

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

Division of Air Resources, Bureau of Air Quality Analysis and Research

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Memorandum

To: Steven Flint, Director, Division of Air Resources
From: Thomas Gentile, Chief, Air Toxics Section
Subject: Results of PTFE Sintering Oven Emissions Characterization Study
Date: December 17, 2019

Background

The New York State Department of Environmental Conservation (DEC) requested the US Environmental Protection Agency (EPA) Office of Research and Development (ORD) qualitatively characterize the emissions from polytetrafluoroethylene (PTFE) sintering ovens. ORD has the ability to perform targeted and non-targeted poly and perfluoroalkyl substance (PFAS) analyses using state-of-the-art laboratory instrumentation and techniques. As part of the EPA PFAS action plan, ORD has been collaborating with State environmental agencies to characterize PFAS stack emissions from manufacturers that are end users of PTFE dispersions and powders. The St. Gobain McCaffrey Street facility in Hoosick Falls is an end user of PTFE powders. This is the first targeted and non-targeted PFAS emissions characterization studies conducted by EPA on the potential emissions from these sintering ovens. In addition to the targeted and nontargeted PFAS testing, testing was conducted for PTFE decomposition products and volatile organic compounds (VOCs).

Targeted PFAS compounds are primarily the legacy Method 537 PFASs that includes the perfluorinated carboxylic acids and perfluorinated sulfonic acids, as well as some of the new replacements for perfluorooctanoic acid (PFOA). These are referred to as targets since there are laboratory standards that could be used to precisely identify their chemical identity. Non-targeted PFAS compounds are the emerging fluorinated compounds or fluorinated compounds that are tentatively identified which do not have a laboratory standard that can be used for precise chemical identification.

Emission testing was conducted over the course of the typical 70-hour heating cycle. The entire sintering process is approximately 121 hours and the emission testing ended as the maximum oven temperature hold times started to decrease. The test began at noon on March 19 and ended at noon on March 22, 2019.

Methods

A real-time high resolution chemical ionization mass spectrometer (CIMS) was used on site. This instrument ran almost continuously over the course of the 70 hours. The CIMS is capable of detecting per and polyfluorinated carboxylic acids, fluorotelomer alcohols, and perfluoro ether carboxylic acids. It is also capable of detecting additional hydroxylated fluorinated compounds that do not have a laboratory standard.

Midget impinger sampling trains were used to collect hydrophilic (water soluble) PFAS compounds for targeted and non-targeted qualitative analysis.

SUMMA Canisters were used for targeted qualitative analysis of VOCs, fluorotelomer alcohols, and PTFE decomposition products that included tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and perfluoroisobutylene (PFIB).

A total of 16, two-hour SUMMA cans and midget impinger stack emission samples were collected over the course of the 70-hour oven heating cycle.

Results

Overall results indicate extremely low emissions from PTFE sintering oven process operations at the facility. The real time CIMS monitor detected the slow release of three perfluorinated carboxylic acids over time as the sintering oven temperatures increased. Perfluoroethanoic acid (C2), Perfluoropropanoic acid (C3), and Perfluorobutanoic acid (C4) were detected. EPA has noted the relative responses from the CIMS should not be interpreted as concentrations relative to each other since the absolute CIMS response varies among the individual compounds. No other perfluorinated carboxylic acids above C4 were detected by the real-time monitor in the stack emissions.

The midget impinger samples tentatively identified 15 polyfluorinated compounds present in the emissions. A compound was considered present if it was greater than or equal to 10 times the nitrogen system blank level.

The SUMMA canisters detected a 4:2 fluorotelomer alcohol and only one PTFE decomposition product, tetrafluoroethylene. Thirty nine individual VOCs were present in the stack emissions.

Discussion

ORD reported conclusively that PFOA was not present in emissions, and no other long chain legacy perfluorinated carboxylic acids (PFCA) were found. The CIMS identified shorter chain fluoropolymer aide replacements that have been phased in, two ultra-short and one short chain PFCAs.

Fifteen polyfluorinated alkyl substances were tentatively identified, two of which were tentatively identified by ORD on the USEPA Computational Toxicology Chemicals

Dashboard.¹ Based on a literature review, these tentatively identified PFASs are consistent with those used in cosmetics and paint adhesives.

The actual chemical identity of the 13 others could not be determined, but ORD reported their mass and chemical formulas. The peaks detected from non-targeted analysis do not yield quantitative estimates of the concentrations of the materials detected. Further, the identity of true unknowns can be difficult to confirm because novel compounds are absent from publicly available databases (McCord and Stryner, 2019)².

The source of these polyfluorinated alkyl substances was not conclusively determined. These substances appeared only in sample 1 (train 2) and were carried over into the alternating train 2 midjet impinger samples. The trains were rinsed in methanol between sampling and it is likely the rinse could not remove these compounds from train 2. Nor did they appear in the train 1 samples, including sample 2, collected immediately following sample 1. These substances do not appear to be related to the PTFE sintering process operation.

The fluorotelomer alcohol detected (4:2 FTOH) was most likely used in the production of the PTFE powder. The 4:2 fluorotelomer alcohol is extremely volatile and has the potential to form perfluorinated butanoic acid (C4). (Herzke, Posner and Olsson, 2009)³

PTFE decomposition products, specifically tetrafluoroethylene, was detected as expected. However, known PTFE decomposition products, such as hexafluoropropylene and perfluoroisobutylene, were not detected. The current oven operating temperatures do not result in the formation of these PTFE decomposition products.

The 39 VOCs detected are routinely found in DEC's ambient air toxics sampling program and we noted that some of these compounds are used at the facility. Overall the results of the VOC testing were unremarkable.

Conclusions

The qualitative emissions characterization study identified very low, trace emissions for ultra-low chain perfluoroalkyl substance replacements, a fluorotelomer alcohol, and expected PTFE decomposition products. Some polyfluoroalkyl substances were

¹ United States Environmental Protection Agency (USEPA). CompTox Chemicals Dashboard. <https://www.epa.gov/chemical-research/comptox-chemicals-dashboard>

² McCord, J., Strynar, M. Identifying Per- and Polyfluorinated Chemical Species with a Combined Targeted and Non-Targeted-Screening High-Resolution Mass Spectrometry Workflow. *J. Vis. Exp.* (146), e59142, doi:10.3791/59142 (2019). <https://www.jove.com/video/59142/identifying-per-polyfluorinated-chemical-species-with-combined>

³ Herzke, D., Posner, S., Olsson, E. Survey, Screening and Analyses of PFCs in Consumer Products. TA-2578/2009. Swera IVF Project Report 09/47. (2009). <http://tema.miljodirektoratet.no/old/klif/publikasjoner/2578/ta2578.pdf>

tentatively identified, which are not believed to be associated with the process operation. We are continuing to evaluate the literature to identify possible sources of these emissions.

Since this was a qualitative stack emissions study, we cannot precisely quantify the emissions present. However, we can use this qualitative information in tandem with other information collected during the emission testing to determine that the emissions of the polyfluorinated alkyl substances, PTFE decomposition products, and VOCs from the PTFE sintering oven operations at the St. Gobain McCaffrey Street facility are very low.

Prior to the emissions testing, the PTFE billets were weighed on an industrial scale to determine their weight loss over the 121-hour heating cycle. Two billets lost no weight, one gained a pound, and one lost a pound. The scale is not precise but provides us with an indication of any mass lost during the sintering process. Based on the observed weight loss of the billets, information from ORD about the testing of these PTFE powders under laboratory conditions and information from the fluoropolymer manufacturers it can be concluded that any PFAS and PTFE decomposition emissions from the sintering ovens are minimal and are primarily the TFE monomer that is a known degradation product of the sintering process. TFE was the primary emission detected.