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Alternative methods for transferring mosquito repellent capsules containing bio-based citronella oil to upholstery fabrics: coating and printing

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Abstract The aim of this study was to prepare insect repellent textiles and compare the application methods. Bio-based insect repellent agent citronella oil was encapsulated with ethyl cellulose shell with coacervation method. Morphological assessment showed that capsules had smooth surfaces and their shape was spherical. The homogenous size distribution of the capsules was supported and the mean particle size of the optimum formulations was almost 50 μm. Outdoor upholstery fabrics were treated with citronella capsules by coating and printing to compare the application methods. After application, the insecticide effects of the fabrics were investigated and compared with the impregnation method. Insecticide activity was evaluated against common house mosquitoes (*Culex pipiens*), with respect to cone bioassay of World Health Organization. Mosquitoes tended to stay away from treated fabrics, and mortality rates of mosquitos were noted as 72, 65 and 55% for printing, coating and impregnation, respectively, and the fabrics still showed repellency after five washing cycles. This study showed that the developed product might be used as an alternative to the other products in the market for avoiding mosquito-borne diseases and these results showed that capsules can be transferred by printing and coating processes when compared with the impregnation method.

Keywords Insecticide, Microencapsulation, Complex coacervation method, Citronella oil

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Introduction

An insect, which is any member of the largest class of the *Phylum arthropoda*, is itself the largest of the animal phyla. In a popular sense, ''insect'' usually refers to familiar pests or disease carriers, such as bedbugs, houseflies, clothes moths, mosquitoes, fleas, horseflies and hornets. On the other hand, many insects are beneficial from a human viewpoint; they pollinate plants, produce useful substances, control pest insects, act as scavengers and serve as food for other animals. Furthermore, insects are valuable objects of study in elucidating many aspects of biology and ecology.[1,2]

Mosquitos, any of approximately 3500 species of familiar insects in the fly order, are diptera that are important in public health because of the bloodsucking habits of the females. Mosquitoes are known to transmit serious diseases, including yellow fever, Zika fever, malaria, filariasis and dengue. Therefore, mosquito repellency is important for the human body and there are numerous methods developed to protect humans from mosquitoes. An insect repellent is a substance applied to skin, clothing or other surfaces, which discourages insects from landing or climbing on that surface. Insect repellents help prevent and control the outbreak of insect-borne diseases. Besides mass insecticide applications, there are several types of personal applications like mosquito nets, spray, aerosol or lotions.[3–6] On the other hand, these methods have some disadvantages. Sprays dispensed directly on the body may have side effects on the body, and nets used can only be effective where they are located. Therefore, encapsulation of insecticides is an alternative way to avoid excessive usage of insecticides.[7]

In the textile industry, microencapsulation is a rapidly developing technology in the field of chemical processes due to its versatility and flexibility. An important advantage of the use of microencapsulation technology is the ability to protect the active ingredient

from dangerous conditions such as oxidation, heat, acidity, alkalinity, moisture or evaporation.[7–9] Microencapsulation is the process of coating solid, liquid or gas with an inert polymeric material as a film. Generally, the active substance is called the ''core'' and the coating substance is called the ''shell.'' Encapsulation process produces small spheres covered with a thin shell film to protect the active substance. With this technology, it is possible to protect easily perishable substances such as insecticides, antibacterials and antioxidants from environmental factors like heat, light and oxygen. In addition, people are exposed to much lower doses of these substances. By using microcapsules in textile finishing, it is possible to produce wash resistant textile products that are effective even if less active substance is used.[10–20]

The versatility of microencapsulation technologies offers unlimited combinations of core and shell materials in its production, allowing microcapsules to be used in a wide variety of applications. To date, very little research has been done on possible applications of microcapsules in functional coating and printing processes. Microcapsules produced in the textile industry are generally transferred by the impregnation method. In this study, we aimed to increase the strength of microcapsules by providing application for coating and printing processes.[9,21]

Citronella oil is an essential oil that is made from the distillation of the Asian grass plant in the *Cymbopogon* genus. Citronella selected as a naturally sourced active ingredient consists of citronellic acid, borneol, citronellol, geraniol, nerol, citral, citronellal, camphene, dipentene and limonene. Citronella oil is a plant-based insect repellent and has been registered for this use. Citronella oil is popular as a natural insect repellent. Its mosquito repellent qualities have been verified by research,[22] including effectiveness in repelling *Aedes aegypti* (dengue fever mosquito). To be continually effective, most citronella repellent formulas need to be reapplied to the skin every 30–60 min.[23,24] Ethyl cellulose (EC), which is chosen as shell material, is a rigid, thermoplastic and hydrophobic material. This polymer is resistant to water, alkali and salt. It is compatible with the coacervation technique and can be applied to textile surface.[25–27]

This study aimed to evaluate the behavior of microcapsules that contain citronella oil. First, citronella oil carrying ethyl cellulose microcapsules were produced with the coacervation method. As part of characterization studies of microcapsules, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and gas chromatography–mass spectrometry (GC-MS) analyses were performed. The optimum formula was applied to outdoor upholstery fabrics by the printing, coating and impregnation methods in order to investigate whether the coating and printing methods can be an alternative to the conventional impregnation method. To evaluate the effect of active agent and capsule endurance on fabric, insecticide efficiency tests were conducted. After application of microcapsules that were produced with citronella oil to textile materials, odor release behaviors from fabrics were examined after five washing cycles. Insecticide efficiency test of fabrics, dimensional change after washing, weight change, color measurements and fastness analysis were performed on the fabrics after the treatment with capsules to evaluate the effect of the encapsulation process on outdoor upholstery fabric properties.

Experimental

Materials

In this research, desized, plain weave cotton fabric (specific weight 210 g/m^2, 65% cotton/35% polyester blend panama fabric with weft/warp density 12/60 thread/cm) was used. The shell material EC Premium 4 was donated from Dow Chemicals, Istanbul, Turkey. Citronella oil (Sigma-Aldrich) was employed as core material. Tween 20 was used as a surfactant. The surface active agents, ethanol and ethyl acetate (EA), were supplied from Merck, Darmstadt, Germany. Acrylic-based pigment printing paste was supplied from Harput Tekstil, Turkey. All other auxiliary chemicals used in the study were of laboratory-reagent grade.

Preparation of the microcapsules

In order to obtain citronella oil capsules, the complex coacervation method was employed. In this process, the interactions of water-insoluble polymers with water were utilized to form the capsules. Citronella oil and EC in a specific ratio were dissolved homogenously in organic solvent. Polymer-rich organic phase was then added to polymer-free aqueous phase. Active ingredients were separated into microdroplets with the help of Silverson high shear mixer at 8000 rpm, and every single droplet was coated with a thin film of shell material, simultaneously. Afterward, the liquid film was solidified by adding water into the system. A centrifuge machine was used at 5000 rpm (3689 RCF/g) for 15 min for removing water and obtaining microcapsule slurry.[28,29] At the final step, the slurry was treated with an ultrasonic bath for having smoother structure and drying at laboratory conditions. The spherical shaped capsules are obtained successfully at 1:1; 2:1, 4:1 and 10:1 (w/w) shell-to-core ratio and named as Cit 1, Cit 2, Cit 3 and Cit 4, respectively. An experimental diagram of the production of capsules and application methods is given in Fig. 1.

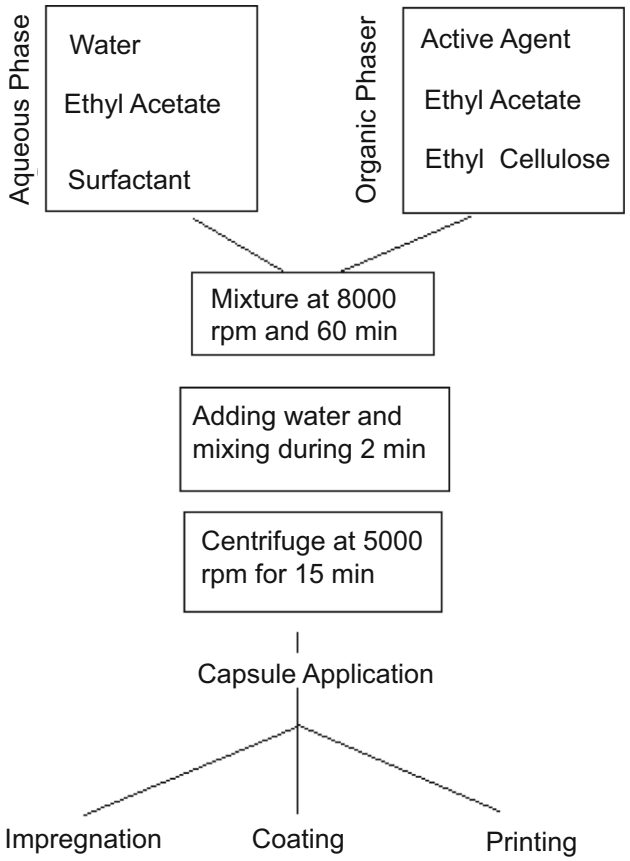


Fig. 1: Experimental diagram of the production of capsules and application methods

Mass yield of microcapsule

The total powder obtained after coacervation was weighed, and the process yield was calculated as a percentage of the amount of solids added during the preparation process according to equation (1):

$$R\% = (Q_f/Q_i) \times 100 \quad (1)$$

where $R\%$ is the yield of the process, Q_i is the amount of solids initially added for the preparation of capsules and Q_f is the quantity of microparticles (MPs) obtained at the end of the process.

Particle morphology of microcapsules

The morphologic properties of the capsules were evaluated using scanning electron microscopy (SEM-Quanta 250 FEG). Samples were gold-coated (15 mA, 2 min) to assure electrical conductivity. The measurements were taken at 2 kV accelerating voltage. According to the capsule images obtained as a result of SEM analysis, the optimum capsule formulation was determined and other characterization studies were made according to this formulation.

Particle size of microcapsules

To determine the size of the resulting optimum capsule, a Malvern Zetasizer Nano-S particle size distribution tester was used. Before measurement, an aqueous solution of capsules in a certain rate was prepared and sonicated in an ultrasonic bath until forming a good mixture. After that, the capsule dispersion was put in disposable cuvettes. Then, the light emitted by the laser Doppler passed through the dispersion.

Fourier transform infrared spectrophotometer (FTIR) analysis

Fourier transform infrared spectroscopy (FTIR) analysis was performed to determine encapsulation performance with the changes in the IR spectrum for optimum capsule formula. Measurements were taken at a wavelength range of 4000–400 cm^{-1} using a PerkinElmer Frontier FTIR device. The obtained spectra were smoothed to remove the noise with official software of the device.

Thermogravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) of the capsules was carried out in the SDT Q600 device with nitrogen gas in the temperature range of 0–600°C. This is a technique based on the observation of the change in mass with the temperature increase.

Application of the microcapsules to the outdoor upholstery fabrics

The impregnation, coating and printing methods were used to transfer the microparticles to upholstery fabrics to be used in garden furniture. Crosslinking chemicals were used in the bonding of microcapsules with fiber.

In the printing method, microcapsules were added into the printing paste and transferred to the textile material by direct printing. In the printing process, pigment printing paste and glitter (largest porous) template, the contents of which are given in Table 1, were used. Alginate thickener was used in the printing paste.

Before the coating process, the fabrics were kept in a laboratory type Stenter for an average of 30 sec for fabric smoothness. Waterproof acrylic coating polymer was used in coating processes. With the help of a squeegee, the coating material containing microcapsules was transferred onto the fabric (Table 2).

The optimum capsule sample was impregnated in a solution bath containing capsules (40 g/L) and acrylic binding agent (50 g/L) and then squeezed between rollers to 89% wet pick-up. Achieving long-lasting effect on wearable cosmetic textiles, the fabric was

Table 1: Capsule transfer prescription for printing method

Pigment printing paste (g)	Pigment dye (g)	Dispersing agent (mL)	Microcapsule (g)	Drying + fixing
994	6	9	40	120°C 3 min

Table 2: Capsule transfer prescription for coating method

Acrylic (g)	Dispersing agent (mL)	Defoamers (mL)	Microcapsule (g)	Drying + fixing
1000	9	9	40	120°C 3 min

Table 3: Capsule transfer prescription for impregnation method

Acrylic binder (g/L)	CMC (g/L)	Microcapsule (g/L)	Drying + fixing
50	1.5	40	120°C 3 min

exposed to combined drying and fixation processes for 4 min at 120°C in a laboratory Stenter (Table 3).

In order to compare the impregnation method most used in capsule transfer processes with the printing and coating methods, capsules were preferred at the same capsule ratio in these methods.

Evaluation of treated fabrics

SEM images were taken to obtain the existence of capsules on the textile surface from both five washed and unwashed samples. Samples were gold-coated (15 mA, 2 min) to assure electrical conductivity. The measurements were taken at 2 kV accelerating voltage.

FTIR analysis was used to examine the bonding of capsules to fabrics on capsule-transferred fabrics. FTIR analysis studies were carried out on a Nicolet iS50R device. The samples to be measured were homogeneously mixed with potassium bromide (KBr) compound and compressed under pressure. The IR spectra of the mixture in the wavelength range of 400–4000 cm^{-1} were measured.

GC-MS analysis was performed to determine the citronella content in the fabrics and after five washes which were transferred by coating, printing and impregnation methods. The samples were cut, weighed 1 g and mixed in an ultrasonic bath for 1 h in ethanol/hexane. GC cycle time was determined as 5 min, sample volume 0.5 mL, incubation time 10 min and incubation temperature 85°C. Volatiles were dissolved in the HP-ONNOWAX capillary column. Helium was used as the carrier gas at a flow rate of 0.7 mL/min. 60°C was determined as the initial temperature and operation was carried out at this temperature for 1 minute. Then, 240°C was reached at 10°C/min and kept for 2 min. Finally, 320°C was reached at 10°C/min and kept at this temperature for 3 min. The injection was done in split mode (1:50). To identify the compounds, MS spectra database was compared with Wiley and mass spectra were made as basis. The analysis was performed by using Agilent Tech 7890GB GC-System branded GC-MS device.

The fabric samples containing citronella oil capsules were washed five times separately. Trials were carried out to determine the insect repellent activity of samples that were not washed and had five washes. As stated in the WHO method, fabrics attached to the wide mouth of the cones were prepared and 20–25 females did not absorb blood. *Culex* sp. mosquito specimen (2–3 days old) was placed in a cone and kept for 10 min as in Fig. 2.[28] The % repellent effect was tested at two-minute intervals. All tests were completed in repetitions of 24°C ± 2°C and 60% ± 10% RH.

$$\%\ \text{repellent effect:} \left(\frac{\text{Number of individuals not placed on the fabric surface}}{\text{Total number of individuals}}\right) \times 100.$$

One of the important features expected in upholstery fabrics is low-dimensional changes after washing. For this purpose, the dimensional change of the fabrics containing capsules in washing was determined according to TS EN ISO 6330.

In order to determine the strength of capsule-transferred fabrics against washing, testing was performed according to TS EN ISO 105-C06: Textile-Color Fastness Tests Section C06 Determination of Color Fastness to Domestic Washing and Washing in Commercial Establishments and fastness evaluations were carried out according to gray scales. In addition, five washes were applied to the fabrics, they were dried

Fig. 2: Cone test for insect repellent effect

under room conditions and their evaluation was made after washing.

The resistance of the fabrics containing capsules to wet and dry rubbing was measured according to the standard of TS EN ISO 105-X12: Textile-Color Fastness Tests Section X12 Determination of Color Fastness to Rubbing in the Atlas brand Krokmeter rubbing device.

Color fastness to light is one of the most important features in summer garden furniture. For this purpose, light fastness analyzes of fabrics containing capsules were carried out according to TS EN ISO 105-B02.

Color measurement analysis of the fabrics were carried out with the Minolta CM 3600 D brand spectrophotometer. K/S and ΔE values obtained as a result of the analysis were made according to the following calculations.

$$\text{Kubelka Munk formulas: } K/S = (1-R)^2/2R \tag{2}$$

K light absorption, S light reflection, R the remission value at the maximum absorption wavelength.

Color coordinates in the CIE-LAB system were used for color evaluations. The a value in the CIE-LAB system refers to red-green, b value to yellow-blue, and L value to the aperture values. In addition, K/S values were used to calculate the color efficiency of dyed fabrics.

$$\Delta E = \left[(\Delta L)^2+(\Delta a)^2+(\Delta b)^2\right]^{1/2} \tag{3}$$

Results and discussion

In this study, capsules were successfully prepared by the coacervation method. Encapsulation studies were carried out at 1:1, 2:1, 4:1 and 10:1 polymer/active agent (w/w) ratio.

Mass yield of microcapsules

Formulations of citronella oil capsules and the production yield are given in Table 4. In the centrifuge step, no precipitate was formed for Cit 1 formulation. This may be due to the fact that the active substance concentration is too high, and therefore, the encapsulation does not occur. For the other formulations, the yield of the capsules ranged between 62 and 80% (w/w), which can be considered relatively high (Table 4). A reduction in the amount of active substance in the formulation affected the production efficiency positively.

Particle morphology of microcapsules

Citronella microcapsules were usually characterized by spherical shape and narrow particle size distribution. Typical photomicrographs obtained by SEM of the microcapsules show that the product is composed mainly of spherical shaped particles (Fig. 3).

According to SEM analysis, microcapsules filled with active substance (citronella oil) were obtained. In the formulations of Cit 2, Cit 3 and Cit 4, spherical and smaller capsules were successfully formed. It was also indicated that the capsule formulations have homogeneous characteristics with smooth appearance and do not show the presence of free active agents on their surfaces.

Particle size of microcapsules

The mean particle size of MPs was determined by laser diffraction method for microcapsules. Particle size distribution graph of microcapsules is indicated in Fig. 4.

The mean particle size and distribution of these particles are also important for the textile application. When the particle size analysis of the capsules produced at different ratios was evaluated, the Cit 2 coded capsules had a particle size of 50 μm and had 98.59% high homogeneity. According to the data obtained as a result of the analysis, it was determined that 96.22% of the capsules were around 50 μm for Cit 3 coded capsules. It was determined that the particle size analysis graphic area showed a uniform distribution. The particle size was 50 μm for Cit 4 coded capsules (71.78%). When particle analysis results were evaluated, it was determined that Cit 2 capsules have a higher uniformity compared to other ratios.

Fourier transform infrared spectrophotometer (FTIR) analysis

The FTIR spectra of citronella oil capsules and the materials forming them are given in Fig. 5.

Table 4: Mass yield of microcapsules

Capsule code	EC: Citronella oil (w/w)	Mass yield (% w/w)
Cit 1	1:1	–
Cit 2	2:1	75
Cit 3	4:1	62
Cit 4	10:1	53

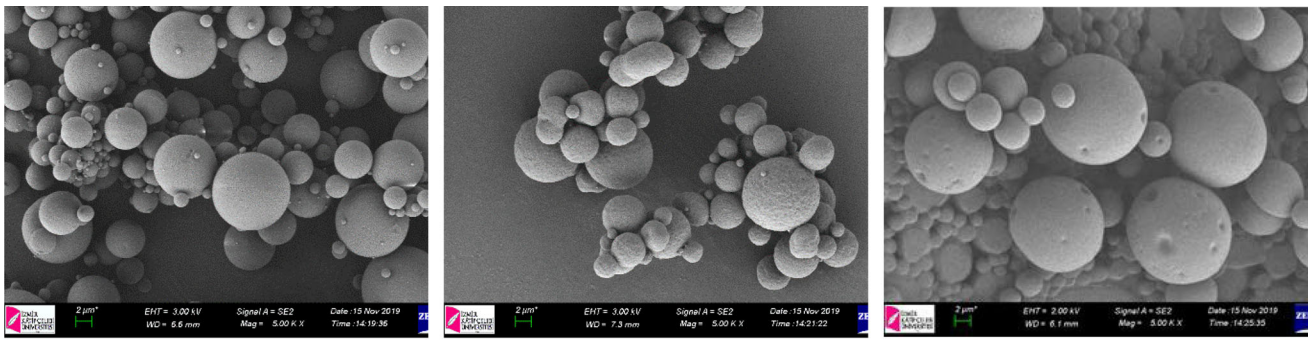


Fig. 3: SEM images of microcapsules

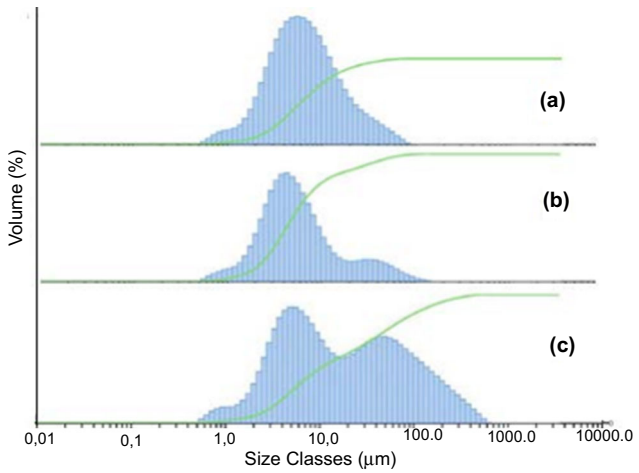


Fig. 4: Particle size distribution of (a) Cit 2 capsules, (b) Cit 3 capsules and (c) Cit 4 capsules

Figure 6b shows characteristics absorptions of citronella oil, like the axial deformation of the OH (3363 cm^{-1}) also related to water absorption. The CH stretch at 2976 cm^{-1} and 2899 cm^{-1} and the C=C at 1647 cm^{-1} were detected. It can be also observed the vibration of methylene, i.e., the folding CH in 1451 cm^{-1} and 1381 cm^{-1} and the folding OH in 1044 cm^{-1}, according to the literature. There was an intense broad peak within the range of 3600–3200 cm^{-1} particularly at 3365.78 cm^{-1} corresponding to the polymeric hydroxyl (OH) group. Another intense and bifurcated peak within the range of 2935–2915 cm^{-1}, which corresponds to the C–H methyl and methylene asymmetric stretch, mostly aliphatic alkyl groups were observed. The medium peak at 2719.63 cm^{-1} validated a terminal aldehydic C–H stretch of carbonyl compound. Another distinct and sharp peak within the range of 1750–1705 cm^{-1} signified aldo, keto, estero and or acido (C=O) stretch. A strong and relatively narrow absorption peak at 1668.43 cm^{-1} contributed to olefinic unsaturated C= group. The sharp and strong peaks were observed for methylene C–H (1485–1445 cm^{-1}), methyl C–H symmetric bend (1380–1371 cm^{-1}) and aryl–O–H stretch (1270–1230 cm^{-1}). Moreover, C–O bend (1140–1050 cm^{-1}), simple OH stretch (1200–1000 cm^{-1}) and CH=CH trans-unsaturated (910–860 cm^{-1}) functional groups with medium peaks were also observed. A medium peak depicting di or tri-substituted alkenes (C=H) stretch was detected at 825.53 cm^{-1}. Minor vibrations within the range of 750–660 cm^{-1} were attributed to the presence of aromatic, vinyl C–H group. These results were in absolute accord with the literature.[29]

When the IR spectrum of EC was examined, the stretching vibrations of characteristic –C–O–C– band and –C–H band were observed at 1054 cm^{-1} and at 2870 and 2972 cm^{-1}, respectively. C–H bending was located at 1375 cm^{-1}.[30] When the spectra of the capsules were examined, both EC and citronella peaks were identified. The strong peak of EC at 1053 cm^{-1} aroused from –C–O–C– band was observed in all formulations. The C–H bands, obtained at 2973 and 2870 cm^{-1}, were found to be deeper than EC peaks and close to the peak intensity of citronella. This may indicate successful encapsulation. The missing citronella bands in the spectrum of capsules were considered as a result of capsulation. Thus, it was considered that the active agents were captured inside the EC shell.

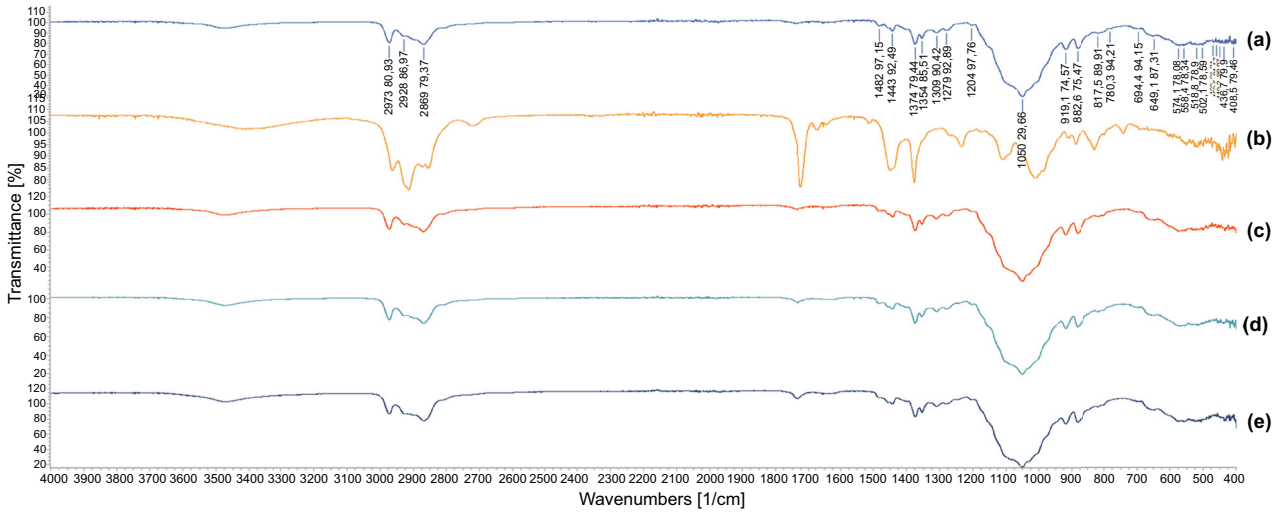


Fig. 5: FTIR spectra of (a) ethyl cellulose, (b) citronella oil, (c) citronella capsules which is coded Cit 2, (d) citronella capsules which is coded Cit 3 and (e) citronella capsules which is coded Cit 4

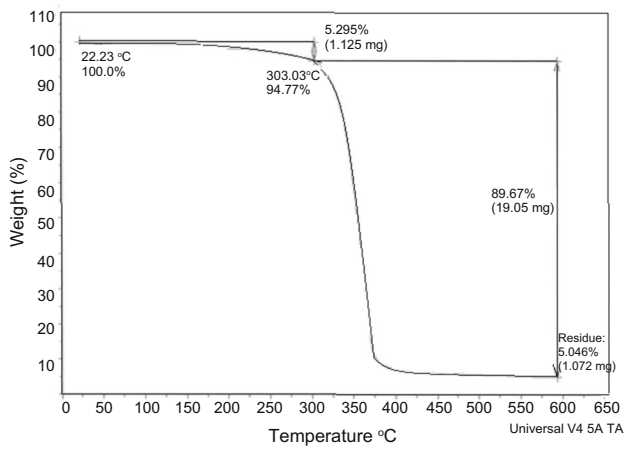


Fig. 6: TGA thermogram of ethyl cellulose

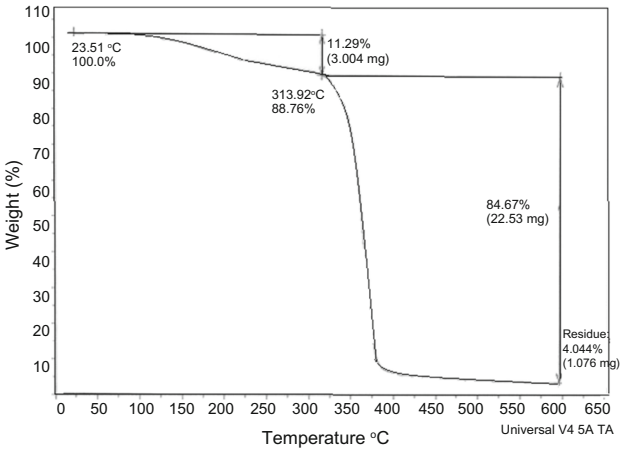


Fig. 7: TGA thermogram of Cit 2 (2:1) coded capsules containing citronella oil

Thermogravimetric analysis (TGA)

TGA graphics of ethyl cellulose and the capsules obtained are given in Figs. 6, 7, 8 and 9.

The TGA graph of capsules containing citronella shows that the degradation started at 300°C and pyrolysis accelerated above 350°C. As a result of the analysis, 4% residues were formed in the samples coded Cit 2 (2:1), Cit 3 (4:1) and Cit 4 (10:1). No specific difference was detected for all three concentrations according to the TGA thermograms.

Evaluation of treated fabrics

After characterization studies like SEM, particle size and mass yield of microcapsules, the Cit 2 coded capsules have been determined as the optimum capsule due to homogeneous capsule distribution, higher active

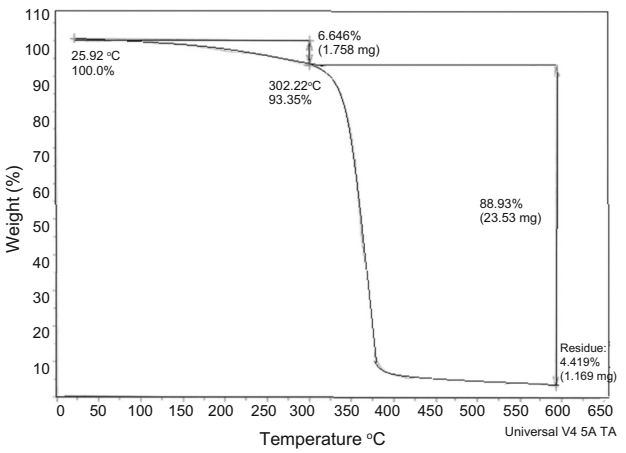


Fig. 8: TGA thermogram of Cit 3 (4:1) coded capsules containing citronella oil

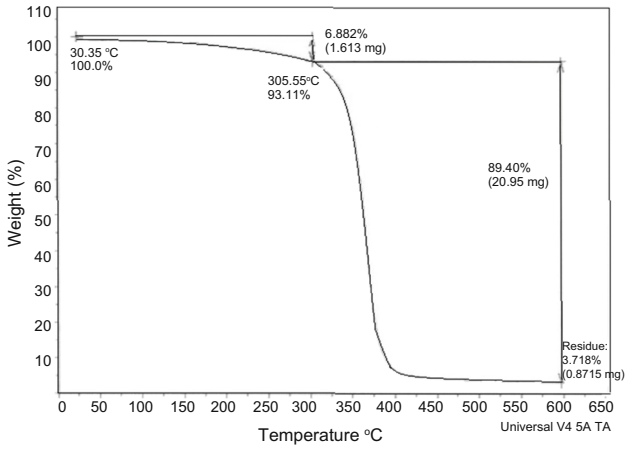


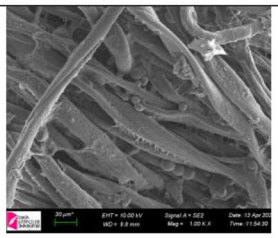
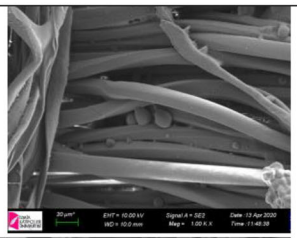
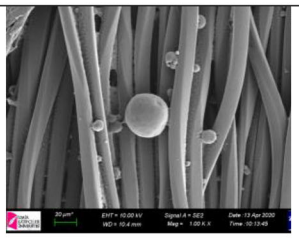
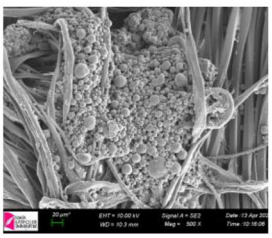
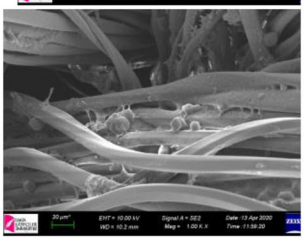
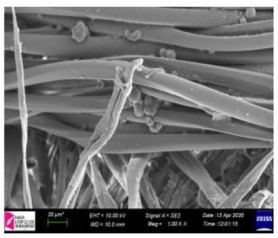
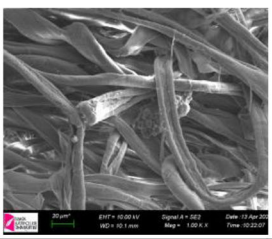
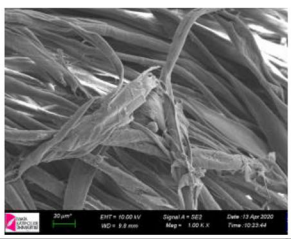
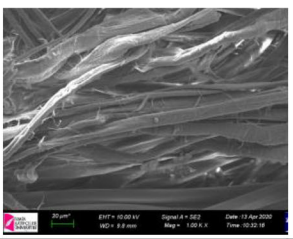
Fig. 9: TGA thermogram of Cit 4 (10:1) coded capsules containing citronella oil

substance ratio and high efficiency. The capsules were transferred to outdoor upholstery fabrics by printing, coating and impregnation methods and compared with each other.

SEM images of outdoor upholstery fabrics are shown in Table 5.

SEM images of the capsules containing citronella transferred to upholstery fabrics by printing, coating and impregnation methods, taken before and after five washing cycles and enlarged 1000 times, are given in Table 5. When the images of the capsules transferred to upholstery fabrics by different methods were examined, it was seen that the most intense capsule presence was in coated fabrics. It has been determined that the transferred capsules were located between the fabric surface and the acrylic binder layer. In the impregnation method, it was determined that the rate of capsules was less. It was determined that capsules

Table 5: SEM photomicrographs of outdoor upholstery fabrics treated with citronella capsules with no wash, after 5 washing cycles and after rubbing

Process	Before Washing	After 5 Washings	After Rubbing
Pigment Printing			
Coating			
Impregnation			

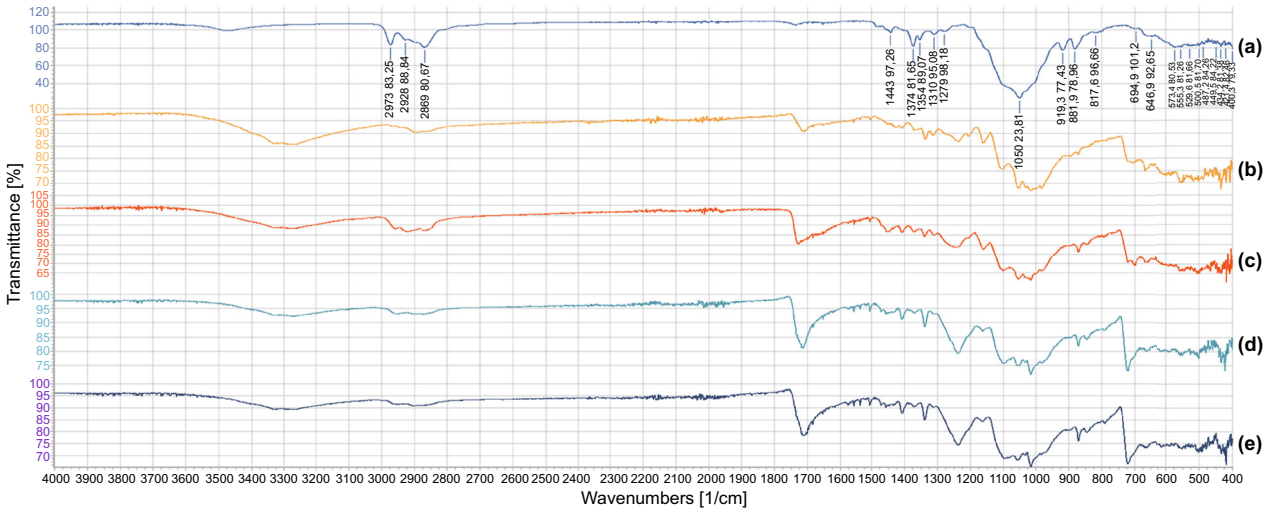


Fig. 10: FTIR spectrum of (a) citronella capsules, (b) raw fabric, (c) the fabric to which the capsules containing citronella were transferred by printing method, (d) the fabric to which the capsules containing citronella were transferred by coating method and (e) the fabric to which the capsules containing citronella were transferred by impregnation method

survived on the fabric for all methods after fiver washes. However, it was determined that the method in which the presence of capsules seemed most intense after five washes was again the coating method.

SEM analysis was applied to examine the behavior of fabrics treated with citronella oil capsules after rubbing tests (Table 5). It is seen that the fibers on the fabric surface were their elliptical shape as a result of rubbing and became flat. This indicates that the capsules on the surface were more affected by friction than those between the fibers. It has been concluded that mechanical movements cause the capsules to break and cause rapid release of the active substance. However, it was determined that this situation was observed less for capsules transferred to fabrics by the coating method than by the other methods.

Figure 10 shows FTIR spectra of citronella oil containing microcapsules and microcapsule applied fabrics.

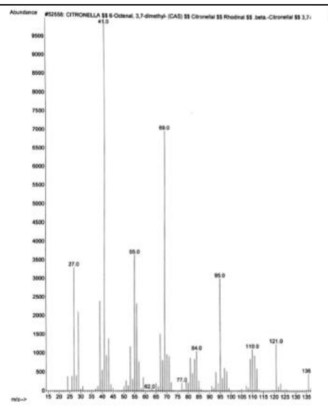
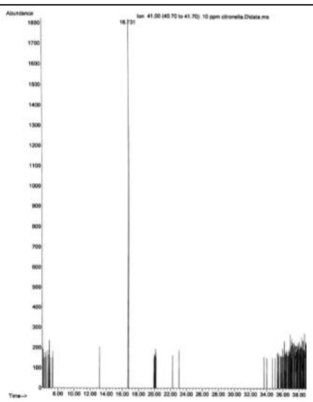
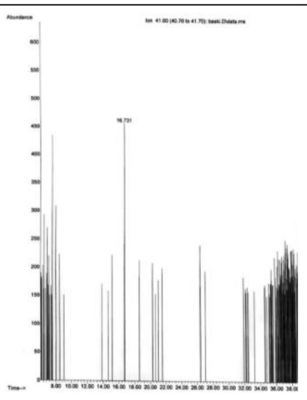
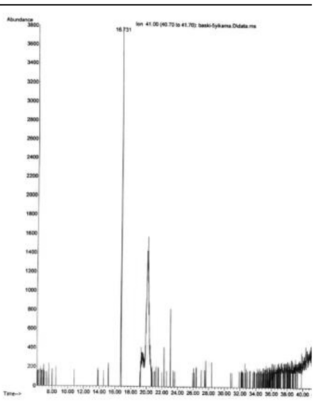
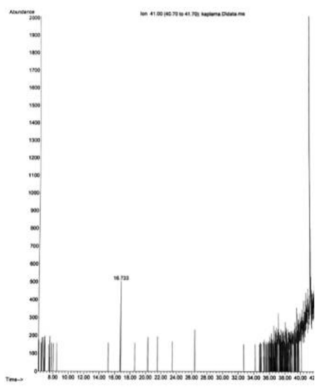
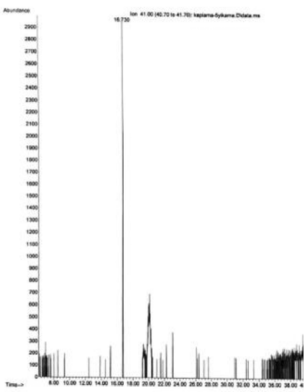
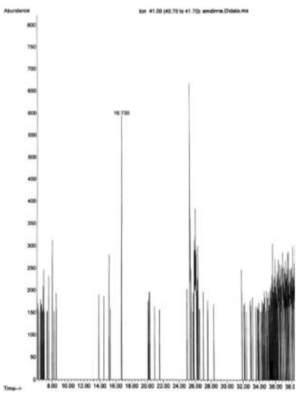
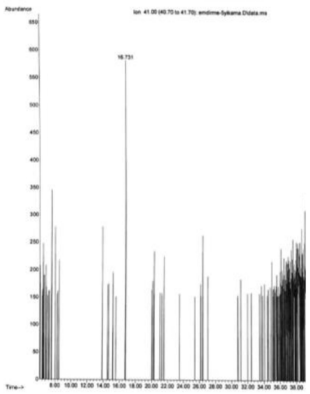
FTIR analysis was performed to chemically explain the presence of microcapsules in the fabric structure on microcapsule applied fabrics. Figure 10b shows the FTIR spectrum of the raw fabric. In the raw fabric, the tensile vibrations belonging to –OH groups in the structure of the cotton fiber gave wide and strong bands at 3325 cm^{-1}. And also, the stress range of the C–O groups is seen at 1083–1088 cm^{-1}. When the FTIR spectra obtained after the capsules were transferred to fabrics by different methods, sharp peaks were not observed. However, it has been determined that some bands were concentrated in some wavelengths due to the capsule. In the FTIR results, specific peaks of the acrylic coating material have been determined to be C–H rock bands at 808–839 cm^{-1}, C–H twist/rock band at 1299 cm^{-1} and C–H bending at 1449 cm^{-1}.[31]

Besides that, due to the alginate thickener used in the printing paste, bands were observed in the 2960–2840 cm^{-1} region assigned to C–H stretching, C–O stretching of the carboxyl group between 1750 and 1400 cm^{-1}, several bending modes between 1500 and 1200 cm^{-1} and C–O and C–C stretching modes between 1200 and 1000 cm^{-1}.[32] These peaks showed that application of microcapsules with the printing and coating process has been carried out successfully.

Peaks at 1735 cm^{-1} in the spectrum of microcapsule and microcapsule applied fabrics are also caused by C=O stresses and it has been determined that these peaks become sharp due to the presence of the capsule. It is seen that the carbonyl group of the aliphatic esters were given a sharper peak at 1740 cm^{-1} than the carbonyl groups in the isocyanate structure. This shows that the capsules transferred bind better to the cotton fiber. In addition, it was determined that when capsules were transferred by coating method, the peaks became sharper and due to this situation, the capsules adhere better to the fabrics. However, it has been found that the transfer methods in general do not make a big difference in bonding the capsules to fabrics.

GC-MS analysis was carried out to determine the citronella content in the fabrics after five washes where capsules containing citronella were transferred by coating, printing and impregnation methods. First, the GC diagram of the citronella active substance was determined and the ion chromatogram was evaluated. Accordingly, since m/z (m mass and z charge ion) with the highest concentration of citronella was 41, all injections were measured accordingly. After determining the ion chromatogram, citronella and extracted

Table 6: The ion chromatogram of citronella oil and GC-MS diagrams of outdoor upholstery fabrics treated with citronella capsules with no wash and after 5 washing cycles

			
Ion chromatogram of citronella	GC-MS diagram of citronella	GC-MS diagram of printed fabric extension containing microcapsules	GC-MS diagram of printed fabric with microcapsules after 5 washes
			
GC-MS diagram of the coated fabric containing microcapsules	GC-MS diagram of the coated fabric containing microcapsules after 5 washes	GC-MS diagram of impregnated fabric containing microcapsules	GC-MS diagram of microcapsule impregnated fabric after 5 washes

samples were measured according to Ion 41. The obtained ion chromatogram of citronella and GC-MS diagrams are given in Table 6.

As a result of the GC-MS analysis, the citronella content in the fabrics and after five washes which were transferred by coating, printing and impregnation methods are shown in Table 7.

When the data in Table 7 are examined, a lower rate of citronella was detected before washing with the printing and coating methods, compared to the impregnation method. It has been determined that the rate of active substance is higher when the capsules were transferred by the coating and printing after washing. This suggests that the capsules transferred in a viscous matrix by printing and coating methods were released more with the decrease of this matrix after washing. For this reason, m^2 weights before and after washing were determined for all samples.

As can be understood from Table 8, weight decrease was detected in the fabrics to which the capsules were transferred after washing, especially by coating and printing methods. This shows that the chemicals on the fabric, which were used for capsule transfer, were decreased after washing. It was thought that the

Table 7: Citronella amount in the samples as a result of GC-MS analysis

Fabric	ppm
Capsule transferred by printing method	0.2977
Capsule transferred by printing method (after five washings)	2.6139
Capsule transferred by coating method	0.2697
Capsule transferred by coating method (after five washings)	2.0043
Capsule transferred by impregnation method	0.3646
Capsule transferred by impregnation method (after five washings)	0.3704

Table 8: m^2 weight changes of samples before and after washing

Fabric	Before washing (g/m^2)	After five washings (g/m^2)
Capsule transferred by printing method	220	210
Capsule transferred by coating method	235	215
Capsule transferred by impregnation method	202	198

Table 9: Insect repellent effect results of samples

Fabric	Insect repellent ratio (%)			
	2 min	4 min	8 min	10 min
Capsule transferred by printing method	51.0	43.3	44.7	39.0
Capsule transferred by printing method (after five washings)	61.0	62.7	72.0	62.7
Capsule transferred by coating method	44.7	42.7	56.3	56.3
Capsule transferred by coating method (after five washings)	38.7	56.3	65.0	62.3
Capsule transferred by impregnation method	56.0	44.7	55.0	54.3
Capsule transferred by impregnation method (after five washings)	63.3	53.0	48.7	61.7

removal of printing and coating chemicals by washing was caused more emergence of citronella from fabric. This situation was consistent with the results obtained by GC analysis.

The fabrics including insect repellent capsules were also subjected to insect repellent activity tests in accordance with WHO standard. The assays were performed for treated and washed fabrics. The insect repellent effect percentage of the samples are listed in Table 9.

According to the cone test results, it was determined that the insect repellent activity increased after washing for the printing and coating methods. Insect repellent ratio was found to be 72, 65 and 55% for fabrics finished with printed, coated and impregnated citronella capsules, respectively. This shows that the contents of the capsules are released more easily from the shells for the printed and coated fabrics, as confirmed by the GS-MS analysis. Contrary to this, in the impregnation method, the insect repellent efficiency obtained after washing was decreased. The insect repellent effect percentages were better with the coating and printing methods, so it suggests that coating and printing methods can be an alternative to the conventional impregnation method.

One of the important features expected in upholstery fabrics is the dimensional changes after washing. For this purpose, the dimensional change of the fabrics containing capsules in washing was determined according to TS EN ISO 6330 and indicated in Table 10.

According to the dimensional change analysis; it was determined that the presence of microcapsules did not cause any negative effect on dimensional change. It was determined that the percentage of dimensional change obtained in the presence of microcapsules were the same in each method.

The results of rubbing, washing and light fastness of the fabrics to which the microcapsules containing citronella were transferred are given in Table 11. In order to examine the effect of capsule presence on fastness properties, impregnation, printing and coating processes were compared with the forms that do not contain capsules.

When the light fastness, washing fastness and rubbing fastness analyses were examined, it was determined that the presence of microcapsules did not affect the fastness analysis results positively or

Table 10: Dimensional change percentage for fabrics

Fabric	Dimensional change (%)	
	Width	Length
Raw fabric	− 3	− 4
Printed fabric (without capsule)	− 2.5	− 3
Capsule transferred by printing method	− 2.5	− 3
Coated fabric (without capsule)	− 3	− 2.5
Capsule transferred by coating method	− 3	− 2.5
Capsule transferred by impregnation method	− 3	− 2.5

Table 11: Fastness test results of capsule-transferred fabrics containing citronella

Fabric	Fastness to light	Fastness to washing							Fastness to rubbing	
		A02	CA	CO	PES	PA	PAC	Wo	Wet	Dry
Printed fabric (without capsule)	6–7	5	5	4–5	5	5	5	5	4	3–4
Capsule transferred by printing method	6–7	5	5	4–5	5	5	5	5	4	4
Coated fabric (without capsule)	6–7	5	5	5	5	5	4–5	5	4–5	4–5
Capsule transferred by coating method	6–7	5	5	5	5	5	4–5	5	4–5	4–5
Capsule transferred by impregnation method	6–7	5	5	5	4–5	5	4–5	5	5	5

Table 12: Color measurements of fabrics

Fabric	L^*	a^*	b^*	C^*	H^*	K/S	R %	ΔE
Impregnated	68.5	2.92	7.21	7.78	67.9	0.74	31.5	–
Impregnated with citronella capsules	67.9	3.01	7.34	7.93	67.8	0.78	30.7	0.56
Coated	68.3	3.06	7.69	8.27	68.3	0.78	30.8	–
Coated with citronella capsules	68.1	3.04	7.56	8.14	68.1	0.78	30.7	0.26
Printed	39.9	− 3.55	− 30.1	30.3	263.1	7.01	6.34	–
Printed with citronella capsules	39.5	− 3.73	− 29.2	29.5	262.7	7.13	6.17	0.98

negatively. The fastness analysis was given very good results in terms of the use of upholstery fabrics and it was determined that the fabrics preserved their colors due to usage.

In order to examine whether the capsules have an effect on the color values of the fabrics, color measurements of the fabrics with and without capsules on which impregnation, coating and printing prescription were applied. The color values of the fabrics are included in Table 12.

According to the color measurement results, it was determined that the presence of capsules did not cause a big change in the fabric color for all methods. When the color difference (ΔE) values were compared to the fabrics without capsules, the fact that all of these values were less than 1 indicates that the colors obtained in the presence or absence of capsules were not significantly different.

Conclusions

In this study, microcapsules containing a bio-based active agent citronella oil with insecticide effect were obtained by using the complex coacervation method, and their optimization was performed with FTIR ATR, SEM, particle size and TGA analyses. The homogenous size distribution of the capsules was supported by laser diffraction analysis and the mean particle size of the optimum formulations for citronella was almost 50 μm. As a result of the conducted studies, the concentration of 2:1 (EC: active substance) was deter-

mined as the optimum prescription. Capsules were transferred on fabrics to be used in garden furniture and curtains by impregnation, coating and pigment printing methods.

As a result of the analysis, the encapsulation process has been carried out successfully. With the characterization studies, the presence of capsules on the fabric was detected even after five washes. This shows that the transferred capsules are washing resistant. It has been determined that microcapsules transferred on upholstery fabrics do not change the fastness properties, size or color values of the fabrics.

According to the results of GC-MS analysis, it was determined that the capsules containing citronella active substances released more citronella oil after washing in the fabrics transferred by coating and printing processes. This suggests that the capsules transferred in a viscous matrix by printing and coating methods release more with the decrease of this matrix after washing. In parallel with these results, as a result of the insecticide analysis, it was determined that the insect repellent activity after washing for the printing and coating method was increased. Mosquitoes tended to stay away from treated fabrics, and mortality rates of mosquitos were noted as 72, 65 and 55% for printing, coating and impregnation, respectively, and the fabrics still showed repellency after five washing cycles. Compared to previous studies, it has been determined that bio-based citronella oil has a better insect repellent effect than synthetic agents.

When the analysis of insect repellent effect obtained was examined, it is suggested that coating and printing methods provide a better effect after than the conventional impregnation method washing and therefore can be an alternative to the impregnation method.

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Conflict of interest The authors declare that they have no conflict of interest.

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