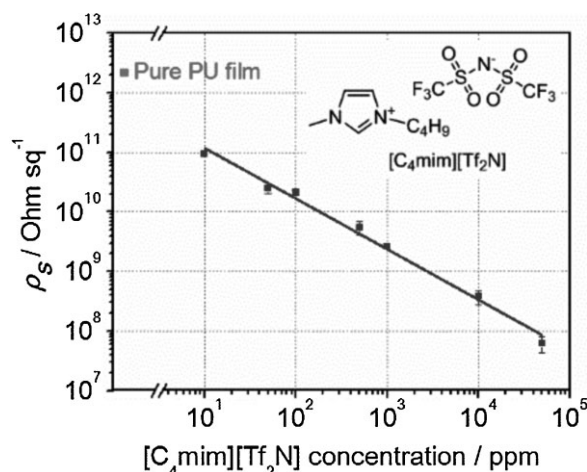


# Bis(trifluoromethanesulfonyl)imide-Type Ionic Liquids as Excellent Antistatic Agents for Polyurethanes<sup>a</sup>

Takuya Iwata, Akiko Tsurumaki, Saori Tajima, Hiroyuki Ohno\*

Surface resistivity ( $\rho_s$ ) of polyurethane (PU) films is reduced from  $2.1 \times 10^{12}$  to  $9.4 \times 10^{10}$  ohm sq<sup>-1</sup> by addition of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C<sub>4</sub>mim][Tf<sub>2</sub>N]) for only 10 ppm. Addition of [Tf<sub>2</sub>N]-type ionic liquids (ILs) for 1 000 ppm leads to the reduction of not only  $\rho_s$  from  $10^{12}$  to  $10^9$  ohm sq<sup>-1</sup> but also volume resistivity ( $\rho_v$ ) from  $10^9$  to  $10^7$  ohm cm, suggesting that the ILs are uniformly incorporated into the PU films. These PU films have  $\rho_s$  in the order of  $10^9$  ohm sq<sup>-1</sup> even after methanol washing. The antistatic effects are attributed to ionic conductivity of the PU films, which is achieved by low glass transition temperatures of both PU films and [Tf<sub>2</sub>N]-type ILs. These results suggest that [Tf<sub>2</sub>N]-type ILs are excellent antistatic agents for PUs.



## 1. Introduction

Polyurethane (PU) is widely used as an important material in industry due to a wide possibility of properties achieved by combining variable PU precursors such as diol/polyols and isocyanate.<sup>[1]</sup> PUs are applied as foams, coatings, and

sealants not only for automotive and construction fields but also for electronics.<sup>[2]</sup> However, PUs, as well as most organic polymers, possess very high resistivity, and accordingly they are easily charged. This causes electrostatic discharge (ESD) damage on sensitive electronic devices during production, packing, shipping, and final use.

In order to prevent ESD of PUs, resistivity of PUs has to be reduced because low resistivity is effective to prevent charge accumulation. Surface and volume resistivity ( $\rho_s$  and  $\rho_v$ ) are frequently used to classify ESD protective materials together with charge decay time and triboelectric properties. Materials with  $\rho_s > 10^{12}$  ohm sq<sup>-1</sup> are generally classified in the insulator, whereas those with  $\rho_s$  in between  $10^5$  and  $10^{12}$  ohm sq<sup>-1</sup> are static dissipative ones.<sup>[3]</sup> There is no clear range of  $\rho_s$  to define antistatic materials; however, the  $\rho_s$  from  $10^{10}$  to  $10^{12}$  ohm sq<sup>-1</sup> is practically recognized to realize antistatic effects.<sup>[4]</sup>

To reduce the  $\rho_s$ , antistatic agents are added to insulative polymer materials. According to the antistatic mechanisms, antistatic additives can be divided into three such categories as surfactants, conductive inorganic additives,

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and conductive polymers. In the case of surfactants, they are classified into ionic surfactants and non-ionic ones.<sup>[5]</sup> As examples of ionic surfactants, imidazolium salts with long alkyl chains, which are solid at room temperature, have been applied as antistatic agents for polypropylenes. For this case, their good antistatic properties are enhanced due to hydrophilic properties of the imidazolium salts and accordingly improved surface wettability. This effect can be comprehended due to surface activated properties of the imidazolium salts. A similar mechanism of antistatic effect has been reported for non-ionic surfactant-added systems. Accordingly, excellent antistatic effects are achieved under humid conditions, and durability of some surfactants against washing is very short. In order to improve washing durability, conductive additives such as carbon materials<sup>[6]</sup> and metallic fillers<sup>[7]</sup> are blended into polymer materials. As these inorganic additives hardly diffuse in the polymer matrix, antistatic properties are realized by forming conduction pathways: in other words, successive phase of the additives. Accordingly, a small percentage of additives is at least necessary to form such successive phase. The addition of conductive materials deteriorates sometimes mechanical and optical properties of materials. From the viewpoint of methods used to keep physical properties of polymer matrices, a use of intrinsically conductive polymers is very attractive.<sup>[8]</sup> However, in this case, we have to consider the compatibility between additive polymers and matrix polymers to generate homogeneous or microphase separated mixtures. It should also be indispensable to form successive phase of the added conductive polymers in the matrix polymers. However, as control of compatibility of both polymers is not easy, we are obliged to add a relatively large amount of conductive polymers to form a successive phase in matrix polymers.

In the area of solid state electrolytes, the composites based on polyether (e.g., poly(ethylene oxide) [PEO]) and salts have long been proposed as potential ion conductive materials. As PEO is composed of ether oxygen as a repeating unit, inorganic salts are dissociated into ions by the large dipole moment on ether oxygen atoms. The dissociated ions migrate in the amorphous region of PEO due to very low glass transition temperatures ( $T_g$ ). Their ionic conductivity is therefore deeply related to the degree of dissociation of the added inorganic salts and mobility of ions. Because of this, these polymer matrices are essentially required to have relatively high polarity and low  $T_g$ .<sup>[9]</sup> Recently, ionic liquids (ILs) have been recognized as potential additives instead of inorganic salts owing to their low  $T_g$ .<sup>[10]</sup> ILs are generally highly dissociated, and there is no need to design strong ion–dipole interaction with polymer matrices to induce salt dissociation aiming to enhance ion conduction.<sup>[11]</sup> This suggests that some ILs are potential additives to improve ionic conductivity of many

polymers as long as they show moderate affinity with each other.

PU composed of polyether-based polyol and polymeric isocyanate are considered to show moderate affinity with ILs due to the presence of polyether network, and their composite should be effective in terms of antistatic properties. In the present study, we prepared IL-doped PU films and discuss their antistatic properties with physico-chemical properties of ILs.

## 2. Experimental Section

### 2.1. Materials

A series of bis(trifluoromethanesulfonyl)imide ([Tf<sub>2</sub>N]) type ILs containing such cations as 1-butyl-3-methylimidazolium ([C<sub>4</sub>mim][Tf<sub>2</sub>N]), 1-(2-hydroxyethyl)-3-methylimidazolium ([C<sub>2</sub>OHmim][Tf<sub>2</sub>N]), tris(2-hydroxyethyl)methylammonium ([thema][Tf<sub>2</sub>N]), 1-ethylpyridinium ([C<sub>2</sub>py][Tf<sub>2</sub>N]), *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium ([DEME][Tf<sub>2</sub>N]), 1-butyl-1-methylpyrrolidinium ([Py<sub>14</sub>][Tf<sub>2</sub>N]), tributyl-*N*-octylphosphonium ([P<sub>4448</sub>][Tf<sub>2</sub>N]), and 1-butyl-2,3-dimethylimidazolium ([C<sub>4</sub>mmim][Tf<sub>2</sub>N]), were used in this study. Also, [C<sub>4</sub>mim]Br and [P<sub>4448</sub>]Br were used. These ILs were incorporated to PU films, and [C<sub>4</sub>mim][Tf<sub>2</sub>N] were also incorporated to films of polyethylene (PE), poly(methyl methacrylate) (PMMA), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP). The source, chemical structure, and purity of all materials are provided in the Supporting Information.

### 2.2. Resistivity Measurements

Resistivities,  $\rho_s$  and  $\rho_v$ , were measured with a Modulab system (from Solartron) at room temperature. In the case of  $\rho_s$  measurements, cells with a comb-shaped gold electrodes, with a four-pair-toothed formation with a distance between electrodes, were used. From the IL-doped PU films, a square with 0.5 cm per side was cut out for the measurement. The cut films were dried in a vacuum at room temperature for at least 3 h. These films were layered to a cell and tightly packed under N<sub>2</sub> atmosphere, and measurements were carried out under an ambient atmosphere. Prior to the measurements, +5 and –5 V were applied for 60 s to generate the same static environment on the film surfaces, then direct currents were measured by applying +5 V to the cell. The  $\rho_s$  was calculated with modified Ohm's law (Equation (1)), where  $V$  is applied potential,  $l$  is the total length of electrodes ( $l = 3.5$  cm),  $I$  is the measured current intensity, and  $d$  is the distance between the electrodes ( $d = 0.03$  cm).

$$\rho_s = \frac{Vl}{Id} \quad (1)$$

In the case of  $\rho_v$  measurements, cells were fabricated by sandwiching a film with two ITO-glass electrodes. As a spacer to keep the electrode gap distance constant, a 0.1 mm thickness tape based on polyethylene terephthalate polyester was used. The measurements were carried out in the same condition as that for

the  $\rho_s$  measurements. The  $\rho_v$  was calculated with Equation (2), where  $t$  is thickness of the sample film ( $t = 0.1 \pm 0.05$  mm) and  $a$  is an area of the sample film ( $0.25$  cm<sup>2</sup>).

$$\rho_v = \frac{Vlt}{Id} \quad (2)$$

### 3. Results and Discussion

#### 3.1. Surface and Volume Resistivity of [Tf<sub>2</sub>N]-Type IL-Doped PU Films

To evaluate antistatic properties, we prepared PU films containing [Tf<sub>2</sub>N]-type ILs (see Supporting Information). The ILs were added to polyether-based polyol prior to plasticization of the PU films. Figure 1 shows the  $\rho_s$  and  $\rho_v$  of the films containing 1 000 ppm of [Tf<sub>2</sub>N]-type ILs, and the  $\rho_s$  after methanol washing is also depicted. Resistivity was measured for well-dried PU films. The  $\rho_s$  for pure PU film was found to be  $2.1 \times 10^{12}$  ohm sq<sup>-1</sup>. In the presence of the ILs, the  $\rho_s$  of the films was reduced in the order of  $10^9$  ohm sq<sup>-1</sup>, which is small enough to leak accumulated static electricity on PU surfaces.

When the effect of IL addition is found only for the lowering of the  $\rho_s$ , there should be a fear of bleeding out of the ILs. As seen in Figure 1; gray and black bars, both  $\rho_s$  and  $\rho_v$  are lowered in same tendency, suggesting that the ILs are uniformly incorporated in the PU films.

Some antistatic agents with low molecular weight are easily removed; consequently, their life time is relatively short. For example, hydrophilic surfactants are easily washed off from polymer surfaces with water, and this causes low durability of their antistatic effects. As all [Tf<sub>2</sub>N]-type ILs used in this study are soluble in methanol, washing durability was evaluated by comparing  $\rho_s$  values before and

after methanol washing for 3 s of the films. The washed PU films were freeze dried for one night and then dried at room temperature for 3 h. There was no remarkable change of  $\rho_s$  before and after methanol washing (see Figure 1; gray and white bars), confirming the durability of antistatic effects of the film against methanol washing is quite high. The  $\rho_s$  of PU films containing 1 000 ppm of [C<sub>4</sub>mim][Tf<sub>2</sub>N] was also investigated after ultra-sonication treatment in methanol for 1, 5, and 10 min. The  $\rho_s$  was found to be in the order of  $10^9$  and  $10^{10}$  ohm sq<sup>-1</sup> even after ultra-sonication for 1 and 10 min, respectively (see Figure S1 in the Supporting Information). In spite that the ILs delocalized on the PU surfaces were washed off, the ILs presented in bulk of the film were still effective to leak the static electricity even after methanol washing. We confirmed that [Tf<sub>2</sub>N]-type ILs are potential additives as antistatic agents for PUs.

#### 3.2. Mechanisms of Antistatic Effect of ILs in the PU Films

Figure 2a shows the effect of [C<sub>4</sub>mim][Tf<sub>2</sub>N] concentration on current decay up to 500 s when 5 V was applied to the films. For pure PU film, small leakage current was observed. For the case of [C<sub>4</sub>mim][Tf<sub>2</sub>N]-doped PU films, larger leakage currents were observed for all the films, and clear charge currents were observed for the films incorporating [C<sub>4</sub>mim][Tf<sub>2</sub>N] for more than 50 ppm. When carbon materials are used as antistatic additives, the antistatic effect is realized by electronic conductivity via successive three-dimensional path or "sea-island" structure of carbon materials.<sup>[12]</sup> These composites are frequently characterized by the percolation theory, and it is well known that antistatic effects are enriched above the concentration ( $C_0$ ) at which antistatic agents reach the percolation threshold. For a successive three-dimensional path system,  $C_0$  is basically defined as 15 wt.-%.<sup>[13]</sup> The number of  $C_0$  can be larger when additives form clusters, and it can be lower when additives have larger surface area.<sup>[14]</sup> For example,  $C_0$  for PU/carbon black is 15 wt.-%, and it is lowered by replacing the carbon black with graphite nanosheets.<sup>[6a]</sup> Moreover, by using the additives with high aspect ratio such as carbon nanotube,  $C_0$  was found to be 0.13 wt.-%.<sup>[15]</sup> However, in our case, we obtained the larger leakage current even with 10 ppm of [C<sub>4</sub>mim][Tf<sub>2</sub>N] and the clear charge current with 50 ppm of [C<sub>4</sub>mim][Tf<sub>2</sub>N]. Because the 10 and 50 ppm of [C<sub>4</sub>mim][Tf<sub>2</sub>N] were not enough to generate a successive conduction pathway, antistatic effects of IL-doped PU films should be originated by different mechanisms reported before.

Figure 2b shows the effect of [C<sub>4</sub>mim][Tf<sub>2</sub>N] concentration on the  $\rho_s$ . The logarithmic  $\rho_s$  and logarithmic [C<sub>4</sub>mim][Tf<sub>2</sub>N] concentration was found to be close to the straight line with a slope of -1.0, suggesting antistatic properties are not based on the percolation threshold of the additives.

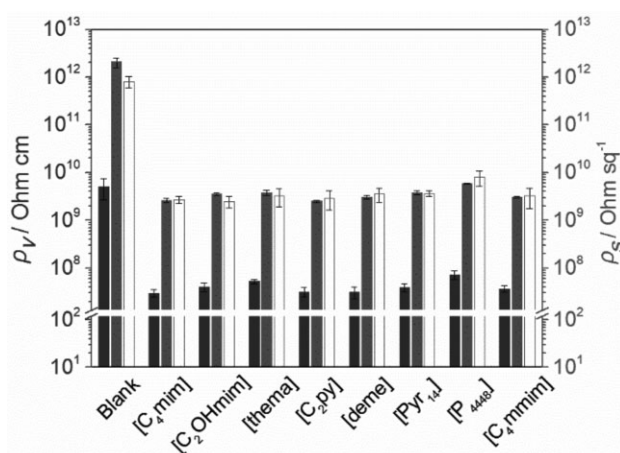
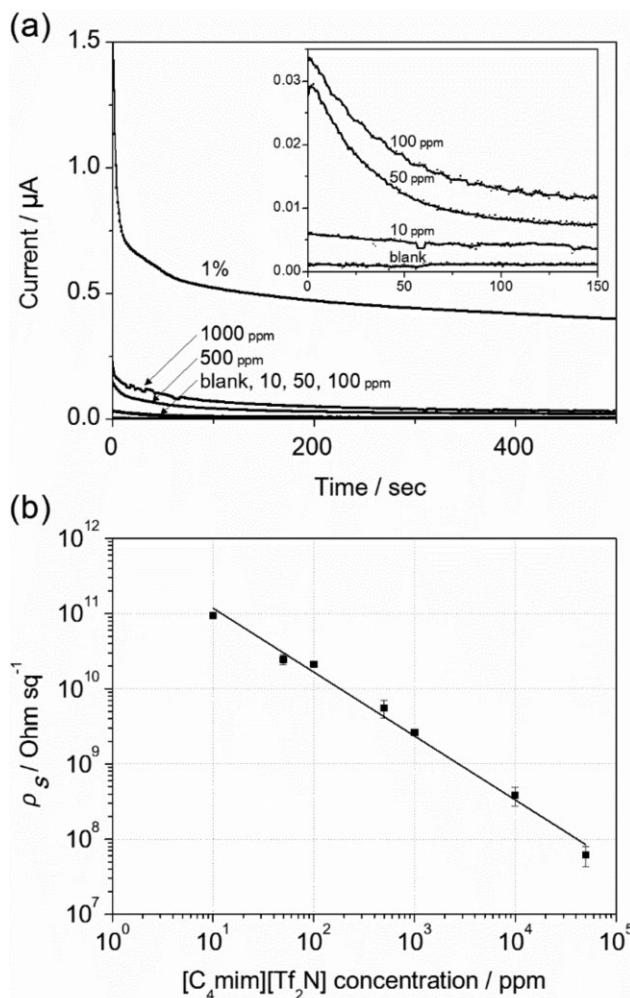


Figure 1. The  $\rho_v$  (black) and  $\rho_s$  (gray) of the PU films containing 1 000 ppm of [Tf<sub>2</sub>N]-type ILs, and the  $\rho_s$  after methanol washing (white).

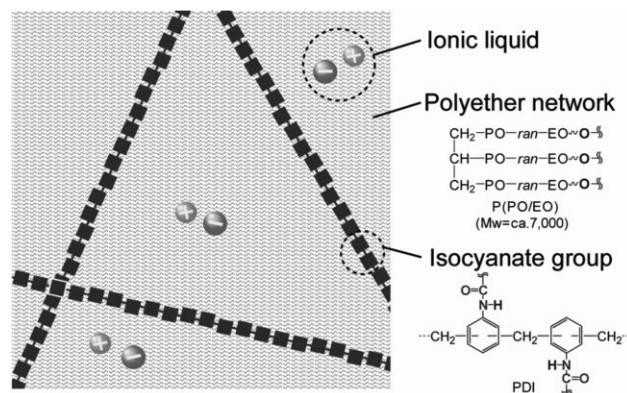


**Figure 2.** Effect of [C<sub>4</sub>mim][Tf<sub>2</sub>N] concentration on (a) the direct current and (b) the  $\rho_s$  of the [C<sub>4</sub>mim][Tf<sub>2</sub>N]-doped PU films.

According to the previous report on polymer gel electrolyte containing trifluoromethanesulfonic acid, logarithmic conductivity of the electrolyte as a function of logarithmic acid concentration shows a straight line behavior at low acid concentration and deviates from a straight line behavior at high acid concentration.<sup>[16]</sup> The deviation was considered to be due to the aggregation of ions. In our case, the  $\rho_s$  can be linearly controlled up to  $10^7$  ohm sq<sup>-1</sup> within 5 wt.-% of [C<sub>4</sub>mim][Tf<sub>2</sub>N]. This means, in the concentration range from 10 ppm to 5 wt.-%, [C<sub>4</sub>mim][Tf<sub>2</sub>N] are dispersed into PU films and dissociated into ions which contribute to the ion conduction. As a result, antistatic effects were obtained after IL-doping into PU films.

### 3.3. Important Factors for the Antistatic Properties of IL-Doped PU Films

Basing on the results above, here we propose the schematic depiction of IL-doped PU films (Scheme 1).

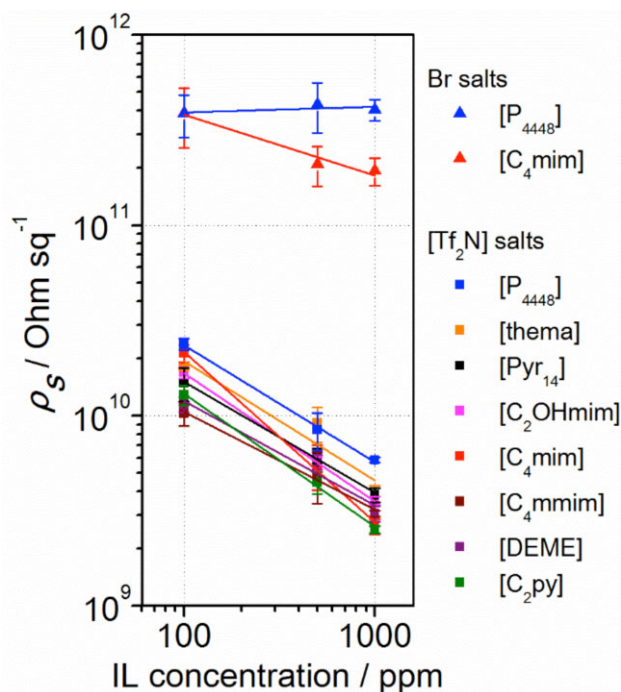


**Scheme 1.** Schematic illustration of IL-doped PU films.

Considering the formulation ratio of the PU films used in this study, ILs should distribute mainly in polyether network of the PU. ILs are then considered to enhance ionic conductivity and compensate the surface charge accumulation. A linear relation of logarithmic [C<sub>4</sub>mim][Tf<sub>2</sub>N] concentration and logarithmic  $\rho_s$  also supports considerable contribution of ionic conductivity to the antistatic effect.

To confirm that the combination of ILs and PUs is the key to realize antistatic effects, we prepared composites with other polymers and salts. First, we prepared films with PE, PMMA, PVdF-HFP with 1000 ppm of [C<sub>4</sub>mim][Tf<sub>2</sub>N]. Structural difference between PU and other polymers examined here is the presence of polyether network. The  $\rho_s$  for the PE film was found larger than  $9.4 \times 10^{14}$  ohm sq<sup>-1</sup> (measured in Sumika Chemical Analysis Service, Ltd.), and  $1.1 \times 10^{12}$  and  $1.2 \times 10^{12}$  ohm sq<sup>-1</sup> for PMMA and PVdF-HFP films, respectively. There were small changes before and after addition of [C<sub>4</sub>mim][Tf<sub>2</sub>N] for 1000 ppm. These data show that polyether network in the PU films is suitable for realizing antistatic effect.

On the other hand, we analyzed the  $\rho_s$  of PU films incorporating Br and [Tf<sub>2</sub>N] salts (Figure 3). For the case of the PU films with [Tf<sub>2</sub>N]-type ILs, the  $\rho_s$  decreased depending on the concentration of [Tf<sub>2</sub>N]-type ILs. By contrast, the addition of Br salts to PU films showed a small effect in terms of the  $\rho_s$ . This may be due to low dissociation degree and high  $T_g$  of Br salts. As ionic conductivity of polymer/salt composites is the function of the number of ions and their mobility, properties of the added salts are great factors in order to control the conductivity. Considering the ionic conductivity, ILs which are highly dissociated and have low  $T_g$ , such as [Tf<sub>2</sub>N]-type ILs, are favorable to reduce the  $\rho_s$  of PU films. These obtained data clearly showed that low  $T_g$  of both polyether network as a major component of the PU films and [Tf<sub>2</sub>N]-type ILs is important to improve antistatic effect of IL-doped PU films.



■ Figure 3. Effect of ion species on the  $\rho_s$  of IL-doped PU films.

#### 4. Conclusion

Addition of [Tf<sub>2</sub>N]-type ILs lowered both  $\rho_s$  and  $\rho_v$ , and enhanced antistatic properties with PU films. The reduction of  $\rho_s$  from  $2.1 \times 10^{12}$  to  $9.4 \times 10^{10}$  ohm sq<sup>-1</sup> was also found when [C<sub>4</sub>mim][Tf<sub>2</sub>N] was added for 10 ppm. Because the 10 ppm of [C<sub>4</sub>mim][Tf<sub>2</sub>N] is not enough to generate a successive conduction pathway, the antistatic effect cannot be explained by the percolation theory. The antistatic effect may be derived from the conduction of free ions generated in polyether network. A linear correlation between logarithmic  $\rho_s$  and logarithmic [C<sub>4</sub>mim][Tf<sub>2</sub>N] concentration strongly supported the importance of ion conduction for realizing antistatic properties. The effect of [C<sub>4</sub>mim][Tf<sub>2</sub>N] addition on the antistatic properties of the PU films was much larger than that of [C<sub>4</sub>mim]Br addition. ILs with highly dissociative properties and low  $T_g$  were concluded to be excellent antistatic agents for PUs.

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