

New aroma chemical applications

Fabric Care

Distribution of aroma chemicals on textile fibers^a

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Understanding the factors that influence retention and release of aroma chemicals from textiles is important for development of consumer products for fabric care applications. Olfactometry, as well as gas chromatographic, techniques have been extensively used to investigate the deposition of aroma chemicals on fabrics and to evaluate their performance in consumer products.¹ However, the distributions of aroma chemicals within the textiles are less well defined. Electron microscopy techniques have been used to study the distribution of chemical finishing agents and soils on fibers and within yarns. Studies show that the penetration and distribution of these materials can be understood in terms of the chemical and physical properties of the textile.²⁻⁷

This study focused on defining the distribution of osmium-tagged aroma chemicals on and within the fiber structures using scanning electron microscopy and X-ray microanalysis. Our overall goal was to understand mechanisms of deposition, adsorption, and retention based on aroma chemical properties (such as vapor pressure and surface tension) and textile characteristics (such as morphology, capillary structure and fiber chemistry).

Experimental Methods

Fabrics: Bleached cotton print cloth style 400 and polyester (100 percent Dacron, type 54, style 777) were purchased from Testfabrics Inc., West Pittston, PA. Lyocell (Tencel chambray) was obtained from Courtaulds Inc., Axis, AL. Prior to use, all three fabrics were rinsed in running tap water for 1 h, followed by Soxhlet extraction with ethanol for 24 h. The fabrics were then air-dried at 23°C and conditioned at 65 ± 2 percent relative humidity for at least 24 h.

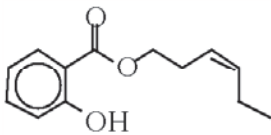
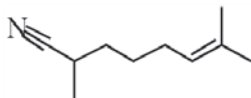
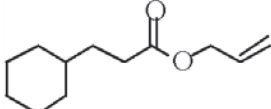
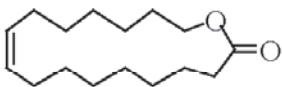
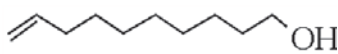
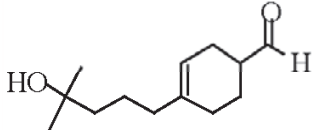
Chemicals: Aroma chemicals were supplied by International Flavors & Fragrances Inc. (Union Beach, NJ), and were used as received (T-1). All other reagents were used as received.

Osmium tetroxide (2 percent aqueous solution) and Spurr's low viscosity resin were purchased from Electron Microscopy Sciences (Fort Washington, PA). The quantity of electrons backscattered from a given surface is proportional to the atomic number (such as osmium) of the sample material, and thereby provide contrast for imaging with electron microscopy. Osmium tetroxide is a commonly used stain for electron microscopy since it reacts readily with unsaturated

Study Overview

A combination of backscattered electron microscopy (BSE) and X-ray microanalysis were employed to probe the distribution of aroma chemicals on cotton, lyocell and poly(ethylene terephthalate) (PET) fabrics. *cis*-3-Hexenyl salicylate (CHS) deposited itself on both the internal and external surfaces of cotton fibers, with higher concentrations found in the lumen and crenulations, whereas CHS was uniformly distributed between the internal and external fiber surfaces of lyocell. This was attributed to differences in the pore and capillary structures, fiber morphology, surface roughness, and the high polarity of the fibers. In contrast, CHS accumulated only at a few locations on the fiber surfaces and in the interfiber spaces of PET yarns. Compared to cellulosic fibers, PET is of lower polarity, possesses an isotropic cross-sectional shape, has smoother surfaces, and exhibits fewer voids. Deposition and retention of aroma chemicals will be explained in terms of surface tension and aroma chemical vapor pressure.

^aMicroscopical Analysis of Aroma Chemical Distribution on Fibers. I. *cis*-3-Hexenyl salicylate," Haiqing Liu, S. Kay Obendorf, Timothy J. Young, Michael J. Incorvia, *Journal of Applied Polymer Science*, Vol. 91, 2004 (John Wiley & Sons, Inc.).

Chemical	Structure	p^* [Pa]	Retention on cotton fabric [percent]		
			10 min	70 min	480 min
<i>cis</i> -3-hexenyl salicylate		0.04	98	nm	nm
agrunitrile		7.46	nm	43	5
allyl cyclohexyl propionate		1.36	nm	78	20
ambrettolide		0.03	nm	100	100
rosalva		0.79	87	nm	26
lyral		0.01	100	nm	75

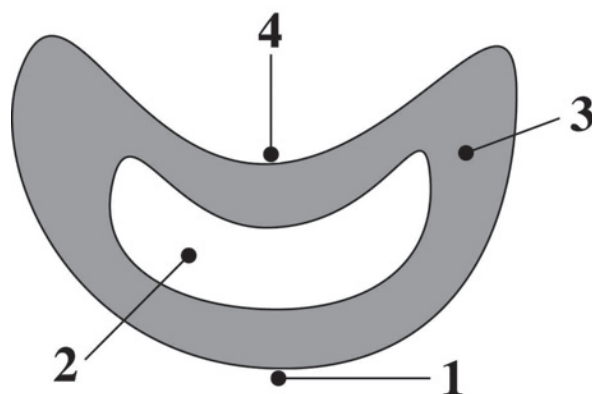
p^* = pure vapor pressure; nm = not measured

organic compounds and is not naturally occurring in organic materials.

Application method: Aroma chemicals were delivered onto circular fabric swatches (diameter = 5 cm) using a pipette method, which has been described previously.⁸ Briefly, a 0.2 ml aliquot of 1 percent (w/v) aroma chemical/ethanol solution was delivered by pipette onto each fabric swatch, followed by air-drying; when evaluating the effect of vapor pressure on retention, 5 percent (w/v) aroma chemical solutions were used to give sufficient contrast for BSE images. To prepare the samples for electron microscopy, a small piece of each treated fabric was exposed to osmium tetroxide vapor for several hours in an enclosed container, thereby fixing the aroma chemical on the textile. Control cotton specimens were not treated with aroma chemical but were exposed to osmium tetroxide vapor. It should be noted that osmium tetroxide does not react with cellulose or PET.

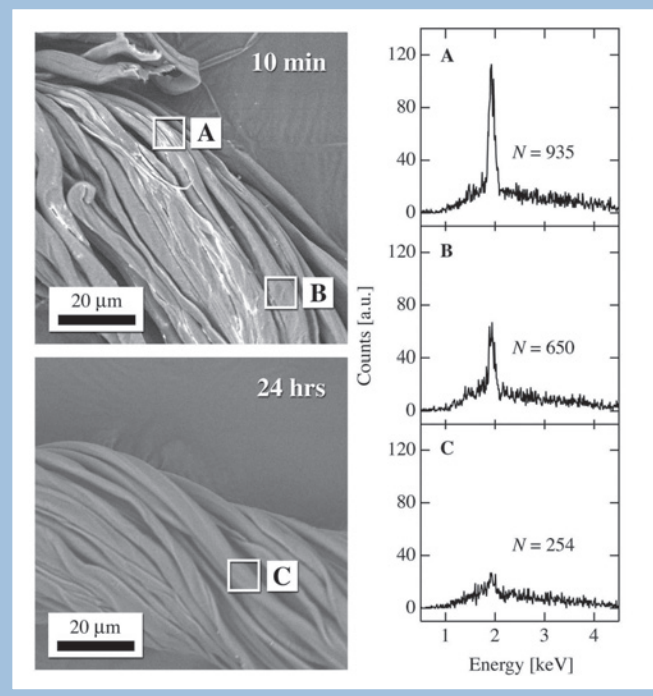
Key morphological features of cotton fiber:
(1) fiber surface (2) lumen (3) secondary wall
(4) crenulation

F-1



BSE and X-ray spectra of cotton treated with 1 percent *cis*-3-hexenyl salicylate, after 10 min and 24 h

F-2

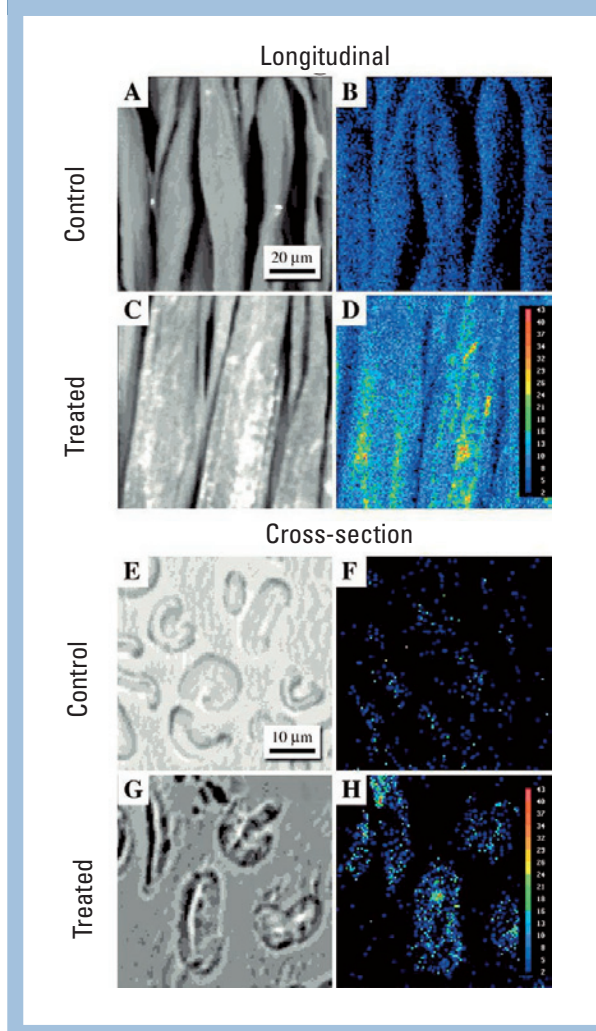


Microscopy analysis: Both longitudinal and cross sectional fiber specimens were prepared from the treated and untreated fabrics. Osmium tetroxide treated warp yarns were embedded in resin and cured at 70°C for roughly 10 h. Thick cross-sections (ca. 5 μm) were microtomed from this resin block, and were subsequently carbon-coated. Backscattered electron images (BSE) were recorded on a Scanning Electron Microscopy JEOL 440 (LEO Electron Microscopy Ltd., Japan). X-ray maps and energy dispersive X-ray analyses (EDX) were obtained using a JEOL Superprobe JXA-8900R WD/ED combined microanalyzer. Energy dispersive X-ray analysis provided net X-ray counts from Os at an energy range of 1.64-2.11 keV at selected morphological locations (F-1).

The BSE technique is sensitive to its chemical composition as well as surface roughness. Regions of brightness in BSE images indicate osmium-rich regions, and thus the location of labeled aroma chemical (F-2). It should be noted that BSE does not detect low concentrations or uniform distributions of osmium on the fiber surfaces or in the cross-sections. Therefore, it is necessary to use energy dispersive X-ray analyses (EDX) in tandem with BSE

Longitudinal and cross-sectional BSE images and X-ray maps of control cotton and cotton treated with 1 percent *cis*-3-hexenyl salicylate after 10 min

F-3



to fully define aroma chemical distribution on the fibers. Using EDX, an “X-ray map” of the surface can be produced by tuning the spectrometer to a specific element or energy window of interest while the beam scans the sample.

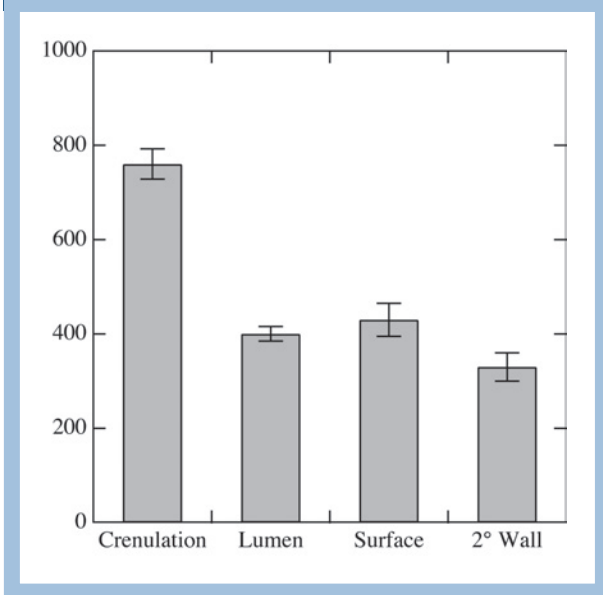
Results and Discussion

Distribution of aroma chemical on cotton fibers:

Backscattered electron images and X-ray maps show the distributions of aroma chemical on the cotton fiber surfaces and within the fiber structure (F-3). The surfaces of the untreated fibers do not show areas of high contrast indicating that osmium tetroxide is selectively tagging the aroma chemical.

Distribution of CHS on cotton fibers was found to be non-uniform, due to individual fiber morphology, surface roughness, and capillary structure of the yarns (F-2, F-3); high concentrations of CHS were found in crevices and irregular morphological locations within the fiber and yarn structure. This is illustrated in F-2;

Relative concentration of *cis*-3-hexenyl salicylate at key morphological locations on cotton fiber after 10 min (error bars represent standard deviations) **F-4**

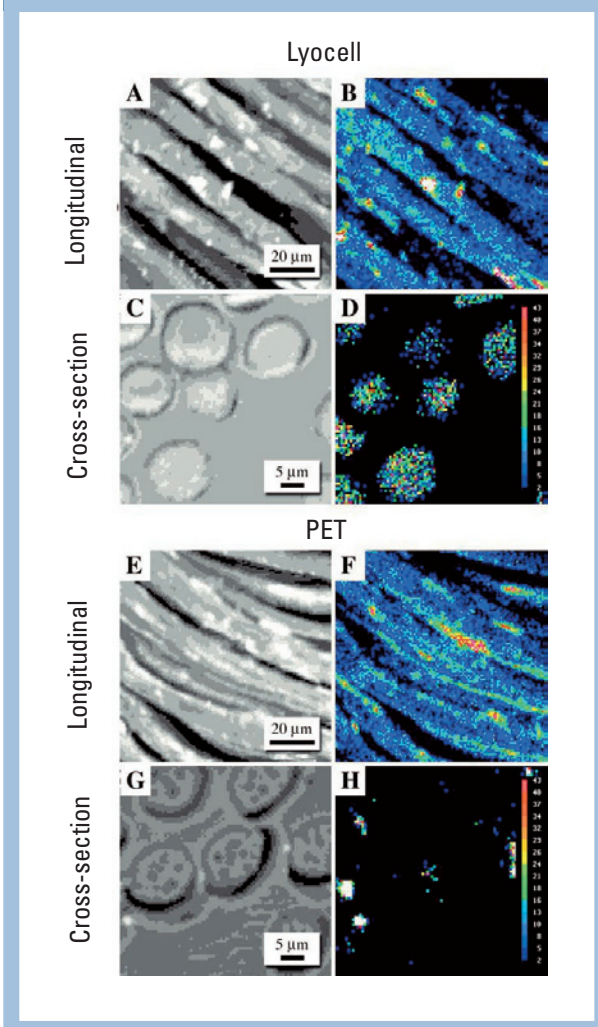


the marked bright spot (A) had net counts of 935, and the total net counts of a darker spot in the same image (B) was 650. After storing the treated fabric under ambient conditions for 24 h, regions of high CHS concentration were substantially diminished in intensity suggesting aroma chemical release over time. The fiber surface at a spot probe location of the darker surface (C) had counts of 254, showing retention of some aroma chemical on the fiber surface but of a lesser amount than that observed on the surfaces after only 10 min (F-2). From the X-ray analysis, we conclude that aroma chemicals deposit themselves on most fiber surfaces, but with different concentrations at various morphological locations. Most of the surfaces of treated fibers had X-ray intensities above background after 10 min.

Cotton fiber surfaces are irregular, and the fiber shape is commonly described as a “collapsed tube.”^{3-7,9} Distinct morphological regions exist within a cotton fiber (F-1): external fiber surface, lumen, secondary wall, and crenulation (also known as the V-groove). The characteristic irregular morphological shape and non-uniform sizes of cotton fibers can be seen in F-3, and each morphological region can be identified. For cotton fibers treated with CHS solution, X-ray microanalysis shows that the crenulation of cotton fiber had the highest concentration (ca. 760 net counts), while fiber surface, secondary wall, and lumen had similar concentrations (ca. 400 net counts) (F-4).

We observed that aroma chemicals were retained in the interfiber capillaries, surface irregularities, and pores within the fibers. The largest concentration was observed in small surface grooves or crenulations. The crenulation acts as “micro-container” (small capillary)

Longitudinal and cross-sectional BSE images and X-ray maps of lyocell, and PET treated with 1 percent *cis*-3-hexenyl salicylate after 10 min **F-5**



to hold solution.

Transport of oily soils, chemical finishes, and detergents into the interior of cotton fibers has been well documented.^{2-7,9} Cotton fibers have a characteristic microporous structure. Rowland et al. defined pores in the cotton structure into which molecules with diameters greater than 16 Å penetrate. Nelson and Oliver found that the actual diameters of some pores are as large as 32-64 Å, which is two to four times the size of some solutes.^{10,11} As well, small interfibrillar spaces of 12-50 Å width are present in the cotton fiber structure; these spaces vary in size with the processing treatment of the fibers and the extent of swelling in water or other liquid media.^{12,13} These micropores and interfibrillar spaces greatly affect water uptake, dyeability, washability.⁷ Since the

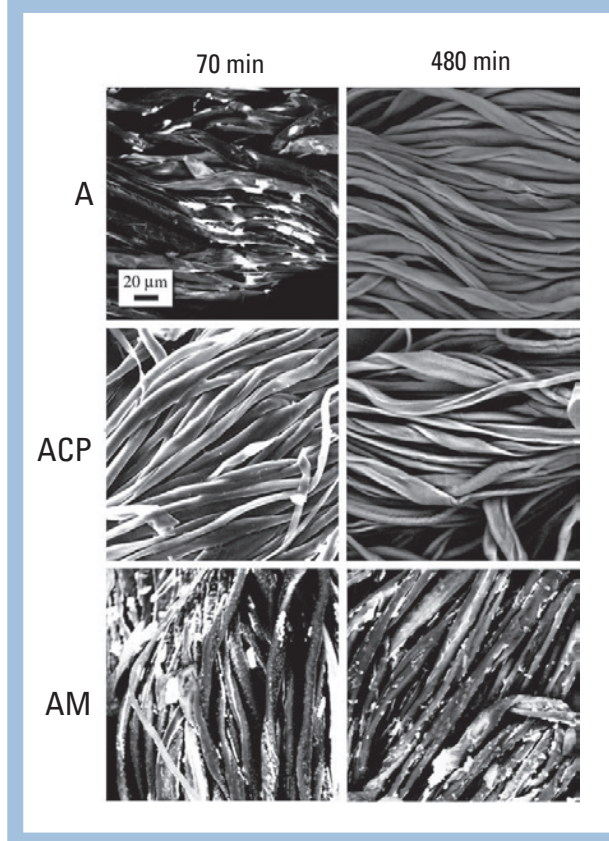
diameters of aroma molecules are around 10-20 Å, they can be carried into these micro-pores and micro-spaces by the movement of the solvent where they deposit on surfaces internal to the cotton fiber. This phenomenon explains our finding of aroma chemicals on internal surfaces within the interior of cotton fibers including the secondary wall.

Effect of fiber morphology, comparison of cotton to lyocell and PET: To study the role of fiber morphology and physical structure on aroma chemical deposition, X-ray maps and BSE images of CHS on lyocell and PET fibers (F-5) were collected for comparison with cotton (F-3). Round morphological shape of lyocell fiber is shown in the BSE image in F-5C, which can be compared to the twisted ribbon structure of cotton (F-3). Aroma chemicals are observed distributed over the surfaces of the lyocell fibers (F-5A, F-5B); surface irregularities and defects along the fiber result in areas of higher concentrations of aroma chemical.

In comparing cotton and lyocell, which are both cellulosic fibers possessing different fiber morphologies, we observed

BSE images of cotton fabric treated with agrunitrile (A), allyl cyclohexyl propionate (ACP), and ambrettolide (AM); data were collected 70 min and 480 min after application for each sample

F-6



that CHS was distributed more evenly throughout the lyocell fiber cross-section (F-5D) than in cotton (F-3H). Lyocell fibers contain larger air-filled voids, and smaller defect regions that are formed during the solvent-spun manufacturing process. Void diameters range from 28-50 Å.¹⁴ CHS/ethanol solution should easily penetrate into those voids and be retained after solvent evaporation.

PET fibers differ in chemical composition from cotton and lyocell; PET fibers treated with CHS are shown in F-5. Like lyocell, the cross-sectional shape of PET is round and more uniform than that of cotton fiber. Again for PET, higher concentrations were retained by irregularities on the PET fiber surfaces as well as in interfiber spaces of yarns. The appearance of the aroma chemical deposition on the fiber surface was similar to that observed for lyocell which is also a manufactured fiber. The X-ray map of PET cross-section further defines the higher concentrations in closely packed fiber spaces. PET fibers have very few, if any, voids or surface irregularities and exhibited no observable penetration of aroma chemical into the fiber (F-5H).¹⁵

The distribution of CHS on PET fibers illustrates the strong effect of the surface tension of the substrate on the distribution of the aroma chemical. For a liquid

to spread across a surface, the surface tension of the liquid must be less than that of the surface. Surface tensions of cellulose, PET, ethanol and CHS are 42, 35, 22.8 and 37 mN/m at 20°C, respectively. Aroma chemicals in ethanol solution will readily wet both cellulose and PET fiber surfaces based upon the surface tension of ethanol. However, after evaporation of solvent ethanol, CHS, as a single component, is expected to spread over cellulose, but not over PET surfaces. Consistent with these expectations, we observed accumulation of CHS on PET fiber surface particularly between closely spaced fibers (F-5G and H).

Effect of vapor pressure: As expected, low vapor pressure resulted in higher retention of aroma chemical on cotton fabric (T-1). For ambrettolide, with vapor pressure of 0.03 Pa, most of the applied aroma chemical was retained on the cotton fabric after 480 min, while after the same time period only 5 percent of agrunitrile with higher vapor pressure of 7.46 Pa was retained. Lyril and rosalba on cotton fabric showed a similar effect of vapor pressure.

In the BSE images of treated cotton yarn, high concentrations of agrunitrile or allyl cyclohexyl propionate were not observed after 480 min (F-6, A-480 min and ACP-480 min). Between 5 percent and 20 percent of agrunitrile and allyl cyclohexyl propionate was retained, respectively, according to GC (T-1). However, we observed greater retention on the yarn treated

with ambrettolide, an aroma chemical with a lower vapor pressure (0.03 Pa) (F-6, AM-480 min).

Future work: We are currently investigating the deposition of aroma chemicals on textiles from aqueous surfactant systems using a complementary gas chromatography/electron microscopy approach. Retention and release characteristics of aroma chemicals delivered in this way are also being investigated. It should be noted that such systems present unique challenges that are not directly addressed by this paper.

Conclusions

The combination of BSE imaging and X-ray microanalysis can be used to define the distribution of aroma chemicals on textiles. The physical and chemical nature of the fiber is important in the retention and distribution of aroma chemical. During this study, we observed that CHS was retained and distributed over the entire fiber surface of cotton and lyocell, with higher concentrations in surface irregularities and morphological structures such as the crenulations in cotton. The capillary structure formed by close-packing of fibers

as observed for lyocell and PET yarns gave rise to higher levels of aroma chemical accumulation. Lower concentrations of CHS were retained in micropores within the cotton and lyocell fibers. Higher surface tension of CHS than that of PET fiber led to its build-up in a few locations particularly between closely-spaced yarn fibers. Vapor pressure of aroma chemicals has the expected effect on the retention and release from a textile.

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