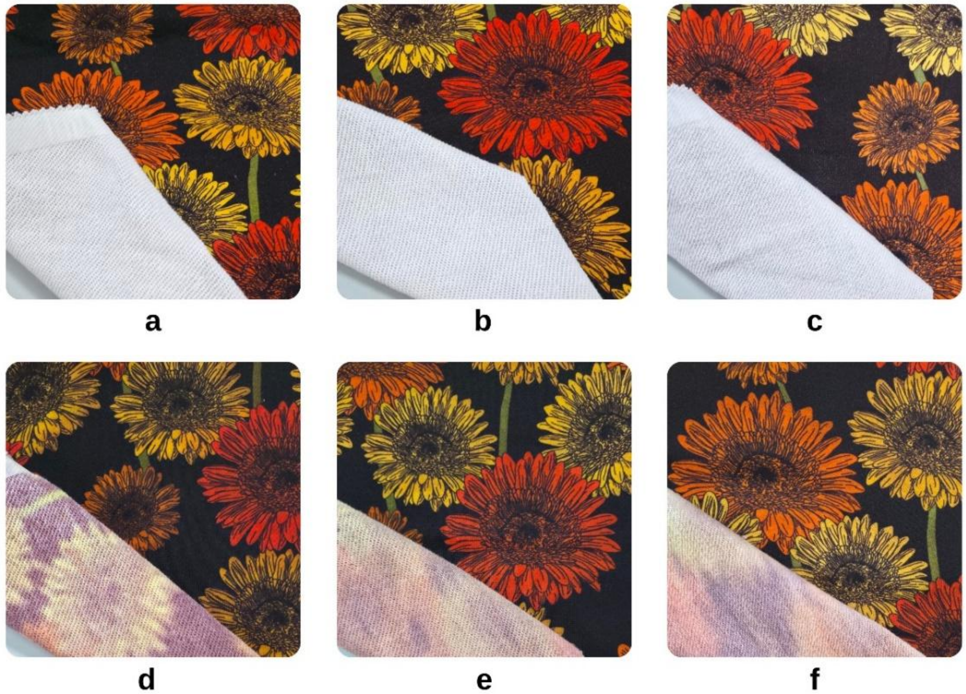

Figure 3: a), b), c) Visual evaluation of paste 1, 2 and 3 applicated fabrics after digital printing and rope washing, d), e), f) Visual evaluation of paste 1, 2 and 3 applicated fabrics after digital printing and open width washing.

In Figure 3, we can see that by applying cationic paste only to the front side of the fabric by rotary screen printing, post-washing back contamination is virtually eliminated. Furthermore, it is once again clear that rope washing is the most suitable post-printing washing method.

4. Discussion and Conclusion

This study investigated the industrial potential of a novel, one-step approach applying cationic pretreatment on cotton knitted fabrics to address key challenges in reactive digital printing processes. Considering that traditional two-stage cationization methods are time-consuming, consume high amounts of water and chemicals, and commonly cause back staining problems during post-printing washing, the main objective was to determine whether a single-step process implemented with the rotational printing technique could solve these problems.

The visual evaluation results of our study show that the application method of the cationic printing paste to the fabric and the washing method play a critical role in preventing back staining. Serious back staining was observed on the fabric to which cationic agent containing printing paste was applied using the traditional pad-drying method, after rope washing and open width washing (Figure 2a, 2b).

The results are much different for new, one-step cationic pretreatment pastes applied with the rotational printing technique. No back staining was observed in the white areas of all pastes applied with rotary printing after rope washing (Figures 3a, 3b, 3c). This shows that local application of the cationic agent (not spreading over the entire fabric surface) and rope washing with rotational application are successful in preventing the back staining of free dyes. It was observed that all of the pastes applied with rotational printing were ineffective in removing dyes that were not bound to the fabric after open-width washing and that there was significant back staining (Figures 3d, 3e, 3f).

In light of these findings, it was concluded that the rotational printing process, which is a single-step cationization method proposed to overcome the back-staining problem, should be combined with the rope washing machine as the final washing step.

While the primary goal is to prevent back staining, fastness testing must also support the ability of this new process to meet commercial standards.

When perspiration and water fastness was examined, cationic paste applied fabrics that went through the rope washing process generally showed better perspiration fastness compared to open width washed fabrics. Additionally, open-width washing resulted in a decrease in the water fastness values of the fabrics. This suggests that rope washing better removes the applied dye and cationic structure from the fabric fibers.

When the general fastness values were examined, the color change of the samples remained at acceptable levels in both washing methods. Light fastness values are also within acceptable limits. These results confirm that the newly developed process enhances the fixation of reactive dyes, ensuring that the final product has sufficient commercial fastness properties. In addition, the highest dye retention rates were observed in fabrics treated with cationic pastes, indicating that the cationization process was successful, but increasing the cationic agent beyond a certain amount did not further increase the color yield.

5. Acknowledge

This study was carried out by the Almaxtex Tekstil Sanayi ve Ticaret A.Ş. R&D Center, supported by the Republic of Turkiye Ministry of Industry and Technology, with the AGM-S3-P19 project code.

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