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Performance study of silicone and acrylic chemical resin binders on color fastness, colorimetric and drape propriety of cotton fabric dyed with thermochromic pigments.

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Abstract: The present research highlights the use of thermochromic dye via two different processes applied on cotton fabrics. Two different chemical binders, silicone and acrylic resins were investigated and their influence on mechanical characteristics and colorimetric behavior was studied. Comparison of the two used chemical binders was made and varied results were obtained revealing significant differences and clear influence in dyeing performance via the evaluation of color strength and the different colorimetric coordinates after the thermochromic dye application under the same condition (dye concentration, binder rate, thermo-fixation time and temperature). In addition, the two tested binders revealed varied influences on handle, color fastness and mechanical properties of dyed fabrics. Knowing the importance of dyeing with thermochromic pigments allowing functional and smart textiles, the selection of appropriate and efficient binder could improve an effective application of these dyes in various medical, protection and environmental fields.

Keywords: Thermochromic dyeing; Cotton fabric; Chemical binder; Silicone resin; Acrylic resin; Spectro-colorimetric study.

1. Introduction:

Smart textile fabrics are the result of the great development in material formulations, and methods of manufacturing textile and clothing. In this perspective, many efforts are made to develop and innovate a new generation of fabrics and textiles that are expected to be used in different fashions targeting various applications such as defense, medicine, and sports [1]. The use of thermochromic dyes is among the innovative textile finishing process allowing new functionalities investigated in different vital applied fields. The thermal chromaticity of the thermochromic finished fabrics is a unique novel core which was first noticed in the nineteenth century and until now has not been sufficiently exploited in the field of technical textiles [2]. These functional fabrics are also considered of great importance to artists and designers, as they are inspired by their capabilities to develop new creative design trends towards interaction and response in a functional and aesthetic manner [3] [4].

Thermal coloring is applied, usually with thermochromics colorants also called thermal dyes. On textile materials as is the case on t-shirts and dresses, to produce aesthetic and functional design, also known as smart materials, the change in the ambient temperature or the heat of direct sunlight can cause analytical change in color. Thermochromic colorants are also used nowadays to make camouflage patterns for military protective clothing [5, 6].

Figure (1-a) presents a sample of separately screen-printed fabric with a green, purple, and blue leuco-thermochromic dye, which shows the individual brilliant colors that can be obtained at ambient temperatures. Figure (1-b) shows the same samples after heating, causing the pattern to disappear, and then the designs appear again when the samples cool and return to room temperature [3].

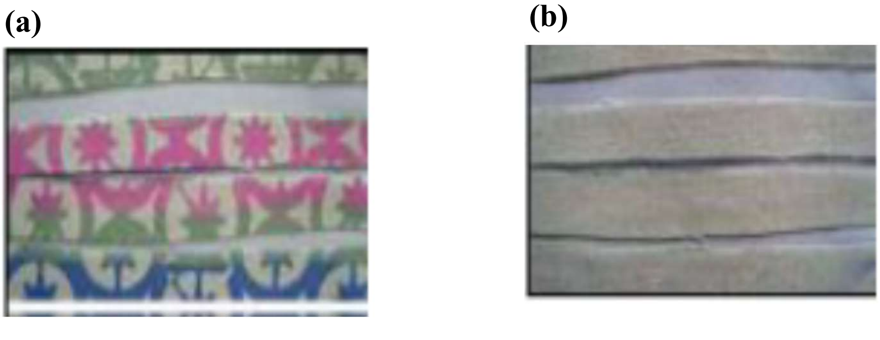

Fig 1. Textiles printed by thermochromic, (a) before and (b) after heating. The design disappeared after heating [3]

There are two main types of thermochromic systems that can be applied to textile materials. The first is a dye acting by the formation of colors from the interaction of three materials: color component (Leuco dye), acid (activator) and a low solvent solution. The working pattern with these substances includes a series of physical transformations within the complex system, which leads to a chemical shift between colored and colorless shapes depending on the chemistry of the Leuco dye, and the thermal coloration effect usually observed is the change from colored to colorless appearance (which is reversible) with increased temperature [7,8].

The second type of thermochromic system that can be applied to textiles depends on liquid crystals, which are often called an intermediate state of matter. Color appearing depends on the orientation of the particles and their randomness. The "thermochromic" effect provided by liquid crystals is completely different compared to Leuco dyes. The color change occurs because of the interaction of light with the liquid crystals to produce a colored diffraction depending on the interplanar distance variation with temperature [9].

The thermochromic dyes are preferably applied in the form of capsules, to ensure the presence of the substances and provide them with protection from their environment in which the substances may be sensitive (Figure 2). They are applied as separate fine solid particles. The primary problem encountered in applying thermochromic microcapsules to both synthetic and natural fibers is that the compressed thermochromic system is impermeable and insoluble in water. Indeed, they are not able to dye the fibers directly due to their lack of affinity with the fibers [10].

There are different methods and processes of applying thermochromic pigment on textile fabrics. Generally, the formulation-dyeing bath contains pigments, which are anchored to the substrate textile material by the binder, which adheres to the fiber and encloses the pigment particles. Besides the pigment and the binder, and the thickening agents that are effective for textile printing or coating, generally of the emulsion type, other auxiliaries could be incorporated. These include processing additions to enhance particularly the fastness and handle, with the use of dispersing agents, protective colloids, water-retention agents, crosslinkers, adhesion promoters, catalysts, handle modifiers and defoamers.

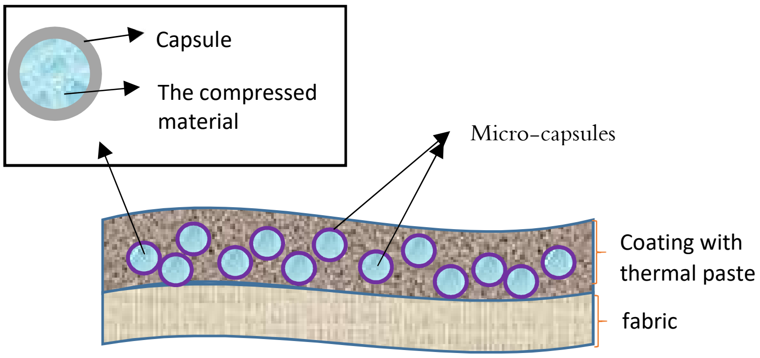

Fig 2. Textile surface coated with thermochromic micro-capsule pigments.

The two main processes of thermochromic pigments application are dyeing in full bath by impregnation and thermo-fixation or via printing procedure. For the first process, pigment emulsion is applied by direct impregnation of the textile or using the pad-dry-cure process. The dye molecules make an unbroken and solid chemical bond with the fiber molecules, as both curing temperature and time control are two main factors in the dyeing process. The second process is printing during which the dye has a uniform color. The printing allows a range of different colors to be applied to a fabric. Usually, the number of pastes used in the printing process is between 1 to 10 pastes required for a single sample, and the color can be supplied by either using dyes or other coloring materials. Printing is usually done with dyes that display an affinity for the fibers. On the other hand, it can be performed superficially with pigments, which can be fixed using thermoplastic resins [11].

Silicone and acrylic resins are among the most chemical binders used in textile pigment finishing. The application of thermochromic pigments as dyes to textile natural or synthetic fibers, faces difficulties due to the lack of affinity and insolubility in water. They are usually applied in presence of specific binding systems on the surface of fabrics [12]. The silicone and acrylic resins provide excellent adhesion, durability and protection when used as binders.

Silicone resins are made of highly crosslinked networks with high silicon and oxygen bonding energy, making them stable in harsh environments.

Acrylic resins are formed by polymerization of the esters of acrylic or methacrylic acids with different acrylate monomers. These resins create a durable, UV resistant film. The use of dye binders is very important in the production of colored fabrics in the textile industry, which should be inexpensive, provide good productivity and color fastness, and are non-toxic [13]. Hence the current research aims to compare the performance of the application of silicone and acrylic resins to fix thermochromic pigment dye on cotton fabric and an evaluation of the effect of each on the durability, color behavior and dye fastness properties against washing, sweat and friction.

2. Experimental

Cotton fabric was dyed with a thermochromic dye by the intermediate of two types of binders, silicone resin and acrylic resin. Then the effect of these chemical crosslinking agents on the fabric's drip and on the stability of the thermochromic dye was evaluated against washing, sweat and friction.

2.1. Materials

The material used for dyeing was a cotton textile knitted fabric. Table 1 shows an overview of its different properties.

Table (1). Characteristics of the cotton fabric used material

Variable	specification
Fabric	100% cotton
Surfacic weight	355 g/m^2
Thickness	1.3 mm
Structure	Jersy

The dyeing solution was prepared using thermochromic dye powder (ORANGE-RE-O21) in the form of fine microcapsules carrying thermal ink, which was produced by the company (GEM'INNOV). It is a metamorphic thermal dye with an orange color. This dye is thermally transformed, so whenever the dye is exposed to a temperature higher than 37°C, it changes its orange color to more clear shade until reaching the whiteness. Acrylic and silicon chemical resin binders (Figure 3) were supplied from Brenntag Company (USA) in the form of suspension solutions.

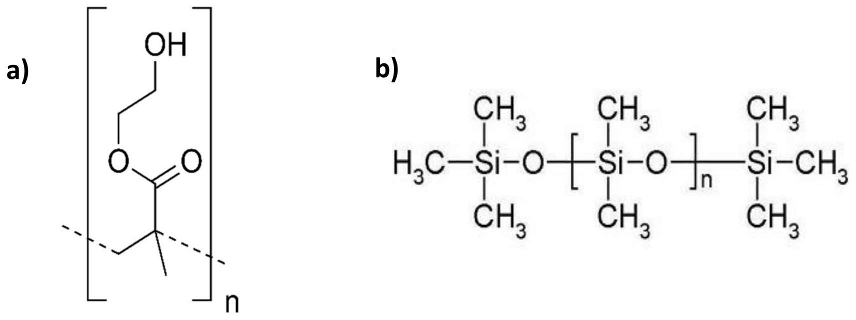

Fig.3: Chemical structures of acrylic (a) and silicon resin binders

2.2. Methods

2.2.1. Color measurements

The reflectance spectra of the dyed samples were measured using a spectrocolorimeter 3NH YD5010 within the visible spectrum at 39 wavelengths with 10 nm intervals from 380 nm to 780 nm. The K/ S values were determined using the Kubelka–Munk equation (Equation 1) [14].

$$\left(\frac{K}{S}\right)_\lambda = \frac{(1-R_\lambda)^2}{2\times R_\lambda} \quad (1)$$

where K and S are the absorption and scattering coefficients, respectively, and R_λ is the spectral reflectance of the dyed fabric at λ_{max} [15]

CIELab coordinates of color (L*, a*, b *) and the total color difference (ΔE) were measured under 10 degrees standard observer and D65 standard illuminant. Where, L* describes lightness, a* represents redness-greenness, b* represents yellowness-blueness [16, 17].

2.2.2. Drape Assessment test

For the drape assessment test, samples were cut in circular form and then placed between two small disks. The free ends of the fabric sample hang around the lower disk. The shadow resulting from the shape of the test sample is not circular. The test was performed using two samples of fabrics after placing them in a standard atmosphere for 24 hours. Each measurement represents the average of three essays [18]. The average drape coefficient of the total reading is determined according to the specification: Determination of drape coefficient (ISO 9073-9).

To estimate the Drape Coefficient، the following equation was used:

$$F\ (\%) = ((\mathrm{AS}\ \times\ \mathrm{Ad}\ )/\mathrm{AD}) \times 100 \tag{2}$$

Whereas:

F: Drape coefficient
AD: Total area of sample
Ad: Disk surface
AS: Total shadow area

2.2.3. Color fastness upon washing test:

Samples were washed in presence of detergent at a temperature of 40 °C for 45 minutes. Before washing, the samples were divided into six parts and then each part was knitted with a test white fabric of different textile origins (wool, acrylic, polyester, polyamide, cotton, and acetate). A gray scale, which ranges from no. 1 to no. 5 was used to determine the degree of color fastness. No. 5 represented the highest rate of color fastness and no. 1 the lowest rate.

The color fastness upon washing was determined according to the American Standard -AATCC 61c- 06.

2.2.4. Color fastness to perspiration test

Tested samples were placed in an acidic sweat solution. It was divided into five parts; each one was sewn to a different textile material test: wool, cotton, acetate, polyester, and acrylic. Then the sample was placed in the test device.

The device exerts slowly mechanical pressure on the sample with a temperature of 38 ± 1°C for 6 hours until the sample dries. The degree of color change of the sample, as well as the percentage of staining on the tested sample were measured to determine their color stability.

The color fastness to perspiration was determined according to the standardized test: ISO 105 E04: 2008.

2.2.5. Preparing of the dye bath:

For the two tested binders, the same dye bath was used. It contained:

- Ovarian Fabric

- Water used to maintain the liquid substance at a ratio of 1: 20

- Cationic agent to provide the fibers a very strong cationic charge: 15 mL

- Thermochromic dye in the form of capsules containing thermal ink: 20 g/L.

- Non-ionic dispersion adjustment factor (Alpadet CLW): 15-10 mL/L.

- Soft binder: Acrylic resin: 20 g/L.

Silicon resin: 20 g/L.

-Temperature: room temperature.

Drying at 90 °C for 20 minutes.

- Thermal stabilization of the treated fabric was performed via thermo fixation using an oven at 140 °C for 10 minutes.

3. Results and discussion

This part included the results of characterization tests on the dyed materials and the study of the effect of binder resins on the drop propriety of cotton fabrics as well as the degree of color stability and the different colorimetric measurements.

3.1. Colorimetric measurements

Colorimetric coordinates, total color difference and color strength were summarized in Table 2.

Table (2). Colorimetric coordinates, total color difference and color strength of dyed fabrics using silicon chemical resin and acrylic chemical resin.

	L*	a*	b*	C*	R%	K/S	ΔE
Dyed Fabric + Silicon Binder	74.32	29.83	18.50	35.10	13.44	5.75	7.512
Dyed Fabric + Acrylic Binder	73.36	35.28	23.58	42.43	13.73	5.95	

The different colorimetric results in Table 2 revealed a significant difference in dyeing behavior between the two chemical binders used to fix thermochromic pigments to the cotton fabric. Indeed, we noticed that with the acrylic resin the dyed sample was more reddish (a*) and more bluish (b*) than with the use of silicon binder. In addition, with the use of acrylic binder the resulting shade was more saturated (C*), so darker and this was confirmed by the reflectance which was more important. We also noticed a higher color strength (K/S) in the case of acrylic binder. This implied a more color uptake and fixation for the thermochromic dyeing using acrylic resin binder. The total color difference (ΔE) confirmed the variation in dyeing performance between the two chemical binders. Therefore, we could conclude that in the case of acrylic binder the bath exhaustion and the dyeing behavior was more efficient.

3.2. Strain measurement test:

Results in Figure 4 and Table 3 show that the drop coefficient for the sample dyed with the thermochromic dye using the acrylic resin (53.19%) was higher compared to the drop coefficient for the fabric dyed with the thermochromic dye using silicone resin (44.52%). This meant that the obtained rigidity and flexibility was better with silicon resin.

Table (3). Results of the drape factor test with the two types of binders used:

	Drop coefficient %
Virgin fabric	٤٣,٢٣
Dyed Fabric + Silicon Binder	٤٤,٥٢
Dyed Fabric + Acrylic Binder	٥٣,١٩

In the two cases with the use of acrylic or silicone binder, the evaluation of the fabric drape after dyeing was acceptable since the drape coefficient did not exceed the typical values of the drop coefficient ranging from 30% to 90%. Through these results, it was clear that the fabric's rigidity was not affected using silicone resin. Besides, for the fabric dyed using the acrylic resin we noticed a clearer modification of this mechanical property. Therefore, we could conclude that with the use of silicon binder we obtained better handle and tactile properties, implying an improving comfort in clothing.

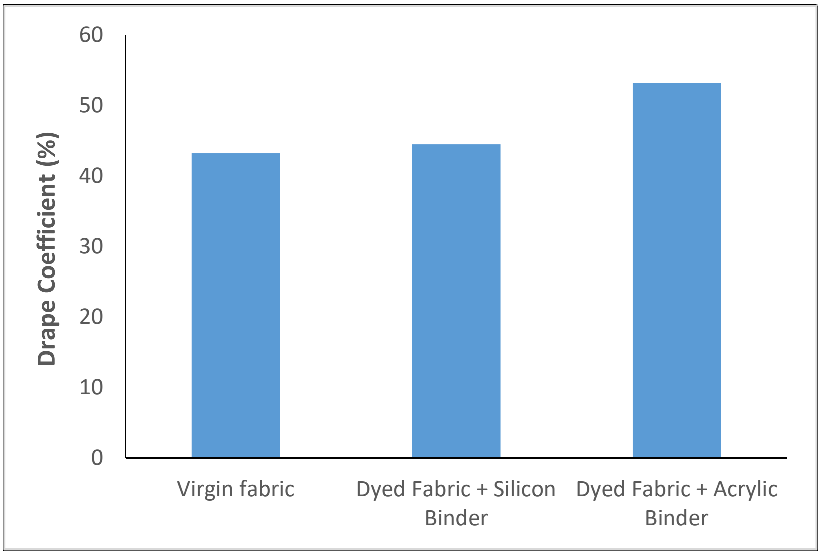

Fig 4. Drape coefficient properties of thermochromic dyed samples using acrylic and silicon resin binders.

3.3. Color fastness against washing standardized tests

The different color fastness results of dyed textile cotton fabrics fixed with the two chemical binders were presented in Table 4.

Table (4). Color fastness against washing tests

	Color fastness					
Textile testing fabrics	Wool	Acrylique	Polyester	Polyamide	Cotton	Acetate
Dyed Fabric + Acrylic Binder	4	4	4	4	4	4
Dyed Fabric + Silicon Binder	3	3	4	4	3	4

Results in Table 4 and Figure 5 presented the color fastness of thermochromic dyed samples after washing test which was made in contact with different natural and synthetic textile materials. In general overview of results, we noticed a good color stability for the two used resins silicon with a value of 3-4 (evaluation on the gray scale) and acrylic with a slightly better rating of 4. Therefore, these results of washing revealed a slightly higher color stability and fastness with the use of acrylic resin binder.

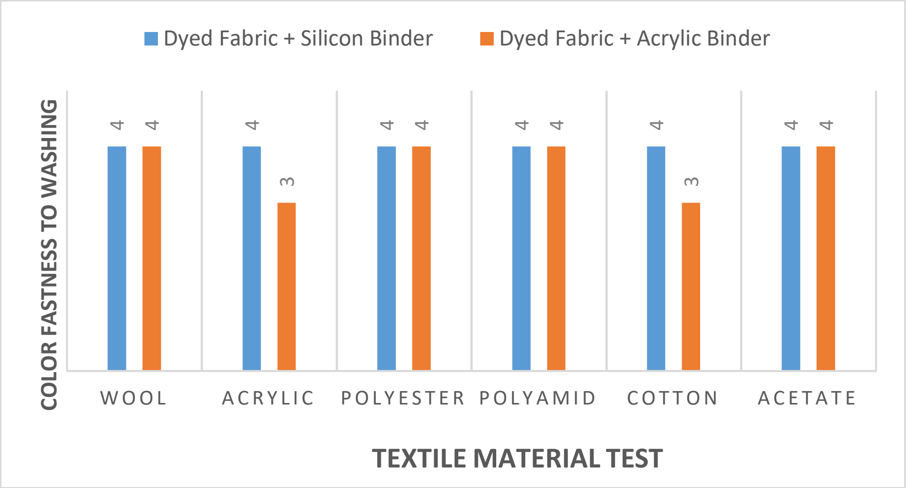

Fig 5. Color fastness results after standardized washing test using different textile materials in contact with the thermochromic dyed cotton sample. Gray scale was used.

3.4. Color fastness evaluation to perspiration

Different results of color fastness to perspiration were summarized in the following Table 5.

Table (5). Color fastness results to acid perspiration test

	Color fastness to acid perspiration						
		Degree of color change					
	Dyed sample alone	wool	Acrylique	Polyester	Polyamide	cotton	Acetate
Dyed Fabric + Acrylic Binder	٥	4	4	4	4	4	4
Dyed Fabric + Silicon Binder	٥	٤	٤	٥	٥	٤	٥

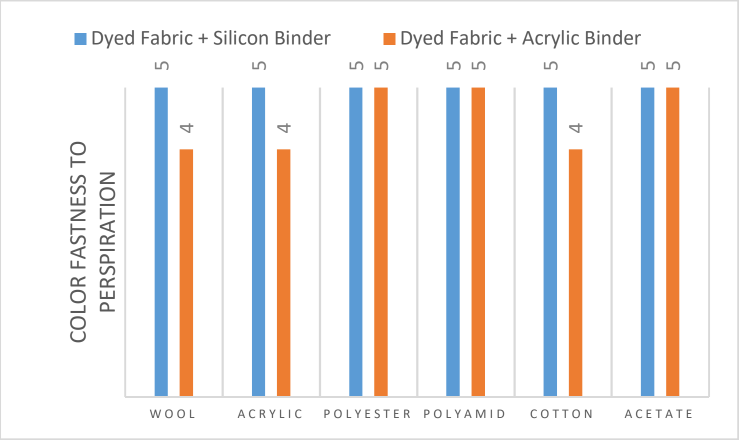

Fig 6. Color fastness results after standardized acid perspiration test using different textile materials in contact with the thermochromic dyed cotton sample. Gray scale was used.

Table 5 and Figure 6 show that textile materials revealed a good color stability in the acid perspiration solution. The samples scored high values ranging between 4-5. The samples in which acrylic resin was used as a fixed material recorded a high degree of 5 on the gray scale. The dyed samples using silicone resin scored from 4 to 5. Therefore, we could conclude the slightly higher color stability of dyeing after acid perspiration test using the acrylic resin binder as fixed and crosslinking agent.

3.5. Color fastness test against friction

Table 6 and Figure 7 showed that all the studied samples presented good color stabilities for dry friction. The samples recorded a high rating of 4 on the gray scale with the use of acrylic or silicon resin binder. Results revealed a slight decrease of color stability to 3 with the silicon binder. Therefore, for wet friction the acrylic binder was more efficient than silicon resin and presented a higher color fastness in thermochromic dyeing evaluation.

Table (6). The different friction results using gray scale evaluation after thermochromic dyeing of cotton samples. A comparison could be made after the use of the two silicon and acrylic resin binders.

	Color fastness test for dry friction	Color fastness test for wet friction
Dyed Fabric + Acrylic Binder	4	4
Dyed Fabric + Silicon Binder	4	3

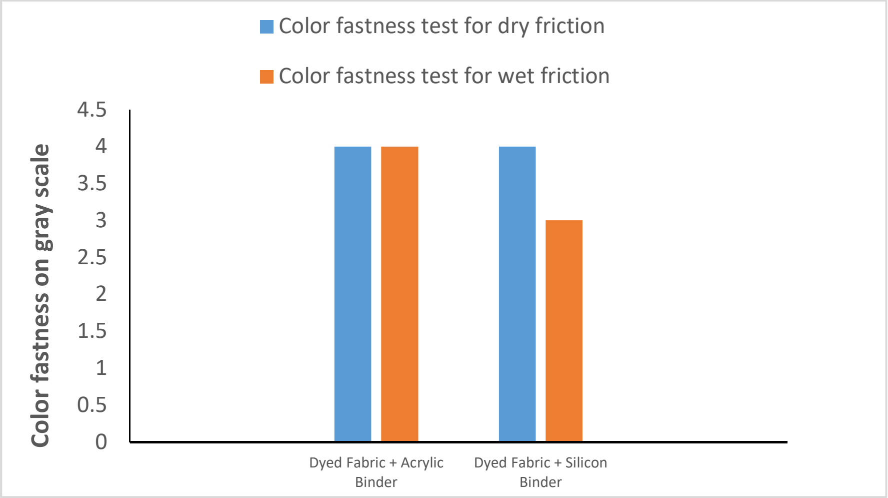

Fig 7. Color fastness evaluation of thermochromic dyeing after standardized friction test. Gray scale was used.

Conclusion

In this study, a comparison study was performed between silicon and acrylic chemical binders in their use in thermochromic pad-dry-cure dyeing process for cotton textile material. The two chemical resins showed an efficient dyeing performance with some variations in their influence on the cotton properties. Colorimetric study revealed that the use of acrylic binder was slightly more effective than silicon resin and presented improved exhaustion and color strength characteristics. Different tests of color fastness showed a more efficient dyeing stability after the use of acrylic resin binder. However, with the silicon binder the different mechanical properties were more effective. Indeed, the obtained handle, tactile and flexibility properties of dyed samples were more enhanced, implying an improving comfort in clothing. This study therefore revealed the influence of the use of silicone or acrylic as a binder in the thermochromic dyeing of cotton. An influence generating varying properties of the finished textile, hence an obvious selection of the binder according to the intended application.

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