Plastic Repellent Paint™: Outgassing and Utility at Common FFF Printing Temperatures

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***Abstract*—Plastic Repellent Paint™ (PRP) is a solution used to prevent Fused Filament Fabrication (FFF) filaments from adhering to the nozzle and hotend of a 3D printer while it is printing. The solution must meet minimal emission levels for use at temperatures as high as 290°C, so it can be used in the same range as most low-temperature filaments. To determine if the possible hazardous emissions are at a low level, the total amount of volatile organic compounds (TVOC) emitted by PRP at 290°C was measured. This was accomplished by applying PRP to aluminum foil trays, curing it, heating it to 290°C, and performing gravimetric analysis. A PRP sample size of 146 mg was determined to have a TVOC emission rate of 42 µg/h over 24 hours which is much lower than the TVOC emission rate of many filaments used in the FFF process. The concentration of outgassed PRP at 1 mg/m^3 was below the individual VOC concentration exposure limits defined by OSHA and NIOSH. This 1 mg/m^3 concentration occurred for a 1 m^3 space, so for a typical two car garage with a volume of 163 m^3 it would be 6 µg/m^3. The total tested surface area of PRP was 15 times larger than a practical surface area making the mass of the TVOC to be approximately 0.067 mg for the typical use case on one hotend. In addition, PRP still repelled plastics after the 290°C exposure.**

***Index Terms*—Plastic Repellent Paint, Fused Filament Fabrication, Total Volatile Organic Compounds.**

I. Introduction

THIS report details the process of determining the total amount of volatile organic compounds (TVOC) outgassed when using a water-based polytetrafluoroethylene (PTFE) nanosuspension as an accessory for Fused Filament Fabrication (FFF) printing at elevated temperatures. The product name for the aqueous PTFE nanosuspension is Plastic Repellent Paint™ (PRP). In addition, this report determines the utility of PRP after it has been subjected to the process temperatures.

To understand this report, it is important to understand why PRP is being used in FFF printing. PRP is a liquid milky-white substance that is applied to the outside surface of a nozzle and hot block used on the printhead of an FFF 3D printer. Once cured, it inhibits adhering of common filaments with melting temperatures below 290°C like polylactic acid (PLA), polyethylene terephthalate glycol (PETG), and thermoplastic polyurethanes (TPU) from applied surfaces. This is especially useful in FFF printing as the nozzles are constantly in direct contact with the filament and it is common for the filament to adhere to the surface of the nozzle. Filament adhering to the exposed surfaces of the nozzle and hot block can interfere with the FFF process and even result in process failure.

PRP is a compound made by Miller-Stephenson Chemical and is distributed by Slice Engineering, LLC for its use in FFF 3D printing [1,2]. Miller-Stephenson Chemical has determined thermal decomposition of PRP occurs at 300°C, and Slice Engineering, LLC advertises a maximum usage temperature of 290°C [1,2]. The main purpose of this study is to determine the rate and concentration of outgassing from PRP at 290°C and compare it to the Occupational Safety and Health Administration's (OSHA) and the National Institute for Occupational Safety and Health's (NIOSH) limits for air contaminants. These outgassed amounts will be compared to amounts of VOCs typically outgassed during standard FFF 3D printing processes [3]. In addition, the utility of PRP is tested after baking at 290°C in order to determine qualitatively by checking whether PLA, PETG, and TPU can be easily removed without tools from a PRP-treated surface.

Through testing, it was determined that PRP outgassed 1 mg/m^3 after being heated to 290°C for 24 hours. This is below OSHA's and NIOSH's long and short-term exposure limits for the compounds listed on the Safety Data Sheet (SDS) for PRP [4,5,6]. This value equates to a release of 42 µg/h. Also, the PLA and PETG filaments were easier to remove from PRP applied surface after the surface was baked at 290°C.

II. Procedure

Mass of Outgassing

PRP was applied to the surface of three 5x5 cm aluminum foil trays. These will be considered coated specimens. This surface area is much larger than the typical use case to create a worst-case scenario. Aluminum foil was chosen because it would not outgas any particles when heated to 290°C. The total mass of the three trays before any PRP was applied was recorded using an Ohaus PA224C Pioneer analytical balance accurate to 0.1 mg [7]. The total mass was measured to ensure the measurement was not bounded by the resolution of the scale. The ambient room temperature was recorded before any heating occurred. The bare aluminum trays were then inserted into a tabletop furnace under a fume hood and heated to 290°C for one hour to ensure no contaminants remained. The mass of the bare aluminum trays was recorded again after they cooled to the

ambient room temperature. PRP was then applied to the top surface of the bare aluminum trays with one thin coat per instructions provided by Slice Engineering, LLC [2]. The mass of the coated specimens was recorded after PRP dried. The coated specimens were then inserted into the tabletop furnace and baked at 204°C for one hour. This was done to cure PRP and remove the water-based carrier liquid from the heterogeneous mixture as it is not a VOC. The coated specimens were allowed to cool to ambient room temperature and were weighed. Again, the coated specimens were inserted into the tabletop furnace and heated to 290°C for 24 hours. They were cooled to ambient room temperature and their masses were recorded. Each time the coated specimens were moved, tongs were utilized to prevent oils from the skin from contaminating the samples. Additionally, the total mass of the three coated specimens were recorded at once each time a recording was made to minimize error.

The mass of PRP before heating was calculated by taking the mass of the coated specimens and subtracting that by the mass of the bare aluminum trays. The mass of PRP after the water-based carrier liquid was removed was calculated by subtracting the mass of the coated specimens after being baked to 204°C by the mass of the bare aluminum trays before heating. The mass of the collective outgassed compounds was calculated by subtracting the mass of the coated specimens after being baked to 290°C by the mass of the coated specimens after being baked to 204°C.

Repellent Utility Testing

Three 5x5 cm bare aluminum foil trays, uncoated specimens, were prepared in addition to the three previously prepared coated specimens baked at 290°C. Two 3 cm segments of PLA, PETG, and TPU filament with 1.75 mm diameter were placed on the specimens. Each type of filament was placed on one coated specimen and one uncoated specimen. Each pair of specimens with the same filament were inserted into the tabletop furnace and baked at the recommended printing temperature for a period of time that allowed the filament to melt. They were cooled to ambient room temperature and a picture was taken to show the relative spreading of each filament type. The more attracted to the surface the molten plastic is, the more it tends to spread. An attempt was made to remove each filament from its respective specimen to determine if PRP was still effective after being baked at 290°C.

III. Results

Mass of Outgassing

The recorded and calculated masses and the ambient room temperature are shown in Table I. Heating the coated specimens from 25°C to 204°C reduced the mass of PRP by 71.99% which equates to a 105 mg change. Heating from 204°C to 290°C caused a decrease in the mass of PRP by 2.44% which equates to a 1 mg change. This 1 mg change is the mass of the TVOC.

TABLE I
VALUES FROM GRAVIMETRIC ANALYSIS

Quantity	Value ± Uncertainty
Ambient Room Temperature	25.0°C ± 0.1°C
Mass of Bare Aluminum Foil Tray	755.0 mg ± 0.1 mg
Mass of Bare Aluminum Foil Tray after initial heating of 290°C	755.2 mg ± 0.1 mg
Mass of Coated Specimen	901.2 mg ± 0.1 mg
Mass of Coated Specimen after being heated to 204°C	796.1 mg ± 0.1 mg
Mass of Coated Specimen after being heated to 290°C	795.1 mg ± 0.1 mg
Mass of PRP before being heated to 204°C	146.0 mg ± 0.1 mg
Mass of PRP after water-based carrier liquid was removed	40.9 mg ± 0.1 mg
Mass of collective outgassed compounds	1 mg ± 0.1 mg

The compounds outgassed at thermal decomposition and the OSHA and NIOSH time weighted average (TWA) and short term (ST) exposure limits for each compound are shown in Table II [4,5,6]. The TWA is for a 10-hour period while the ST is a 15-minute period. When assuming a volume of 1 m^3, the TVOC concentration for PRP is 1 mg/m^3.

TABLE II
OUTGASSED COMPOUNDS AND OSHA EXPOSURE LIMITS

Compound	TWA (mg/m^3)	ST (mg/m^3)
Hydrogen Fluoride	2.46	4.9
Carbonyl Fluoride	5	15.0
Carbon Dioxide	18000	54000.0
Carbon Monoxide	40	229.0

Repellent Utility Testing

The melted PLA in Fig. 1, has indications showing that the filament on PRP tray had greater spreading than the non-PRP applied tray. It also required less force to remove from the tray. It was melted at 220°C for 5 minutes.

Fig. 1. PLA melted in foil trays. Coated specimen on the left.

The melted PETG in Fig. 2, has indications showing that the filament on PRP tray had greater spreading than the non-PRP applied tray. It also required less force to remove from the tray. It was melted at 220°C for five minutes.

Fig. 2. PETG melted in foil trays. Coated specimen on the left.

The TPU in Fig. 3, did have indications of decent spreading. Neither sample removed easily from its tray. It was melted at 240°C for five minutes.

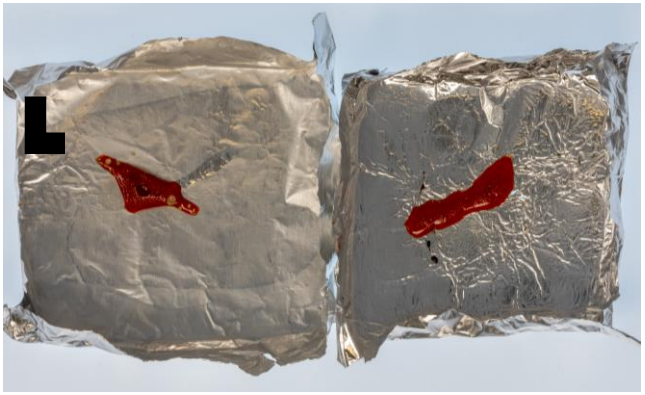

Fig. 3. TPU melted in foil trays. Coated specimen on the left.

IV. Discussion

TVOC Comparison to Typical FFF Materials

PRP was heated to 290°C for 24 hours after being cured. The mass loss during this time was 1 mg which equates to a mass loss rate of 42 µg/h. Compared to common FFF filaments like acrylonitrile butadiene styrene (ABS), PLA, Nylon, high impact polystyrene (HIPS), and polyvinyl alcohol (PVA), the TVOC emission rate of PRP is substantially smaller as shown in Table III [3]. In addition, the TVOC yield for PRP is on the lower end of these materials.

TABLE III
FFF Materials And PRP TVOC Emission

	ABS	PLA	Nylon	HIPS	PVA	PRP
Avg. TVOC ER (µg/h)	835	193.0	1660	888	147.0	42
Avg. TVOC Yield (µg/g material)	77	13.0	134	71	13.0	24

OSHA and NIOSH Exposure Limits

With the assumption of a volume of 1 m^3, the concentration of TVOC is 1 mg/m^3. Because this total value is smaller than each of the compounds from Table II that are outgassed when thermal decomposition occurs, it was not necessary to perform gravimetric analysis to determine the amount of each compound emitted by PRP.

Testing Quantity Compared to Typical Usage

The total surface area PRP is applied to on a hotend amounts to approximately 500 mm^3. This accounts for the bottom of a Mosquito™ hot block and the exposed surfaces of a Vanadium™ nozzle. Comparing this to the specimens' total surface area of 7,500 mm^3, shows that the 1 mg outgassed would be 15 times smaller at 0.067 mg for the typical use case with one hotend. Then it could be assumed that the mass loss would be 2.8 µg/h for a 24-hour period, and the TVOC emission concentration would be 0.067 mg/m^3.

PRP Utility After High Temperatures

The maximum temperature PRP should be heated to according to Slice Engineering, LLC is 290°C [2]. It was then important to determine if PRP still performs its main function which is to make it easier to remove filaments that have adhered to the nozzles of FFF printers. The testing determined that PRP is still effective after being heated to 290°C as both the PLA and PETG were easier to remove from the aluminum foil tray that had PRP applied to it over the tray without PRP. The TPU adhered to both types of trays. Aluminum foil is not representative of the application. A rigid specimen would tend to show more of a difference especially with TPU.

V. Conclusion

As seen in the results, PRP emits a small amount of TVOCs after being heated to the maximum temperature of 290°C. These results are compared to the TVOC amount emitted by typical FFF filament types during regular use. In addition, the TVOC amount is smaller than the individual exposure limits listed by OSHA and NIOSH for the individual compounds that are emitted by thermal decomposition. PRP remains useful after a 290°C 24-hour exposure as it allowed for easy removal of PLA and PETG material samples from the aluminum foil trays.

References

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