

Air Emissions from Carpet Manufacturing Processes

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To better characterize stack emissions from carpet manufacturing processes, volatile organic compound (VOC) emissions were measured and hazardous air pollutants (HAPs) were identified for four processes: suessen heatsetting, beck dyeing, continuous dyeing, and latex coating. The study included field and laboratory investigations performed during the 1996-99 time period.

In nylon 6 fiber heatsetting, caprolactam is the major VOC emitted, released at a rate of 400 mg per pound of fiber. For nylon 66 fiber heatsetting, on the other hand, VOC emissions are predominantly long-chain acids and esters found in yarn spinning lubricant. Total VOC emissions ranged from 240 to 600 mg per pound of fiber processed. Total VOC emissions from beck dyeing ranged from 500 to 1000 mg/yd² carpet; for continuous dyeing, the VOC emission estimate ranged from 100 to 200 mg/yd² carpet. VOC emissions included long-chain hydrocarbons at plants using powder dyes, and glycol ethers and other oxygenated compounds at plants using liquid dyes. Alkyl benzenes from stainblock application were also observed. Laboratory results demonstrate that water-soluble VOCs partition between gas and water effluents. Pure hydrocarbon auxiliary compounds present in the dye applications, on the other hand, were entirely released to the stack gas. VOC emission factors for styrene-butadiene latex coating were estimated to range from 150 to 280 mg/yd². Laboratory simulation results were in close agreement with the field measurements.

In total, it is estimated that 1-2 g of VOCs are released to the air in the manufacture of one square yard of nylon carpet.

Introduction

Emission source inventories of volatile organic compounds (VOCs) are inadequate in part due to incomplete characterization of a large number of minor sources. The need to better characterize air emissions from carpet manufacturing processes was identified as a research priority by the Consortium on Competitiveness for the Apparel, Carpet, and Textile Industries (CCTI), a Georgia traditional industries program.¹ In July 1996, a three-year project was undertaken to estimate emissions of VOCs and hazardous air pollutants (HAPs) at carpet manufacturing plants. Carpet manufacturing processes that can result in significant air emissions are yarn heatsetting, carpet dyeing, and carpet backing.

Nylon and polyester yarns are prepared in a spinning mill. Staple fibers, which are unaligned, and continuous filament fibers are received with residual lubricant from the fiber manufacturer. More lubricant is added at the spinning plant ("overspray"), particularly to staple fiber. Fibers are drawn out to increase fiber alignment and twisted to form a yarn. The resulting plied yarns are coarse and thick. Yarns are heatset to stabilize shrinkage which may occur in subsequent thermal processing. Heatsetting typically occurs in an autoclave or superba at elevated temperature and pressure, or in a suessen at higher temperature and atmospheric pressure. After heatsetting, the yarn is attached to a primary backing material (tufting process).

Both batch and continuous methods are used to dye carpet. In the batch process, carpet is immersed in dye solution contained in large, enclosed dye becks for about one hour. Batch, or beck, dyeing is followed by carpet rinsing and drying. In the continuous dyeing process, dye is typically sprayed on carpet as it passes through a dye range. The dye is then steam set, rinsed to remove any excess dyes and chemicals, and dried in a gas-fired oven. Anti-soil and anti-staining agents may be applied.

In the final carpet manufacturing step, a foam or woven secondary backing is applied to the carpet. This backing is applied by coating the surface of the primary backing with latex adhesive. The two backings are rolled together to form a tight bond, and the adhesive is cured in a gas-fired oven. The carpet is then ready for distribution to stores and consumers.

Potential stack emissions associated with these carpet manufacturing processes that may be of concern include the following. The high heatset temperatures may result in the release of volatile components of yarn finishing as well as from the yarn itself. Auxiliary chemicals used in dyeing, including oxygenated VOCs and HAPs, may be emitted. In the secondary backing application, free latex constituents, such as styrene and butadiene, may be released. Although much is known about water and solid effluents from carpet manufacturing, little is known about air emissions. Indoor air quality and its impacts on both textile workers within the carpet mills and on end-use consumers have been assessed in numerous studies. While stack emission tests have been performed to address specific concerns, such as caprolactam from nylon 6 heatsetting² and water soluble VOCs from carpet dyeing,³ these test results are not widely available. Moreover, comprehensive emissions testing for the carpet industry has not been performed.

The overall goal of this work was to gain a better understanding of air emissions from carpet manufacturing processes through field measurement and laboratory simulation. This collaborative effort involved three industry partners. Field studies were performed at eight plants: two suessen heatsetting plants, two beck dye plants, two continuous dye plants, and two latex coating plants. Laboratory studies were also performed to assess emission of any VOCs that could not be measured in the field due to limitations in sample collection methods, as well as to assess effects of temperature and alternative applications on air emissions.

Analytical Methods

Field tests were performed over two-week periods during April of 1997 (two continuous dye plants and two latex coating plants) and April of 1998 (two suessen heatsetting plants and two beck dye plants). Stack measurements were conducted during normal operation of the process lines; stacks were assumed to operate with constant volume flows. Particularly challenging aspects of the field assessment were the large number of stacks and high moisture content of the stack gas. Access holes were drilled on a straight section of the exhaust stack to minimize disturbances from rain-caps, fan blades, and elbows. Dry and wet-bulb temperatures, relative humidity and velocity were measured with a TSI VelociCalc Plus Meter, Model 8388. At least three locations within each exhaust flow were checked to ensure that even temperature distributions existed. Volume flow rates were determined for each stack by conducting velocity measurements across the traverse plane of the stack. The error in mass flow measurement is estimated to be within 5% of the calculated value for stacks allowing good access for a full traverse flow.

Various methods were used for stack gas collection and analysis, as summarized in Table 1. Non-polar and slightly polar VOCs were trapped on Tenax-GR[®] and analyzed by gas chromatography with mass spectroscopy (GC/MS). Artifacts associated with these samples were identified.⁴ For stacks with very high moisture content gas, water impinger samples were taken and VOCs were extracted by solid-phase microextraction (SPME) fibers and analyzed by GC/MS. Aldehydes and ketones were collected in dinitrophenyl hydrazine (DNPH), either coated on extraction tubes or contained in impinger bottles, and analyzed by liquid chromatography with UV detection (LC/UV). Silica gel tubes were used to collect ammonia from latex coating plant stacks, with analysis by ion chromatography with conductivity detector (IC/CD).

Table 1. Sample Collection and Analytical Methods

target compounds	collection medium	analytical method
non-polar VOCs	Tenax-GR [®]	GC/MS
dissolved gases	impinger water	
phosphoric acid		UV colorimetry
polar VOCs		GC/MS
targeted VOC analytes	SPME fiber	GC/MS
aldehydes & ketones	DNPH	LC/UV
ammonia	silica gel	IC/CD

Prior to field testing, samples of chemical applications were analyzed to target potential VOC emissions. These results were also useful in relating the field emissions that were observed to particular chemical applications. After field testing, simple laboratory tests were developed to simulate the time-temperature environment of the carpet during processing. These tests allowed for the assessment of any VOC emissions that could not be measured in the field due to limitations in sample collection methods, as well as the assessment of effects of temperature and alternative applications on air emissions.

Results and Discussion

Air emission factors (mass emission per production unit) for VOCs and HAPs were estimated for four processes: suessen heatsetting, beck dyeing, continuous dyeing, and latex coating. Results, summarized in Table 2, were obtained by studying two plants as follows. First, site visits were conducted to identify process conditions and to collect material and chemical application samples. Second, laboratory analyses of process chemicals were performed to identify potential air emissions. Third, field measurements of stack flow rates and VOC concentrations were taken to determine air emissions. Fourth, laboratory simulation tests were performed to assess effects of process conditions and applications on gas emissions. Emission factors and maximum production capacity were then used in potential-to-emit calculations for the eight plants studied. In total, it is estimated that 1-2 g of VOCs are released to the air in the manufacture of one square yard of nylon carpet. For the maximum production capacity at the plants studied, this translates to an annual VOC emission of 50 to 100 tons. Select results for each process are highlighted in the subsections that follow.

Table 2. Emission Factors and Major Species for Carpet Manufacturing Processes

suessen heatsetting			
lab	nylon 6	VOCs	400 mg/lb fiber (caprolactam)
	lubricant	VOCs	0.8% (diethylene glycol; long-chain esters, acids and alkanes)
field	suessen	VOCs	500 mg/lb fiber ^a (nylon 66 – esters, acids, alkanes)
		HAPs	10 mg/lb fiber (aldehydes; glycol ethers)
beck dyeing			
lab	powder dyes	VOCs	C ₁₄ - C ₂₀ alkanes
	liquid dyes	VOCs	diphenyl ether, esters (butyl hexadecanoate, butyl stearate), glycol ethers
	stainblock	VOCs	alkylbenzenes
field	beck	VOCs	450 mg/yd ² carpet (powder dyes – C ₁₄ - C ₂₀ alkanes; liquid dyes – diphenyl ether)
		HAPs	80 mg/yd ² carpet (aldehydes)
	dryer	VOCs	350 mg/yd ² carpet (C ₁₂ - C ₂₀ HCs; diphenyl ether; alkylbenzenes)
		HAPs	20 mg/yd ² carpet (acetaldehyde and other aldehydes)
continuous dyeing			
lab	dyebaths	VOCs	140 mg/yd ² (isopropanol, 2-ethyl-1-hexanol)
		HAPs	< 7 mg/yd ² (glycol ether - butyl cellosolve; acetaldehyde)
field	dryer only	VOCs	30 mg/yd ² carpet (C ₉ - C ₁₈ HCs, 2-ethyl-1-hexanol)
		HAPs	3 mg/yd ² carpet (propionaldehyde and other aldehydes; glycol ethers)
latex coating			
lab	adhesive & precoat	VOCs	250 mg/yd ² (long-chain alkanes and alkenes)
		HAPs	10 mg/yd ² (styrene, ethylbenzene, cumene, 4-PC)
field	curing oven	VOCs	220 mg/yd ² carpet (C ₁₀ - C ₁₈ HCs, C ₂ - C ₁₆ alcohols)
		HAPs	20 mg/yd ² carpet (acetaldehyde and other aldehydes; styrene, cumene, 4-PC)
		ammonia	200 mg/yd ² carpet

^a To compare with dyeing/coating emission factors, multiply by face weight, typically about 2 lb fiber per yd² carpet.

Yarn Heatsetting

Raw staple fiber is delivered to the plant in 550 lb bales; continuous filament fiber is delivered on spools. Approximately 4 gallons of lubricant is added to each 550 lb bale of staple fiber. Tints may be added to differentiate yarn types. Spinning involves the repeated drawing out of fiber along rotating rollers. Heatsetting reintroduces texture to the yarn. In suessen heatsetting, the yarn is exposed to saturated steam at 200°C for 1 minute. The nominal yarn processing rate is 325 lb/hr. Stock lubricants obtained from each plant contained up to 0.8% (wt) VOCs. Major species included diethylene glycol and long-chain esters (most notably butyl hexadecanoate and butyl stearate), acids and alkanes.

Nylon 6 and 66 yarn heatsetting resulted in very different VOC emissions, as evidenced by the GC/MS chromatograms of Tenax samples from suessen stacks shown in Figures 1 and 2. The major species emitted from nylon 6 processing was caprolactam (peak 9). The release of caprolactam may result from unpolymerized nylon 6 precursor or reaction during heatsetting.⁵ Laboratory experiments with four different types of nylon 6 fiber resulted in caprolactam emission rates ranging from 0.6 to 1% (wt), with an average of 400 mg per pound of nylon 6 fiber processed. In contrast, major species emitted from nylon 66 processing were spinning lubricant constituents, particularly butyl hexadecanoate (peak 16) and butyl stearate (peak 22). Over 80% of spinning lubricant VOCs appears to be released. Nylon 66 thermal decomposition products were not observed.⁶

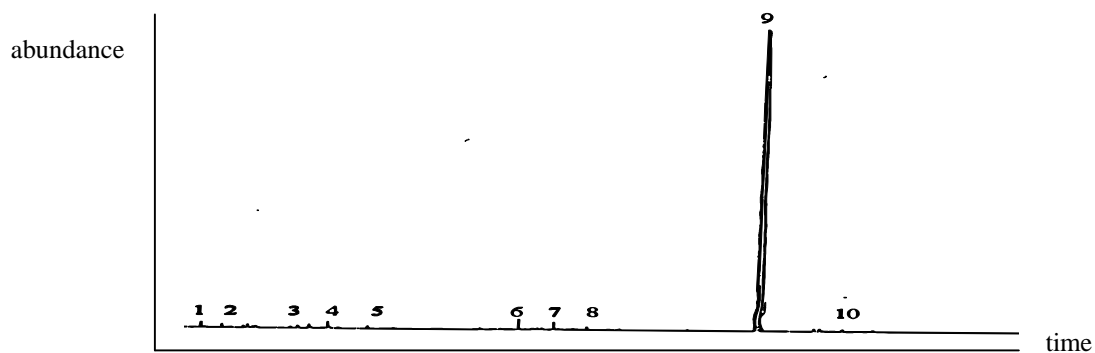


Figure 1. Chromatogram for nylon 6 heatsetting.

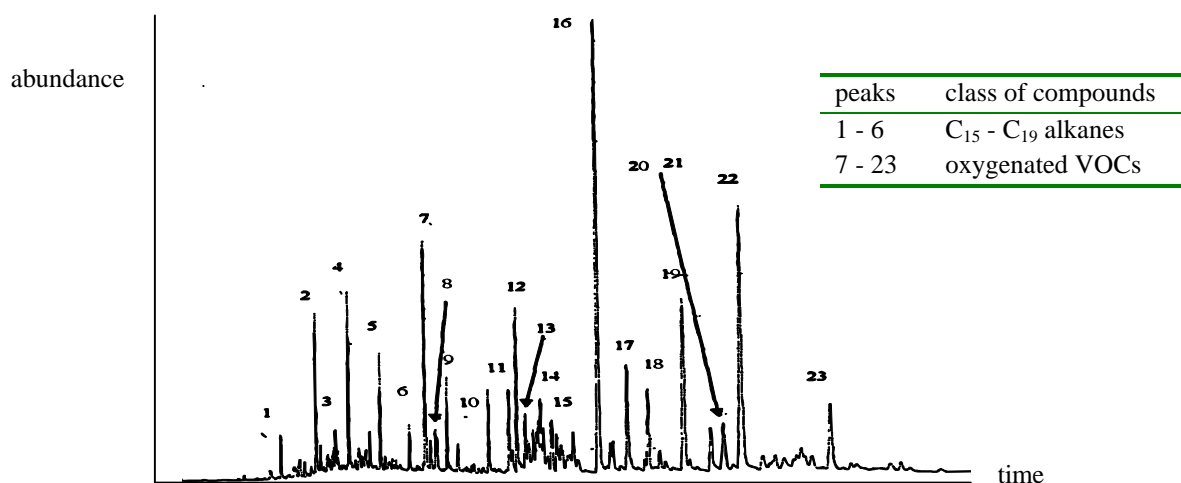


Figure 2. Chromatogram for nylon 66 heatsetting.

Carpet Dyeing

The beck dye plants studied used stainless steel, atmospheric dye tanks, with a liquor-to-carpet weight ratio of 25:1. Nominally, there is a 30 minute warm-up period, 30 to 60 minute boil period, and 30 minute cool-down period. After batch dyeing, the carpet is dried in a continuous process. Stainblock may be applied, containing alkyl benzene compounds.

Samples of stock dyeing solutions were obtained prior to field testing. Both powder and liquid dyes are used. The major species detected in the powder dye solution were numerous long-chain hydrocarbons (12-20 carbon length). In contrast, dyebath containing liquid dyes contained oxygenated organics, including butyl hexadecanoate and butyl stearate. The total VOC content of the dyebaths ranged from 0.1% to 0.5% (wt).

In the field study, beck stacks were sampled four to six times during a cycle to allow for an integrated emission assessment. Major VOC emissions detected were C₁₄ – C₂₀ alkanes from becks using powder dyes and oxygenated VOCs from becks using liquid dyes. These results were consistent with laboratory simulation results. The laboratory and experimental results suggest that nearly all of the non-polar VOCs in the dyebath solution are released to the stack, but only a fraction of the oxygenated VOCs are found in the stack gas.

The continuous dye plants studied used only powder dyes. Carpet entering the plant goes through a pre-steamer which stretches the carpet and opens fiber pores to better accept the dye chemicals. The carpet is then prewashed, followed by application of a gumming agent and dyebath solution. The carpet is steamed to set the dye, and then washed and dried. A fluorochemical spray containing a scotchguard chemical and an anti-soiling agent containing stainblock may be applied prior to drying. At the time of the field tests, only the dryer stacks could be sampled. VOC emissions from steamer stacks were estimated from laboratory simulation tests.

Chemical analysis of samples of chemical bath applications applied during continuous dyeing indicated that these aqueous solutions contained less than 1% VOCs. Laboratory simulation tests indicated that the fraction of VOCs released to the exhaust gas during steaming ranged from over 90% for the more volatile, less water-soluble components to about 10% for the more water-soluble components. The gumming agent had the highest VOC content, with 2-ethyl-1-hexanol the major constituent and glycol ethers (e.g. butyl cellosolve and butyl carbitol) minor constituents.

Results of both the beck and continuous dye emission studies indicate that a large fraction of the VOC emissions are released during carpet dyeing and steaming (rather than drying), and that water-soluble VOCs partition between gas and aqueous effluents. Laboratory results illustrating the latter finding are shown in Figure 3 below.

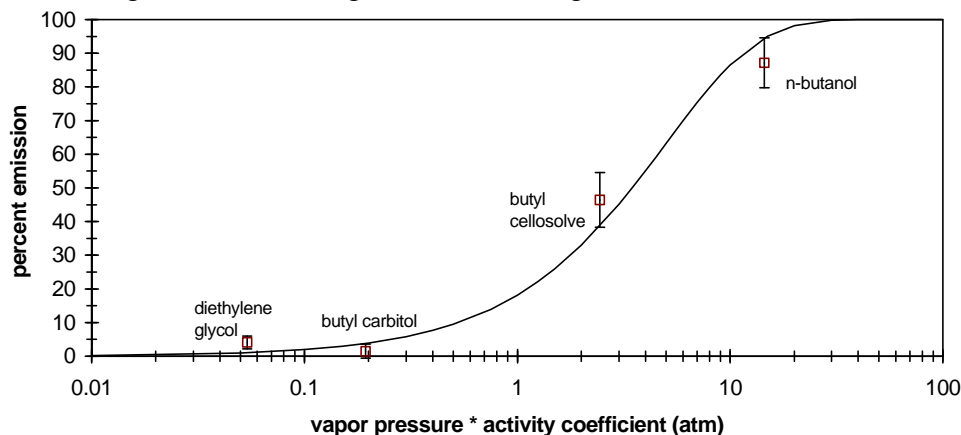


Figure 3. Percent VOC released to gas phase in carpet dyeing.

Latex coating

In the carpet finishing process, a secondary backing fabric is bound to a primary backing to provide strength and support. Precoat and adhesive are applied and cured at about 200°C in a gas-fired oven. This process is run on a continuous line. Precoat and adhesive formulations differ only slightly. Components include styrene-butadiene latex, thickener, filler, and water.

Major VOC constituents found in the precoat and adhesive are long-chain hydrocarbons. In addition, several compounds derived from the latex were observed: styrene and butadiene (unpolymerized), ethyl benzene (styrene precursor), cumene (styrene-butadiene polymer catalyst), and 4-ethyl cyclohexene (4-EC) and 4-phenyl cyclohexene (4-PC), which are Diels-Alder reaction products of styrene and butadiene. Estimated emission factors for these latex-derived compounds are listed in Table 3.

Table 3. Emission Factors for Latex-derived Compounds from Curing

	emission factor: average (range), mg/yd ² carpet
styrene	3.0 (2.3-4.7)
ethyl benzene	3.3 (2.2-4.9)
cumene	2.3 (0.9-5.1)
4-ethenyl cyclohexene	2.4 (1.1-4.6)
4-phenyl cyclohexene	3.5 (2.3-6.6)

Conclusions

VOC and HAP emission factors were estimated for four carpet manufacturing processes: suessen heatsetting, beck dyeing, continuous dyeing, and latex coating. Field measurements and laboratory simulation experiments were used to estimate total emissions and emission factors. It is estimated that 1-2 g of VOCs are released to the air in the manufacture of one square yard of nylon carpet. For the maximum production capacity at the plants studied, this translates to an annual VOC emission of 50 to 100 tons.

Suessen heatsetting and beck dyeing were found to have the highest VOC emission rates. In yarn heatsetting, the amount of lubricant, which contains mineral oil alkane constituents, is a controlling factor for VOC emissions, particularly for staple fiber. Caprolactam is the major VOC emitted in nylon 6 heatsetting. In carpet dyeing, VOC emissions are derived from dyebath auxiliary compounds. For powder dyes, these are mostly long-chain hydrocarbons. For liquid dyes, oxygenated VOCs are principle components. HAP emissions from beck and continuous dyeing processes included glycol ethers. Emissions from latex coating included styrene, ethyl benzene, cumene, and two styrene-butadiene Diels-Alder products: 4-phenyl cyclohexene and 4-ethenyl cyclohexene.

These field and laboratory results provide the most complete characterization of VOC emissions from carpet manufacturing to date. Auxiliary compounds in chemical applications were responsible for much of the VOC emissions. Significant emission reduction is possible through reformulating applications and improved process control.

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Keywords

VOC emissions, carpet plant stack emissions, nylon heatsetting, carpet dyeing, latex coating