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ABSTRACT

A laboratory thermal desorption apparatus was used to measure emissions from a number of nominally identical photocopier toners – manufactured for use in a specific model copier – when these toners were heated to fuser temperature (180 - 200 °C). The objective was to determine whether VOC emissions from a toner might be reduced through judicious selection of the process and the raw polymer feedstock used in its manufacture. Tests were performed on: a series of toner and feedstock samples obtained directly from a toner manufacturer, systematically varying process and feedstock; and toner cartridges – from different lots (for which process and feedstock were unknown) – purchased from local retailers. The results showed that the retailer toners consistently had up to 350% higher emissions of some major compounds, and up to 100% lower emissions of others, relative to the manufacturer toners ($p < 0.05$), probably due to differences in process and/or feedstock. The manufacturer toners showed essentially no effect of process or feedstock, probably because the two processes and two feedstocks used by the manufacturer were not significantly different from each other. It is concluded that process and feedstock can have a significant effect on emissions of individual compounds, but it is not possible from this study to make specific recommendations regarding how process or feedstock might be modified to produce lower-emitting toners for a given copier.

INTRODUCTION

Dry-process photocopiers (and laser printers and fax machines) are ubiquitous potential sources of volatile organic compounds (VOCs), ozone, and particulates in indoor air. The VOCs result primarily from the organic polymers present in the toners used in these machines. While low VOC emissions can be observed even when the copier is off or idling, most emissions occur during copying, when the toner polymer is being melted in the high-temperature fuser that fixes the copied image onto the paper^{1, 2}. Some VOCs (e.g., acetaldehyde and hexanal) have been observed in emissions from plain paper, in the absence of toner (unpublished data); but the toner is the predominant source of most VOCs.

Polymers commonly present in commercial toners are copolymers of styrene and acrylates, the resins most common for copiers utilizing hot-roll (heat and pressure) fusers^{3, 4, 5}. Upon heating to fuser temperature, these polystyrene/polyacrylate resins have consistently been found^{1, 2, 6, 7} to emit styrene, ethylbenzene, xylenes, and acetophenone – all of which are labeled as hazardous air

pollutants (HAPs)⁸ – as well as benzaldehyde, an array of other substituted benzenes, and a number of other VOCs. The precise composition of the proprietary styrene/acrylate copolymer that is used in a given toner product – and the nature of the pigment and the other additives in the toner – will vary between brands and models of copiers, depending upon machine requirements. Differences in the design and operating characteristics of different machines – e.g., fuser temperature – might also impact emissions. Even for a given model copier, emissions might be impacted by the toner manufacturing process and by the purity of the raw materials used in toner manufacture. Perhaps for these reasons, chamber tests on different copiers using polystyrene/polyacrylate toners have shown different VOC emission factors^{1,2}. And thermal desorption tests on toners from different machines have shown some variation in the specific VOCs that are released upon heating⁶.

In prior testing¹, three different lots of nominally identical toner – manufactured for one specific copier – were heated to 150 °C in a vial, and the headspace gas in the vial was analyzed for styrene, ethylbenzene, and xylenes. For each compound, the headspace concentrations obtained with one of the toner lots were 50 to 80% lower than with the other two lots. The toner supplier indicated that the lower-concentration lot had been manufactured using an extrusion process, the process currently favored for new production facilities. By comparison, the other two had been manufactured using the older batch mixing approach (employing Banbury mixers) for melt-mixing the polymer, pigment, and charge control additives to generate the final toner product. It was postulated that the difference in manufacturing process might be responsible for the difference in headspace concentrations. Since the three toner lots had been manufactured in plants that were widely separated geographically, the raw materials used in manufacture could well have been obtained from different resin suppliers, and it is also possible that the concentration difference could be due in part to differences in the purity of the polymer feedstocks.

The objective of the current study was to expand upon that prior work. In particular, it was desired to determine more rigorously the extent to which VOC emissions from a given toner – manufactured for a specific dry-process photocopier – might be reduced through judicious selection of the process and the polymer feedstock used in the manufacture of that toner.

TECHNICAL APPROACH AND PROCEDURES

Basic Approach

The Selected Photocopier

The specific photocopier selected for study is a 70 copy/min monochrome unit using a heat and pressure fuser, widely marketed in the U.S. The fuser nominally operates at 185 °C; a warning light illuminates if this temperature drops below 180 °C, and the machine shuts down if it exceeds 200 °C. The Material Safety Data Sheet for the toner indicates that it is 80 to 90% proprietary styrene/acrylate polymer (binder), 10 to 15% carbon black (pigment), 1 to 5% quaternary ammonium compound (charge control agent^{3,5}), and 1 to 5% polyolefin (wax to reduce adhesion to fuser rollers^{4,5}). This is a typical composition for dry toners used with hot-roll fusers.

Toners Obtained from a Manufacturer

A cooperating toner manufacturer produced four nominally identical batches of toner for the selected copier for this project, according to a 2x2 matrix: using two different manufacturing

processes; and using two different lots of polymer feedstock. The two processes included: vented (or “devolatilizing”) extrusion, in which there is a low-pressure relief port along the barrel surrounding the extruder screw, to allow removal of volatiles released during the extrusion process^{9, 10}; and unvented extrusion, in which there is no such relief port. (It had initially been hoped that toners might also be obtained using a third manufacturing process – batch mixing – but the manufacturer did not produce toners for the selected copier using that process.) The two lots of polymer feedstock – referred to as “Feedstock A” and “Feedstock B” – were presumably obtained from the same resin supplier, and were probably produced at about the same time.

During each of the four production runs, the manufacturer provided two or more toner cartridges that were filled at each of three different times during the run. Samples were also provided of the unprocessed feedstock that was being fed to the extruder.

Using these samples, a systematic matrix of 44 thermal desorption tests was conducted to determine VOC emissions from the toners as a function of: manufacturing process; feedstock; sampling time during the manufacturing run (“within-run variability”); toner cartridge, for cartridges filled at the same time during a run (“between-cartridge variability”); and sample location within a given cartridge (“within-cartridge variability”). This matrix also enabled comparison of the toner emissions against emissions from the corresponding unprocessed feedstocks.

As it turned out, the toners produced by vented extrusion were manufactured with the relief port operating at a vacuum only 2 Pa below atmospheric, due to operating problems. This vacuum is so small that one might expect only limited extraction of volatiles from the vented process, and thus limited differences in emissions from the toners produced by vented vs. unvented extrusion. Contacts with several individuals in the polymer industry – and available literature on polystyrene devolatilization¹¹ – suggest that vacuums more than 4 orders of magnitude greater than this might be required for effective removal of VOCs from this copolymer, based on diffusion considerations.

Toners Obtained from Local Retailers

In addition to the toners obtained directly from the manufacturer, four cartridges of toner for the selected copier were purchased from local retailers. The manufacturer, the manufacturing process, and the feedstock characteristics represented by these retailer toners were unknown. Thus, it would not be possible to analyze these parameters and to rigorously explain any differences in the emissions between these toners and the manufacturer toners. However, the retailer toners provided an opportunity to demonstrate the magnitude of the difference that toner manufacturer, process, and/or feedstock might make in the VOC emissions from a given copier.

Two cartridges, representing two different manufacturing lots, were purchased from one retailer. Two additional cartridges were obtained from a second retailer; both cartridges from this second retailer were from the same lot, different from either of the lots obtained from the first retailer.

Thermal desorption tests were run on two samples from each of these cartridges.

Thermal Desorption Test Method

The toner samples described above were tested using a thermal desorption procedure developed for this project. In this procedure, a sample of the toner was ballistically heated to the fuser temperature operating range for the selected copier (180 to 200 °C), and the resulting VOCs captured either on Tenax[®] or on dinitrophenylhydrazine (DNPH)-impregnated silica gel. Only the results with Tenax[®] are reported here.

A thermal desorption approach was selected over a headspace procedure as the method for quantitative screening of the large number of toner samples in this study. Flow-through thermal desorption tests avoid vapor pressure constraints inherent in static headspace tests, and thus should more accurately reflect the total potential mass of the individual toner VOCs that might be emitted from a copier. Thermal desorption testing also reduces the risk of artifact formation, that might occur when samples are heated for the extended periods commonly employed in headspace testing. But it must be recognized that the mass emissions measured using this thermal desorption screening approach cannot currently be related to the emission factors that would be observed from an actual copier.

The ballistic heating approach used here could not duplicate the temperature profile that would exist in a fuser, where the thin layer of toner on the paper is raised to temperature in milliseconds³. However, it might reveal some effects that the rapid heating could have on emissions. Initial efforts were devoted to demonstrating the reproducibility of this test method.

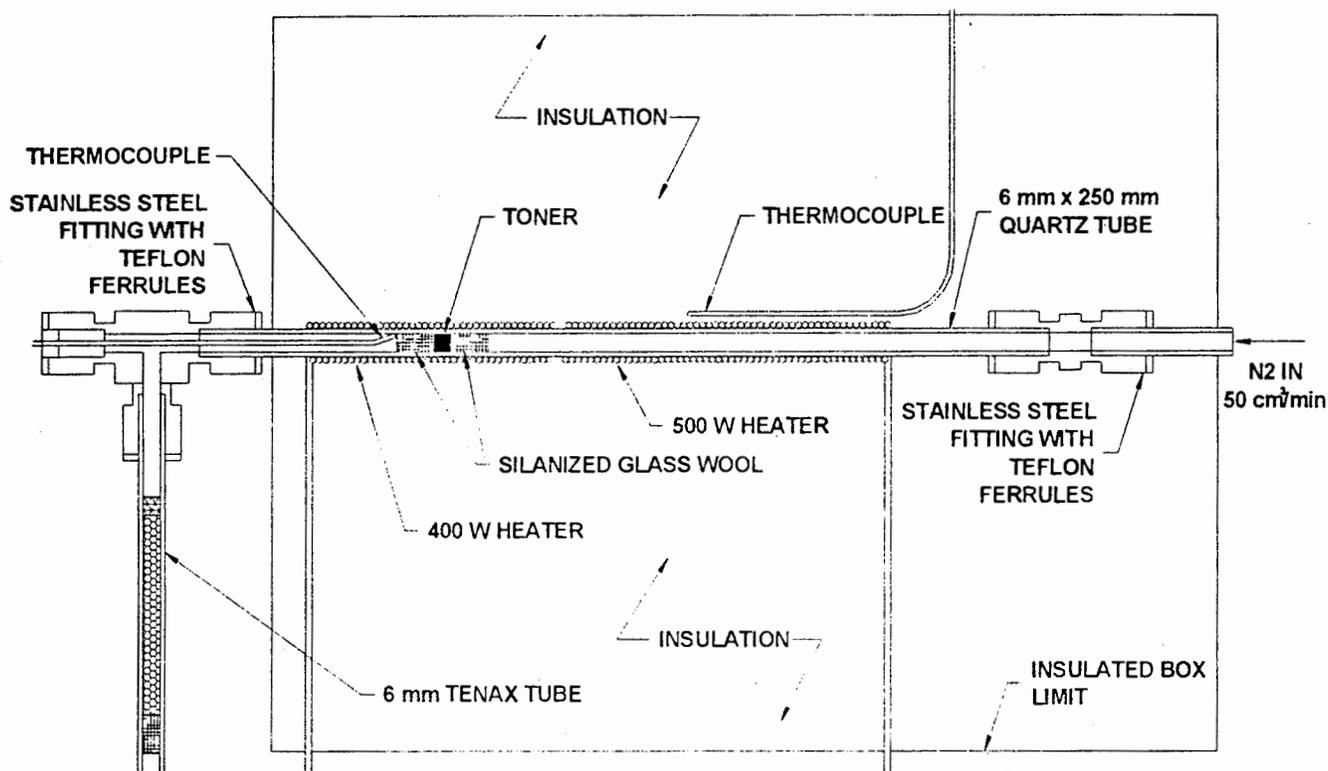
The thermal desorption test apparatus is illustrated in Figure 1, set up for sampling on Tenax[®]. The sample of toner or feedstock powder (10.2 ± 0.4 mg) was held in place inside a 6 mm o.d. quartz tube using glass wool plugs. The tube was mounted inside two electrical heating elements, totaling 900 W, in an insulated oven. Dry nitrogen carrier gas flowed through the tube (50 mL/min), transporting the released VOCs out of the oven and into a sampling tube containing 250 mg of 60/80 mesh Tenax[®] TA. Nitrogen (N₂) was used as the carrier, rather than air, to avoid possible oxygenation of the VOCs. A thermocouple inside the tube measured the temperature at the location of the sample.

During a test, N₂ flow would be initiated, and the heaters turned on briefly, raising sample temperature to 190 ± 4 °C in about 30 sec. Both heaters were turned off at the proper point during this heat-up period (after 5 - 6 sec), to prevent the sample from overheating. Flow continued for an additional 90 sec, during which time the sample cooled to 145 ± 3 °C. The Tenax[®] sample tube was then taken off-line, after a total sampling period of 120 sec. It was not possible to control the heating with sufficient sensitivity to hit the desired peak temperature of 185 °C on each run. If the peak temperature reached in a given test fell outside the range of the selected copier's fuser – i.e., below 180 or above 200 °C – that sample was discarded and re-run.

Analytical Methods for Thermal Desorption Samples

The Tenax[®] sample tubes from the thermal desorption tests were analyzed using an Envirochem multiple tube desorber and an Envirochem Model 85 Unacon concentrator/desorber, interfaced to a Hewlett Packard 5890A gas chromatograph (GC) equipped with a flame ionization detector

Figure 1. Thermal desorption test apparatus.



(FID). Chromatography was performed with a DB-Wax column (30 m long, 0.53 mm i.d., 1 μ m film thickness).

For the toner tests reported here, this GC/FID system was calibrated for 11 individual VOCs, selected based upon separate GC/mass spectrometry (GC/MS) headspace analyses, as discussed below. Calibration was achieved using liquid standards loaded onto Tenax[®] by flash vaporization, at five concentrations spanning the range anticipated from the toner samples (with triplicate analyses at each concentration).

Following the toner thermal desorption testing reported here, the GC/FID system was re-calibrated using standards that included the original 11 compounds plus 10 additional VOCs. The chromatograms from the current toner tests were subsequently re-evaluated to estimate whether any of the 10 additional compounds were present.

Headspace Testing for Compound Identification

Prior to the thermal desorption testing, headspace screening tests were performed to qualitatively identify which individual VOCs were released from the heated toner samples. In tests with the manufacturer toners, 1 g of toner or feedstock was placed in a capped 20 mL sample vial

(containing air) and heated to 185 °C for either 20 or 75 minutes. At the end of that time, a 300 µL sample of the headspace gas was withdrawn and injected into a Hewlett Packard 5890/5970 GC/MS (30 m Hewlett Packard 1301 column, 0.25 mm i.d., 0.25 µm film). Tests with the retailer toners were similar, except that 100 µL of headspace gas was injected into a Hewlett Packard 6890/5973 GC/MS (30 m DB-Wax column, 0.25 mm i.d., 0.15 µm film).

Headspace testing was conducted on single samples of: four of the manufacturer toners (representing both manufacturing processes and feedstocks); each of the feedstocks; and each of the four retailer toners.

The compounds identified in the manufacturer samples were used in selecting the 11 individual VOCs that were quantitated in the GC/FID analyses on the Tenax[®] samples, discussed above. The compounds identified in the retailer samples contributed to the selection of the 10 additional compounds that were added to the subsequent standard.

RESULTS

Compound Identification in Headspace Testing

Table 1 lists the compounds that were identified by GC/MS in the headspace samples taken after 20 min (corrected for background). The table identifies only the compounds that had a matching quality greater than 85% when compared against the available computer library of mass spectra. In addition to these identified compounds, each sample contained two or more significant peaks that could not be identified.

Essentially all of the toners and feedstocks release ethylbenzene, xylenes, styrene, benzaldehyde, and acetophenone upon heating to 185 °C, consistent with expectations and prior data^{1, 2, 6, 7}. In addition, most of the toners release 10 or more additional compounds, with the identities of these additional compounds sometimes differing between the manufacturer and retailer toners. Some of these additional compounds were also detected by other investigators during extensive analysis of nine copier and laser printer toners⁶.

It is unclear why the manufacturer toners from Feedstock A appear in Table 1 to contain so many fewer compounds than the toners from Feedstock B (or than the retailer toners). The subsequent GC/FID chromatograms for the Feedstock A toners, in general, had the same number of peaks as the Feedstock B toners, with similar retention times and area counts.

Source of the Observed Compounds

Most of the compounds observed from the manufacturer toners in Table 1 are also observed from the corresponding feedstocks. Thus, most of the compounds seen in the manufacturer toners clearly result, at least in part, from impurities that had been present in the unprocessed polystyrene/polyacrylate feedstock. In some cases, the source of these feedstock impurities is apparent. In particular, ethylbenzene is the raw material used to produce styrene¹², so that low levels of ethylbenzene and unreacted styrene monomer in the polystyrene could be expected. Benzaldehyde and benzoic acid in the feedstock might result, in part, from degradation of benzoyl peroxide, sometimes used as an initiator in the polymerization of styrene¹³.

Table 1. Compounds tentatively identified in GC/MS headspace testing^{A, B} (>85% matching quality).

| Compound | Manufacturer | | | | Retailer Toners | | | |
|--|--------------|---|--------|---|-----------------|------------|--------------------|----------|
| | Feedstock | | Toners | | Retailer 1 | Retailer 1 | Retailer 2, Lot #3 | |
| | A | B | A | B | Lot #1 | Lot #2 | Cart. #1 | Cart. #2 |
| <i>Benzenes substituted with simple aliphatics</i> | | | | | | | | |
| Benzene | X | X | - | - | - | - | - | - |
| Ethylbenzene ^C | X | X | X | X | X | X | X | - |
| m,p-Xylene ^C | X | X | X | X | X | X | - | X |
| o-Xylene ^C | X | X | X | X | - | - | - | - |
| Isopropyl benzene | X | X | - | X | X | X | X | X |
| n-Propylbenzene | - | - | - | X | X | X | X | X |
| 1-Ethyl-2-methyl benzene | - | - | - | X | X | X | - | - |
| Cyclopropyl benzene | - | - | - | - | X | - | - | X |
| Styrene ^C | X | X | X | X | X | X | X | X |
| α -Methylstyrene ^C | - | - | - | X | - | - | - | - |
| 1-Methylene propylbenzene | X | X | - | X | - | - | - | - |
| <i>Aldehydes and ketones (often containing a phenyl group)</i> | | | | | | | | |
| 3,3,5-Trimethylcyclohexanone ^C | X | X | X | X | - | - | - | - |
| Benzaldehyde ^C | X | X | X | X | X | X | X | X |
| Acetophenone ^C | X | X | X | X | X | X | - | X |
| 2-Phenylpropenal | X | X | - | - | - | - | - | - |
| <i>Phenols</i> | | | | | | | | |
| Phenol | - | - | - | X | X | X | X | X |
| 2-(2-Propenyl) phenol | - | - | - | - | X | - | - | X |
| <i>Ether alcohols (often containing a phenyl group)</i> | | | | | | | | |
| 1,1-Dimethylethoxy benzene | - | - | - | - | X | X | X | X |
| 3-Phenoxy-1-propanol | - | - | - | - | X | X | X | X |
| 2-Phenoxy-1-propanol | - | - | - | - | X | X | X | X |
| <i>Aliphatic alcohols and di-alcohols</i> | | | | | | | | |
| 1-Butanol | X | X | - | X | - | X | X | - |
| 2-Methyl-1-pentanol | - | - | - | - | X | - | - | X |
| 2-Ethyl-1-hexanol | - | - | - | - | X | X | X | X |
| Propylene glycol | - | - | - | - | X | X | X | X |
| <i>Long-chain aliphatics</i> | | | | | | | | |
| Tetradecane | - | - | - | - | - | - | - | X |
| Pentadecane | - | - | - | - | X | - | - | X |
| Hexadecane | - | - | - | - | X | X | X | X |
| Heptadecane | - | - | - | - | - | X | - | X |
| <i>Carboxylic acids</i> | | | | | | | | |
| Benzoic acid | X | X | - | X | - | - | - | - |
| <i>Compounds with two aromatic rings</i> | | | | | | | | |
| 2-Ethenyl naphthalene | - | - | - | - | X | - | - | - |
| Biphenyl | - | - | - | - | - | - | - | X |
| Bibenzyl | - | - | - | - | X | - | - | - |
| 1,1-(1,3-Propanediyl)bis-benzene | - | - | - | X | - | - | - | - |
| 1,3-Diphenyl cyclobutane | - | X | - | X | - | - | - | - |

^A Analysis on headspace from 1 g sample heated to 185 °C for 20 min in 20 mL vial.

^B "X" = detected; "-" = not detected with >85% matching quality.

^C Selected as target compounds for quantitation in subsequent GC/FID analyses.

Benzene is observed from the feedstocks but not from the toners. Benzene is present during styrene manufacture¹², and thus could be an impurity in the raw polystyrene that escapes from the hot mixture, or reacts, during melt-mixing.

Some compounds in Table 1 could be degradation products resulting from the heating and shearing of the polymer during extrusion (or from the heating during the headspace testing here). Among the major byproducts reported from thermal-oxidative degradation of polystyrene¹³ are: styrene, benzaldehyde, and acetophenone (observed from essentially all samples in Table 1); phenol (observed from all of the retailer toners); and benzoic acid (observed from some manufacturer toners). Some level of these degradation products in the toners might be expected. The hot toner mix can reach perhaps 150 °C in the extruder^{3, 4, 5} under high shear forces, and it has been demonstrated that some styrene/acrylate copolymer degradation – in terms of reduced molecular weight, if not byproduct formation – does occur during extrusion¹⁴.

The presence of these potential degradation products in the unprocessed feedstocks – which have not been heated to extrusion temperatures – raises the question regarding the extent to which these observed oxygenated compounds might be an artifact. Perhaps they could be resulting from oxidative degradation occurring during the headspace test procedure, when the sample is heated for 20 min in a vial containing air. But the subsequent thermal desorption testing in this study – in which the samples were heated under N₂ – also resulted in the release of these oxygenated species from the feedstocks. Thus, it seems clear that these compounds are not an artifact. They are, in fact, present in the raw polymer, perhaps created from the polymer during polymerization or, as discussed previously, from degradation of benzoyl peroxide initiator.

Extraction Tests

To further confirm whether the observed compounds are present even when the samples are not heated, three selected samples of the feedstocks and toners were extracted with methylene chloride. The extracts were analyzed by injection into the Hewlett Packard 6890/5973 GC/MS. Probably because the sub-micron carbon black in the toners is an effective sorbent for organic compounds, recoveries of a surrogate standard (and, presumably, of the target analytes) in the extracts were low. As a result, only qualitative results were obtained – and only for the compounds that were present at the highest concentrations.

These extraction results indicated that the major compounds observed during headspace tests on the manufacturer toners – ethylbenzene, xylenes, styrene, benzaldehyde, acetophenone, and 3,3,5-trimethylcyclohexanone – are detected in the extracts both from Feedstock A and from a toner produced using that feedstock. Thus, at least some portion of the emissions of these compounds from this toner is the result of impurities that were present in the unprocessed polymer used to manufacture the toner. These compounds are not solely the result of thermal degradation during the extrusion process, or during heating in the laboratory.

Selection of Target Analytes for GC/FID Quantitation

Nine of the 11 compounds that were selected for quantitation during the GC/FID analyses on thermal desorption Tenax[®] samples are noted in Table 1. The other two target analytes are m-diethylbenzene and 2,4-dimethylstyrene. These 11 compounds were selected based upon: the

consistency with which they appeared in the headspace results for the manufacturer samples; their detection in studies by others; and the availability of standards.

The 10 additional target analytes that were subsequently added to the GC/FID standard were: benzene; toluene; 1-butanol; n-propylbenzene; 2-ethyl-1-hexanol; 2,3-dihydro-2-methyl furan; hexadecane; phenol; 2-phenoxyethanol; and phenyl benzoate. These were selected based on the headspace results from the retailer toners, and based on further efforts to identify unknown peaks.

Validation of Thermal Desorption Method

Method Precision

To verify the precision of the ballistic heating thermal desorption technique (and of the GC/FID analysis), ten different samples of the manufacturer feedstocks and toners were each divided into two or three 10 mg aliquots, with each aliquot being ballistically heated, sampled on Tenax[®], and analyzed for the 11 target analytes.

Eight of the target analytes were present at concentrations above the practical quantitation limit (PQL) of the GC/FID system (5 to 6 µg of compound per g of sample). Within each of the ten sets of replicated samples, the concentrations of each of these eight compounds varied with a percent relative standard deviation (% RSD) ranging from <1 to 17%. The average % RSD, averaged over all of the compounds and all of the replicate sets, was 6%. This agreement is considered to be good, and the precision of the method is deemed to be acceptable.

Role of Peak Temperature

In one ballistic heating test, the sample inadvertently reached a peak temperature of 210 °C, exceeding the 200 °C maximum. The test was then repeated with a replicate sample, reaching a peak temperature of 196 °C. The measured emissions of each of the eight target analytes (present above the PQL) were 17 to 36% greater in the test that reached 210 °C, suggesting the importance of controlling the peak temperature.

The peak temperatures that were reached in this matrix of tests ranged from 181 to 198 °C. Within this temperature range, there was no apparent correlation between the peak temperature and the emissions of any of the target compounds.

Completeness of VOC Recovery from Sample

Since the sample is at elevated temperature for only 2 minutes – and is at the peak temperature only momentarily in this procedure – it is of interest to determine the extent to which volatiles have been driven from the sample. Accordingly, following one test with one of the samples, the quartz sample tube was removed from the oven and sealed while the oven cooled. It was then re-installed and run through the ballistic heating protocol a second time.

Only five of the target analytes were emitted above the PQL during the second heating. The mass of each compound released during the second heating was 13 to 34% of the mass emitted during the first heating. This result indicates that some modest amount of the volatiles still remain after the first heating, or that additional volatiles are created by thermal degradation upon re-heating.

Effect of Air vs. N₂ Carrier Gas

The ballistic heating tests were conducted with N₂ as the carrier to avoid formation of oxygenated species through oxidative degradation of the polymer. Two toner samples were tested using purified dry air as the carrier, to assess the extent of additional degradation that might occur during the tests if oxygen (O₂) were present. The results showed that – with isolated exceptions – there was no statistical difference in the emissions of any of the compounds caused by the use of air as the carrier ($p < 0.05$). Even in the isolated cases where there was a difference, the emissions in air were only about 5 to 20% higher. Thus – for the temperature profile seen by these samples – the presence of O₂ does not seem to create significant additional emissions from polymer degradation in this test system.

Analysis of Thermal Desorption Results

Manufacturer Toners and Feedstocks

The results indicate that there is no effect on the observed emissions resulting from: the sampling time during the manufacturing run; the toner cartridge, for cartridges filled at the same time during the run; or the sampling location within a given cartridge. Thus, the discussion here focuses solely on the effects of the manufacturing process and the feedstock.

The emissions from the thermal desorption tests on the manufacturer samples (expressed as micrograms of compound emitted per gram of sample) are presented in Table 2.

As shown, 8 of the 11 target analytes consistently appear at concentrations above the PQL in all of the samples; the other 3 targets are present, but below the PQL. Of the 10 additional analytes that were added later, only n-propylbenzene could be identified in these samples, at low levels. The eight major target compounds represent about 50% of the total VOC (TVOC) mass emitted from the toners (estimated using the response factor for ethylbenzene), and about 60% of the TVOC mass from the feedstocks. There were also four major unidentified compounds consistently present. Using the ethylbenzene response factor, these compounds accounted for an estimated additional 30% of the toner TVOC mass, and 20% of the feedstock TVOC mass.

As shown, the % RSD for each compound in each sample set is usually less than 15%, which is good.

The means in Table 2 were statistically compared using the two-sided t-test with pooled standard deviations. This analysis yields the following results, with $p < 0.05$.

- The manufacturing process has no effect on toner emissions in this study. For toners produced using either feedstock, the mean emission of each compound is statistically the same regardless of whether the toners were produced by unvented or vented extrusion. Since vented extrusion is specifically intended to reduce the volatiles content in the polymer product^{9, 10, 11}, it is suspected that the lack of an effect seen here for vented extrusion is the result of the negligible vacuum applied in producing the vented toners available for this study.

Table 2. Summary of thermal desorption test results with the manufacturer toners.

| Values in micrograms of VOC emitted per gram of solid sample (average \pm standard deviation, % RSD in parentheses) | | | | | | |
|---|-----------------------|--------------------------------------|------------------------------------|-----------------------|--------------------------------------|------------------------------------|
| Compound ^A | Feedstock A | | | Feedstock B | | |
| | Unprocessed Feedstock | Toner Produced by Unvented Extrusion | Toner Produced by Vented Extrusion | Unprocessed Feedstock | Toner Produced by Unvented Extrusion | Toner Produced by Vented Extrusion |
| Ethylbenzene | 37 \pm 5 (13) | 33 \pm 0.8 (2) | 32 \pm 0.6 (2) | 39 \pm 4 (10) | 30 \pm 2 (7) | 32 \pm 2 (6) |
| p-Xylene | 32 \pm 4 (12) | 27 \pm 0.7 (3) | 27 \pm 0.6 (2) | 32 \pm 3 (10) | 25 \pm 2 (8) | 26 \pm 2 (7) |
| m-Xylene | 91 \pm 11 (12) | 83 \pm 2 (3) | 83 \pm 2 (2) | 96 \pm 10 (10) | 76 \pm 6 (8) | 83 \pm 5 (7) |
| o-Xylene | 52 \pm 7 (14) | 53 \pm 1 (3) | 53 \pm 1 (2) | 56 \pm 6 (10) | 48 \pm 4 (8) | 53 \pm 4 (7) |
| Styrene | 155 \pm 19 (12) | 123 \pm 4 (4) | 123 \pm 3 (2) | 148 \pm 11 (8) | 103 \pm 12 (12) | 115 \pm 10 (9) |
| 3,3,5-Trimethyl-cyclohexanone | 18 \pm 4 (22) | 26 \pm 1 (4) | 27 \pm 0.8 (3) | 22 \pm 2 (10) | 22 \pm 3 (13) | 25 \pm 3 (11) |
| Benzaldehyde | 9 \pm 1 (15) | 17 \pm 0.9 (5) | 18 \pm 0.6 (3) | 10 \pm 0.9 (9) | 14 \pm 2 (13) | 16 \pm 2 (12) |
| Acetophenone | 9 \pm 1 (13) | 21 \pm 2 (7) | 23 \pm 0.4 (2) | 10 \pm 0.9 (9) | 17 \pm 3 (17) | 20 \pm 2 (11) |
| Σ of all quantitated VOCs | 410 \pm 53 (13) | 388 \pm 13 (3) | 390 \pm 7 (2) | 418 \pm 39 (9) | 339 \pm 33 (10) | 375 \pm 30 (8) |
| TVOC (as ethylbenzene) ^B | 672 \pm 113 (17) | 812 \pm 68 (8) | 840 \pm 49 (6) | 705 \pm 57 (8) | 647 \pm 95 (15) | 741 \pm 99 (13) |
| TVOC accounted for | 61% | 48% | 47% | 59% | 53% | 51% |
| Estimated mass in 4 unknown peaks ^C | 124 \pm 29 (24) | 243 \pm 35 (14) | 262 \pm 20 (8) | 123 \pm 9 (7) | 171 \pm 38 (22) | 205 \pm 44 (22) |
| TVOC accounted for (incl. 4 unknowns) | 80% | 78% | 77% | 77% | 79% | 79% |
| No. of samples | 5 | 7 | 4 | 2 | 5 | 5 |

^A Commonly detected, but below the practical quantitation limit (PQL): diethylbenzene; α -methylstyrene; and 2,4-dimethylstyrene. Tentatively identified in all manufacturer samples, below the PQL: n-propylbenzene. The PQL is 5 to 6 μ g/g.

^B TVOC is defined as the total VOC mass eluting after 2.0 min on this column, computed using the response factor for ethylbenzene.

^C Computed using the response factor for ethylbenzene. The peaks elute at 13.4, 28.3, 29.9, and 30.4 min on the DB-Wax column.

- The feedstock has a small but statistically significant effect on the emissions from toners produced by unvented extrusion. Emissions of each compound, and of TVOCs, average 8 to 20% higher with the unvented toners made from Feedstock A, compared to unvented toners from Feedstock B. Feedstock has no statistically discernable effect on toners from vented extrusion.
- No difference can be discerned between the emissions from the two feedstocks used in this study. Thus, differences between the unprocessed feedstocks would not seem to be the sole explanation for the small differences between the unvented toners made from them, cited above.
- With a few exceptions, each unprocessed feedstock generally has 15 to 30% higher emissions of ethylbenzene, p-xylene, and styrene, compared to the toners manufactured using that feedstock. This observation would be consistent with the thesis that some fraction of these compounds – present as impurities in the feedstock – is driven off during the extrusion process.
- Each unprocessed feedstock consistently has about 30 to 60% *lower* emissions of benzaldehyde and acetophenone, compared to the toners manufactured using that feedstock. In addition, Feedstock A has about 30% lower emissions of 3,3,5-trimethylcyclohexanone, compared to the toners from that feedstock. These observations would be consistent with the thesis that some amount of these oxygenated compounds is created by thermal-oxidative degradation of the polymer during the extrusion process.
- Feedstock A has about 50% less mass in the four unknown peaks than do the toners made from this feedstock, suggesting that these compounds also are created, in part, during extrusion. There is insufficient statistical power to discern whether these four unknowns are different between Feedstock B and its toners.

Retailer Toners

Table 3 presents the thermal desorption emissions from the four retailer toners, and compares them against the results from the manufacturer toners. The manufacturer toner results are presented according to the feedstock from which the toner was made, since feedstock seemed to have a somewhat greater effect on emissions than did the manufacturing process.

As shown, three compounds consistently observed at significant concentrations from the manufacturer toners – p-xylene, 3,3,5-trimethylcyclohexanone, and acetophenone – were below the PQL in all of the retailer toners. Thus, only 5 of the 11 target analytes were present above the PQL in the retailer toners, accounting for only about 20 to 30% of the TVOC mass.

Of the 10 additional analytes that were added later, 5 could be tentatively identified in all of the retailer chromatograms, at levels above the PQL: n-propylbenzene, 2-ethyl-1-hexanol, phenol, 2-phenoxyethanol, and phenyl benzoate. These five compounds – plus four other significant, unidentified peaks that were consistently present from all of the retailer toners – accounted for an estimated 35 to 40% of the TVOC mass.

Table 3. Thermal desorption test results comparing manufacturer toners vs. retailer toners.

Values in micrograms of VOC emitted per gram of solid sample (average \pm standard deviation, % RSD in parentheses)

| Compound ^A | Manufacturer Toners | | Retailer Toners | | | |
|---|---|---|----------------------------------|----------------------------------|--------------------------------|---------------------------------|
| | Toners Produced from Feedstock A ^B | Toners Produced from Feedstock B ^B | Retailer 1, Lot #1, Cartridge #1 | Retailer 1, Lot #2, Cartridge #1 | Retailer 2, Lot #3 | |
| | | | | | Cartridge #1 | Cartridge #2 |
| Ethylbenzene | 32 \pm 0.8 (2) | 31 \pm 2 (7) | 16 \pm 2 (10) _c | 20 \pm 2 (12) _c | 27 \pm 1 (4) _c | 25 \pm 4 (17) _c |
| p-Xylene | 27 \pm 0.7 (2) | 26 \pm 2 (8) | | | | |
| m-Xylene | 83 \pm 2 (2) | 79 \pm 6 (8) | 7 \pm 0.7(11) | | 6 \pm 0.3 (5) | 6 \pm 1 (20) |
| o-Xylene | 53 \pm 1 (2) | 51 \pm 4 (9) | 13 \pm 2 (11) | 7 \pm 0.6 (9) | 9 \pm 0.4 (4) | 10 \pm 1 (9) |
| Styrene | 123 \pm 4 (3) | 109 \pm 12 (11) | 48 \pm 5 (10) | 28 \pm 4 (12) | 64 \pm 3 (4) | 60 \pm 10 (16) |
| 3,3,5-Trimethyl-cyclohexanone | 26 \pm 1 (4) | 23 \pm 3 (14) | _c | _c | _c | _c |
| Benzaldehyde | 18 \pm 0.9 (5) | 15 \pm 2 (13) | 47 \pm 5 (11) | 68 \pm 10 (9) | 43 \pm 2 (5) | 40 \pm 8 (19) |
| Acetophenone | 22 \pm 1 (7) | 19 \pm 3 (16) | _c | _c | _c | _c |
| Σ of all quantitated VOCs | 389 \pm 11 (3) | 357 \pm 35 (10) | 143 \pm 15 (11) | 138 \pm 18 (13) | 163 \pm 10 (6) | 155 \pm 26 (17) |
| TVOC (as ethylbenzene) | 822 \pm 61 (7) | 694 \pm 104 (15) | 592 \pm 75 (13) | 515 \pm 67 (13) | 771 \pm 104(14) | 683 \pm 153(23) |
| TVOC accounted for | 47% | 52% | 24% | 27% | 21% | 23% |
| Est. mass in other major peaks ^D | 250 \pm 31 (12) | 188 \pm 43 (23) | 234 \pm 34 (14) | 200 \pm 31 (16) | 275 \pm 18 (6) | 248 \pm 64 (26) |
| TVOC accounted for (incl. other peaks) | 78% | 79% | 64% | 66% | 57% | 59% |
| No. of samples | 11 | 10 | 2 | 2 | 2 | 2 |

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^A Commonly detected in both manufacturer and retailer toners, but below the PQL: diethylbenzene; α -methylstyrene; and 2,4-dimethylstyrene. Tentatively identified in all manufacturer samples, below the PQL: n-propylbenzene. Tentatively identified in all retailer samples, above the PQL: n-propylbenzene; 2-ethyl-1-hexanol; phenol; 2-phenoxyethanol; and phenyl benzoate. The PQL is 5 to 6 μ g/g.

^B Includes toners produced using both non-vented and vented extrusion.

^C Detected at levels below the PQL.

^D For manufacturer toners, includes the four unknown peaks cited in Table 2. For retailer toners, includes: five peaks which have been identified (n-propylbenzene, 2-ethyl-1-hexanol, phenol, 2-phenoxyethanol, and phenyl benzoate) but which were not included in the calibration standard; plus four unknown peaks (eluting at 7.7, 22.1, 24.9, and 31.0 min). Mass computed using ethylbenzene response factor.

Statistical comparison of the means in Table 3 indicates the following, with $p < 0.05$.

- All of the retailer toners have emissions of ethylbenzene, xylenes, styrene, and acetophenone that are significantly lower than those from the manufacturer toners (with either feedstock). Retailer ethylbenzene emissions range from 15 to 50% lower; styrene emissions from 40 to 75% lower; xylene emissions from 70 to 100% lower; and acetophenone emissions (which are below the PQL in the retailer toners) roughly 75% lower.
- All of the retailer toners have emissions of benzaldehyde that are significantly higher – 125 to 350% higher – than those from the manufacturer toners.
- TVOC emissions from the two Retailer 1 toners (Lot #1 and Lot #2) are lower than the TVOC mass from the manufacturer Feedstock A toners (by about 25 to 35%). For the other retailer toners and the manufacturer Feedstock B toners, the difference between the retailer and manufacturer TVOC emissions is generally not statistically significant.
- The emissions of o-xylene and styrene from one retailer toner (Retailer 1/Lot #2) are statistically lower than the emissions of those compounds from the other three retailer toners. But with that exception, there is no statistical difference between the four retailer toners, within the statistical power of this analysis (two samples per toner). There is no difference between toners: for the individual target analytes (except as noted for Lot #2); or for the estimated mass in other major peaks; or for TVOC mass.

The manufacturer, the process, and the feedstock characteristics represented by the four retailer cartridges are unknown. It is known only that the two cartridges from Lot #3 had the same manufacturer, process, and feedstock. Thus, it is uncertain whether the three retailer lots might have been produced by the same manufacturer and process, and whether the similarities between the toners might result for that reason.

As discussed previously in connection with the headspace results, ethylbenzene, xylenes, and styrene appear to result in large part from impurities in the raw polymer feedstock. The lower emissions of these compounds from the retailer toners could be suggesting that: a) the feedstocks used to produce the retailer toners had lower concentrations of these compounds; and/or b) the manufacturing process for these toners enabled more complete devolatilization of the melt (e.g., through effective venting, higher temperature, or longer residence time).

Since benzaldehyde and acetophenone originate in part as impurities in the feedstock polymer, the higher emission of benzaldehyde (and the lower emission of acetophenone) from the retailer toners could be suggesting differing concentrations of these compounds in the feedstocks used to produce those toners. But both of these compounds can also be created by thermal-oxidative degradation of the polymer during toner manufacture, as indicated by the results from the manufacturer toners and feedstocks. Thus, the higher emissions of benzaldehyde could also be suggesting that the process used to manufacture the retailer toners promotes a greater degree of

degradation producing this by-product (e.g., through higher temperature or longer residence time).

The retailer toners also show significant emissions of another degradation product – phenol – at concentrations on the order of (but less than) the benzaldehyde levels. By comparison, the manufacturer toners do not emit meaningful levels of phenol. Thus, to the extent that process-induced thermal-oxidative degradation is contributing to the increased level of oxygenated species in the retailer toners, it would be doing so in a manner that tends to produce benzaldehyde and phenol, and not acetophenone. The degradation process with the manufacturer toners, by comparison, clearly would be favoring 3,3,5-trimethylcyclohexanone and acetophenone to the same degree as benzaldehyde, and would not be tending to produce phenol.

CONCLUSIONS

1. From comparison of the manufacturer and retailer toners tested here, it is clear that nominally identical toners – manufactured to meet the fuser specifications for a single photocopier – can have significantly different emissions of individual VOCs when heated in the laboratory. Emissions of a given compound can vary by a factor of 2 or more between toners.
2. Even when there are significant differences in emissions of individual VOCs between toners, it might not be possible to recommend one as a clearly preferable low-emitting product. Comparison of the manufacturer and retailer toners indicates that – while the retailer toners had much lower emissions of some compounds (ethylbenzene, xylenes, styrene, acetophenone) – they had higher emissions of other compounds (benzaldehyde, phenol). (All of these compounds, except benzaldehyde, are HAPs.) And the difference in TVOC emissions between the two toner sets is modest at best, and often not statistically significant.
3. The differences in emissions between the manufacturer and retailer toners are almost certainly due to differences between the manufacturing processes and/or the feedstock polymers used in the two cases. But without information on the retailer process(es) and feedstocks, the specific factors creating the differences could not be identified in this study.
4. Because the specific factors creating the emission differences between the manufacturer and retailer toners could not be identified, it is not possible from this study to make specific recommendations regarding how process or feedstock might be modified in order to produce lower-emitting toners for a given copier.
5. The tests on the manufacturer toners showed that vented extrusion did not produce toners having lower emissions than did unvented extrusion; but this result was probably obtained because only negligible vacuum (2 Pa) was applied during vented extrusion. These tests also showed that the feedstock had only modest, if any, impact on toner emissions; but the feedstocks were almost identical, creating this result.

6. The tests on the manufacturer toners and feedstocks demonstrated that essentially all of the compounds observed in the toner emissions result, at least in part, from impurities that are present in the feedstocks to begin with. The tests also demonstrated that the concentrations of some species can be increased during the extrusion process, presumably by oxidative degradation of the polymer. These observations can be used to postulate explanations for the differences in emissions between the manufacturer and retailer toners.

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| 16. ABSTRACT The paper gives results of the measurement of emissions--using a laboratory thermal desorption apparatus--from a number of nominally identical photocopier toners (manufactured for use in a specific model copier) when the toners were heated to fuser temperature (180-200 C). The objective was to determine if VOC emissions from a toner can be reduced by judiciously selecting the process and the raw polymer feedstock used in its manufacture. Tests were performed on toner and feedstock samples obtained directly from a toner manufacturer, systematically varying process and feedstock, and on toner cartridges from different lots (for which process and feedstock were unknown) purchased from local retailers. Results showed that the retailer toners consistently had up to 350% higher emissions of some major compounds, and up to 100% lower emissions of others, relative to the manufacturer toners (p<0.05), probably due to differences in process and/or feedstock. The manufacturer toners showed essentially no effect of process or feedstock, probably because the two processes and two feedstocks used by the manufacturer were not significantly different from each other. It is concluded that process and feedstock can have a significant effect on emissions of individual compounds, but it is not possible from this study to recommend changes for lower-emitting toners. | | | | | |
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