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Influence of Resin Color and Printer Brand on Emissions from Stereolithography (SLA) 3-D Printers

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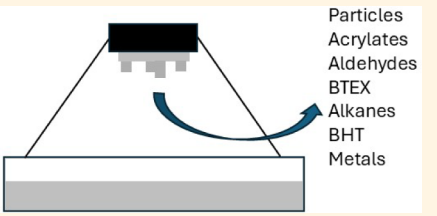
ABSTRACT: Vat photopolymerization (VP) is an additive manufacturing process that uses light to harden resin and build a 3-dimensional shape. Stereolithography (SLA) printing is a variant of VP that uses a laser beam as the light source to initiate a polymerization reaction. During SLA printing, particles and gases can be emitted into the air; however, factors that influence emissions are poorly understood for this technology. Emissions from two brands of SLA printers from different manufacturers (herein termed A and B) were measured using real-time (particle number and size, total volatile organic compound [TVOC] concentration) and time-integrated (aldehydes, acrylates, aromatics, alkanes, butylated hydroxy toluene, and elements) techniques in an environmental test chamber. Three colors of resins (black, clear, and gray), all from the same manufacturer, were tested on each printer. All statistical comparisons used a significance level of 0.05. Printer brand strongly influenced the emission yields. Printer A had significantly higher particle number yield, smaller particle size, and higher 2-hydroxyethyl methacrylate (2-HEMA) and 2-hydroxypropyl methacrylate yields for all resin colors compared with printer B. There were also significant differences between brands in yield values for several aldehydes (acetaldehyde, butyraldehyde, hexaldehyde, isovaleraldehyde, *o,m,p*-tolualdehyde, and propionaldehyde). Resin color had a minor influence on yields for particle number, some aldehydes, and 2-HEMA for printer A only. The strong influence of printer brand on emissions was partially explained by printer configuration, i.e., printer A had a built-in resin heater, whereas printer B did not. Emission yields of organic chemicals were not always higher for printer A compared with printer B, which indicated that other factors also influenced emissions. Improved understanding of factors that influence emissions from SLA printers is critical for developing exposure mitigation strategies using a hierarchy of controls.



KEYWORDS: *ultraviolet curable resins, additive manufacturing, vat photopolymerization, ultrafine particles, aldehydes, acrylates, volatile organic compounds*

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INTRODUCTION

Additive manufacturing (AM) refers to a family of processes that use a computer design file to build a 3-dimensional (3-D) object, usually by a layer-upon-layer methodology.[1] One AM process category is vat photopolymerization (VP). Since the 1980s, AM machines have primarily been used in manufacturing environments for prototyping. More recently, there has been an increase in the availability of low-cost "desktop" AM machines (herein referred to as 3-D printers). As such, VP-type 3-D printers are now affordable for use in schools, libraries, home-based manufacturing businesses, and even for home recreation. The use of any 3-D printer in these spaces requires attention because general room ventilation in nonindustrial spaces is often insufficient for contaminant control.[2−4] Further, these indoor spaces might be occupied by children, the elderly, and others who might not fully understand the safe use of these printers and could be particularly vulnerable to their emissions.[5]

VP-type 3-D printers use ultraviolet (UV) light to cure liquid resins to build objects.[6] There are many resins on the market that differ in color, additives, and properties based on the intended application.[7] The main components of UV light-curing resins used in VP printing are monomers/oligomers, cross-linkers, and photoinitiators. Upon exposure to light, photoinitiators generate radicals that react with the cross-linkers, monomers, and oligomers to form polymer chains. This is an irreversible process that results in hardening of the resin.[7] There are several variations of VP-type 3-D printers on the commercial market, including stereolithography (SLA), digital light processing (DLP), and liquid crystal display (LCD). SLA printers scan a laser beam across the bottom of a vat that contains a resin to initiate a polymerization reaction. DLP and LCD printers flash slices of each object layer across the entire bottom surface of the vat at once; photopolymerization is initiated wherever the UV or multi-

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wavelength light (DLP printers), or light-emitting diodes shining through a liquid crystal display (LCD printers), illuminate the resin.[7]

Multiple published reports cite release of particles and/or gases that could present an inhalation hazard during operation of VP-type printers in environmental test chambers (ETCs) and real-world spaces.[8−23] Bowers et al. performed a task-based assessment of emissions in ETCs for SLA and DLP printers and noted that particle concentrations tended to be highest during printing; gases released during printing included 2-hydroxypropyl methacrylate (2-HPMA, skin sensitizer), acetaldehyde (potential occupational carcinogen), and acetone (central nervous system depressant).[8] Zhang et al. also performed a task-based assessment for the SLA process in an ETC and reported that up to 100 different VOCs were released among tasks, with 40 from printing alone. Dominant VOCs during printing included 2-HPMA, 2-hydroxyethyl methacrylate (2-HEMA, skin sensitizer), propylene glycol, and acetone.[22] Importantly, both studies indicated the potential for exposure throughout the VP process, from start (loading resin into vats) to finish (washing and curing). Han et al. measured total volatile organic compound (TVOC) levels during SLA printing with resins that respond to thermal stimuli to change their shape and reported concentrations of 1500−1800 $\mu g/m^3$ during the printing and shape programming tasks.[12,13] Stefaniak et al. characterized aerosols released during SLA printing in an ETC and noted particle sizes of approximately 40−45 nm that contained chromium and nickel (potential occupational carcinogens), as well as iron and zinc (reactive metals capable of generating reactive oxygen species).[17] Results of emissions assessments in field settings vary. For example, Zisook et al. reported that, with the exception of acetone and isopropyl alcohol, VOC emissions from a VP printer were below background levels in a room.[23] In a series of field evaluations, Väisänen et al. evaluated particle- and gas-phase emissions from VP printers using several different types and colors of resins. On a number basis, particle emissions were similar or lower compared with fused filament fabrication 3-D printers that use a solid thermoplastic filament as feedstock. The authors noted that VOCs were the dominant emissions and included alcohols, aldehydes (e.g., formaldehyde and acetaldehyde), ketones (e.g., acetone), acrylates (e.g., methyl methacrylate, 2-HPMA), and hydrocarbons. While most studies of VP printers in the literature to date have focused on emissions, attention has also been given to control technologies. The NIOSH hierarchy of controls specifies that exposure controls be implemented in the following order of effectiveness: elimination > substitution > engineering > administrative > personal protective equipment. Yang and Li evaluated a titanium dioxide photocatalyst and activated carbon as potential engineering controls for TVOC emissions and reported reductions of up to 71% and 68.5%, respectively.[21] It is also noted that skin contact with feedstock resins could present a dermal exposure hazard[24] and that off-gassing from printed parts could pose an additional inhalation exposure risk to downstream users.[15,19] These potential inhalation and dermal exposure hazards highlight that it is critical to better understand VP printing to support effective, science-based guidance for safe work practices.

Only a few reports provided insights on factors that influence emissions during VP-type 3-D printing (Table 1). Factors influencing VP-type 3-D printing emissions can be grouped as resin (feedstock)-related, print-related, and printer-related. Resin-related factors that increased organic gas emissions included viscosity, composition, and grade.[12,18,21,25] Print-related factors include the surface area of printed parts and resin temperature.[12,21,25] Yang and Li reported that as print surface area increased, TVOC concentration increased, though Miller-Schulze and Williams reported that print surface area did not have a clear impact on individual VOC emissions. Han et al. indicate that TVOC emission rate increased with resin temperature increase.[12] The main printer-related factor that influenced both particle and organic gas emissions was printer type.[8,17]

Table 1. Factors That Influence Particle- and Gas-Phase Emissions from Vat Photopolymerization 3-D Printers[a]

Factor	Influence on emissions	
Resin-related		
Viscosity	TVOC concentration increases as viscosity increases (SLA)	ref 21
Composition	TVOC yield decreases as cross-linker content increases (SLA)	ref 12
Grade	Individual VOCs differed between standard and castable grades (SLA)	ref 18
	Carbonyl levels 2-fold higher for standard than castable grade (SLA)	
Grade	Individual VOCs mostly higher for standard resin versus "Eco" resin	ref 25
Print-related		
Area printed	TVOC concentration increases as surface area increases (SLA)	ref 21
Area printed	Individual VOC concentration not influenced by surface area (SLA)	ref 25
Resin heating	TVOC ER increases as resin temperature increases (SLA)	ref 12
Printer-related		
VP-type	Particle and TVOC yields higher for DLP than SLA	ref 17
	Particle size smaller for DLP than SLA	
VP-type	Particle concentration higher for DLP than SLA	ref 8
	TVOC concentration higher for SLA than DLP	

[a]DLP, digital light processing; ER, emission rate; SLA, stereolithography; TVOC, total volatile organic compounds; VOC, volatile organic compounds; VP, vat photopolymerization.

The purpose of this study was to evaluate the influence of two factors: resin color (resin-related factor) and printer brand (printer-related factor) on emissions during SLA printing. The focus was only on the print step, as this study was part of a broader evaluation of VP-style 3-D printers to identify a combination of printer and resin that could generate consistent exposure for future toxicology studies. For the factor resin color, there were three levels, and for the factor printer brand, there were two levels. All tests were performed in an ETC while emissions were monitored using complementary real-time and time-integrated sampling techniques.

MATERIALS AND METHODS

For all tests, emissions were monitored in a temperature-controlled (21 ± 1 °C) and humidity-controlled (50 ± 5%) 0.6 m^3 stainless steel chamber that meets international guidelines for emissions testing.[26−28] The air exchange rate was 1.3 air changes per hour. Air entering the chamber was passed through a carbon filter and a high-efficiency particulate air filter to remove organic vapors and particles, respectively.

Two popular brands of desktop SLA printers from different manufacturers (herein referred to as A and B) were evaluated in our tests. For each brand of printer, the same three colors of

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resins (black, clear, and gray) were tested. The resins were made by the same manufacturer as printer A and were compatible with printer B (i.e., polymerized at 405 nm by laser). During background, printer A was unplugged because it had a heater for the vat, but printer B, which did not have a heater for the vat, was plugged into an electrical receptacle and powered on. At the end of background, printer A was powered on and allowed to come to temperature before starting the print job. During both background and printing phases (including printer A warm-up), particulates and gases in the chamber were characterized using real-time and time-integrated sampling techniques. Real-time instruments logged data at 1 Hz throughout each test. Separate time-integrated samples were collected during the background and printing phases (approximately 160 to 190 min for printer A and 215 to 230 min for printer B) stages. Background sampling was performed for at least 30 min to achieve a stable particle concentration of <2000/cm^3 and a total organic gas level of <10 μg/m^3 inside the chamber, as prescribed in UL 2904. The potential for buildup of gases inside printer A during background when it was powered down and, therefore, its internal electronic component cooling fan off, was evaluated during method development to ensure it did not bias results. Inspection of real-time organic gas monitoring results (described in the next paragraph) demonstrated that concentrations were negligible during background, nor did they increase when the printer was powered and the resin heater on; concentrations only increased during the print phase.

Real-time particle size and number concentration were monitored from 5.6 to 560 nm by using a fast mobility particle sizer (FMPS, TSI Inc., Shoreview, MN). Attempts were also made to monitor particle size and number from 1 to 4 nm using a particle size magnifier;[29] however, the data were not amenable to determination of an emission yield because counts in the 1 to 4 nm size range increased only after the end of each print run. Metals and metalloids are used as photoinitiators in resins.[6] For this reason, chamber air was drawn through mixed cellulose ester (MCE) filters housed in close-faced cassettes using a personal sampling pump (AirChek XR5000, SKC Inc., Eighty Four, PA) calibrated to 3.0 L/min, followed by analysis using inductively coupled plasma-optical emission spectrometry (ICP-OES) in accordance with NIOSH Method 7303.[30] Additionally, chamber air was drawn through 5-μm pore size track-etched polycarbonate (TEPC) filters at 4 L/min for subsequent analysis using field emission scanning electron microscopy (FE-SEM) (Hitachi High-Tech America, Inc., Dallas, TX) with energy-dispersive X-ray spectroscopy (EDX) (Bruker, Madison, WI) to observe particle morphology and identify their elemental composition.[17] Assessment of gas-phase emissions included real-time total volatile organic compound (TVOC) concentration measurements using a photoionization detector (PID) (Tiger, Ion Sciences, Stafford, Texas). Identities and amounts of specific VOCs were determined by using time-integrated sampling. The compounds for which results are presented herein were chosen for monitoring based on characterization results of the bulk resins (unpublished data by two of the study authors, S.R. and M.R.) and availability of sampling and analytical methods. Qualitative characterization of the bulk resins included gas chromatography−mass spectrometry (GC-MS) for acrylates and phenol derivatives, Direct Analysis in Real Time Mass Spectrometry (DART-MS) for monomers (tri(propylene glycol) diacrylate, 4-acryloylmorphiline, 2-hydroxylethyl acrylate [2-HEAC]), Fourier-transform infrared spectroscopy for acrylates, and headspace GC-MS for volatile organic compounds. Aldehydes were selected based on findings from prior studies.[18,19] Air was drawn through DNPH-coated silica gel cartridges (cat. no. 226-119, SKC Inc.) using a personal sampling pump (AirChek XR5000, SKC Inc.) calibrated to 1.0 L/min followed by analysis for aldehydes using EPA TO-11.[31] Hydrocarbons were monitored by drawing air through charcoal tubes (Cat.# 226-01, SKC Inc.) at 0.2 L/min using calibrated personal sampling pumps (Pocket Pump TOUCH 220−1000TC, SKC Inc.) followed by analysis using NIOSH Methods 1500 and 1501.[32,33] The compounds 2-hydroxyethyl acrylate (2-HEA), 2-HEMA, and 2-HPMA were monitored by drawing air through charcoal tubes (Cat.# 226-01, SKC Inc.) at 0.2 L/min using calibrated personal sampling pumps (Pocket Pump TOUCH 220−1000TC, SKC Inc.), followed by analysis using OSHA Method PV2252.[34] Finally, butylated hydroxytoluene (BHT) was sampled by drawing air through OVS-7 tubes (Cat.# 226-57, SKC Inc.) at 1.0 L/min using calibrated personal sampling pumps (AirChek XR5000, SKC Inc.), followed by analysis using OSHA Method PV2108.[35]

The same object, an artifact created by the National Institute of Standards and Technology (NIST), was printed for all tests.[36] For efficiency, the object was printed at a 40% scale (5 cm × 5 cm x 1 cm) of full size. Real-time instruments were used to monitor particle- and gas-phase emissions during all seven replicate tests, though time-integrated samples for particles and gases were only collected during four of the replicate tests (typically tests 1, 3, 5, and 7). The time required to print the object was longer for black resin compared with other colors because it was more opaque, and longer for printer B because it had a lower laser power. As such, to eliminate time as a variable in the results, particle- and gas-phase emissions were expressed in terms of yield (i.e., emission metric per gram of resin printed). After the sample was rinsed with acetone and allowed to air-dry overnight, the mass of the printed object (including supports) was determined by weighing it on a calibrated balance. Particle number and individual organic compound yields were calculated in accordance with standard UL 2904.[28] TVOC and individual element yields were calculated in accordance with the standard RAL-UZ-205 for determination of emissions from office equipment.[37] The equations used to calculate yields are given in the Supplemental File. Note that all emissions calculations account for background levels in the chamber, so the figures and tables present background-corrected yield values. Inhalation exposure potential was monitored using a one-box model assuming well-mixed air, and the only emission source was an SLA printer as given in UL 2904. For a personal exposure scenario, we assumed the same parameters as Zhang et al. to permit intercomparison of data, i.e., the user is positioned immediately near the printer (i.e., within a 1 m^3 volume) and a room air exchange rate of 0.23 h^{-1}.[22]

Statistical Analysis. Based on a prior study, there was a 59% difference in particle number-based emission yields and a 145% difference in TVOC yields between SLA- and DLP-type VP 3-D printers.[17] Using these data, a posterior analysis was performed using the Design of Experiment function in JMP (version 13.2.0, SAS Institute Inc., Cary, NC). Assuming a similar difference in particle number and TVOC yield values between different brands of SLA printers and colors of resin, a sample size of seven replicates was needed to detect a

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difference at significance level $\alpha = 0.05$ and power = 0.90. The data were non-normally distributed, so the nonparametric Kruskal–Wallis test was used to assess the assumption that medians of groups were different between printer brands. For the factor color, which had three levels, the Wilcoxon-Mann–Whitney test was used to calculate pairwise differences to assess its influence on emissions. All statistics were calculated by using JMP (at a significance level of 0.05).

RESULTS

Figure 1 presents the background-corrected real-time monitoring emission results for the brand A and B printers using each resin color (see Table S1 for the tabulated median values). Between brands, printer A's particle emission yields for black, gray, and clear resins were significantly higher compared with printer B's yields for the respective resin colors. Furthermore, for printer A, the geometric mean (GM) particle sizes for black, gray, and clear resins were significantly smaller compared with those emitted from printer B for the respective resin colors ($p < 0.05$). The TVOC emission yield for printer A with black color resin was significantly higher compared with printer B ($p < 0.05$). The brand A printer's particle emission yields differed among all resin colors ($p < 0.05$), but there were no differences in GM particle size or TVOC yield. For the brand B printer, among resin colors, there were no statistical differences in particle yield, GM particle size, or TVOC yield.

FE-SEM-EDX was used for the qualitative analysis of filter samples collected during background and printing. Inspection of background filter samples identified a few particles over several fields of view. These particles were several micrometers in diameter, with compact morphology and composed of aluminum, silicon, sodium, chlorine, and potassium. Filter samples collected during printing identified some compact particles as well as particles with morphology not seen in the background, i.e., collections of smaller particles (possibly agglomerates). Elements present in these particles but not in particles observed on background samples included titanium, iron, chromium, nickel, and zinc (Figures S1 and S2).

The Supporting Information presents median background-corrected yield values for airborne elements (Table S2), aromatic hydrocarbons (Table S3), alkane hydrocarbons (Table S4), and BHT (Table S5) during SLA printing. These substances were detected in only a few samples, so their yields were not included in the statistical analyses.

Figure 2 presents the background-corrected aldehyde yield values (see Table S6 for the tabulated median values). Between printer brands, the acetaldehyde yield values for printer A were significantly lower compared with printer B for each respective resin color (all $p < 0.05$). The butyraldehyde yield from printer A was significantly higher compared with printer B for black resin only. The hexaldehyde yield value from printer A was significantly lower, but the isovaleraldehyde yield value was significantly higher compared with printer B for clear resin only. For *o,m,p*-tolualdehyde, the yield value was significantly lower for printer A compared with printer B for black resin, whereas the opposite was true for gray and clear resins, i.e., significantly higher for printer A compared with printer B. Finally, the propionaldehyde yield value for printer A was significantly higher compared with printer B for black resin only. For the brand A printer, the acetaldehyde yield for black resin was significantly higher compared with clear and gray resins. There were no differences in the butyraldehyde or propionaldehyde yields between black and gray resins;

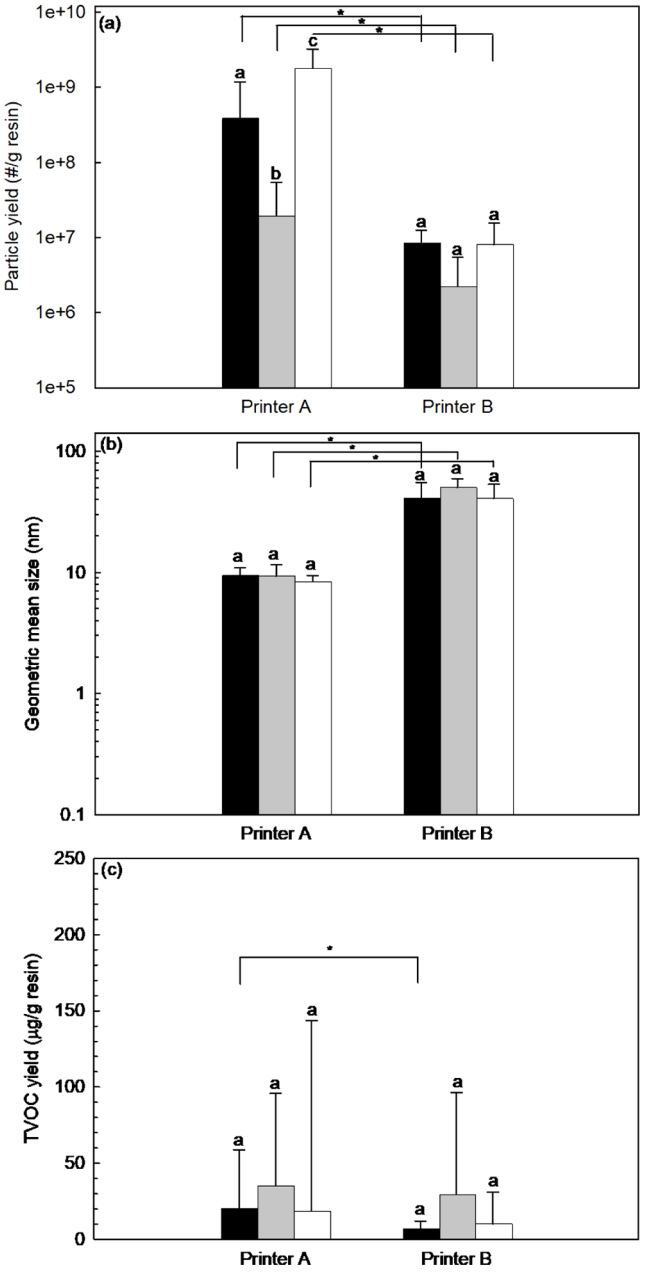

Figure 1. Real-time emission metrics for two brands of SLA 3-D printers using black, gray, and clear resins: (a) median particle number yield, (b) geometric mean (geometric standard deviation) particle size, and (c) median total volatile organic compound (TVOC) yield. Bar colors correspond to resin colors. For panels (a) and (c), error bars represent the interquartile range (25th and 75th percentiles). Within each printer brand, bars not connected by the same letter indicate significant difference. Between printers, horizontal bracket with an asterisk symbol indicates a significant difference.

however, both colors were significantly higher compared with clear resin. The hexaldehyde yield for black resin was significantly higher compared with both gray and clear resins. The isovaleraldehyde yield was significantly higher for gray resin compared with clear resin (but nondetectable for black resin), and the *o,m,p*-tolualdehyde yield for clear resin was significantly higher compared with black resin. For the brand B printer, there were no differences in aldehyde yields among colors.

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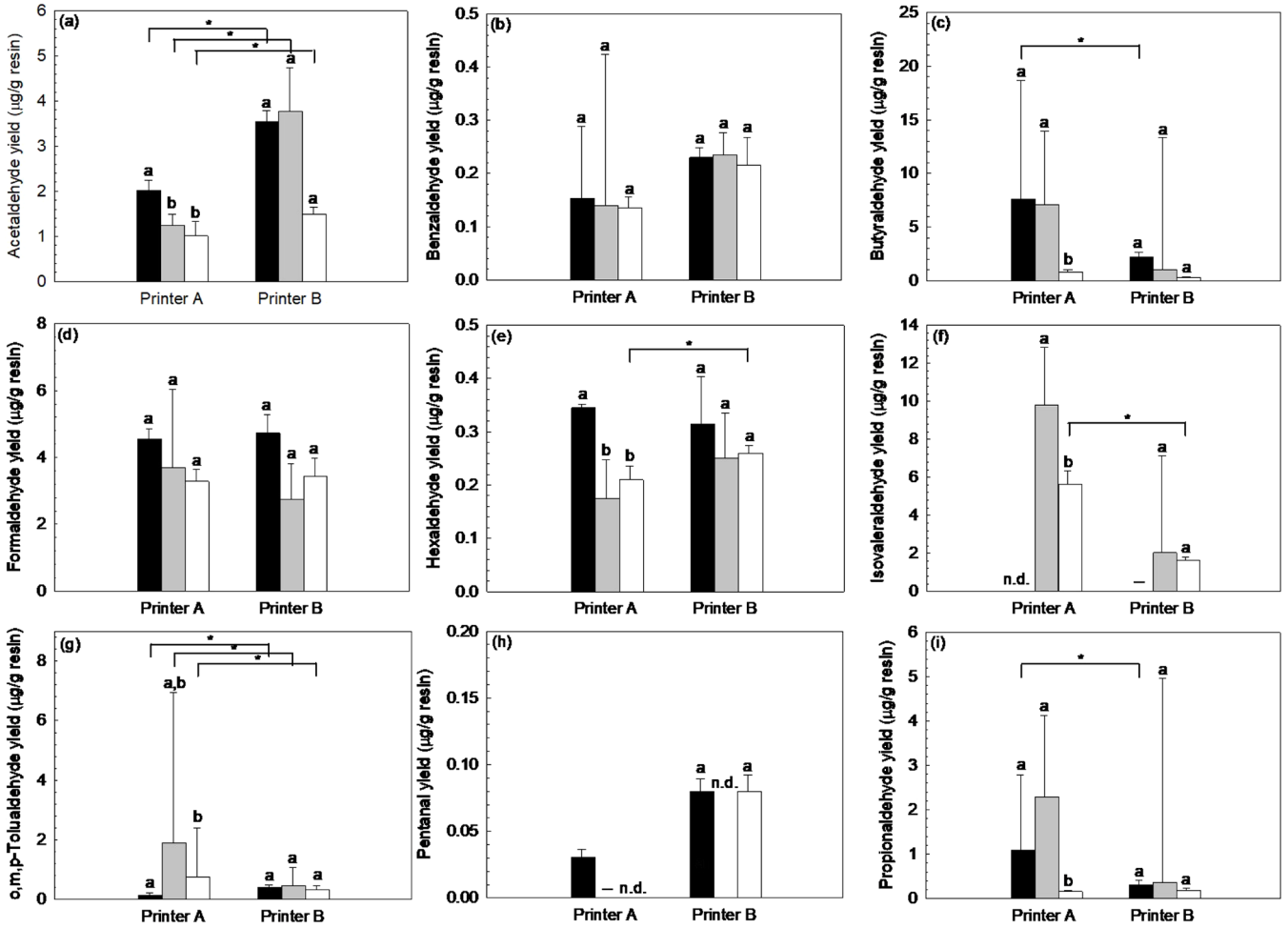

Figure 2. Median aldehyde yields for two brands of SLA 3-D printers using black, gray, and clear resins: (a) acetaldehyde, (b) benzaldehyde, (c) butyraldehyde, (d) formaldehyde, (e) hexaldehyde, (f) isovaleraldehyde, (g) *o,m,p*-tolualdehyde, (h) pentanal, and (i) propionaldehyde. Bar colors correspond to resin colors. Error bars represent interquartile range (25th and 75th percentiles). Within each printer brand, bars not connected by the same letter indicate significant difference. Between printers, horizontal bracket with an asterisk symbol indicates a significant difference. n.d. = not detected. – = quantified on one sample (no median – see Table S6 for yield value).

Figure 3 presents the background-corrected acrylate yield values (Table S7 for the tabulated median values). 2-HEA was not detected in any sample. Between printer brands, 2-HEMA and 2-HPMA yield values from printer A for black, gray, and clear resins were significantly higher compared with printer B for the respective colors (all $p < 0.05$). For the brand A printer, only the 2-HEMA yield for gray resin was significantly higher compared with both black and clear resins. For the brand B printer, there were no differences in acrylate yields among resin colors.

Personal exposure was modeled for contaminants quantified on substance-specific sampling media (Table S8). Modeled values for the personal exposure scenario were all below occupational exposure limits (OELs), where available, except for formaldehyde. The modeled formaldehyde exposure (107.8 $\mu g/m^3$) exceeded the NIOSH Recommended Exposure Limit (REL) of 19.7 $\mu g/m^3$ but was slightly below the American Conference of Governmental Industrial Hygienists Threshold Limit Value (123 $\mu g/m^3$).

DISCUSSION

This study evaluated the influence of a resin-related factor (color) and a printer-related factor (brand) on particle- and gas-phase emissions from desktop SLA-type VP 3-D printers. Results presented herein (Figures 1–3) indicated that color had a minor influence, and printer brand had a strong influence on emissions.

Resin color influenced particle number yield, six aldehyde yields, and 2-HEMA yield for printer A only. Resin color had no influence on any other emission metrics for either of the printer brands. As summarized in Table 1, prior investigations have observed an influence of the resin-related factors of viscosity, composition (cross-linker content), and grade on total and individual VOC emissions from SLA printers.[12,18,21,25] In the current study, the overall minor influence of resin color on emission yields could reflect that the resin brand was the same for all colors, so their basic properties (viscosity, cross-linker content, and grade) were likely similar. Of the six aldehydes and 2-HEMA that were significantly influenced by resin color, yield values were often lower for clear resin among the colors. The safety data sheets for these resins only listed classes of ingredients, so it is unknown if the propensity for clear resin to have lower aldehyde yields was an effect of the amount of these substances in the formulation compared with gray and black resins. Given the paucity of ingredient information on many resin safety data sheets,[24] a

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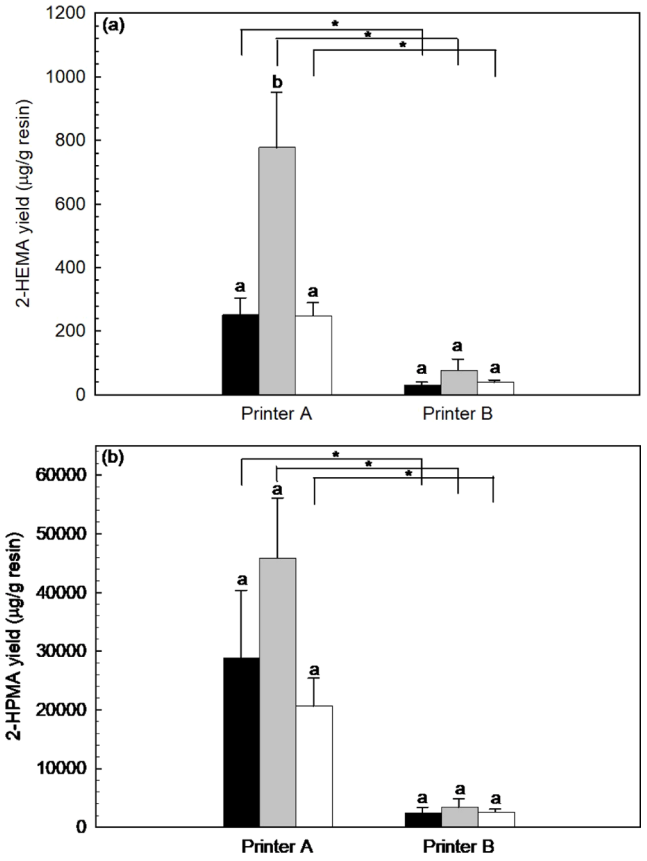

Figure 3. Median acrylate emissions for two brands of SLA 3-D printers using black, gray, and clear resins: (a) median of 2-hydroxyethyl methacrylate (2-HEMA) yield and (b) median of 2-hydroxypropyl methacrylate (2-HPMA) yield. Bar colors correspond to resin colors. Error bars represent interquartile range (25th and 75th percentiles). Within each printer brand, bars not connected by the same letter indicate a significant difference. Between printers, horizontal brackets with an asterisk symbol indicate a significant difference.

recommendation cannot be made at this time as to whether choosing clear resin for printing, when feasible, could be a reliable means to help reduce aldehyde and acrylate emissions.

With regard to the effect of brand, printer A had significantly higher particle number yield, smaller GM particle size, and higher acrylate (2-HEMA and 2-HPMA) yields for all resin colors compared with printer B. Further, printer A had a significantly higher TVOC yield compared with printer B for black resin. Individual printer brands had significantly different aldehyde emission signatures (Figure 2). The literature is inconsistent on the role of print object surface area in organic chemical emissions (Table 1), with one study reporting that the area of an object printed can influence TVOC emissions and another suggesting that object surface area did not impact individual VOC emissions.[21,25] Available literature indicates that printer type influences particle and TVOC emissions.[8,17] In the current study, the same object was printed for all runs, and both brand printers were SLA-type, so these print- and printer-related factors, respectively, can be ruled out as explanations for the observed differences between printer brands. Han et al. reported that TVOC emissions increased as resin temperature rose during operation of an SLA-type printer.[12] In their study, localized heating from the laser or printer enclosure resulted in a change in resin temperature from 22.8 to 24.6 °C, which was sufficient to measurably affect TVOC concentration. Further, Yang and Li postulated that as resin temperature rises, more liquid resin volatilization or other chemical reactions might occur, thereby increasing TVOC emissions.[21] Though both brands of printers used in this study operated on the principle of SLA, printer A had a built-in heater that maintained resin at approximately 31 °C (the heater cannot be turned off or adjusted), whereas printer B did not have a heater. Hence, it is plausible that observed differences in emission characteristics between printer brands in our study were at least partially influenced by resin heating. Elucidation of the exact mechanism by which printer A resin heating resulted in higher particle number release and smaller particle size compared with printer B unheated resin was beyond the scope of this study. A possible mechanism was that heating the resin resulted in volatilization of constituents that would not otherwise evaporate at ambient temperature to form small particles by condensation of vapor. Particle concentration in the chamber during runs with printer A was ca. $10^4/cm^3$, a level sufficiently low enough that significant agglomeration of ca. 8 to 10 nm particles would not take place during the approximately 3 h print time.[38] Heating resin reduces its viscosity and, in turn, the energy needed for curing and print time. These heat-induced savings are the principle behind an emerging variation of vat printing referred to as "hot lithography," which prints at resin temperatures up to 70 °C.[39] Given the relevance of resin temperature to emissions, awareness is warranted for future assessments to account for this factor.

In the current study, the impact of resin heating on organic compound emissions was variable between printer brands. Han et al. suggested that the boiling point of individual resin constituents could explain changes in VOC emission profiles, as compounds with lower boiling points will volatilize before compounds with higher boiling points.[12] In this study, we did not observe a correlative relationship between the resin organic chemical ingredient boiling point and measured concentration at either resin temperature (printer A [heated] or printer B [not heated]) that explained observed differences in yield values. Other printer-related factors that were not tested in this study included laser power and air tightness of the built-in chamber enclosure (used to block ambient light). In the current study, printer A used a 250 mW laser, whereas printer B used a 150 mW laser. Higher laser power does not explain the observed differences because yields of some organics were higher for printer B compared with printer A. If the build chamber of a printer did not form an airtight seal, there is potential for fugitive emissions to escape into the test chamber; however, such an error would be expected to result in systematically higher yields for all emissions across all runs for all colors, since their boiling points were almost all above the vat resin temperatures, which was not the case. Recently, Matoc et al. used a machine learning model to evaluate the impact of resin polymerization layer thickness, light exposure time, and light intensity on VOC emissions from an LCD-type vat printer.[40] Of these factors, light exposure time (duration shown on the resin) most influenced emissions, with much less impact from light intensity and only a minor role for layer thickness. In the current study, light (laser) intensity was also not a major explanation for the emissions. Whether light exposure time impacts emissions from SLA-type vat printers has not been evaluated to our knowledge.

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Individual organic substances quantified in emissions during SLA printing included aldehydes (Figure 2), acrylates (Figure 3), aromatics (Table S3), alkanes (Table S4), and BHT (Table S5). In the current study, nine aldehydes were quantified in the SLA emissions. Existing literature mentions six of these compounds (acetaldehyde, benzaldehyde, butyraldehyde, formaldehyde, hexaldehyde, and propionaldehyde) in emissions from SLA printers using black, gray, and/or clear resins.[8,18,19,22] Three of the aldehydes reported in the current study (isovaleraldehyde, *o,m,p*-tolualdehyde, and pentanal) have not been identified in the literature to date. Several of these aldehydes are associated with adverse health effects. Specifically, acetaldehyde, formaldehyde, and pentanal are eye, nose, throat, and/or respiratory irritants, and NIOSH classifies acetaldehyde and formaldehyde as potential occupational carcinogens.[41] Prior studies have reported the release of 2-HEMA and 2-HPMA during SLA printing.[8,16,18,22] Väisänen et al. noted that 2-HPMA was among the three most common VOCs they measured during SLA printing with clear and castable wax resins,[18] while Zhang et al. had 2-HPMA and 2-HEMA among their top five highest emitting chemicals during SLA printing with clear resin.[22] Acrylates such as 2-HPMA and 2-HEMA are known to cause allergic contact dermatitis, but inhalation of these compounds is also important as they are associated with occupational asthma in dentists.[42] Depending on the resin, other acrylates of health concern might also be emitted during VP printing. For example, Miller-Schulze and Williams evaluated emissions from standard and "eco" resins and reported release of 2-hydroxyethyl acrylate (2-HEAC) and dipropylene glycol diacrylate (DPGDA).[25] In the current study, the aromatic compounds ethylbenzene, *m,p*-xylene, *o*-xylene, and toluene were quantified in emissions during some print runs. Several investigators have measured toluene release during SLA printing with gray and clear resins.[10,19,22] Toluene is an eye and nose irritant, and xylenes are known eye, nose, and throat irritants.[41] The Zhang group also measured alkanes during SLA printing, including dodecane, which was consistent with that in our study. Two studies reported release of BHT during SLA printing and its presence might be as a stabilizer in resin.[22,25] BHT is an eye irritant.[41] Finally, as noted in Tables S2−S6, levels of some compounds emitted during the background step exceeded those released during the print step. Yang and Li developed a mathematical model to describe TVOC emissions from an SLA printer in terms of volatilization from bulk resin in the vat and from the print process. Zhang et al., as well as Miller-Schulze and Williams, characterized substance-specific gas-phase emissions and reported that some chemicals were released at similar or higher levels during background compared with the print step.[22,25] For example, it was reported that the resin monomers (4-acryloylmorpholine, 2-HEAC, and DPGDA), oligomers, and stabilizers (BHT) could be directly emitted from the resin vat and therefore released at similar levels between background and printing. In the current study, for printer A, background levels of the acrylate monomer 2-HEMA were 6−11% of the measured concentrations during printing, and background levels of the acrylate monomer 2-HPMA were 4−6% of that measured during printing. For printer B, background levels of 2-HEMA were 51−93% of that measured during printing, and background levels of 2-HPMA were 34−63% of levels during printing. These data are consistent with these prior studies that there is volatilization of some resin constituents from the printer vat under ambient conditions. As noted above, these background concentrations were accounted for in the emission yield calculations, and the values presented herein are background-corrected. Numerous reasons contribute to variability between the reported literature and current research, including study setting (chamber, real-world), sample collection and analysis techniques, printer configurations, and feedstock resin sources and formulations.

Previously, we reported measurable levels of chromium, iron, lead, manganese, and zinc in particles released during SLA printing with a gray resin.[8] In the current study, ICP quantified three of these elements (chromium, iron, and manganese) in aerosol emissions during SLA printing with various color resins. Bowers et al. reported over 20 elements in VP resins used in the automotive industry.[24] As such, the elements quantified herein (Table S2) are likely a subset of metals that might be present in resins. EDX analysis of individual particles on TEPC filters identified iron and zinc (Figure S2). FMPS measurements indicated that GM particle sizes were approximately 10−50 nm; however, the collection efficiency of the TEPC filter used for SEM-EDX analysis for particles in this observed size range was approximately 40% or less.[43] As such, a limitation of this study is that some smaller particles were likely not collected and characterized by SEM-EDX.

Zhang et al. measured emissions from an SLA printer with clear resin and modeled personal exposures for 16 compounds associated with adverse health effects from inhalation. Of these 16 compounds, four were also quantified in the current study (toluene, BHT, acetaldehyde, and formaldehyde) using black, gray, and or clear resins. Using their modeling scenario, predicted exposures in the current study were higher than those determined by Zhang et al. for three of these chemicals, i.e., 76.4 vs 20.8 $\mu g/m^3$ (toluene), 51.5 vs 21.5 $\mu g/m^3$ (acetaldehyde), and 107.8 vs 24.4 $\mu g/m^3$ (formaldehyde). In contrast, the exposure concentration for BHT modeled by Zhang et al. was higher than that in our study, i.e., 344 vs 27.8 $\mu g/m^3$. Exposure modeling from our chamber measurements indicated that levels of contaminants quantified on air samples were below occupational exposure limits, except for formaldehyde (107.8 $\mu g/m^3$), which was above the NIOSH Recommended Exposure Limit (19.7 $\mu g/m^3$). Given the potential carcinogenicity of formaldehyde, if exposure to this substance were to exceed the REL in the workplace, the hierarchy of controls should be implemented to reduce levels. Two substances with modeled exposures, butyraldehyde and propionaldehyde, do not have OELs, though NIOSH recommends that careful consideration should be given to reducing exposures to these aldehydes.[41]

In summary, this study elucidated that a resin-related factor (color) had a minor influence on gas- and particle-phase emissions from SLA-type 3-D printers, whereas a printer-related factor (brand) had a strong influence on these emissions. The stronger impact of printer brand on emissions was, at least partially, affected by printer configuration; i.e., printer A had a built-in resin heater, whereas printer B did not. Emission yields of organic chemicals did not follow a clear, consistent relationship between the VOC boiling point and whether a printer heated (A) or did not heat (B) the resin, which indicated that other factors not considered in the current study design also likely influenced emissions. As noted previously, the NIOSH hierarchy of controls specifies that exposure controls be implemented in order from most (elimination) to least (personal protective equipment)

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effectiveness.[44] In some instances, VP printing can be the superior technology for 3-D printing of an object, which can make the most preferred controls, such as elimination or substitution, difficult to implement. In this study, printer A, which heated resin, had a higher particle yield and smaller particle size for all resin colors (and TVOC yield for black resin) compared with printer B. Use of a printer that does not heat resin could be a substitution control to help reduce particle and gas emissions. It must be noted that elimination of a resin heater would not fully eliminate particle and organic gas emissions and would only be a supplement to the use of effective ventilation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chas.5c00076.

The file contains formulas for emission yield calculations, example electron micrographs of particles released during vat printing, tabulated values of real-time and substance-specific sampling emission yields, and modeled exposure values for a printer operator scenario (PDF)

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Notes

The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of NIOSH, Centers for Disease Control and Prevention (CDC). Mention of any company or product does not constitute endorsement by NIOSH/CDC. Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the Consumer Product Safety Commission, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.
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■ REFERENCES

(1) ISO *ISO/ASTM: 52900: 2021(en) Additive manufacturing — General principles —Fundamentals and vocabulary*, ISO: Geneva, Switzerland, 2021.

(2) Ding, S.; Ng, B. F. Particle emission levels in the user operating environment of powder, ink and filament-based 3D printers. *Rapid Prototyp. J.* **2021**, *27* (6), 1124−1132.

(3) Secondo, L. E.; Adawi, H. I.; Cuddehe, J.; Hopson, K.; Schumacher, A.; Mendoza, L.; et al. Comparative analysis of ventilation efficiency on ultrafine particle removal in university MakerSpaces. *Atmos. Environ.* **2020**, *224*, 117321.

(4) Viitanen, A.-K.; Kallonen, K.; Kukko, K.; Kanerva, T.; Saukko, E.; Hussein, T.; et al. Technical control of nanoparticle emissions from desktop 3D printing. *Indoor Air* **2021**, *31* (4), 1061−1071.

(5) CPSC *Safety Concerns Associated with 3D Printing and 3D Printed Consumer Products*, CPSC: Washington, DC, 2020.

(6) Bao, Y. Recent Trends in Advanced Photoinitiators for Vat Photopolymerization 3D Printing. *Macromol. Rapid Commun.* **2022**, *43*, 2200202.

(7) Pagac, M.; Hajnys, J.; Ma, Q.-P.; Jancar, L.; Jansa, J.; Stefek, P.; Mesicek, J. A review of vat photopolymerization technology: Materials, applications, challenges, and future trends of 3d printing. *Polymers* **2021**, *13* (4), 598.

(8) Bowers, L. N.; Stefaniak, A. B.; Knepp, A. K.; LeBouf, R. F.; Martin, S. B.; Ranpara, A. C.; et al. Potential for Exposure to Particles and Gases throughout Vat Photopolymerization Additive Manufacturing Processes. *Buildings* **2022**, *12* (8), 1222.

(9) Bressot, C.; Morgeneyer, M.; Aguerre-Chariol, O.; Bouillard, J.; Zaras, K.; Visser, G. W.; et al. Sanding and analysis of dust from nanosilica filled composite resins for stereolithography. *Chem. Eng. Res. Des.* **2020**, *156*, 23−30.

(10) Chuang, Y.-S.; Berekute, A. K.; Hsu, H.-Y.; Wei, H.-S.; Gong, W.-C.; Hsu, Y.-Y.; et al. Assessment of emissions and exposure in 3D printing workplaces in Taiwan. *J. Occup. Environ. Hyg.* **2024**, *21* (4), 270−286.

(11) Felici, G.; Lachowicz, J. I.; Milia, S.; Cannizzaro, E.; Cirrincione, L.; Congiu, T.; Jaremko, M.; Campagna, M.; Lecca, L. I.; et al. A pilot study of occupational exposure to ultrafine particles during 3D printing in research laboratories. *Front. Public Health* **2023**, *11*, 1144475.
(12) Han, M.; Li, L.; Zhao, J. Volatile organic compound emissions from 4D printing: Effects of material composition and external stimulus. *Addit. Manuf.* **2022**, *56*, 102894.
(13) Han, M.; Zhao, J.; Li, L. Emissions of volatile organic compounds from 4D printing and associated control strategies towards workplace safety. In *International Manufacturing Science and Engineering Conference*, American Society of Mechanical Engineers, 2021; Vol: *85079*; p. V002T09A005.
(14) Hayes, A. C.; Osio-Norgaard, J.; Miller, S.; Whiting, G. L.; Vance, M. E. Air pollutant emissions from multi jet fusion, material-jetting, and digital light synthesis commercial 3D printers in a service bureau. *Build. Environ.* **2021**, *202*, 108008.
(15) Pham, Y. L.; Wojnowski, W.; Beauchamp, J. Online Volatile Compound Emissions Analysis Using a Microchamber/Thermal Extractor Coupled to Proton Transfer Reaction-Mass Spectrometry. *Anal. Chem.* **2022**, *94* (50), 17354−17359.
(16) Runstrom Eden, G.; Tinnerberg, H.; Rosell, L.; Möller, R.; Almstrand, A.-C.; Bredberg, A. Exploring Methods for Surveillance of Occupational Exposure from Additive Manufacturing in Four Different Industrial Facilities. *Ann. Work Exposures Health* **2022**, *66* (2), 163−177.
(17) Stefaniak, A. B.; Bowers, L. N.; Knepp, A. K.; Luxton, T. P.; Peloquin, D. M.; Baumann, E. J.; et al. Particle and vapor emissions from vat polymerization desktop-scale 3-dimensional printers. *J. Occup. Environ. Hyg.* **2019**, *16* (8), 519−531.
(18) Väisänen, A.; Alonen, L.; Ylönen, S.; Hyttinen, M. Organic compound and particle emissions of additive manufacturing with photopolymer resins and chemical outgassing of manufactured resin products. *J. Toxicol. Environ. Health, Part A* **2022**, *85* (5), 198−216.
(19) Väisänen, A. J. K.; Hyttinen, M.; Ylönen, S.; Alonen, L. Occupational exposure to gaseous and particulate contaminants originating from additive manufacturing of liquid, powdered, and filament plastic materials and related post-processes. *J. Occup. Environ. Hyg.* **2019**, *16* (3), 258−271.
(20) Vasilescu, M. D. Influence of technological parameters on the emision on DLP 3D printing process. *Rev. Chim* **2019**, *70* (12), 4387−4392.
(21) Yang, Y.; Li, L. Total volatile organic compound emission evaluation and control for stereolithography additive manufacturing process. *J. Cleaner Prod.* **2018**, *170*, 1268−1278.
(22) Zhang, Q.; Davis, A. Y.; Black, M. S. Emissions and Chemical Exposure Potentials from Stereolithography Vat Polymerization 3D Printing and Post-processing Units. *ACS Chem. Health Saf.* **2022**, *29* (2), 184−191.
(23) Zisook, R. E.; Simmons, B. D.; Vater, M.; Perez, A.; Donovan, E. P.; Paustenbach, D. J.; et al. Emissions associated with operations of four different additive manufacturing or 3D printing technologies. *J. Occup. Environ. Hyg.* **2020**, *17* (10), 464−479.
(24) Bowers, L. N.; Ranpara, A. C.; Roach, K. A.; Knepp, A. K.; Arnold, E. D.; Stefaniak, A. B.; et al. Comparison of product safety data sheet ingredient lists with skin irritants and sensitizers present in a convenience sample of light-curing resins used in additive manufacturing. *Regul. Toxicol. Pharmacol.* **2022**, *133*, 105198.
(25) Miller-Schulze, J. P.; Williams, N. D. Volatile Organic Chemical Emissions from Standard and "Eco" Resins for Vat Photopolymerization Additive Manufacturing ("3D") Printers and Potential Mitigation Strategies. *ACS Chem. Health Saf.* **2025**, *32* (2), 175−185.
(26) ASTM International *ASTM: D6670: Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products*, ASTM International: West Conshohocken, PA, 2013.
(27) International Organization for Standardization *ISO: 28360: 2007 Information technology — Office equipment — Determination of chemical emission rates from electronic equipment*, International Organization for Standardization: Geneva, Switzerland, 2007.
(28) UL *UL: ANSI/CAN/UL 2904: Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers*; UL: Northbrook, IL, 2019.
(29) Mendes, L.; Kangas, A.; Kukko, K.; Mølgaard, B.; Säämänen, A.; Kanerva, T.; Flores Ituarte, I.; Huhtiniemi, M.; Stockmann-Juvala, H.; Partanen, J.; et al. Characterization of Emissions from a Desktop 3D Printer. *J. Ind. Ecol.* **2017**, *21* (S1), S94−S106.
(30) NIOSH Method 7303: Elements by ICP (Hot Block/HCl/HNO3 Digestion). In *NIOSH Manual of Analytical Methods*, 4th ed.; Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, U.S National Institute for Occupational Safety and Health: Cincinnati, OH, 2003.
(31) U.S. EPA *Method TO-11A: determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]*, U.S. Environmental Protection Agency: Cincinnati, OH, 1999.
(32) NIOSH Method 1501: Hydrocarbons, Aromatic. In *NIOSH Manual of Analytical Methods*, 4th ed., Ashley, K.; O'Connor, P. F., Eds.; DHHS/CDC/NIOSH: Cincinnati, OH,2003.
(33) NIOSH Method 1500: Hydrocarbons, BP 36 C - 216 C. In *NIOSH Manual of Analytical Methods*, Ashley, K.; O'Connor, P. F., Eds.; DHHS/CDC/NIOSH: Cincinnati, OH, 2003.
(34) OSHA *Method PV2252: Hydroxyethyl Methacrylate*, U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Salt Lake Technical Center: Salt Lake City, UT, 1989.
(35) OSHA *Method PV2108: Di-tert-butyl-p-Cresol*, U.S. Department of Labor, Occupational Safety and Health Administration, Salt Lake Technical Center: Salt Lake City, UT, 1992.
(36) Moylan, S.; Slotwinski, J.; Cooke, A.; Jurrens, K.; Donmez, M. A. An additive manufacturing test artifact. *J. Res. Natl. Inst. Stand. Technol.* **2014**, *119*, 429−459.
(37) Bundesanstalt für Materialforschung und -prüfung Test Method for the Determination of Emissions from Hardcopy Devices. In *RAL-UZ-205*, BAM: St, Augustin, Germany, 2017.
(38) Hinds, W. C. *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, 2nd, ed.; John Wiley & Sons, Inc: New York, 1999.
(39) Steyrer, B.; Busetti, B.; Harakály, G.; Liska, R.; Stampfl, J. Hot Lithography vs. room temperature DLP 3D-printing of a dimethacrylate. *Addit. Manuf.* **2018**, *21*, 209−214.
(40) Matoc, D. A.; Kanabar, B. K.; Sata, A. Machine learning-driven prediction and digital twins implementation for VOC emissions in VAT photopolymerization additive manufacturing. *Eng. Res. Express* **2025**, *7* (1), 015554.
(41) *NIOSH: Pocket Guide to Chemical Hazards*, http://www.cdc.gov/niosh/npg/default.html, 2005. Accessed 30 April 2024.
(42) Lindström, M.; Alanko, K.; Keskinen, H.; Kanerva, L. Dentist's occupational asthma, rhinoconjunctivitis, and allergic contact dermatitis from methacrylates. *Allergy* **2002**, *57* (6), 543−545.
(43) Lindsley, W. G. Filter Pore Size and Aerosol Sample Collection. In *NIOSH Manual of Analytical Methods*, 5th ed., ed., Andrews, R., Ed.; Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health: Cincinnati, OH, 2016.
(44) *NIOSH.: Hierarchy of Controls*. https://www.cdc.gov/niosh/topics/hierarchy/default.html 2015. Accessed 30 April 2024.

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Influence of resin color and printer brand on emissions from stereolithography (SLA) 3-D printers

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Supplemental File

Emission yield calculations

Particle number emission rates (PER) were calculated from the real-time measurement data collected during printing and converted to yields in accordance with the mass-balance model in UL 2904:

$$PER(t) = V_c[\frac{C_p(t) - C_p(t-\Delta t)\exp(-\beta \cdot \Delta t)}{\Delta t \ exp(-\beta \cdot \Delta t)}]$$

Where, PER(t) = particle emission rate as a function of time;

V_c = chamber volume, cm^3;

$C_p(t)$ = particle number concentration at time t, #/cm^3;

Δt = time difference between two successive data points, sec;

β = particle loss coefficient (calculated from decay phase after printing), sec^{-1}.

Integrating over the print interval gives the total number of particles (TP)

$$TP = \int_{tstart}^{tstop} PER(t) \quad d_t = \sum_{tstart}^{tstop} PER(t) \cdot \Delta t$$

Where, t_{start} = time when printing begins;

t_{stop} = end of print.

$$Yield = \frac{TP}{g \ printed}$$

Individual organic compound emission rates were calculated from the time-integrated sampling results and converted to yields in accordance with standard UL 2904 as follows:

$$ER_i = \frac{Q(C_{i,t} - C_{i,0} \cdot \exp(-\frac{Q}{V_c}(t - t_0))}{1 - \exp(-\frac{Q}{V_c}((t - t_0))}$$

Where, $ER(i)$ = individual gas-phase emission rate, µg/hr;

Q = flow rate into the chamber, m^3/hr;

$C_{i,t}$ = concentration of compound in chamber during printing (at t), µg/m^3;

$C_{i,0}$ = concentration of compound in chamber during background (t_0), µg/m^3;

V_c = chamber volume, m^3.

$$Yield_i = \frac{ER_{i \cdot t_{print}}}{g\ printed}$$

Where, t_{print} = total print time

Emission rates for TVOCs and elements were calculated in accordance with RAL-UZ-205. ER values for TVOC measurements were calculated from the beginning of the print phase until one air exchange after the end of the print phase and converted to yields as follows:

$$SER_{oper} = \frac{C_{oper} \cdot n_d^2 \cdot V_c \cdot t_g - SER_B \cdot n_d \cdot t_g}{n_d \cdot t_d - e^{-n_d(t_g - t_d)} + e^{-n_d \cdot t_g}}$$

Where, SER_{oper} = TVOC specific emission rate during the print phase, µg/hr;

C_{oper} = TVOC concentration during the print and post-decay phases, µg/m^3;

n_d = air exchange rate in chamber during printing and post-decay phases, hr^{-1};

V_c = chamber volume, m^3;

t_g = total sampling time, hr;

SER_B = specific emission rate during background phase, µg/hr;

t_d = printing time, hr.

$$SER_B = c_{B \cdot n_B \cdot V_c}$$

Where, SER_B = specific emission rate during background phase, µg/hr;

C_B = TVOC concentration during background phase, µg/m^3;

n_b = air exchange rate in chamber during background phase, hr^{-1}.

$$Yield_i = \frac{SER_{oper \cdot t_{print}}}{g\ printed}$$

For elements, the emission rates and yields were calculated as follows:

$$ER_i = \frac{m_{element \cdot n_d \cdot V_c \cdot t_g}}{V_{sample} \cdot t_d}$$

Where, ER_i = Element specific emission rate during the print phase, µg/hr;

$m_{element}$ = background corrected mass of element during print phase, µg;

n_d = air exchange rate in chamber during printing and post-decay phases, hr^{-1};

V_c = chamber volume, m^3;

t_g = total sampling time, hr;

V_{sample} = air volume passed through filter, m^3;

t_{print} = printing time, hr.

$Yield_i = \frac{ER_{i \cdot t_{print}}}{g\ printed}$ (Note: values were converted from µg/g to ng/g for presentation in Table S2).

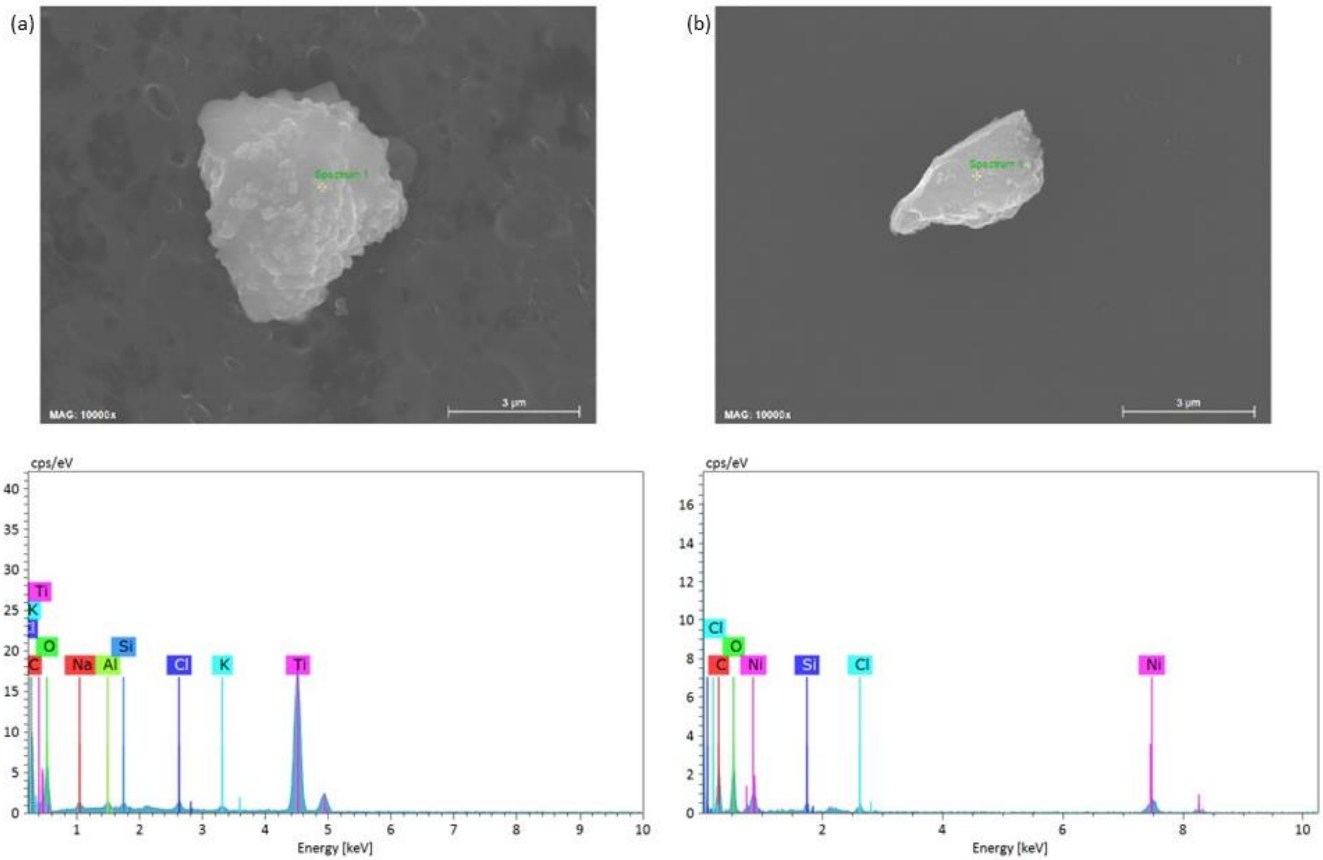

Figure S1. Example images of particles released during stereolithography 3-D printing and their elemental spectra for Printer A: (a) black resin, (b) grey resin. Spectra tags: Al = aluminum, C = carbon, Cl = chlorine, K = potassium, Na = sodium, Ni = nickel, O = oxygen, Si = silicon, Ti = titanium.

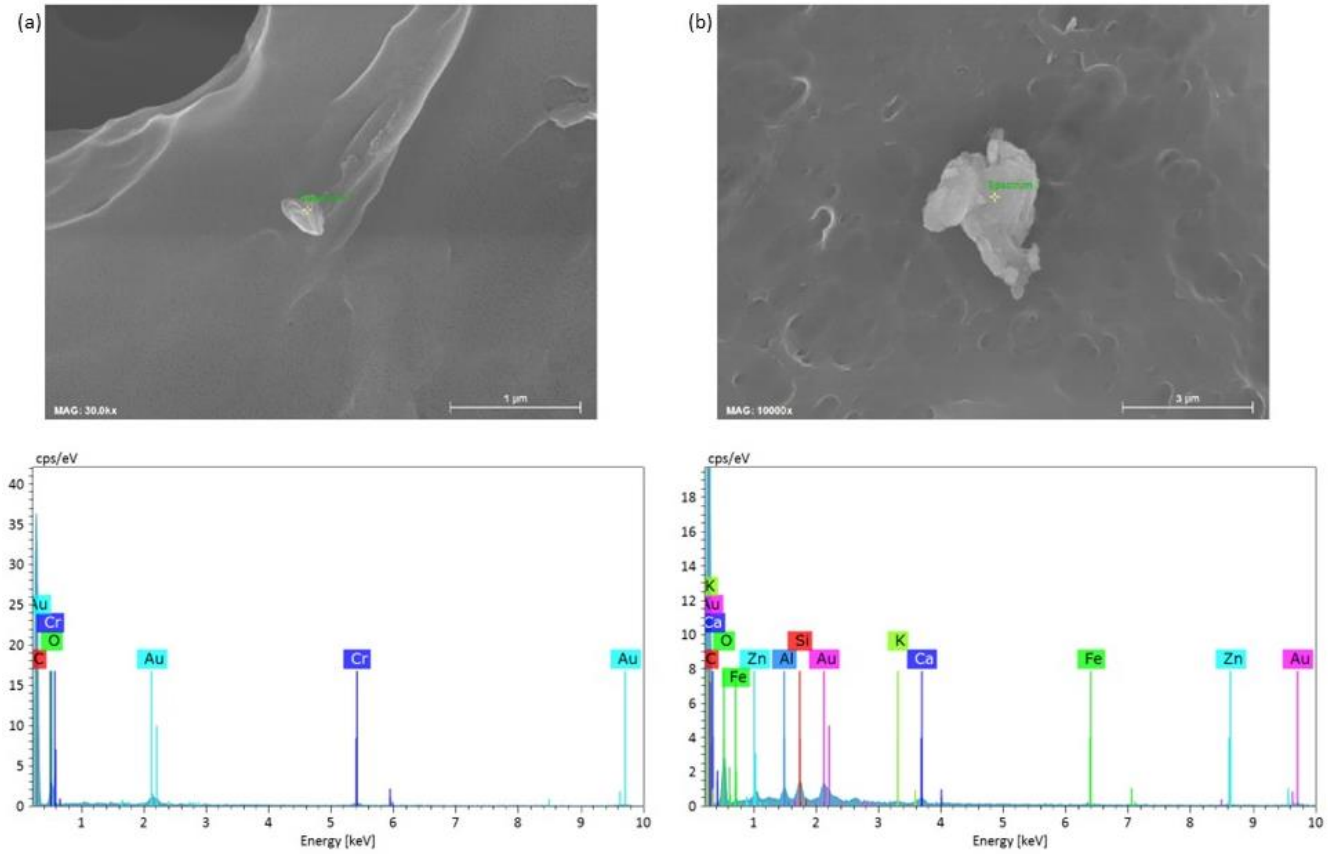

Figure S2. Example images of particles released during stereolithography 3-D printing and their elemental spectra for Printer B: (a) black resin, (b) grey resin. Note that the scale bar differs between images. Spectra tags: Al = aluminum, Au = gold (from coating sample to make conductive), C = carbon, Ca = calcium, Fe = iron, K = potassium, O = oxygen, Si = silicon, Zn = zinc.

Table S1. Median (interquartile range, 25 – 75%) of real-time monitoring emission yields and GM particle sizes for stereolithography 3-D printing*

Printer	Resin	FMPS Yield, #/g	GM, nm (GSD)	TVOC Yield, µg/g
A	Black	3.9 (1.9 – 12.7) x 10^8	9.5 (1.2)	20.3 (18.0 – 53.8)
A	Grey	2.0 (0.7 – 5.2) x 10^7	9.5 (1.3)	35.2 (31.4 – 84.0)
A	Clear	1.8 (0.9 – 3.3) x 10^9	8.4 (1.2)	18.5 (6.7 – 145.3)[a]
B	Black	8.4 (5.5 – 11.3) x $10^{6,\ b}$	42.5 (1.4)	7.2 (0.3 – 11.3)
B	Grey	2.2 (1.9 – 5.6) x $10^{6,\ c}$	50.8 (1.4)	29.5 (7.2 – 97.2)[c]
B	Clear	8.1 (0.5 – 15.6) x $10^{6,\ d}$	41.9 (1.4)	10.2 (2.4 – 26.0)[a]

* Medians calculated using only runs for which an emission yield was calculable

[a] Incalculable for 1/7 runs because of low emission levels

[b] Incalculable for 5/7 runs because of low emission levels

[c] Incalculable for 2/7 runs because of low emission levels

[d] Incalculable for 4/7 runs because of low emission levels

Table S2. Median (interquartile range, 25 – 75%) of elemental yields in ng/g resin printed for stereolithography 3-D printing (n = 4 samples unless specified otherwise)

Printer	Resin	Aluminum	Barium	Chromium	Copper	Iron	Magnesium	Manganese	Phosphorous	Strontium	Vanadium
A	Black	--	--	--	54.65[a]	2.32[a]	0.51[a]	152.35[a]	--	--	--
A	Grey	--	--	--	--	--	--	186.1 (46.2-326.0)[b]	143.39[a]	--	6.53[a]
A	Clear	64.2 (57.9-70.4)[b]	--	5.9 (3.0-8.8)[b]	--	--	11.6[a]	--	20.70[a]	1.80[a]	--
B	Black	--	2.5 (1.2-2.6)[c]			269.8[a]				0.9 (0.9-0.9)[b]	
B	Grey	259.6[a]	--	--	--	--	--	--	--	--	--
B	Clear	60.5[a]	--	--	--	293.3[a]	--	--	--	--	--

--, value not calculable because mass of analyte was non-detectable or below background on all samples

[a] Quantified on 1 of 4 samples

[b] Quantified on 2 of 4 samples

[c] Quantified on 3 of 4 samples

Table S3. Median (interquartile range, 25 – 75%) of aromatic hydrocarbon yields in µg/g resin printed for stereolithography 3-D printing (n = 4 samples unless specified otherwise)

Printer	Resin	Benzene	Ethylbenzene	*m,p*-Xylene	*o*-Xylene	Toluene
A	Black	--	--	8.6 (7.7-9.5)[a]	--	2.6 (0.7-4.7)[b]
A	Grey	--	--	1.6 (1.1-4.7)	118.5 (107.0-225.0)	--
A	Clear	--	0.54[c]	--	--	--
B	Black	--	--	--	--	--
B	Grey	--	--	4.67[c]	22.89[c]	--
B	Clear	--	--	--	--	--

--, value not calculable because mass of analyte was non-detectable or below background on all samples

[a] Quantified on 2 of 4 samples

[b] Quantified on 3 of 4 samples

[c] Quantified on 1 of 4 samples

Table S4. Median (interquartile range, 25 – 75%) of alkane hydrocarbon yields in µg/g resin printed for stereolithography 3-D printing (n = 4 samples unless specified otherwise)

Printer	Resin	Cyclohexane	n-Decane	n-Dodecane	n-Nonane	n-Pentane	n-Undecane
A	Black	--	--	--	--	1.1 (0.6-2.0)	--
A	Grey	0.5 (0.4-2.8)[a]	7.9 (6.0-9.0)[a]	1.9 (1.5-3.4)	3.7 (2.4-11.3)	--	4.9 (2.3-7.2)
A	Clear	--	--	--	--	--	--
B	Black	--	--	--	--	--	--
B	Grey	4.59[b]	13.6 (2.5-24.6)[c]	2.16[b]	15.95[b]	--	8.3[b]
B	Clear	--	--	--	--	--	--

--, value not calculable because mass of analyte was non-detectable or below background on all samples

[a] Quantified on 3 of 4 samples

[b] Quantified on 1 of 4 samples

[c] Quantified on 2 of 4 samples

Table S5. Median (interquartile range, 25 – 75%) of butylated hydroxytoluene (BHT) yields in µg/g resin printed for stereolithography 3-D printing (n = 4 samples unless specified otherwise)

Printer	Resin	BHT
A	Black	--
A	Grey	0.6[a]
A	Clear	0.7 (0.5-1.4)
B	Black	--
B	Grey	--
B	Clear	--

--, value not calculable because mass of analyte was non-detectable or below background on all samples

[a] Quantified on 1 of 4 samples

Table S6. Median (interquartile range, 25 – 75%) of aldehyde yields in µg/g resin printed for stereolithography 3-D printing (n = 4 samples unless specified otherwise)[a]

Printer	Resin	Acetald.	Benzald.	Butyrald.	Formald.	Hexald.	Isovalerald.	*o,m,p*-Toluald.	Pentanal	Propionald.
A	Black	2.0 (1.8-2.2)	0.15 (0.07-0.3)	7.6 (2.9-19.1)	4.5 (3.7-4.6)	0.4 (0.3-0.4)	--	0.2 (0.1-0.2)	0.03 (0.04 – 0.04)[b]	1.1 (0.5 – 2.9)
A	Grey	1.2 (1.0-1.5)	0.1 (0.03-0.5)[c]	7.1 (5.3-14.2)	3.7 (3.2-6.1)	0.2 (0.2-0.3)	9.8 (7.0-12.8)	1.9 (1.9-7.4)[c]	1.8[d]	2.3 (1.2 – 4.2)
A	Clear	1.0 (0.6-1.3)	0.1 (0.1-0.2)	0.8 (0.3-0.9)	3.3 (3.1-3.6)	0.2 (0.1-0.2)[c]	5.6 (5.2-6.4)	0.7 (0.6-0.7)	--	0.2 (0.1 – 0.2)[c]
B	Black	3.5 (2.8-3.6)[c]	0.2 (0.2-0.3)[c]	2.2 (1.0-2.5)[c]	4.7 (3.6-5.1)[c]	0.3 (0.2-0.4)	1.8[d]	0.4 (0.3-0.5)	0.1 (0.1 – 0.1)[c]	0.3 (0.2 – 0.4)
B	Grey	3.8 (2.6-4.7)	0.2 (0.2-0.3)	1.0 (0.4-13.5)	2.7 (2.6-3.9)	0.3 (0.2-0.3)[b]	2.0 (1.3-7.2)	0.5 (0.3-1.1)[c]	--	0.4 (0.2 – 5.4)[c]
B	Clear	1.5 (1.4-1.7)[c]	0.2 (0.1-0.2)	0.3 (0.3-0.3)[c]	3.4 (3.4-4.0)[c]	0.3 (0.2-0.3)[c]	1.7 (1.1-1.7)[c]	0.3 (0.2-0.5)[c]	0.1 (0.1 – 0.1)[c]	0.2 (0.2 – 0.4)

--, value not calculable because mass of analyte was non-detectable or below background on all samples

[a] Acetald., acetaldehyde; Benzald., benzaldehyde; Butyrald., butyraldehyde; Formald., formaldehyde; Hexald., hexaldehyde; Isovalerald., isovaleraldehyde; *o,m,p*-Toluald., *o,m,p*-tolualdehyde; Propionald., propionaldehyde

[b] Quantified on 2 of 4 samples

[c] Quantified on 3 of 4 samples

[d] Quantified on 1 of 4 samples

Table S7. Median (interquartile range, 25 – 75%) of acrylate yields in µg/g resin printed for stereolithography 3-D printing (n = 4 samples)[a]

Printer	Resin	2-HEMA	2-HPMA
A	Black	252.3 (179.0-296.4)	28884.4 (19850.9-39980.2)
A	Grey	777.8 (438.5-886.2)	45840.3 (24876.2-52119.5)
A	Clear	248.8 (227.0-290.7)	20624.7 (20070.3-25513.7)
B	Black	31.0 (19.3-38.8)	2475.9 (1386.6-3297.1)
B	Grey	76.7 (41.1-111.3)	3423.1 (1963.9-4807.7)
B	Clear	39.6 (25.4-43.5)	2616.6 (1815.8-2957.9)

[a] 2-HEMA, 2-hydroxyethyl methacrylate; 2-HPMA, 2-hydroxypropyl methacrylate

Table S8. Modeled personal exposures to contaminants quantified during SLA printing. Values calculated using UL 2904 model and median emission rate value for each contaminant. Exposure limits are 8-hour time-weighted average values unless indicated otherwise.[a]

Contaminant	Concentration (µg/m^3)	REL (µg/m^3)	PEL (µg/m^3)	TLV® (µg/m^3)
Elements				
Aluminum	2.50	10000	15000	1000 (Respirable)
Barium	0.04	n/a	n/a	500
Chromium	0.24	500	1000	500
Copper	1.53	1000	1000	1000
Iron	4.35	5000	100000	5000 (Respirable)
Magnesium	0.43	n/a	15000	10000
Manganese	4.27	1000	5000	100 (Inhalable)
Phosphorous	3.30	100	100	100
Strontium	0.01	n/a	n/a	n/a
Vanadium	0.26	50 (Ceiling)	500 (Ceiling)	n/a
Aromatics				
Ethylbenzene	21.2	435000	435000	86800
m,p-Xylene	78.7	435000	435000	86800
o-Xylene	4395.3	435000	435000	86800
Toluene	76.4	375000	750000	75400
Alkanes				
Cyclohexane	49.2	1050000	1050000	344000
Decane	313.8	n/a	n/a	n/a
Dodecane	66.1	n/a	n/a	n/a
Hexane	47.4	180000	180000	353000

Contaminant	Concentration (µg/m^3)	REL (µg/m^3)	PEL (µg/m^3)	TLV® (µg/m^3)
Nonane	173.8	1050000	n/a	1050000
Pentane	31.9	350000	2950000	2950000
Undecane	149.1			
Phenols[b]				
BHT	27.8	10000	n/a	2000
Aldehydes				
Acetaldehyde	51.5	n/a (Carcinogen)	360000	45000 (Ceiling)
Benzaldehyde	4.09	n/a	n/a	n/a
Butyraldehyde	35.0	n/a	n/a	n/a
Formaldehyde	107.8	19.7 (Carcinogen)	922.5	123
Hexaldehyde	6.28	n/a	n/a	n/a
Isovaleraldehyde	173.9	n/a	n/a	n/a
o,m,p-Toluladehyde	7.65	n/a	n/a	n/a
Pentanal	1.35	175000	n/a	176500
Propionaldehyde	6.43	n/a	n/s	47509
Acrylates[c]				
2-HEMA	3411.7	n/a	n/a	n/a
2-HPMA	323955	n/a	n/a	n/a

[a] REL = NIOSH Recommended Exposure Limit; PEL = U.S. Occupational Safety and Health Administration Permissible Exposure Limit; TLV = ACGIH Threshold Limit Value®

[b] BHT = butylated hydroxytoluene

[c] 2-HEMA, 2-hydroxyethyl methacrylate; 2-HPMA, 2-hydroxypropyl methacrylate