

## PROPERTIES OF NON-FLAMMABLE INSULATING POLYMERS

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### Summary

The basic disadvantages of polymeric materials are low temperature resistance and high flammability. Polymers themselves can be treated as fuels, feeding the fire and, consequently, increasing hazards to people, property and environment. Polymers used as electric insulators are particularly hazardous. That is why in this paper the attempts to make polypropylene (commonly used in electric devices as insulator) non-flammable are presented. The obtained material was tested by means of cone calorimeter which in itself is interesting due to the uniqueness of this kind of apparatus.

**Keywords:** cone calorimeter, flame retardants, polymers

### Właściwości uniepalnionego izolacyjnego materiału polimerowego

#### Streszczenie

Wadą materiałów polimerowych jest mała odporność na wysoką temperaturę i ogień. Są traktowane często jako paliwa podtrzymujące ogień. Cecha ta powoduje, że zwiększa się zagrożenie pożarem, stwarzając niebezpieczeństwo dla ludzi i środowiska. Materiały polimerowe stosowane w różnych gałęziach techniki muszą spełniać określone wymagania dotyczące bezpieczeństwa przeciwpożarowego. Do tej grupy zalicza się również materiały stosowane na obudowy, osłony kabli oraz izolatory elektryczne, szczególnie narażone na działanie wysokiej temperatury. W pracy podjęto próby uniepalniania polipropylenu (materiał stosowany w budownictwie). Wytworzony materiał, po wprowadzeniu uniepalniacza, poddano weryfikacji za pomocą kalorymetru stożkowego, najnowocześniejszego urządzenia do określania palności.

**Słowa kluczowe:** kalorymetr stożkowy, środki zmniejszające palność, materiały polimerowe

## 1. Introduction

Polymers due to their insulating properties are commonly used for a protection applied to electrical conductors, insulating channels, housings of electrical switching stations and similar devices. All materials applied for this purpose, apart from having good dielectric properties, should have one

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important feature: be non-flammable. However, polymers are highly flammable materials which increases propagation of fire. That is why they must be modified by additives called flame retardants which bring about limitation of this undesired property [1, 2]. These additives slow down and dampen the burning process by chemical and physical interaction in either solid or gaseous state. There is a number of flame retardants; the most frequently used are the ones based on halogen compounds, hydrocarbons, nitrogen, aluminum and magnesium. Due to increasing requirements concerning fire protection, the worldwide demand for non-flammable polymers and, consequently, for flame retardants is permanently growing at the rate of 4% annually in the USA, the EU and Japan [3].

The thorough knowledge of the polymer burning process enables us to apply the flame retardants in a proper way. Many testing methods are used in order to determine the behaviour of polymers in a real fire [4]. One of such methods is the testing by means of cone calorimeter which derives its name from the conical shape of the heater. There are just a few such instruments in Europe thus their application is interesting itself. In Poland reasonable results obtained with cone calorimeters be a rare breed [5, 6]. This apparatus applies the principle that the heat released at burning most materials is proportional to the amount of the consumed oxygen. The rate is 13.1 MJ per 1 kg oxygen (+/- 5%).

The apparatus fully simulates the conditions of the real developed fire and measures the following parameters [7-9] :

- Time to Ignition (TTI) ,
- Fuel Load (FL),
- Total Heat Rate (THR) ,
- Total Oxygen Consumed (TOC),
- Total Smoke Release (TSR),
- Total Smoke Production (TSP) ,
- Carbon Monoxide Yield (CMY) ,
- Carbon Dioxide Rate (CDY) .

In this paper one of the most popular polymer applied as electrical insulators, namely polypropylene, has been tested with the mentioned cone calorimeter. The polymer was made non-flammable by admixing two different flame retardants: one halogen based and the other – non-halogen one. The effects of these two fillers upon the properties of the material have been compared. No such kind of comparison is known; the Authors usually compare flame retardants of the same kind [10, 11]. From this point of view the results applied in this paper are novelty.

## 2. Materials used

The basic polymer applied in this work was polypropylene SABIC 531P intended for injection moulding and extrusion, manufactured by Dutch company SABIC. Its Melt Flow Index is 0.30g/10 min (at 2 kg, 230°C).

As mentioned above, two flame retardants were used, both supplied by A. Schulman:

- Organic-halogen POLYBATCH MPL 2171, based on bromium compounds and antimonium trioxide. The manufacturer's information is that some additives (carbon black, calcium carbonate, antistatics) can affect its performance and make it UV sensitive. Also, materials containing this filler must have no contact with food. Its melt temperature is 160°C, ignition temperature is above 300°C, decomposition begins at 250°C.

- Non-halogen POLYBATCH FRLS 1971 which, according to manufacturer, is featured by low heat emission, good smoke reduction and only minor effect on the mechanical properties of the modified material. In fire it releases carbon monoxide, monomers, nitrogen oxides and some other gases and fumes. Its temperatures are: melting – 80-120°C, ignition – above 300°C, decomposition – 240°C.

Four mixtures containing: 5%, 10%, 15%, 20% of the flame retardant were prepared. Paddle-shaped specimens were then injection moulded. Some of them were used for strength testing in accordance with PN-EN ISO 527-2:1998, the others underwent flame and smoke emission tests with the aid of cone calorimeter, in accordance with ISO 5660-1:2002.

## 3. Description of the cone calorimeter

Testing by means of the cone calorimeter is one of the most interesting methods in determining flammability of polymers, smoke emission intensity and toxicity of the fumes. In spite of it, there are no detailed criteria of material flame properties evaluation worked out so far. The scheme of the cone calorimeter can be seen in Fig. 1 [12]. The specimen tested should be a flat square 100x100 mm of the thickness not exceeding 50 mm. It can be positioned either horizontally or vertically. The test consists in exposing the surface of the specimen (2) to the heat flux of up to 100 kW/m<sup>2</sup> generated by the cone heater (4). The released gaseous substances are then ignited by the spark igniter (3). During burning the fumes are collected by the outlet shield (5) and directed for further analysis. Sensors and the accompanying devices (6 to 12) are described in the caption to Fig. 1.

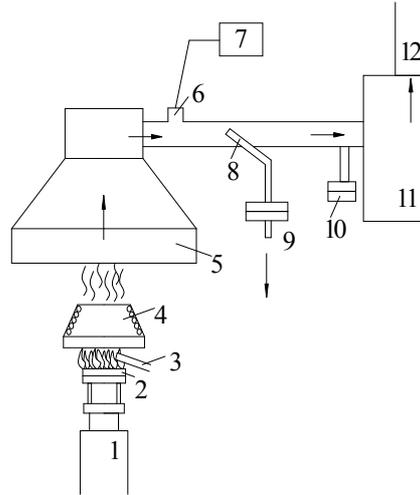


Fig. 1. Scheme of the cone calorimeter [12]: 1 – loss of weight sensor, 2 – Specimen, 3 – spark igniter, 4 – cone heater, 5 – fume cupboard, 6 – fume dispenser, 7 – sensor of oxygen concentration, 8 – carbon black dispenser, 9 – carbon black detector, 10 – laser meter of smoke intensity, 11 – exhaust fan, 12 – temperature measurement point

#### 4. Analysis of the experimental results

In order to determine the effect of the flame retardants upon the mechanical strength of the material, standard tensile tests were performed. The results are presented at Fig. 2. It can be seen that the drop of strength is insignificant; for the non-halogen filler it is, however, slightly bigger.

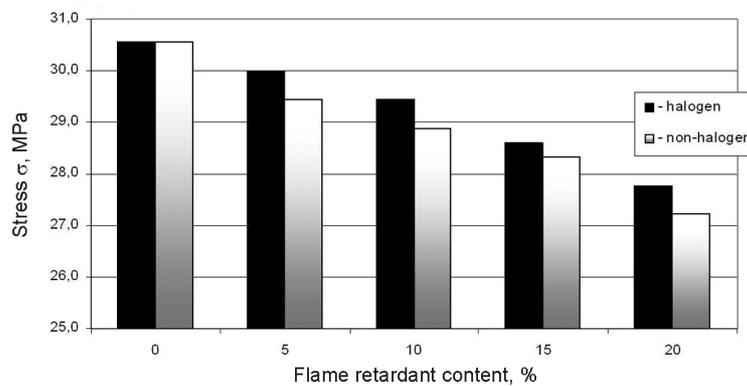


Fig. 2. Effect of the flame retardant content on the tensile strength of the filled polypropylene

Prior to the measurements with the cone calorimeter, the optimal heat flux had to be adjusted. It was started at the level of  $25 \text{ kW/m}^2$  which appeared too low – the specimen did not burn even if the material did not contain any flame retardant (Fig. 3). After some attempts, the flux of  $50 \text{ kW/m}^2$  was found as appropriate and was used throughout. The calorimeter at work can be seen at Fig. 4. The obtained values of flame and smoke parameters are presented in Table 1 and 2 respectively.



Fig. 3. Specimen of material without flame retardant after testing at the flux of  $25 \text{ kW/m}^2$  – no ignition observed



Fig. 4. Cone calorimeter at work

### Evaluation of the flame parameters

The measured flame parameters, mentioned previously in the introduction, are as follows:

- Time to ignition TTI, s,
- Fuel load FL, MJ/kg, energy released from 1 kg of material,
- Total heat rate THR, MJ/m<sup>2</sup>, energy released from 1m<sup>2</sup> of the specimen,
- Total oxygen consumed TOC, g,

Table 1. Values of flame parameters

Mixture number	Flame retardant content, %	Polymer content, %	Time to ignition TTI, s	Fuel load FL, MJ/kg	Total heat rate THR, MJ/m <sup>2</sup>	Total oxygen consumed TOC, g
Non – halogen flame retardant						
1	0	100	44	33,66	129,9	86,7
2	5	95	43	28,07	125,6	84,9
3	10	90	47	27,4	119,35	83,9
4	15	85	45	27,09	116,5	79,1
5	20	80	44	26,99	115,7	76,9
Halogen flame retardant						
6	0	100	44	33,66	129,9	86,7
7	5	95	46	31,75	122,9	84,9
8	10	90	48	29,48	116,9	82,3
9	15	85	60	26,59	105,9	76,1
10	20	80	64	23,08	93,2	69,4

The results presented in Fig. 5 show that the halogen filler performs much better properties than the non-halogen one, particularly when its contents exceed 15%. Time to ignition increases from 44 to 60-64 s which is a positive phenomenon. For the non-halogen flame retardant it remains almost constant.

Both flame retardants cause drop of fuel load (Fig. 6) from 33.66 to 23-27 MJ/kg. The actions of them both seem comparable; at high contents of the filler the halogen one works slightly better.

The results obtained for total heat rate (Fig. 7) and total oxygen consumption (Fig. 8) show again that the halogen flame retardant acts better than its counterpart. The drop of THR is worth noticing; its value is reduced from 130 to 93 MJ/m<sup>2</sup> (drop of 28%) for the halogen one while it is reduced from 130 to 115 MJ/m<sup>2</sup> (only 11.5%) for the non-halogen one. The same trends occur in total oxygen consumption. The drop of the values for the halogen filler and the non-halogen one are 20 and 11% respectively.

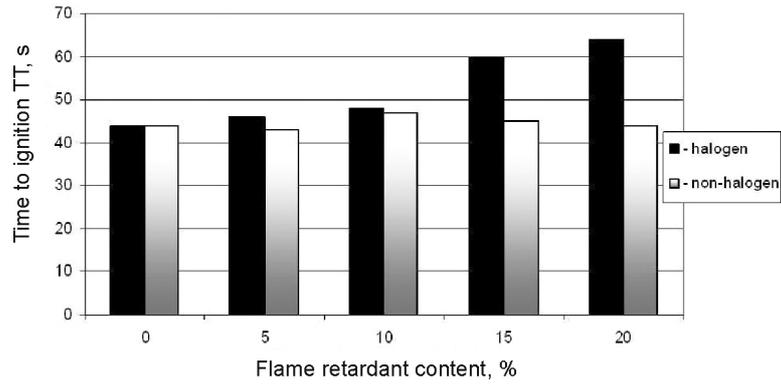


Fig. 5. Time to ignition versus flame retardant content

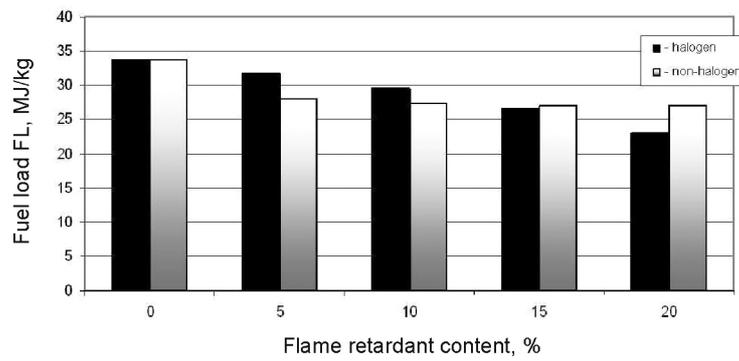


Fig. 6. Fuel load versus flame retardant contents

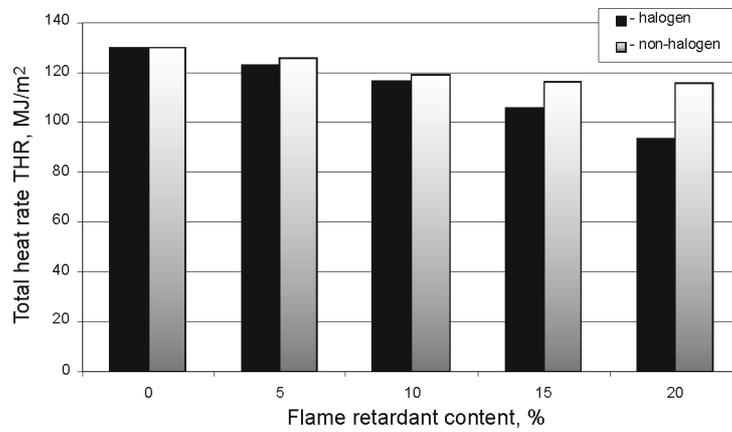


Fig. 7. Total heat rate versus flame retardant content

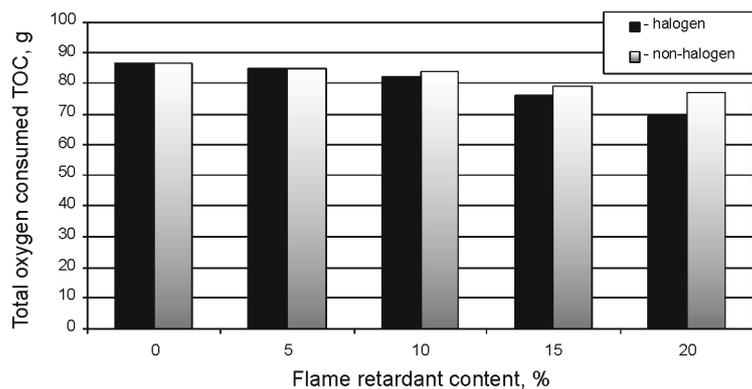


Fig. 8. Total oxygen consumption versus flame retardant content

### Evaluation of the smoke parameters.

The smoke parameters, mentioned previously are as follows:

- Total smoke release TSR,  $m^2/m^2$ ,
- Total smoke production TSP,  $m^2$ ,
- Carbon monoxide yield CMY, kg/kg,
- Carbon dioxide yield CDY, kg/kg,

Their values are presented in Table 2.

Table 2. Values of smoke parameters

Mixture number	Flame retardant content, %	Polymer content, %	Total smoke release TSR, $m^2/m^2$	Total smoke production TSP, $m^2$	Carbon monoxide Yield CMY, kg/kg	Carbon dioxide Yield CDY, kg/kg
Non-halogen flame retardant						
1	0	100	1988	17,6	0,27	2,41
2	5	95	2205,9	19,3	0,41	2,32
3	10	90	2590,5	22,9	0,55	2,24
4	15	85	2941,4	26	0,63	1,99
5	20	80	2835,6	25,1	0,72	1,76
Halogen flame retardant						
6	0	100	1988	17,6	0,27	2,41
7	5	95	1804,8	16,9	0,27	2,6
8	10	90	1691,16	14,95	0,28	2,45
9	15	85	1625	14,3	0,3	2,43
10	20	80	1527	13,5	0,33	2,33

Both parameters indicating smoke emission (TSR – Fig. 9 and TSP – Fig. 10) show the obvious positive effect of the halogen flame retardant and the striking negative effect of the non-halogen one. The former lowers the smoke emission by 23% while the latter raises it by 33-42%.

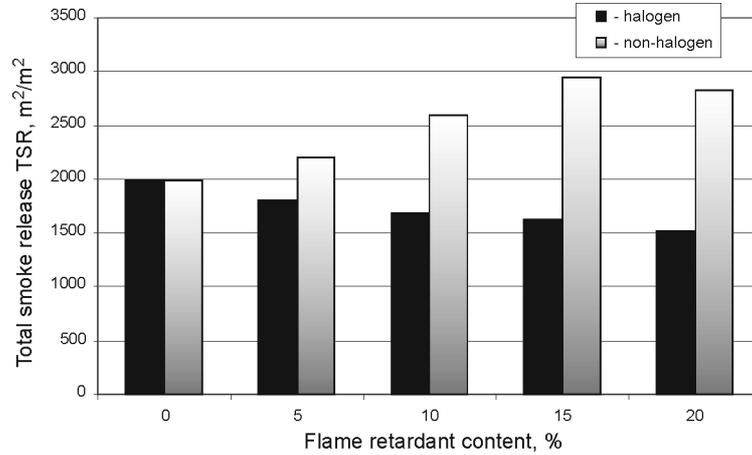


Fig. 9. Total smoke release versus flame retardant content

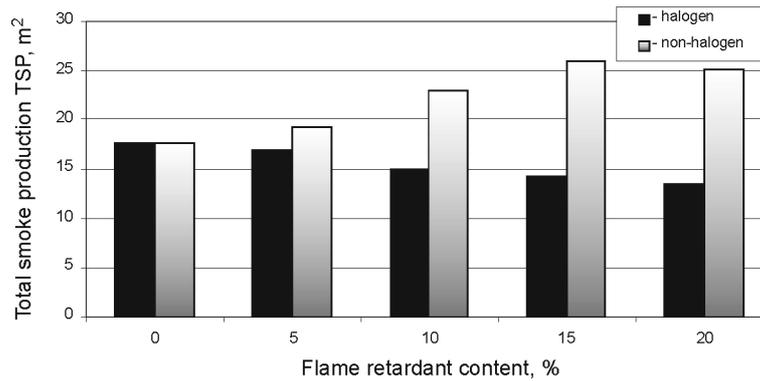


Fig. 10. Total smoke production versus flame retardant content

The last measured parameters: carbon monoxide yield (CMY) and carbon dioxide yield (CDY) are presented in Fig. 11 and 12, respectively. Here both flame retardants rise CO emission but the non-halogen one does it in a dramatic way (160% rise compared to 22% rise for the halogen filler). In the category of CO<sub>2</sub> emission, the non-halogen flame retardant performs much better (drop by 27%) while for the halogen one the CDY parameter remains practically constant. The final drop by 3.3% may be due to the measurement fluctuation.

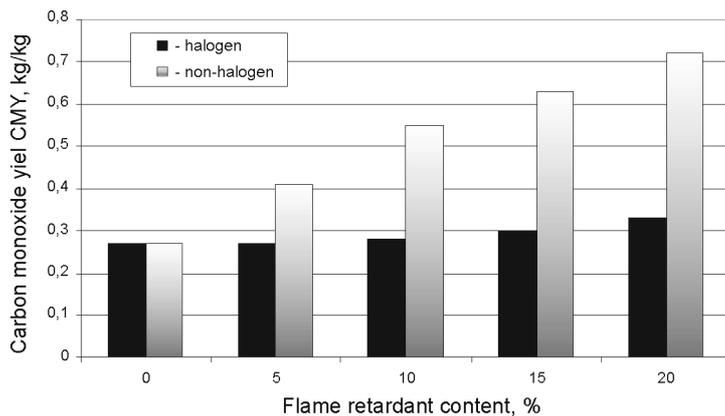


Fig. 11. Carbon monoxide yield versus flame retardant content

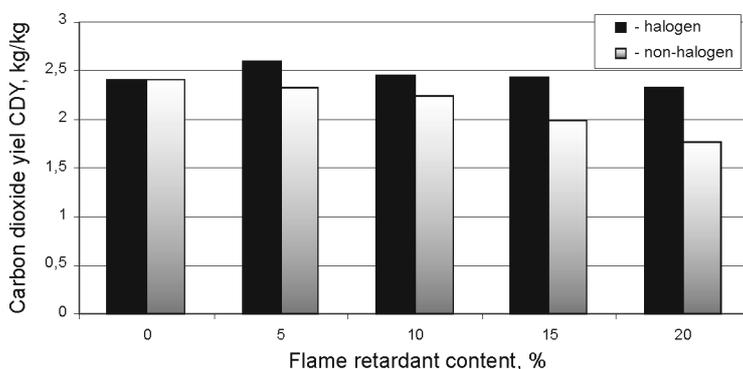


Fig. 12. Carbon dioxide yield versus flame retardant content

## 5. Conclusions

As could be seen, the results obtained with the help of the cone calorimeter are numerous and the number of evaluated parameters equals nine, that is:

- mechanical strength,
- 4 flame parameters,
- 4 smoke parameters.

In order to be able to generalize the results and to draw final conclusions, some synthesis of the values of the obtained parameters seemed necessary. Thus an index which might well represent the change of each parameter was introduced. This index, designated as V (variation), can be defined by the formula (1).

$$V = 100\% \left( \frac{P - P_0}{P_0} \right) \quad (1)$$

where: P – value of the parameter for the given flame retardant contents,  
P<sub>0</sub> – value of the parameter for the pure polymer (a reference value).

Applying the index, the changes of all evaluated parameters can be presented in Table 3. which can be seen below. It should be stressed that this simple method indicates not only the percentage rate of the change but also increasing or decreasing of the values (plus or minus in the table).

Table 3. Statement of the parameters change obtained for the non-flammable polypropylene

Mixture number	Flame retardant content, %	Change of parameters V, %								
		$\sigma_{max}$	TTI	FL	THR	TOC	TSR	TSP	CMY	CDY
Non-halogen flame retardant										
2	5	- 3,6	-2,3	-16,6	-3,3	-2,1	11,0	9,7	51,9	-3,7
3	10	- 5,5	6,8	-18,6	-8,1	-3,2	30,3	30,1	103,7	-7,1
4	15	- 7,3	2,3	-19,5	-10,3	-8,8	48,0	47,7	133,3	-17,4
5	20	-10,9	0,0	-19,8	-10,9	-11,3	42,6	42,6	166,7	-27,0
Halogen flame retardant										
7	5	- 1,8	4,5	-5,7	-5,4	-2,1	-9,2	-4,0	0,0	7,9
8	10	- 3,6	9,1	-12,4	-10,0	-5,1	-14,9	-15,1	3,7	1,7
9	15	- 6,4	36,4	-21,0	-18,5	-12,2	-18,3	-18,8	11,1	0,8
10	20	- 9,1	45,5	-31,4	-28,3	-20,0	-23,2	-23,3	22,2	-3,3

In order to make the table more clear, all variations were subdivided into three groups :

- Shaded – positive changes i.e. betterment of the material. It should be stressed that it has nothing to do with the +/- sign. For most flame and smoke parameters, all – V denotes that the amounts of heat, smoke or toxic fumes have decreased thus it is a positive change,
- Non-shaded, bold type – negative changes,
- Non-shaded, italics – undetermined changes (ambiguous results).

Thus the table gives reason to conclude that the used halogen flame retardant generally performs much better than the non-halogen one. While the drop of mechanical strength is in both cases insignificant and comparable, all flame parameters indicate better positive changes for the halogen flame retardant, particularly for its high contents. When it comes to smoke parameters, the difference is even more striking. Both TSR and TSP are improving for the

halogen filler and are much worsening for the non-halogen one. The CO emission (CMY) increases significantly for the halogen one while for its counter-part the increase is dramatic (166%). Only the CO<sub>2</sub> emission drops for the non halogen flame retardant and it is the only point where it is advantageous compared to its counterpart. Yet it is of much less importance than the negative changes (TSR, TSP, CMY) or less positive changes (all flame parameters) than for the halogen flame retardant. It should be kept in mind that carbon dioxide is a neutral gas while carbon monoxide is a poison. The obtained results are surprising because:

- The flame retardants do not behave exactly as the manufacturers describe them,
- The worse performance of the non-halogen flame retardant compared to the halogen one is in contradiction with the common opinion saying that halogen fillers should be withdrawn from use or, at least, omitted at all cost.

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