

Flame retardant back-coated PET fabric with DOPO-based environmentally friendly formulations

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ABSTRACT

There is a great demand for nontoxic flame retardants (FRs) in textile industry to replace harmful halogenated counterparts. On the other hand, the availability of eco-friendly phosphorus-based FRs for application on synthetic textiles are scarce for, especially for the back coating application. Thus, in this work, non-toxic phosphorus FRs such as EDA-DOPO (ED) and DOPO-PEPA (DP) were applied to PET fabric via a back coating process. For immobilizing these FRs on fabric, three different polymer resins, namely polyurethane, vinylacetate and acryl-copolymer, were utilized. The FR performance of fabrics was evaluated via a vertical burning test (FAR 25.853), a standard used commonly in aviation industry. For ED formulations (all resins), 5 % phosphorus (P) content on coating was sufficient for the textiles to pass the fire test. However, fabrics coated with DP formulations failed the fire test for the same P content. To further improve the FR performance of DP formulations, melamine was incorporated as a synergistic additive. In order to understand their FR behavior, thermogravimetric analysis (TGA) and direct insertion probe-mass spectrometry (DIP-MS) analysis was performed to elucidate the FR action of the additives. Herein, it was shown that DOPO-based FR compounds were first time successfully applied for the back coating application in textiles and their gas phase action was essential to pass the vertical burning test.

1. Introduction

Poly(ethylene terephthalate) (PET) is the most commonly used synthetic fiber [1] in the textile industry today due to its attractive aspects such as low cost, mechanical resistance, chemical stability, easy processability, good elasticity, wrinkle resistance, etc. Therefore, it naturally finds wide range of applications in daily life, and the demand for PET in the textile sector is continuously increasing. In addition to apparel and domestic use, PET is utilized as technical textiles, for example in sails for boats and yachts [2], hanging roofs and other building construction material [3]. On the other hand, PET fabric is flammable [4] and potentially dangerous in case of fire hazards. When ignited, the flame spreads quickly, and the PET polymer melts easily and decomposes readily. This feature of the fabric limits its fire safe application unless treated with a FR.

The FR treatment of PET, a synthetic textile, is a challenging task due to its melt dripping and lack of char formation [5]. For fire inhibition, the FR additive can be incorporated at the fiber stage during melt spinning in case of synthetic textiles, yet in most cases this causes changes in the mechanical properties of the textiles [6]. Alternatively,

post treatments can be carried out for FR treatment, more preferred way of application. Among various methods, back coating is one of the most economical surface treatments especially for furnishing fabrics [7]; therefore, even though it is not a hot topic in the research laboratories [8], it is still commonly employed in industry for FR treatment of mainly upholstery and transportation seat and carpet textiles [7].

For the back coating, the FR is applied to the backside of the fabric in the presence of a carrier matrix so that the appearance and softness/flexibility of the visible part of the textile would not be changed. Besides, it is also a practical method for the reason that the undesired chemical interaction with the fabric would be minimized. Hence, for such a treatment, gas phase active systems are required to inhibit the fire to be effective on the front side of the fabric where there is no direct contact with FR.

Nevertheless, the vast majority of back coating formulations in industry comprise antimony-bromine synergist formulations [7], as they are efficiently active in the gas phase, although halogenated FRs are well known to lead to environmental problems [9]. Especially regarding synthetic textiles [9], the phosphorus-based FRs [10], as effective and eco-friendly counterparts [11], are not equally common for back

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coating. Indeed, ammonium polyphosphate (APP) is frequently utilized for the back coating; however, its application is limited to cotton and cotton/PET blends [10], as it mainly works in the condensed phase; on the other hand, gas phase active FRs are more suitable for polyester due to low hydroxyl content which participates in the condensed phase. For the back coating application of PET fabric, aluminum phosphinates were employed as FR in the lab scale and it was found to enhance char formation and reduced the peak heat release rate [12]. Also, expandable graphite-based back coating formulation was applied to PET for potential upholstery usage for which dermatological test was carried out regarding its permeation and reported to be safe when to human contact [13], yet FR back coating application for PET fabric is limited to few examples.

In order to fulfill the demand to produce environmentally friendly FR additives for commercialization, phosphorus-containing FRs ED (6,6'-(ethane-1,2-diylbis(azanediyl))bis(6H-dibenzo[c,e][1,2]oxaphosphinine-6-oxide)) [14] and DP (6H-dibenz[c,e][1,2]oxaphosphorin,6-[(1-oxido-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-yl)methoxy]-, 6-oxide) [15] were developed with a straightforward and economic synthetic method and shown to be effective on various substrates. Moreover, toxicological assessment on ED was also carried out [16] and registered according to the European Chemicals Regulation (REACH). While ED was shown to be a FR for polyurethane foam for upholstery and mattresses [17] and also exhibited fire retarding activity PA6 for engineering plastics [18], DP was investigated as FR for epoxy resin [19] and polyester [15]. However, their applications in textile coating are still unexplored. As both FRs contain DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) unit in their skeleton, they can be considered for back coating application as an eco-friendly alternative to halogenated FRs, as DOPO [20] has dual activity and gas phase mode of action would be useful for back coating by releasing PO• radicals to quench the fire.

In this work, the effectiveness of ED and DP (Fig. 1), as a potential phosphorus-containing FR, was investigated for PET fabric in order to propose eco-friendly formulations, as DOPO-based compounds are not common for back coating. Moreover, several polymer resins as binders were screened as their chemistry plays a significant role in FR mechanism. The binder interacts with the FR and can potentially control its activity in the gas and condensed phase. The fire performance of the coated fabrics was compared and analyzed by various analytical tools. The influence of melamine as a prospective synergistic additive for DP was also explored and a flame retarding mechanism for different formulations was proposed in this work.

2. Experimental

2.1. Materials

PET fabric with an area density 190 g/m² was provided by Serge Ferrari Group, France. ED and DP (Table 1) were prepared according to previously reported protocols [14,15]. The polymer resins (TUBICOAT PU60, TUBICOAT VA60 and TUBICOAT AC506) were supplied by CHT Switzerland (Table 2). The back-coated PET fabrics were conditioned for 24 h in 65 % relative humidity and 20 °C before the vertical burning test. Ammonium polyphosphate (Exolit AP 423) and melamine were sourced from Clariant and Aldrich respectively and used as received.

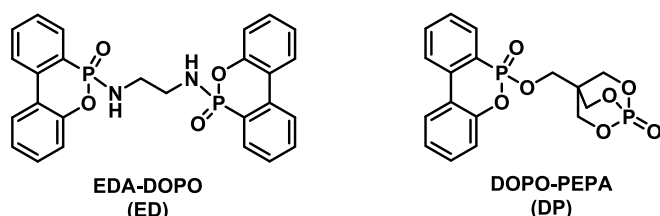


Fig. 1. Chemical structures of DOPO-based FRs.

Table 1
Flame retardants.

FR	P content (%)
EDA-DOPO (ED)	12.68
DOPO-PEPA (DP)	15.71

Table 2
Polymer resin binders.

Trade name	Structural information	Solid content (wt %)	pH value (20 °C)
TUBICOAT PU60 (PU)	Polyurethane	Ca. 60 %	7–9
TUBICOAT VA60 (VA)	Polyvinylacetate	Ca. 60 %	3–6
TUBICOAT AC506 (AC)	Acrylicopolymer	Ca. 45 %	5.2–6.8

2.2. Methods

2.2.1. Preparation of FR dispersions

In order to obtain 5 % P in the dry coating paste, the corresponding amount of FR was added to the polymer resin binders which are in a water-based dispersion form (Table 3). Then, the mixture was blended with IKA T18 digital ULTRA TURRAX to have a homogenous dispersion. The stirring was started with a lower rotation speed of 1000 rpm and gradually increased to 15,000 rpm and it was stirred for 5 min to get the dispersions in Table 3.

2.2.2. Back coating of the PET fabric

After cutting the PET fabric to the size of 30 cm × 34 cm, a paint roller was used to apply the coating dispersion (mentioned in Table 3) evenly on the backside of the fabric. Then, the fabric was dried at 60 °C for 1 h. It was targeted to have around 50 g/m² add-on for each coating. The coating add-on was calculated by measuring the weight gain of the fabric. Before the flammability test, the fabrics were conditioned for at least 24 h. Finally, evenly coated PET fabrics were cut into three pieces (9 cm × 31 cm) for the FAR 25.853 test.

2.2.3. Thermal analysis

TGA was carried in a NETZSCH TG209 F1 Iris instrument. Approximately 4 mg of sample was heated from 25 to 800 °C at a rate of 10 °C/min. The measurements were performed in N₂ and air with a total gas flow of 50 mL/min.

2.2.4. Fire test

Vertical burning tests of PET fabrics were performed according to “FAR 25.853 (a) Appendix F Part I (a) (1) (ii)” designed by Federal

Table 3
Formulation of FR-containing coating paste.

FR dispersion	FR additive	Water-based dispersion of polymer binder	FR percentage in dry coating paste
5 % P ED-PU	10 g of ED	25.6 g of PU (60 %)	39 %
5 % P ED-VA	10 g of ED	25.6 g of VA (60 %)	39 %
5 % P ED-AC	10 g of ED	34.1 g of AC (45 %)	39 %
5 % P DP-PU	10 g of DP	35.7 g of PU (60 %)	32 %
5 % P DP-VA	10 g of DP	35.7 g of VA (60 %)	32 %
5 % P DP-AC	10 g of DP	47.6 g of AC (45 %)	32 %
5 % P APP-PU	10 g of APP	86.7 g of PU (60 %)	10 %
Melamine-PU	10 g melamine	35.7 g of PU (60 %)	32 %
3%P DP/melamine (60/40 wt/wt)-PU	6 g DP + 4 g melamine	35.7 g of PU (60 %)	32 %

Aviation Administration to test materials and textiles (seat, carpet, etc.) used in aviation. The fabrics in a vertical orientation were exposed to a Bunsen burner flame (flame from propane gas – blue flame) for 12 s to record the burn length and time. The flame temperature is $>843^{\circ}\text{C}$ measured in the center of the flame. The flame height is 38 mm and 19 mm of the flame is on the sample. In order to pass the FAR 25.853 test, flame self-extinguishing time should be <15 s, and burn length should be <20.3 cm. Drip self-extinguishing time should also be recorded <5 s. For our experiment, three samples for each coated PET fabric were tested and the average is the result of the test.

2.2.5. Microscale combustion calorimetry (MCC)

Heat release rates (HRR) of FR-containing dry coating pastes were determined using a microscale combustion calorimeter (Fire Testing Technology Instrument, London, UK) following ASTM D7309. Between 3 and 16 mg of sample was exposed to a heating rate of 1.0°C/s from 150 to 750°C in the pyrolysis zone.

2.2.6. Cone calorimetry

Cone calorimetry (Fire Testing Technology, East Grinstead, London, UK) was performed with an irradiative heat flux of 25 kW/m^2 on specimens ($100 \times 100\text{ mm}^2$) placed horizontally with grids. Parameters such as peak heat release rate, total heat release, total smoke release, total smoke production, CO production, and CO_2 output were recorded for each sample. The cone calorimetry samples were prepared via back coating.

2.2.7. Direct insertion probe mass spectrometry

DIP-MS analysis was performed for a 1–2 μg sample using the ThermoQuest FINNIGAN apparatus (Austin, TX, USA). The sample was heated from 30°C to 450°C at a rate of 60 K/min and 10^{-6} mbar pressure.

3. Results and discussion

3.1. Vertical burning test of the coated PET fabrics

3.1.1. The flammability of ED and DP coated samples

As previously mentioned back coating is a commonly practiced method for FR treatment in industry and mainly finds applications mainly for upholstery. In this regard, transportation textiles for seats and floors are also coated with this method and subjected to the corresponding fire test before their use. Accordingly, in this work, the flammability was evaluated in terms of a standard burning test used for aircraft textiles as the back coating formulations developed herein can be potentially applied in the aircraft sector.

The burning test used in this work is FAR 25.853 which is designed by the Federal Aviation Regulations (FAR). It is a vertical Bunsen burner test developed to test materials and textiles (seat, carpet, etc.) used in aviation. There are two results for this flammability test; either pass or fail. In order for a material to be employed in aircraft, it must pass the burning criteria mentioned earlier in the experimental section in detail. In order to satisfy the conditions of the FAR test, flame self-extinguishing time and drip self-extinguishing time should be <15 s and 5 s, respectively. Burn length should be recorded <20.3 cm. For example, the blank PET fabric, even though it has $17.3 (\pm 3.3)$ cm of average burn length less than the maximum allowed length of 20.3 cm, does not pass the FAR test as it does not fulfill the after-flame time requirement which is $28.4 (\pm 18.1)$ s (Table 4, Entry 1). Therefore, FR treatment is necessary to increase the fire resistance of PET fabric.

For back coating, since polymeric binders are required in order to immobilize FR on the backside of the fabric, PET fabric was coated with only polymer matrixes and the flammability was checked in the absence of FR additive (Table 4, Entry 2–4). For this work, three different halogen free polymer binders were used, which are polyurethane (PU), polyvinyl acetate (VA) and acrylicopolymer (AC)-based resins (Table 2).

Table 4

Vertical flammability test results of blank PET and PET fabrics coated with polymer binders without FR.

Entry	PET sample	Add-on (g/m^2)	After-flame time (s)	Burn length (cm)	Result
1	PET (blank)	–	28.4 ± 18.1	17.3 ± 3.3	Fail
2	PET-PU	51	20.4 ± 4.7	29.4 ± 2.0	Fail
3	PET-VA	52	54.0 ± 4.2	30.0 ± 1.0	Fail
4	PET-AC	56	61.0 ± 1.4	31.0 ± 0.0	Fail
5	PET-ED-PU	53	0.0 ± 0.0	11.0 ± 0.2	Pass
6	PET-ED-VA	55	0.0 ± 0.0	13.7 ± 0.3	Pass
7	PET-ED-AC	54	0.0 ± 0.0	11.3 ± 0.6	Pass
8	PET-DP-PU	54	16.3 ± 4.7	21.0 ± 4.6	Fail
9	PET-DP-VA	57	31.5 ± 5.0	23.3 ± 6.0	Fail
10	PET-DP-AC	50	40.0 ± 18.4	28.0 ± 4.2	Fail
11	PET-melamine-PU	56	12.3 ± 6.8	24.0 ± 2.7	Fail
12	PET-DP/melamine (60/40 wt/wt)-PU	61	2.8 ± 3.0	13.3 ± 1.2	Pass
13	PET-APP-PU	60	19.4 ± 4.9	17.4 ± 1.9	Fail

As expected, compared to blank fabric, the flammability increases upon introduction of flammable polymer binders to the PET fabric when there is no FR present (PET-PU, PET-VA and PET-AC). Among all, coating with PU resulted in the least flammable fabric in the vertical burning test, and the flammability increases for VA and AC coatings. On the other hand, even though PET-PU has the best result in the FAR test, it is worth noting that it is the most expensive resin among the three tested.

Afterward, FR additives, namely ED and DP, were applied to improve the fire resistance of PET fabric. All coating pastes were prepared to have the same amount of P content (5 % P) in the dry content for both FRs. The phosphorus content was calculated theoretically and the corresponding amount of ingredients (FR and binder) was blended to have the coating formulations. In order to have a fair comparison regarding the fire performances, the coating amount on PET fabric was kept around of $50 (\pm 10)\text{ g/m}^2$ for back coating.

Table 4 summarizes the result of the flammability test of the PET fabric when treated with ED (Entry 5–7). For all binders, 5 % P was enough to pass the vertical burning test. However, lower %P content was screened to check the limits of the formulations to pass the FR test. While the passing limit was 3 % P for PET-ED-PU and PET-ED-AC fabrics, a minimum concentration of 4 % P was necessary for PET-ED-VA to be successful in the vertical burning test (Tables S1–S3, Supp. info.).

DP-containing formulations offered lower fire performance compared to ED-based formulations. In fact, all the DP coated PET samples (5%P) failed in the FAR 25.853 test (Table 4, Entry 8–10). Since 5 % P in the coating paste, equal to 32 % FR additive, was not sufficient, the P content of the formulations was further increased to 7 % to pass the burning test (Tables S4–S6, Supp. inf.). Among the three polymer binders, formulations of PET-DP-VA (7 % P) clearly failed the vertical burning test. On the other hand, PET-DP-AC (7 % P) was the only one to pass the test with an average burn length of $19.6 (\pm 0.5)$ cm and after-flame time of $10.7 (\pm 4.2)$ s. Although PET-DP-PU (7 %) had slightly better burning results in terms of time and length, it is considered to fail in the FAR test since one of the samples failed among the three replicate.

3.1.2. The effect of synergistic additive on the performance of DP

In the vertical burning test of back-coated PET, it was demonstrated that ED has a better FR performance compared to DP. Thus, to enhance the flame retardancy of DP, a two-component system, consisting of a FR and a synergistic additive, was developed to pass the necessary vertical fire test. Hence, our objective was (i) to reduce the amount of costly reagent, DP in this case, in the FR system with the addition of a cheaper synergistic additive and (ii) to decrease the required phosphorus content in the coating paste.

Melamine was hypothesized to be a suitable synergistic partner for

DP as it is generally utilized as an additive to establish phosphorus-nitrogen synergism [21]. Melamine, having a high nitrogen content in its structure, releases ammonia to dilute flammable gases during pyrolysis, while absorbing heat during the combustion due to endothermic decomposition [22]. Indeed, it can be assumed that the sublimation ability of melamine [23] far below its melting point might basically be effective in a vertical burning test since it can help FR to be transferred to the front side of the fabric and FR system can act before the decomposition of PET fabric. Melamine has been used as an additive for APP to lower onset temperature in TGA, increasing vaporization of FR [24].

For improving the fire performance of DP formulations, PU was preferred as the FR binder since it showed the most promising results in the vertical burning test compared to VA and AC-based formulations. As stated before, PET-DP-PU fabric does not pass the FAR test with 5 % P (Table 4, Entry 8) in which content, FR holds 32 % of the total coating paste. In order to build a comparable system, melamine was dispersed in PU matrix to prepare a coating paste (where 32 % was melamine), whose coating on PET (PET-melamine-PU) did not afford a pass result in the vertical burning test (Table 4, Entry 11). On the other hand, the formulation having DP/melamine (60/40 wt/wt)-PU is an effective FR system for PET as observed in the FAR test, showing an improved after-flame time and burn length (Table 4, Entry 12), even the P content was reduced to 3 % in the coating paste while the amount of total additive was kept constant at 32 %.

From these results, it can be inferred that there is a synergism between DP and melamine in the vertical flame test since DP and melamine individually do not pass the FAR test while their combination with reduced P content was successful (DP/melamine, PU, 60/40 wt/wt, 3% P) in passing the burning test.

3.1.3. Control experiment with APP

As a non-halogenated alternative in conventional FR applications, APP-based formulations are commonly studied for back coating of cotton or blends [10,24,25]. Therefore, the FR performance of ED and DP/melamine was compared with that of APP. For this purpose, an APP-based coating paste with a phosphorus content of 5 % in PU as the polymer matrix was prepared and applied to PET fabric via back coating (PET-APP-PU). The flammability was similarly evaluated via the vertical burning test (Table 4, Entry 13).

Contrary to the fact that ED and DP/melamine coated textiles successfully pass the fire test as presented earlier, PET-APP-PU (as the common FR for back coating) did not pass the FAR. This result confirms the significance of exploring new phosphorus-based FR alternative to existing FR solutions for back coating applications.

3.2. Thermal decomposition pathways and mode of action of FR additives

3.2.1. TGA data

From the FAR test results, it is clearly implied that ED is more effective than DP in FR back coatings of PET. In order to rationalize the different behaviors of two FRs, TGA and DIP-MS experiments were carried out to investigate their volatilization for understanding their comparative action in the gas phase.

Since the FR coating paste is applied to the reverse side of the fabric, the front face does not have a direct interaction with FR. For effective flame retardation, therefore, FR should start to liquefy earlier than the decomposition temperature of fabric during combustion so that diffused FR species can be transferred to act on the front side of the fabric as well. Hence, the relative volatility of the FR is of great importance to determine its FR action. For this reason, thermogravimetric analysis is an essential tool to comprehend the fire behavior of a back-coated sample in a vertical test. The onset temperature obtained from TGA was helpful to estimate the vaporization of FR species in the gas phase.

Although TGA data in air is more relevant to understand the fire performance of fabrics in vertical burning test as the combustion process takes place naturally in the presence of oxygen. Still, TGA in nitrogen

also provides important platform to clearly observe the char formation since the char would not further oxidized by oxygen. Therefore, the more char formation is observed, the more condensed phase activity the FR has, and accordingly it will have less impact on the result of vertical burning test.

According to TGA data, the blank PET has the first onset temperature of around 386 °C (in air) where major mass loss takes place (Fig. S1, Supp. inf.). Therefore, an effective FR for the PET fabric would start to decompose slightly earlier than the fabric so that FR action would take place before the PET ignition.

Thus, TGA results of plain FRs were compared in the absence of polymer binder (Fig. 2), and it was found that ED starts to decompose earlier than DP whereas DP left more char residue. The earlier decomposition of ED could explain its effectiveness as FR in the vertical burning test for the back-coated PET fabric. For ED, the gas phase activity is more pronounced since the early transfer of volatile flame retarding species from the back to the front side of the fabric is important to cease the fire. On the other hand, because of the high char residue left, DP is working mainly in the condensed phase but this property is not reflected in the vertical burning test result because the FR action in the condensed phase is less significant for the back-coated samples [24]. In addition, most thermoplastic polymers including PET form very less char during the burning process. The condensed phase action of DP is not sufficient to significantly increase the char formation of the PET fabric.

Thermogravimetric analysis of plain binders (PU, VA and AC) and FR dispersed in binders (ED-PU, ED-VA, ED-AC, DP-PU, DP-VA and DP-AC) were also conducted (Figs. S2–S4, Supp. inf.). Nitrogen-containing polyurethane PU resin has the lowest onset temperature in TGA compared to other plain binders (VA and AC). For this reason, PU-based FR coating pastes have relatively better results in the vertical burning test as discussed earlier. PU degrades earlier than the other binders in both air and nitrogen, which promotes the volatilization of FR compared to other binders. This could lead to P,N synergism and/or the presence of nitrogen in PU which is effective in the gas phase [26]. Furthermore, a similar degradation trend was observed for ED and DP dispersed in coating pastes, and FRs in PU experienced early thermal transitions in TGA carried out in air. As expected, ED-containing matrixes decomposed earlier compared to the corresponding DP-based binders. These results are in agreement with the outcome of the FAR test.

For the DP/melamine-PU-based system, flammability behavior in the FAR test correlates with the data obtained from TGA (Fig. 3). While DP-PU works in the condensed phase and leaves a considerable char residue, melamine-PU dispersion has a much lower onset decomposition temperature and almost no char residue is left. However, the addition of melamine to DP results in the reduction of the onset temperature of the formulation (DP/melamine (60/40 wt/wt)-PU), showing that melamine accelerates the volatilization of DP; as a result, the combination has a better result in the vertical burning test.

3.2.2. DIP-MS data

DIP-MS experiments were performed to analyze the gas phase active phosphorus-containing volatiles produced during the pyrolysis process. Fig. 4 shows the total ion chromatogram of plain ED and DP. Based on the species detected in DIP-MS experiments, the FR mechanism for DP was previously postulated by Salmeia et al. (Scheme 1) [15]. Accordingly, the DOPO part of DP is responsible for the gas phase fire retardation by releasing PO^\bullet radicals ($m/z = 47$). Even though the relative ion concentration corresponding to $m/z = 47$ is quite low, the presence of DOPO ($m/z = 216$) and dibenzofuran ($m/z = 168$) species in chromatogram indirectly demonstrates the release of PO^\bullet radicals (Fig. S5b). On the other hand, PEPA works in the condensed phase via the formation of phosphoric acid, catalyzing char formation (Scheme 1), which explains the considerable amount of char residue of DP (Fig. 2). ED starts to release volatiles earlier than DP. DOPO moiety in ED produces the same volatiles ($m/z = 47, 168$ and 216) to work in the gas phase as

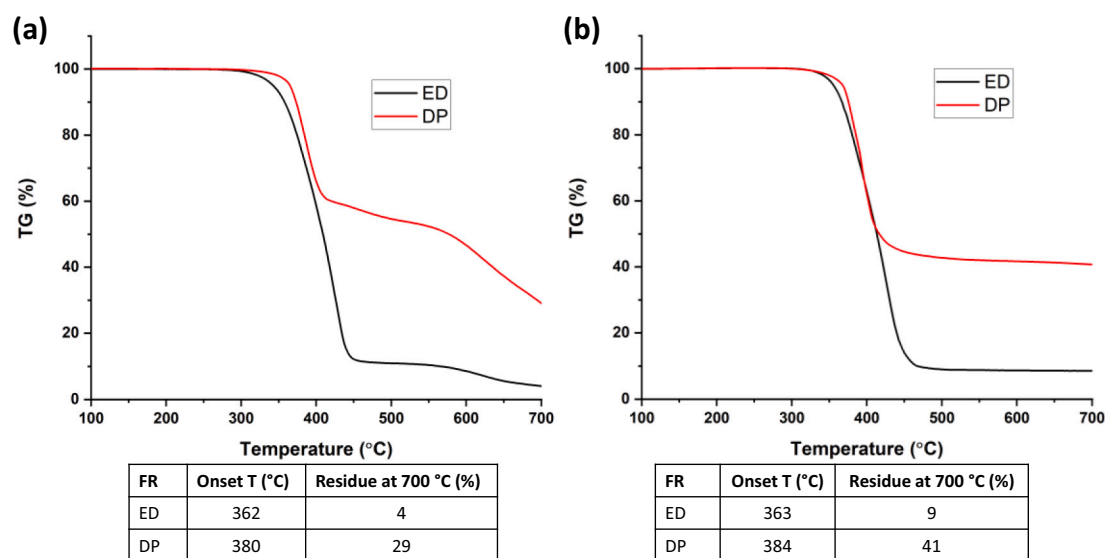


Fig. 2. TGA data of ED and DP (a) in air and (b) in N₂.

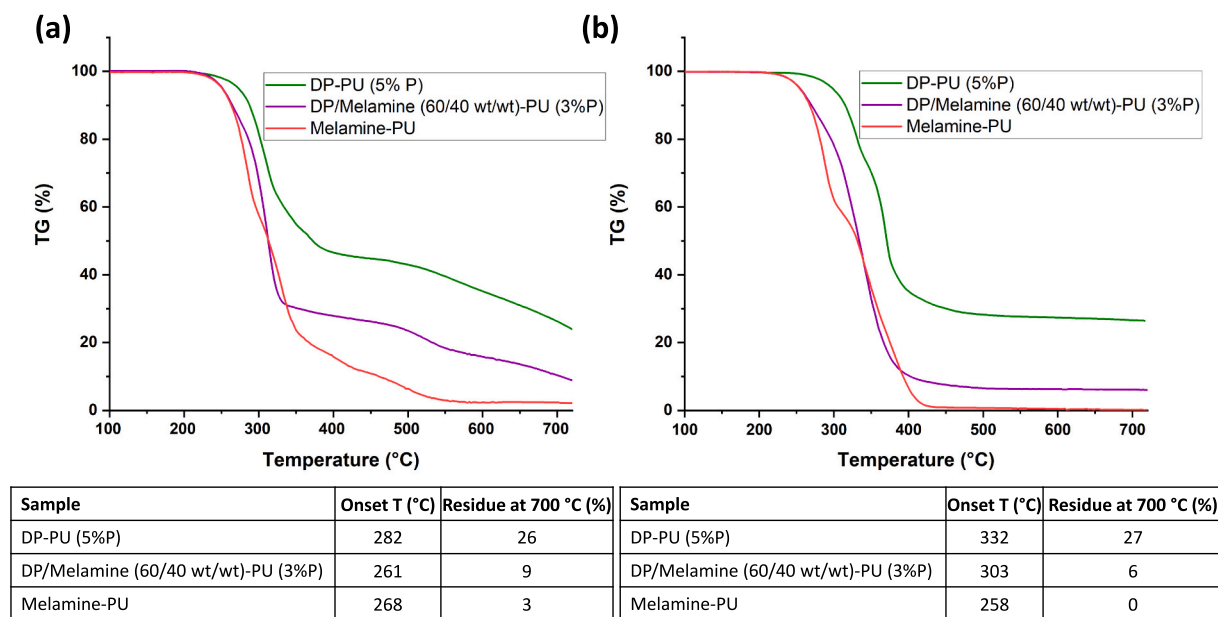


Fig. 3. TGA data of FR coating pastes-containing DP and/or melamine in PU (a) in air and (b) in N₂.

detected by DIP-MS (Fig. S5a).

Furthermore, total ion chromatograms of FRs in binders (PU, VA and AC) were compared (Fig. S6), and it supports the data obtained from TGA. Among all, PU is the most suitable polymer matrix for both DP and ED because FRs in PU start to release volatiles earlier than that in VA and AC. ED-PU starts to produce volatiles around 5 min 50 s (corresponding temperature of 360 °C) while pyrolysis for DP-PU starts to generate volatiles at 6 min 20 s (corresponding temperature of 402 °C). As a result, DIP-MS data correlates well with the successful FAR test results with the early emergence of gas phase active species.

DIP-MS data (Fig. 5) further enlightens the successful vertical burning test result of the DP/melamine-PU system. Melamine-PU starts to release volatiles earlier than DP-PU (around 5 min 30 s). Decomposition of melamine is well studied and known to take place in three steps, condensation products, melam, melem and melon, are formed; as a result, NH₃ gas is released (Scheme 2) [27,28]. In the extracted DIP-MS

data of melamine-PU, the condensation products of melamine (melam, melem and melon) were detected (Fig. S7a, Supp. inf.), indirectly showing the release of ammonia gas. The concentrations of condensation products are quite low in the total chromatogram, and it is due to the fact that condensation products have higher thermal stability [22] and are less likely to fly in MS. On the other hand, DP-PU, as expected, releases volatile species at a higher temperature, appearing after 6 min in the chromatogram.

Nonetheless, gas phase active species were detected earlier for DP/melamine-PU-based formulation than both DP-PU and melamine-PU (Fig. 5). In the extracted ion chromatography, phosphorus-based volatiles coming from DP was observed for DP/melamine-PU. Also, the presence of melamine condensation products is the evident for formation of ammonia gas (Fig. 6). Due to the liberation of ammonia gas as non-combustible gas, flammable volatiles would be diluted and the heat formation would be lowered.

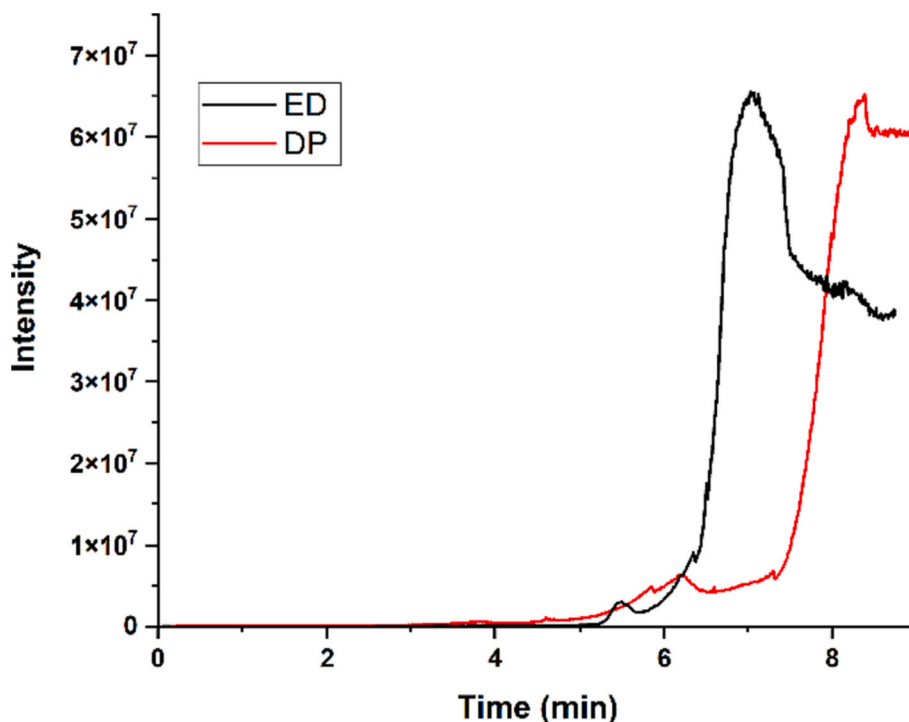
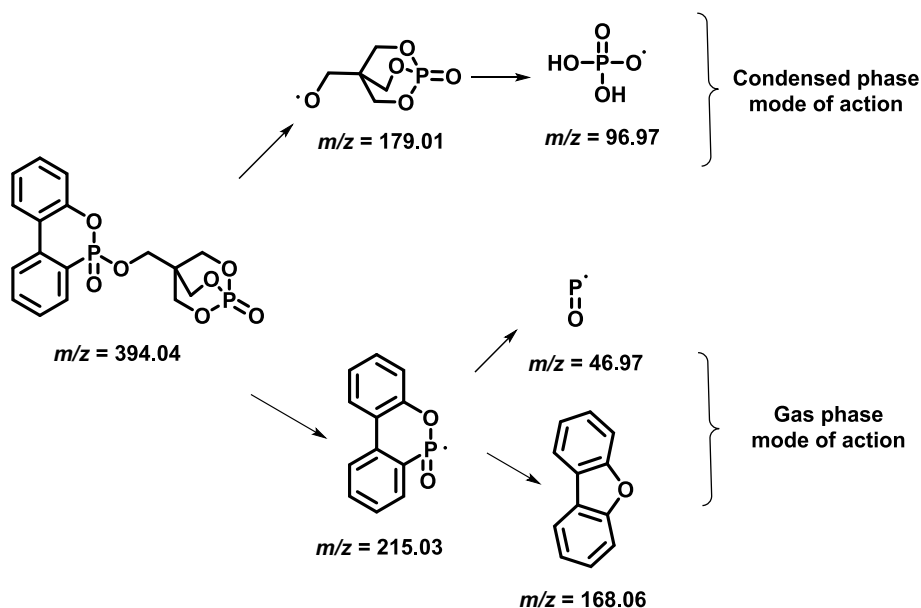


Fig. 4. Total ion chromatogram of ED and DP obtained from DIP-MS.



Scheme 1. Thermal decomposition of DP [15].

3.3. Heat release rate measurement

In a conventional MCC measurement, the pyrolysis was carried out in nitrogen atmosphere and it was followed by the oxidation of pyrolysis products. The resulting HRR is determined based on the oxygen consumption. The curves of the blank polymer resins are presented in Fig. S7. From the analysis it is shown that VA has the lowest value for THR (22.3 ± 0.3 kJ/mol) and pHRR (286.7 ± 11.0 W/g); on the other hand, PU and AC exhibit similar THR values which are $31.4 (\pm 0.1)$ and $30.1 (\pm 0.1)$ kJ/g respectively, and AC shows the highest pHRR which is $601.2 (\pm 13.1)$ W/g.

When the FR additives were blended with polymer resins, they

showed similar heat release trends. FR-VA formulations showed lower THR compared to AC and PU-based counterparts (Fig. 7). In terms of THR of FRs, DP formulations exhibit lower THR values compared to ED formulations with respective resins. This fact can be attributed to the char formation ability of DP, which suppresses the heat release. The results obtained from MCC do not justify the behavior of fabric in the vertical burning test. On the contrary, reduction in heat release is directly proportional to the char formation capacity of the FR, yet it is required to have a mechanism working in the gas phase for the vertical burning test.

Simultaneously, THR and pHRR are also reduced upon the addition of melamine to DP in PU resin (Fig. S8, Supp. inf.) although this

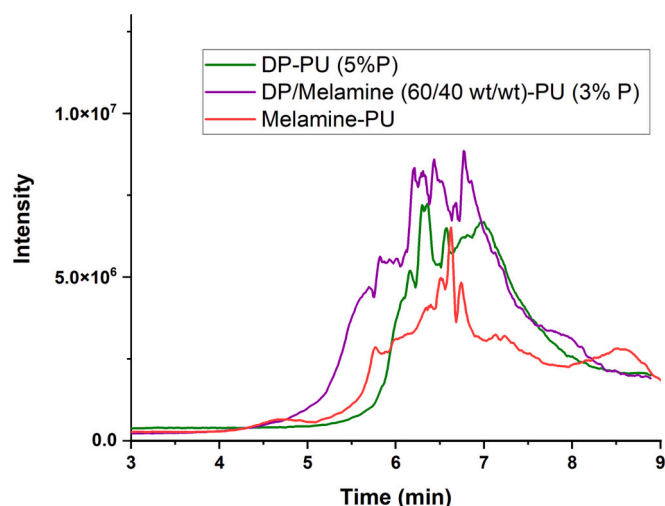
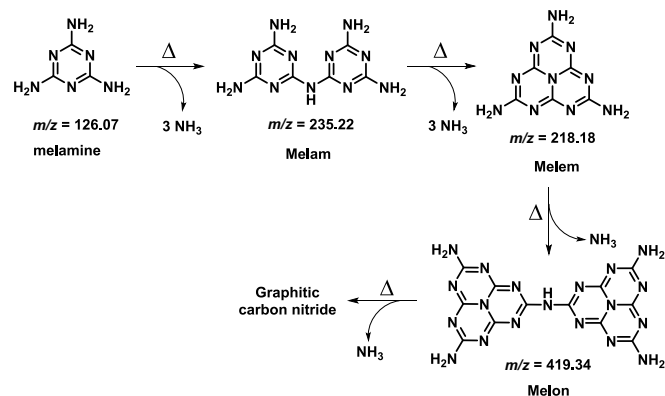


Fig. 5. Total ion chromatogram of coating pastes-containing DP and/or melamine obtained from DIP-MS.



Scheme 2. Thermal decomposition of melamine [22].

reduction may not have a significant role in explaining the successful FAR test result for DP/melamine-PU. While DP-PU and melamine-PU have pHRR of $532.8 (\pm 68.7)$ and $235.3 (\pm 3.5)$ W/g respectively, the pHRR of DP/melamine-PU was measured as $283.5 (\pm 4.4)$ W/g, experiencing a drastic reduction compared to DP-PU.

Cone calorimetry provides additional parameters closely representing the real fire scenario. Thus, further fire evaluations of the coated textiles using cone calorimeter were performed and the relevant data are shown in Figs. S9–11 (Supp. inf.). Compared to the blank PET, the THR increased for binder only coated fabrics. This correlates well the vertical burning results. Among the binder only coated fabrics, PU coated PET (PET-PU) has the highest pHRR (360.7 ± 11.9 kW/m²), whereas the blank PET has the lowest pHRR (245.3 ± 23.0 kW/m²) value. The pHRR values measured for PET-VA and PET-AC was $259.3 (\pm 9.6)$ and $349.5 (\pm 17.6)$ kW/m² respectively. On the other hand, TSR reduced upon coating for PET-PU and PET-AC compared to blank fabric (Fig. S9, Supp. inf.) which could be due to the effect of binders. In comparison, for the FR coated fabrics, ED coatings showed lower pHRR compared to DP coatings, correlating well with the vertical burning results. DP-coated fabrics showed lower TSR (Figs. S10 and 11, Supp. inf.), which could be attributed to preferential condensed phase activity of PEPA component of DP-PET fabrics with VA based coatings exhibited the least reduced pHRR and av-EHC.

3.4. Quantitative expression of synergism between DP and melamine

So far, the phenomenon of synergism between DP and melamine was discussed qualitatively. In order to prove the existence of synergism quantitatively in a defined concentration of FR and synergistic additive, Weil and Lewin propose an equation to determine the synergistic effectivity (SE) [29,30]. Accordingly, by using flammability parameters obtained from a fire test, such as LOI value, synergistic effectivity can be calculated to express whether a synergism occurs between two species. The formula for SE calculation is shown below [31].

$$SE = \frac{(Fp)_{fr+s} - (Fp)_p}{[(Fp)_{fr} - (Fp)_p] + [(Fp)_s - (Fp)_p]}$$

where (Fp) is the parameter obtained from burning tests. In this case, it represents the burn length measured in the FAR 25.853 test. $(Fp)_p$ is the FR parameter of the polymer alone, $(Fp)_{fr}$ is that of the polymer and FR, $(Fp)_s$ is that of the polymer treated with the synergist, and $(Fp)_{fr+s}$ is that of the full formulation-containing FR and synergist.

If the SE value is >1 , it indicates synergism between two additives. In case of SE value between 0 and 1, there is no synergistic effect, but it means just a simple addition effect of two substances. On the other hand, if the SE has a negative value, it indicates that two substances are antagonistic.

For this work, burn length from the FAR test was used as the parameter to determine synergistic effectivity according to the equation given above. Burn length of PET-DP/melamine-PU formulation is 13.3

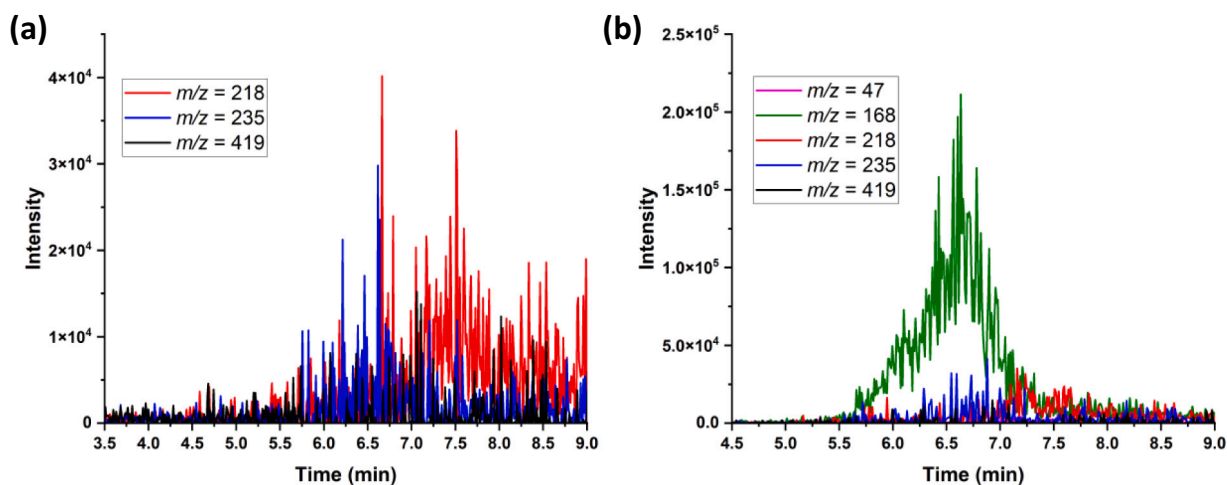


Fig. 6. Extracted ion chromatogram obtained from DIP-MS for (a) melamine-PU and (b) DP/melamine (60/40 wt/wt)-PU with 3%P (The structures of the corresponding m/z values are depicted in Schemes 1 and 2).

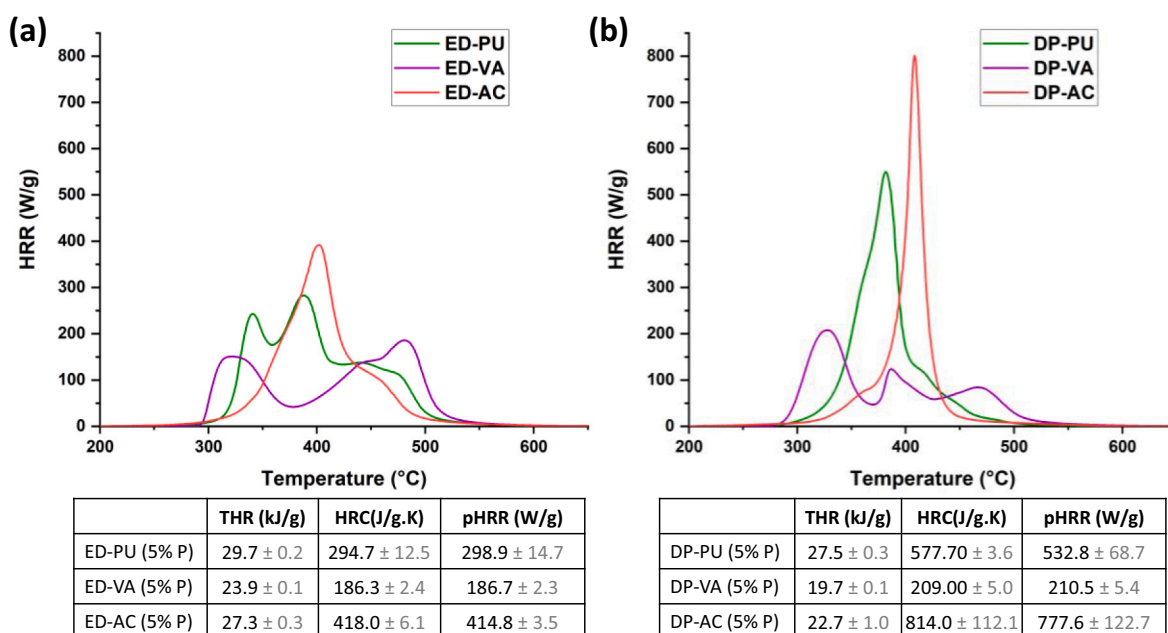


Fig. 7. HRR of coating pastes (5 % P)-containing FR (a) ED and (b) DP in corresponding binders measured via MCC.

Table 5

FAR 25.853 test results of back coated PET fabrics to calculate SE for DP and melamine synergism.

Parameters	PET sample	Burn length (cm)	After-flame time (s)
$(Fp)_p$	PET-PU	29.4	20.4
$(Fp)_{fr}$	PET-DP-PU	21.0	16.3
$(Fp)_s$	PET-melamine-PU	24.0	12.3
$(Fp)_{fr+s}$	PET-DP/melamine (60/40 wt/wt)-PU	13.3	2.8
SE		1.5	1.4

cm $[(Fp)_{fr+s}]$, while that of PET-DP-PU and that of PET-melamine-PU are 21.0 cm $[(Fp)_{fr}]$ and 24.0 cm $[(Fp)_s]$ respectively. As the burning parameter for blank PET fabric, the burn length of PU coated PET (PET-PU) without any FR $[(Fp)_p]$ was used, which is 29.4 cm (Table 4). By using these parameters, SE was calculated as 1.5, which confirms quantitatively the synergistic interaction between DP and melamine (Table 5). In addition to burn length, after-flame time was also used to determine SE, which was calculated as 1.4 as depicted in Table 5. As a result, synergism was observed by using both parameters obtained from the FAR test.

4. Conclusion

Since most back coating formulations used in industry are currently based on halogenated FR solutions, there is an urgent need for replacing the present FR systems with effective eco-friendly solutions. Accordingly, ED and DP as potential halogen free alternative additives were screened for the back coating formulations of PET fabric and the flammability of the coated fabrics was evaluated via a vertical burning test. ED formulations were found to have higher FR efficacy than DP as it releases active FR species in the gas phase at lower decomposition temperature. On the other hand, DP works essentially in the condensed phase, which explains its lack of fire performance in the vertical burning test. Moreover, three different polymer resins were employed for immobilizing the FR on the backside of PET fabric. Compared to polyvinylacetate and acryl copolymer resins, the use of polyurethane-based resin showed favorable results in the FAR test. The fire performance of

DP was enhanced by the introduction of melamine as a synergistic additive. Melamine acts as a source of volatile nitrogen products and enhances the vapor phase activity of DP; thereby, improving the fire performance in the vertical burning test. The flammability behavior of the back coating formulations was rationalized by the reduction of onset temperature in TGA and the relatively early emergence of phosphorus volatiles in DIP-MS. MCC data further provided insight into the burning behavior of these formulations.

For synthetic textiles, there are limited back coating FR solutions currently available. In this work, it was demonstrated that the use of two potential phosphorus-based FRs is suitable for FR back coatings of PET fabric. In the future, such formulations could also be evaluated for flame retardation of technical textiles composed of polyamides and polyolefins.

CRedit authorship contribution statement

Merve S. Özer: conceived, planned, carried out the experiments and wrote the manuscript.

Marie-Jasmine Wesemann: contributed to carry out the experiments.

Sabyasachi Gaan: conceived and planned the experiments, and provided critical feedback and helped shape the research, analysis and writing the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2022.107363>.

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