

Production of Organo-Modified and Amino-Functional Silicone Finishing Chemicals and Their Effects on The Handle and Color Values of Cotton Knitted Fabrics

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ABSTRACT

In this study, silicone finishing chemicals were produced using organo-modified, amino-functional silicone oils and polar additives (polyethyleneglycol). Silicone emulsions are affected by many factors. These are the type of oil used when producing silicone softener emulsions, the ratio of emulsifiers, hydrophile-lipophile balance (HLB) values of emulsifiers, particle size of the silicone finishing chemicals produced, and viscosity of silicone emulsions. After the application, quantitative handle, soft feel, particle size analyzes of the prepared silicone finishing chemicals, CIELab color, and Berger whiteness index measurements were evaluated. As a result, organo-modified and amino-functional silicone finishing chemicals caused the handle, softness properties, and color differences in cotton knitted fabrics. The large particle size of emulsions caused the large color difference, which is calculated from the changes in color coordinates. The main factor affecting the softening (quantitative behavior) of fabric samples applied with silicone finishing chemicals is the number of amino groups. At pH 5.5, the better handle and softness properties were obtained as more secondary amine groups were ionized. The particle size and viscosity of silicone finishing chemicals have an effect on the handle of fabric samples.

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ÖZ

Bu çalışmada organo-modifiye ve amino-fonksiyonel silikon yağları ve polar katkı maddeleri (polietilenglikol) kullanılarak silikon bitim kimyasalları üretilmiştir. Silikon emülsiyonları, birçok faktörden etkilenir. Bunlar, silikon yumuşatıcı emülsiyonları üretilirken kullanılan yağın cinsi, emülgatörlerin oranı, emülgatörlerin hidrofil-lipofil denge (HLB) değerleri, üretilen silikon emülsiyonlarının parçacık boyutları ve silikon emülsiyonlarının viskozitesidir. Uygulama sonrasında kantitatif tutum, yumuşaklık hissi, hazırlanan silikon emülsiyonlarının partikül boyut analizleri, CIELab renk ve Berger beyazlık indeksi ölçümleri değerlendirilmiştir. Sonuç olarak organo modifiye ve amino fonksiyonlu silikon apre kimyasallarının pamuklu örme kumaşlarda tuşe, yumuşaklık özellikleri ve renk farklılıklarına neden olduğu görülmüştür. Emülsiyonların büyük parçacık boyutu, renk koordinatlarındaki değişikliklerden hesaplanan büyük renk farkına neden olmuştur. Silikon apre kimyasalları uygulanan kumaş numunelerinin yumuşamasını (kantitatif davranışını) etkileyen ana faktör amino grup sayısıdır. pH 5.5'te daha fazla ikincil amin grubu iyonize edildiğinden daha iyi tutum ve yumuşaklık özellikleri elde edilmiştir. Silikon bitim kimyasallarının parçacık boyutu ve viskozitesi, kumaş numunelerinin tutumu üzerinde etkiye sahiptir.

1. INTRODUCTION

Cotton has a good handle and moisture absorption properties. The knitted fabric properties depend on many factors, from the fiber properties to the structural properties of the yarn. The moisture properties of knitted fabrics depend on the fibre type, fibre fineness, yarn type, yarn twist, fabric structure, and surface finishing [1-3].

Due to the hydrophilic characteristics of cotton fibres, cotton knitted fabrics have better moisture transmission properties. The minimum wet radius value for the top and bottom surfaces reflects good moisture transport properties and a feeling of dryness. The high hygroscopic property of the fabric increased moisture absorption and allowed sweat to dry faster from the skin [4,5]. 100% cotton knitted fabrics have a longer wetting time and slower absorption rate.

Softeners provide surface softness by reducing the friction coefficient between fibers, and improve the wear feeling of textile materials [6].

Silicones have hydrophobic properties, elasticity, and film-forming ability due to the low interaction between Si-O-Si and methyl groups. Silicones with groups such as amino alkyls show super softness and durability properties. These silicones are cross-linked to fibers by electrostatic forces and H bonds [7-9].

The softening effect of silicones depends on their amino groups. For pure cotton, the amine number is important. Particle size and viscosity have little effect [10,11]. Amines are a class of nitrogen-containing compounds used as dyes, polymers, and surfactants. Amino-functional silicones react with amino epoxy groups to reduce yellowing.

Amino functional silicones provide the feature to knitted fabrics with weak acid bath. After applying amino silicone softener, the fabrics become slightly yellowed. Ethylene amines are used to obtain a soft handle [12].

Amino functional silicones showed softness and lubrication effect on polar fibers and did not cause any change in the tone of the dyed fabric [13]. Amino silicone emulsions are sensitive to changes in bath pH. In an acidic environment, amino groups have a positive charge and form an ammonium ion structure. This group determines the stability of the emulsion. When the ammonium groups lose a proton in the alkaline bath, the polarity of the silicone decreases, and the stability of the emulsion decreases [14].

Poly-ethoxylated amino silicone compounds have good absorption properties with the amino groups in their structure. Amino silicones are most used in textile applications. They provide permanent softness to the fabric [15].

Organo silicone compounds are polymeric materials and consist of a silicon-oxygen chains and hydrocarbon radicals. Organo-silanes have been used in various applications such as adhesion or the surface modification. Organofunctional silicones contain different groups: for instance, $-NH_2$, $-CH-CH_2-O-$ (epoxy), $-NR_3^+$, Cl^- , $-COOH$, $-NHCOR$. Modified silicone materials indicate the hydrophilicity of finished products. They have amino groups and high softness properties [16].

Textile finishing chemicals such as micro ($<0.01\mu m$) and macro ($<0.1\mu m$) have a milky feature [17].

2. REVIEW OF LITERATURE

There are some research works, where different types of silicone emulsions are used in cotton knitted fabrics.

In studies [18,19], the organo-modified silicones were used. Reactivity and permanent softness were achieved with silicone copolymers containing hydrophilic groups such as polyalkylene oxide, amine, amide, or epoxy groups.

In studies [20,21], the amino silicone based softeners were prepared with different emulsifiers. Amino silicone hydrophobic film was applied to cotton and cotton/polyester blend fabrics by a coating process. The polar silicone-oxygen bond was attached to the cotton fabric surface, and the silicone containing methyl group formed a hydrophobic layer on the fabric surface [20]. Fixation of the amino-functional silicone softener onto the cellulose structure enhanced the extent of crosslinking, provided high softness and roughness decreased as the strength increased. Acceptable rubbing fastness results were achieved without losing softness and permanent handle. The modified amine derivatives, such as amino ethyl, amino propyl functional silicones, provided good softness and less yellowing due to their weaker interactions with the fibers [21].

In study [22], the amino-modified silicone oil was synthesized by bulk polymerization. The amino value in the emulsion was measured as 0.71 mmol/g. Amino modified silicone emulsion had a non-ionic character. The handle (softness) property of the finished cotton knitted fabric was 5. In the softness test, the scale was changed from 1 to 8, that 8 is the best softness and 1 is the harshest.

In studies [23, 24], the amino functional silicones were used. They formed hydrophobic film on the fabric surface owing to strong dipole–dipole hydrogen bonding and electrostatic interactions with cellulosic fibres.

The pH of the bath affected the softening properties of aminoalkyl functional siloxanes [25]. The softening mechanism of aminoalkyl functional siloxanes was studied by molecular interaction. Softening mechanisms included the interactions of aminoalkyl siloxane softeners with fiber. The amino groups become cationic ($-\text{NH}_3^+$) in acidic conditions and a strong bond with the fabric was formed through ionization. The structure and particle sizes of mono-aminoalkyl siloxane polymer emulsions varied with pH. At pH 6.0, amino groups become cationic ($-\text{NH}_3^+$), and one end group ionized. When the pH was greater than 8, softness increased due to the change in the molecular structure of the cotton fiber.

Silicone softeners were synthesized in three different chemical ratios and applied to knitted and woven cotton fabrics [26]. Various tests were carried out such as solid content, stability, fabric whiteness, tensile strength and absorbency. As a result, it was determined that the best silicone softener increased the softness of the fabric and imparted it less absorbent.

In this study [27], silicone oil was stabilized into nano or micro droplets by surfactant and guar gum. As a result, it was determined that the use of HP-guar depended on the silicone concentration.

In this study [28], the effects of the silicone emulsions at different particle sizes on the performance of 100 % cotton knitted fabrics were examined. The silicone emulsions were applied to knitted fabric samples by padding and exhausting methods. After treatments, CIELab, Berger whiteness index values, and particle sizes were measured. After these tests, the change on the performance of the fabric samples was evaluated depending on the particle size and the chemical structures of the silicone oils.

The effects of six types of softeners on the handle properties and washing durability of cotton and bamboo knitted fabrics were investigated [29]. The washing durability of the softeners was tested after 5, 10 and 20 washes.

In this study, organo-modified and amino-functional polysilicone finishing chemicals were prepared using different structures of silicone oils and polar additives. The prepared emulsions were applied to 100% cotton (30/1 Ne) knitted fabric samples according to the impregnation-drying method. The effects of emulsifier ratio, amino group content, and particle sizes of silicone emulsions on the softness (handle) and color values of cotton knitted fabrics were examined. The color values and hand feeling of the treated fabrics were evaluated.

3. MATERIALS AND METHODS

In this study, the production of organo-modified and amino-functional finishing silicone chemicals and their effects on the softness and color values of cotton knitted fabrics were examined.

3.1. Materials

100% cotton (30/1 Ne) knitting fabric as a t-shirt (265 g/m²) was employed in this study. Organo-modified and amino-functional silicone oils were supplied by Terrasilicone, and additives (alcohol ethoxylates (IT3, IT6, IT12) (polar auxiliaries) were supplied by Denge Chemistry.

3.2. Preparation of Organo-Modified and Amino-Functional Silicone Emulsion Recipes

To evaluate the effects of organo-modified and amino-functional finishing chemicals on post-application softness and color values in 100% cotton single jersey fabric samples, 14 different oil-in-water-based finishing silicone chemical recipes were prepared by using organo-modified and amino-functional silicone oils. 14 different oil-in-water-based finishing chemical recipes were indicated in Table 1.

Table 1. Organo-modified and amino-functional finishing chemical recipes*

	Water	IT3- emulsifier	IT6- emulsifier	IT12- emulsifier	Oil	Defoamer	Protective chemical	pH
R1	45.6	1.5		2.5	50	0.3	0.1	5.5
R2	43.6	2.3		3.7	50	0.3	0.1	5.5
R3	45.6		3.22	0.78	50	0.3	0.1	5.5
R4	43.6		4.83	1.17	50	0.3	0.1	5.5
R5	45.6	0.92		3.08	50	0.3	0.1	5.5
R6	43.6	1.38		4.62	50	0.3	0.1	5.5
R7	45.6		1.93	2.07	50	0.3	0.1	5.5
R8	45.6	1.5		2.5	50	0.3	0.1	5.5
R9	45.6		1.93	2.07	50	0.3	0.1	5.5
R10	45.6	0.92		3.08	50	0.3	0.1	5.5
R11	43.6	1.38		4.62	50	0.3	0.1	5.5
R12	43.6	2.3		3.7	50	0.3	0.1	5.5
R13	43.6		4.83	1.17	50	0.3	0.1	5.5
R14	45.6		3.22	0.78	50	0.3	0.1	5.5

*Organo-modified silicone oil was used in (R1, R2, R3, R4, R5, R6, R7) and also amino-functional silicone oil was used in (R8, R9, R10, R11, R12, R13, R14)

In this study, IT3, IT6, and IT12 alcohol ethoxylates polar additives in each recipe were dissolved in water for 5 min at 1000 rpm. Then, 50% organo-modified and amino-functional oil were added and mixed for 20 min at 1000 rpm. After, 0.3% defoamer was added to finishing silicone emulsion and mechanically mixed for 2 min at 1000 rpm. Then, 45.6 % and 43.6 % water were added very slowly and mixed mechanically at 800 rpm for 10 min to obtain the desired fluidity. After, 0.1% protective chemical was added and mixed for 5 min at 500 rpm. Finally, the acetic acid was added to adjust the emulsion pH to 5.5 and mixed at 500 rpm to make a fully homogeneous solution.

3.3. Treatment of Cotton Knitting Fabric with Organo-Modified and Amino-Functional Finishing Silicone Chemicals

The organo-modified and amino-functional finishing silicone chemicals were applied to 100% cotton (30/1 Ne) knitted fabrics using a laboratory padder (padding method). 60g/l solution of macro silicone finishing chemicals was applied to grey-colored fabric samples by padder with 90.9% pick-up, and the fabric samples were dried at 100°C for 5 min and cured at 150°C for 5 min. Firstly, the pH of the finishing silicone chemicals was adjusted to 5.5 by using acetic acid. Secondly, the color values, color change, softness, and particle size of finishing silicone chemicals were measured.

3.4. Testing and Analysis

In order to determine the effect of finishing silicone chemicals prepared by additives on the softness and color values of cotton knitted fabrics were tested.

Color measurement was evaluated using a reflectance spectrophotometer according to AATCC 173. 100% cotton knitted fabric without finishing silicone chemical was used as a zero reference sample. CIELab coordinates L*(lightness), a*(red-green axis) and b*(yellow blue axis), C*(chroma), the total color difference (ΔE^*), K/S (color strength) and Berger white index values were obtained from color measuring. Four reflectance measurements were made on each finishing silicone chemical emulsions and the averages of the reflectance values (%) at wavelengths between 400 and 700 nm were obtained.

The particle size of prepared finishing chemicals was measured by a laser particle size analyzer. The particle sizes of macro finishing chemicals were between 150 and 250 nm. In fact, particle sizes of the macroemulsion finishing silicone chemicals were higher, they were deposited on the yarn surface. Macroemulsion finishing silicone chemicals reduced the friction coefficient between fibers to obtain the surface softness [29]. Handle expressed as the quantitative sensory evaluation of fabric samples. Organo-modified and amino-functional silicone emulsions were diluted at 60g/L and the hue changes and Berger whiteness index of dyed knitted fabrics before and after application were compared according to standard test method [30].

4. RESULTS AND DISCUSSION

4.1. Softness of Treated Cotton Knitted Fabrics

The handle effects with softness depend not only on the chemical character but also on their position in the textile. If the softener was penetrated into the yarn, a secondary handle effect was obtained. The macro finishing silicone chemicals consist of particles with a diameter of greater than 150. Macro finishing chemicals provided a very pleasant surface smoothness with a soft voluminous handle to the fabric samples. In this study, the fabric handle was evaluated through subjective assessment by people. 10 researches from the textile and clothing sectors were chosen for fabric handle evaluation. The tests were fulfilled in standard atmosphere conditions ($20 \pm 2^\circ\text{C}$ temperature and $65 \pm 4\%$ relative humidity). 20×20 cm fabric samples were prepared for subjective test method. The researchers made an assessment using a 5-point scale. The softness rating numbers for scale were given in Table 2.

Table 2. Softness rating numbers for scale

Sensory attribute	Rating number
Softness/Stiffness	1-stiffest.....5-softest

In the subjective evaluation procedure, softness-stiffness is related to bending. Fabrics that can be bent easily have been described as soft. During evaluation, researchers held the fabric between their thumbs and palms. While the four fingers of the hand were moving, the durability of the fabric was evaluated. The more resistance, the stiffer the fabric. Low resistance showed that the fabric was soft [31]. Researchers were asked to rate the softness/stiffness of the fabric samples between 5 and 1; 5 being the best and 1 being the worst. After the hand evaluation of the researchers, the softness/stiffness degree of the fabric sample treated with the R8 recipe corresponded to 5 (the best), while the softness/stiffness degree of the untreated fabric sample corresponded to 1(the worst). The other samples were rated by the researchers according to this hand evaluation scale. The corresponding ratings were presented in Table 2. The ratings which did not correspond to exact hand feeling were presented as “in the middle ratings”, i.e., “between 3 and 4”.

Reactive silicones were preferred to obtain a super soft handle. Amino or quaternary functional silicones were superior in hand. Quaternary ammonium groups improved softness and increased bath stability against electrolytes. Amino propyl silicones performed a soft handle. Non-yellowing amino silicone structures can be produced such as alkylation or the N-atom in a ring structure.

When the effect of the applied organo-modified finishing chemical emulsions strength (different structure of emulsifier in recipes) on dyed cotton knitted fabrics was examined, it could be seen that the sample 1(emulsion recipe-1) showed the best softness. The results of samples 5, 4, 6, 2, and 3 had moderate softness. However, the sample 7 had the worst softness. And also, the amino-functional finishing chemicals are applied to dyed cotton knitted fabrics were compared, and it was seen that the sample 8 showed the best handle. The softness of samples 12, 14, 13,10, and 11 were moderate. Additionally, the sample 9 had the worst softness. From the results obtained, it has been determined that amino-functional silicone finishing

chemicals exhibited softening features due to their excellent film forming ability. Furthermore, they were easily emulsified, stable on dilution, compatible with other finishing agents and non-yellowing. The best handle softness was related to the affinity of amino group to fiber and also its linkage to the silicones. Similarly, the structure of the emulsifier used and compatibility of used emulsifier with amino-functional or organo-modified silicone emulsion. The result of softness ratings treated with organo-modified and amino-functional silicone emulsions were given in Table 3.

Table 3. The fabric softness ratings treated with organo-modified and amino-functional silicone emulsions

Fabrics		Softness rating	Fabrics		Softness rating
Organo-modified silicone emulsion recipes	untreated knit fabric	1.0	Amino-functional silicone emulsion recipes	untreated knit fabric	1.0
	R1 treated knit fabric	4.0		R8 treated knit fabric	5.0
	R5 treated knit fabric	between 3.0 and 4.0		R12 treated knit fabric	between 3.0 and 4.0
	R4 treated knit fabric	between 3.0 and 4.0		R14 treated knit fabric	between 3.0 and 4.0
	R6 treated knit fabric	between 3.0 and 4.0		R13 treated knit fabric	between 3.0 and 4.0
	R2 treated knit fabric	between 3.0 and 4.0		R10 treated knit fabric	between 3.0 and 4.0
	R3 treated knit fabric	between 3.0 and 4.0		R11 treated knit fabric	between 3.0 and 4.0
	R7 treated knit fabric	2.0		R9 treated knit fabric	2.0

The functional silicone finishing chemical improved performance properties (such as good softness, smoothness, whiteness and hydrophobicity) of the fabrics [32]. Amino groups were formed hydrogen bonds. These groups were strongly interacted with cellulose. The formation of hydrogen bonds between amino groups and cellulose indicated in Figure 1.

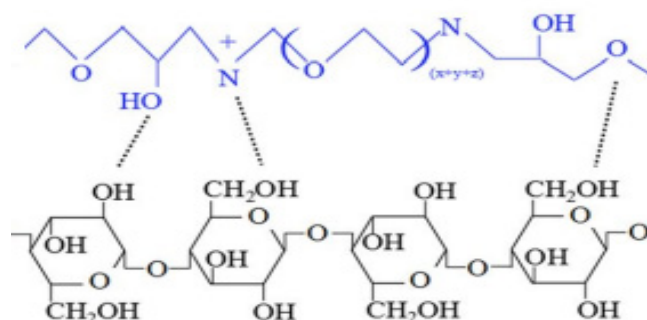


Figure 1. The formation of hydrogen bonds between amino groups and cellulose

The amino-functional silicones had a soft handle on the fiber surface. The amino-functional silicones could form a hydrophobic film on cotton knitted fabrics. Therefore, silicone (Si) also formed covalent ether bonds between cellulose and amino silicone molecules. In amino-functional silicones, the number of functional groups, viscosity and chain length are important.

In amino-functional silicone finishing chemicals, the primary functional (non-ionized NH₂) group was contributed to the electrostatic interaction with the cotton fiber, and also the -NH₃⁺ and -NH₂⁺ groups in the ionized state. As the amount of ionized amino groups (at pH 5.5) was increased, the electrostatic interaction of the cotton fiber with amino-functional finishing chemical was reduced. As the interaction energy was decreased (at pH 5.5), the more secondary amine groups were ionized. Thus, the handle and softness properties were improved.

4.2. Particle Sizes of Organo-Modified and Amino-Functional Silicone Emulsions

The emulsion stability characteristics, molecular conformation, particle size, pH and temperature were played significant roles in desired surface properties.

The particle distribution of emulsions homogeneity value was important. The positively charged emulsions adsorbed on the surface of negatively charged cotton fabrics. In this study, particle size graphs of silicone emulsions with the best softness and worst softness properties in organo-modified and amino-functional finishing chemicals were given in Figure 2a, 2b, 3a, 3b and Table 4.

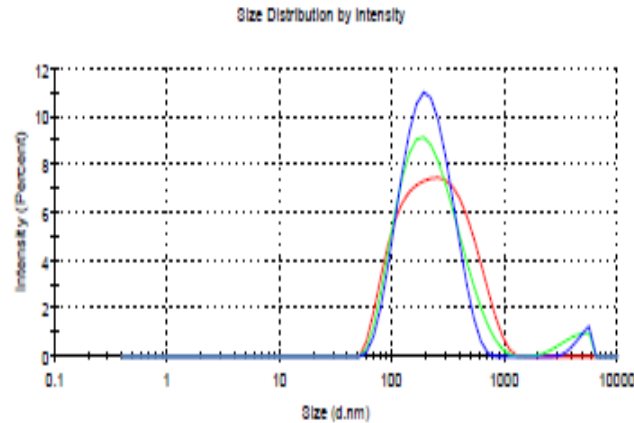


Figure 2a. The particle size of E1 organo-modified finishing chemical (the best softness property) (recipe 1). The particle size of E1 organo-modified was 286.3 nm (100 %) and the solution was cloudy (Figure 2a).

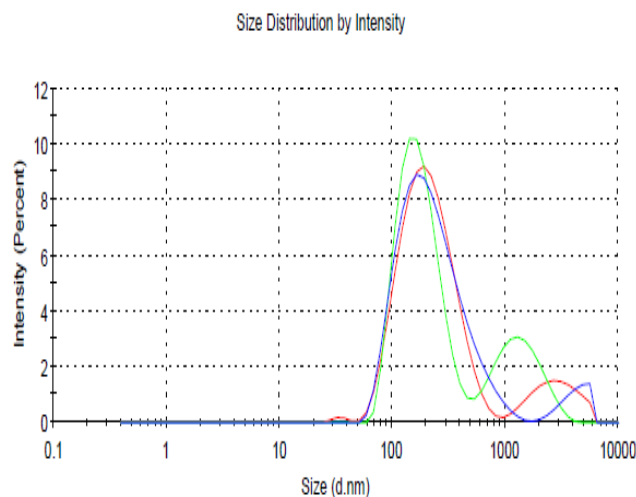


Figure 2b. The particle size of E7 organo-modified finishing chemical (worst softness property) (recipe 7). The particle size of E7 organo-modified was 227.9 nm (86.6 %) and solution was cloudy (Figure 2b).

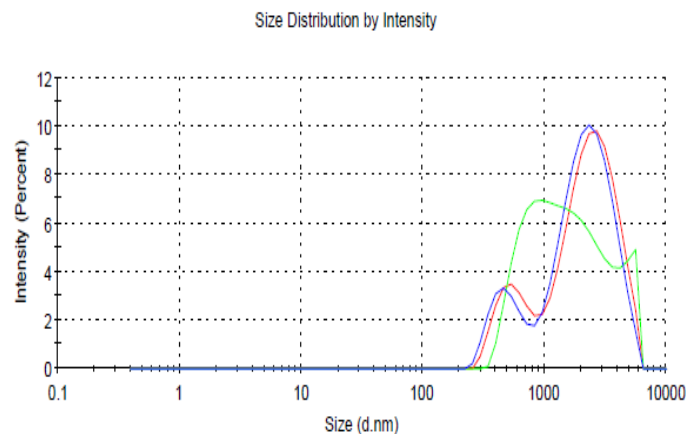


Figure 3a. The particle size of E8 amino-functional finishing chemical (the best softness property) (recipe 8). The particle size of E8 amino-functional was 2601 nm (81%) and solution was cloudy (Figure 3a).

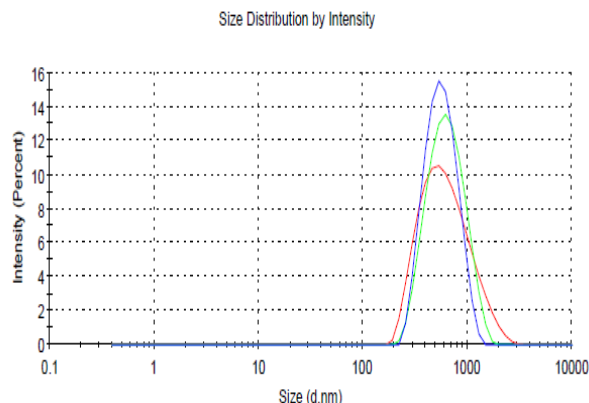


Figure 3b. The particle size of E9 amino-functional finishing chemical (worst softness property) (recipe 9). The particle size of E9 amino-functional was 684.2 nm (100 %), more than 1000nm, and solution was cloudy (Figure 3b).

Table 4. Particle sizes of organo-modified and amino-functional silicone emulsions

		Organo-modified silicone emulsion recipes						
		R1	R5	R4	R6	R2	R3	R7
Particle sizes		286.3 nm	265.5 nm	253.6 nm	251 nm	250.7 nm	239.4 nm	227.9 nm
		Amino-functional silicone emulsion recipes						
		R9	R12	R14	R13	R10	R11	R8
Particle sizes		684.2 nm	783.8 nm	1250 nm	1338 nm	1606 nm	2171 nm	2601 nm

The smaller the particle size, the more stable and the clearer emulsion appearance tends to be. The higher particle size, the more milky feature of the emulsion. Macro emulsions have narrow particle size distributions. The polydispersity values of the organo-modified finishing chemical emulsions were obtained as 0.263 and 0.344, respectively. However, in the emulsion of amino-functional, the polydispersity values were measured as 0.193 and 0.404, respectively. This means that the organo-modified and amino-functional finishing chemical emulsion prepared had a narrow distribution.

4.3. The Effect of HLB System on Emulsifying Property of Organo-Modified and Amino-Functional Silicone Emulsions

The concentration ratios of oil phase components and polar additives played significant roles in stability of the emulsion [33].

In an O/W emulsion, monomer is dispersed and stabilized by the surfactant into large monomer droplets (oil phase) and monomer-swollen micelles in water phase. Emulsifiers with HLB >8 formed oil-in-water emulsions. HLB values of organo-modified and amino-functional silicone emulsions were given in Table 5.

Table 5. HLB values of organo-modified and amino-functional silicone emulsions

		Organo-modified silicone emulsion recipes						
		R1	R5	R4	R6	R2	R3	R7
HLB values		11.25	11.25	11.25	12.95	12.95	12.95	12.95
		Amino-functional silicone emulsion recipes						
		R8	R12	R14	R13	R10	R11	R9
HLB values		11.25	12.95	12.95	11.25	11.25	12.95	12.95

Factors affecting the viscosity of emulsions were HLB value, the emulsifier type and emulsifier ratio.

4.4. Color Values and Color Differences of Organo-modified and Amino-functional Silicone Emulsions

The extent of color change dependent on the structure of the amino side-chain, on curing temperature and time.

The values of L^* were positive, all the fabric samples have become lighter. Furthermore, the fabric samples got more greenish after applied to fabric, the a^* values were negative.

The negative b^* values showed that the samples became increasingly blueish because of organo-modified and amino-functional silicone emulsions. The K/S values of silicone emulsion-containing fabrics were greater than untreated fabric. Color changes were evaluated according to the untreated fabric sample. The color difference tolerance was 1.0 in this study. As a result, all samples received a failing grade because ΔE was greater than 1 (Table 7). As seen in Table 7, higher yellowness was obtained in fabric samples applied with medium particle size of organo-modified silicone emulsions such as E4 and E5. As indicated in Table 7, the smaller particle size of finishing chemicals were obtained less color difference.

Macro silicone emulsions had the least color strength on cotton knitted fabric due to remained on the fabric surface. Macro silicone was increased the color fastness by creating a protective layer on the fabric surface.

Tested the whiteness index (Berger) of the treated fabric results indicated in the Table 6. From this table, the whiteness indexes of fabric samples treated with organo-modified and amino-functional silicone finishing chemicals were decreased at 150 °C.

Color difference was specified as a change in color of treated fabric samples with finishing silicone emulsions. Color-difference was evaluated with the CIELab color space that the reflectance values (%) in the visible wavelengths (400-700 nm). The reflectance difference values of treated and untreated fabric samples at wavelengths of 400-700 nm, as presented in Table 8. The results indicated that the reflectance difference values (%) of the treated fabrics with finishing silicone chemicals was related to the particle size, chemical type and distribution of the finishing chemical applied. As seen in Table 8, the samples treated with organo-modified and amino-functional finishing silicone chemicals exhibited a decrease in the reflectance difference values (%). The particle sizes of finishing chemical emulsions were smaller, the smaller reflectance difference values were obtained.

Table 6. Measured CIELab values of 100% cotton knitted fabrics (60g/L)

Sample	Color values					K/S	Whiteness index (Berger) of treated fabric samples at 150°C drying temperature
	L^*	a^*	b^*	C^*	h°		
0	27.30	-1.2	-1.08	1.62	222.86	9.75	6.42 (raw)
E1	25.50	-0.89	-0.82	1.21	222.53	11.49	5.37
E2	25.74	-0.88	-0.87	1.24	224.89	11.71	5.52
E3	25.47	-0.95	-0.88	1.30	222.91	11.78	5.34
E4	26.01	-0.89	-0.76	1.17	220.26	11.55	5.53
E5	25.07	-0.92	-0.73	1.18	218.62	11.55	5.23
E6	25.28	-1.03	-1.04	1.46	225.28	11.65	5.49
E7	25.59	-0.85	-0.75	1.13	221.32	11.87	5.34
E8	25.04	-0.97	-1.08	1.45	228.23	11.90	5.31
E9	25.47	-1.02	-0.95	1.39	222.90	12.46	5.46
E10	25.19	-0.95	-1.02	1.39	227.08	12.11	5.42
E11	25.26	-1.11	-1.00	1.49	222.00	12.32	5.52
E12	25.18	-0.98	-0.98	1.39	224.96	11.94	5.57
E13	25.55	-0.93	-1.06	1.41	228.82	12.04	5.57
E14	24.99	-1.01	-0.98	1.41	224.39	12.00	5.40

Table 7. The color difference between reference (raw material) and organo-modified & amino-functional treated fabric samples (60g/L)

Sample	Color differences						Assessment
	ΔL^*	Δa^*	Δb^*	ΔC^*	Δh°	ΔE	
E1	-1.80	0.31	0.26	-0.41	-0.33	2.35	Fail (darker, reddish, yellow, duller)
E2	-1.56	0.32	0.21	-0.38	2.03	2.11	Fail (darker, reddish, yellow, duller)
E3	-1.83	0.25	0.20	-0.32	0.05	2.92	Fail (darker, reddish, yellow, duller)
E4	-1.29	0.31	0.32	-0.45	-2.6	2.19	Fail (darker, reddish, yellow, duller)
E5	-2.23	0.28	0.35	-0.44	-4.24	2.85	Fail (darker, reddish, yellow, duller)
E6	-2.02	0.17	0.04	-0.16	3.42	2.50	Fail (darker, reddish, yellow, duller)
E7	-1.71	0.35	0.33	-0.49	-0.54	2.71	Fail (darker, reddish, yellow, duller)
E8	-2.26	0.23	0	-0.17	6.37	3.04	Fail (darker, reddish, yellow, duller)
E9	-1.83	0.18	0.13	-0.23	1.04	3.49	Fail (darker, reddish, yellow, duller)
E10	-2.11	0.25	0.06	-0.23	5.22	2.75	Fail (darker, reddish, yellow, duller)
E11	-2.04	0.09	0.08	-0.13	0.14	2.68	Fail (darker, reddish, yellow, duller)
E12	-2.12	0.22	0.10	-0.23	3.10	2.79	Fail (darker, reddish, yellow, duller)
E13	-1.75	0.27	0.02	-0.21	6.96	2.60	Fail (darker, reddish, yellow, duller)
E14	-2.31	0.19	0.10	-0.21	2.53	2.78	Fail (darker, reddish, yellow, duller)

ΔL^* = Difference in lightness or darkness value, Δa^* = Difference in red/green axis, Δb^* =Differences in yellow / blue axis, ΔC^* = Difference in chroma, Δh° = Difference in hue, ΔE = Color difference value

Table 8. The reflectance difference(ΔR) between untreated and treated fabric samples

	Wavelength (nm)															
ΔR	400	420	440	460	480	500	520	540	560	580	600	620	640	660	680	700
E1	-1	-0.91	-0.88	-0.89	-0.87	-0.87	-0.86	-0.81	-0.74	-0.7	-0.66	-0.64	-0.65	-0.84	-1.02	-1.09
E2	-1.11	-0.99	-0.95	-0.98	-0.96	-0.93	-0.9	-0.83	-0.77	-0.75	-0.69	-0.68	-0.72	-0.78	-0.66	-0.3
E3	-1.12	-0.99	-0.99	-0.99	-0.97	-0.97	-0.96	-0.91	-0.84	-0.81	-0.76	-0.74	-0.68	-0.78	-1.25	-1.2
E4	-1.02	-1.02	-0.98	-0.99	-0.98	-0.98	-0.96	-0.91	-0.84	-0.8	-0.74	-0.67	-0.68	-0.9	-1.14	-1.32
E5	-1.01	-0.99	-0.92	-0.98	-0.96	-0.93	-0.9	-0.83	-0.84	-0.77	-0.69	-0.67	-0.68	-0.78	-0.66	-0.3
E6	-1.06	-0.97	-0.92	-0.91	-0.9	-0.89	-0.9	-0.85	-0.8	-0.77	-0.73	-0.7	-0.72	-0.85	-1.14	-1.08
E7	-1.18	-1.11	-1.05	-1.06	-1.06	-1.05	-1.06	-0.98	-0.9	-0.86	-0.8	-0.77	-0.78	-1.02	-1.43	-1.69
E8	-1.03	-1.03	-0.98	-0.99	-0.99	-0.99	-0.99	-0.93	-0.88	-0.85	-0.8	-0.78	-0.78	-0.95	-1.23	-1.33
E9	-1.23	-1.2	-1.15	-1.17	-1.17	-1.17	-1.17	-1.11	-1.05	-1.03	-0.98	-0.9	-0.87	-1.07	-1.42	-1.45
E10	-1.11	-1.09	-1.06	-1.09	-1.08	-1.07	-1.06	-1.01	-0.94	-0.91	-0.87	-0.84	-0.87	-1.07	-1.42	-1.45
E11	-1.17	-1.13	-1.09	-1.11	-1.11	-1.12	-1.12	-1.07	-1	-0.97	-0.92	-0.88	-0.93	-1.17	-1.62	-1.75
E12	-1.05	-1.05	-1	-1.01	-1	-1.01	-1	-0.95	-0.9	-0.87	-0.83	-0.79	-0.84	-1.03	-1.31	-1.34
E13	-1.08	-1.07	-1.03	-1.04	-1.02	-1.01	-1	-0.95	-0.9	-0.88	-0.85	-0.82	-0.85	-1.07	-1.52	-1.64
E14	-1.08	-1.04	-1	-1.02	-1.02	-1.02	-0.96	-0.89	-0.89	-0.86	-0.8	-0.81	-0.79	-0.97	-1.29	-1.31

* $\Delta R = R_{\text{numune}} - R_{\text{standart}}$ (Reflectance difference value)

5. CONCLUSION

In this study, the effects of emulsion ratio, organo-modified and amino-functional silicone emulsion type, particle size of silicone emulsion on the fabric handle, whiteness index, color values and color difference of cotton knitted fabrics were examined. The main results are summarized as follows:

Produced softener emulsions were applied to the 100% cotton knitted fabrics via pad cure technique.

Application of silicone emulsion affected the values of dyed fabrics.

Macro silicone emulsion provided high softness, minimum shade change and increased color yield. The produced silicone emulsions were characterized via particle size. Macro-silicone softeners increased surface roughness and uniformity.

Emulsion stability and particle size distribution created the desired surface properties on treated with amino-functional silicone emulsion cotton knitted fabric samples. And also, silicone (Si) also formed covalent ether bonds between cellulose and amino silicone molecules that provided a good soft handle. Experimental results showed that softening, as the amount of ionized amino groups in amino-functional finishing chemicals was increased, the softening ability of the fabric was increased. This corresponded to a pH of approximately 6.0 for amino-functional finishing chemicals. As the pH value was decreased (at pH 5.5), the more secondary amine groups were ionized. Thus, the handle and softness properties were improved. With optimum orientation of silicones on the fiber surface, a good softness and smoothness was achieved. The amino groups were become cationic (NH_3^+) at acidic conditions and the strong interaction with the fabric was achieved.

Less yellowing was obtained in fabric samples applied with amino-functional finishing chemicals owing to the oxidation of amino groups in the presence of air, heat or light energy. In amino-functional silicones, azo yellow and azoxy yellow compounds were obtained as a result of oxidation of amino group.

The smaller the particle size, the more stable the emulsion tends to be. Fabrics treated with the organo-modified chemicals that were smaller in particle size gave higher reflectance values (%). Consequently, the smaller particle size of finishing chemicals had a high surface area and gave a smoother reflecting surface. In addition, the less color difference was obtained in the fabric samples applied with the small particle size of finishing silicone chemicals.

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