In this study, two diurethanes were synthesized and blended with thermoplastic polyurethane (TPU), and the effects of the incorporation of these diurethanes on the physical properties of the TPU were evaluated. The diurethanes were obtained reacting 4,4'-diphenylmethane-diisocyanate with 1-butanol (Additive 1) or 1-octanol (Additive 2). An increase in the amount of Additive 1 promoted a reduction in the rigid phase glass transition temperature ($T_g$), while an increase in the amount of Additive 2 caused an increase in the $T_g$ of this phase. Processing of the TPU increased the hardness and elastic modulus and decreased the tensile stress at break. Addition of diurethanes did not promote significant changes in the hardness and stress-strain behavior, compared with the processed TPU; however, increasing the additive content decreased the elongation and tensile stress at break. Scanning electron microscopy micrographs showed that incorporation of diurethanes into TPU led to migration of these additives. POLYM. ENG. SCI., 50:2321–2328, 2010. © 2010 Society of Plastics Engineers

INTRODUCTION

Polyurethanes (PU) are present in many aspects of modern life. They represent a class of polymers that have found widespread use in the medical, automotive, and industrial fields. PU can be found in products such as furniture, coatings, adhesives, construction materials, fibers, paddings, paints, elastomers, and synthetic skin [1].

According to Oertel [2], the general term “polyurethanes” has been used for a multitude of polymers prepared according to the diisocyanate-polyaddition principle. Other authors describe PU as a polymer derived from polyisocyanate and polyl in which the repeating unit contains a urethane moiety [1, 3].

PU elastomers with thermoplastic character were first described in the 1950s, and in the early 1960s, they became commercially available. Today, they are one of the most versatile products in the group of engineering thermoplastics with elastomeric properties [2]. Thermoplastic polyurethanes (TPUs) have been used in several applications, such as the automotive, shoe and automation industries, and in medical articles [1, 4–6].

TPUs are linear-segmented copolymers, composed of micro-phase separated hard and soft segments [7–13]. The properties of these polymers seem to result from a combination of chain segment flexibility, the rigidity of aromatic units, chain entanglement, orientation of segments, hydrogen bonding, and other intermolecular interactions [13].

PU are generally characterized by their poor stability because of the thermally labile urethane group. Thermal decomposition starts in the range of 100–200°C [14]. Above the stability temperature, urethane bonds dissociate and reassociate simultaneously (“transurethanization”) [15]. Such reactions are believed to decrease the molecular weight, leading to reduced strength and elongation, particularly in harder TPUs, because they need to be processed at higher temperatures [16].

The dissociation of urethane bonds causes a considerable molar mass decrease because the equilibrium reaction is shifted toward the free endgroups. As a consequence of transurethanization and change in molar mass, any thermal treatment of TPU elastomers beyond a critical temperature, in particular measurements and processing in the molten liquid state, can change the viscosity, crystallization behavior, and even mechanical properties significantly [7].

Additives for polymers have been used both in scientific and industrial communities, to modify several properties. Furthermore, the incorporation of additives into existing polymers is faster and cheaper than the synthesis of new polymers.
It is well known that the TPU parts attain their optimum properties after a thermal postcure [2]. According to the material type and configuration of the part, a post cure at 80–120°C for 15–20 h is generally sufficient. Without post cure, the part should be stored for 4 to 6 weeks at temperatures above 20°C before being put into service [14–17].

Herrera et al. [18] studied the thermal degradation of two different TPU elastomers based on 4,4’-diphenylmethane-diisocyanate (MDI) and observed that PU degrade at low temperatures (200–300°C). Carbon dioxide was found to be the most abundant product during the first step of degradation in nitrogen, indicating the scission of the urethane bond. For the second degradation stage, a complex mixture of products was identified, most probably originating from the polyol segment.

Finnigan et al. [16] observed that the dissociation and recombination reactions of urethane groups promoted a reduction in molar mass, reducing tensile strength and elongation, particularly in high hardness TPU.

Torró-Palau et al. [19] added different types of silica to a TPU and reported increases in the viscosity and in the storage and loss moduli of the PU/silica composites in solution, but only the hydrophilic fumed silica imparted pseudoplasticity and thixotropy. Interactions between the hydrophilic fumed silica, the polyurethane and/or the solvent seemed to be responsible for the improved rheological properties of the composites. Addition of silica did not modify the glass transition temperature but increased the softening temperature of PU composites.

In this study, two low-molecular-mass additives containing urethane groups were added to TPU, with the aim of evaluating the influence of these additives on the thermal and mechanical properties of TPU, such as glass transition temperature, thermal stability, tensile behavior, and hardness.

**EXPERIMENTAL**

*Materials*

In the diurethane synthesis, MDI (MDI—Isonate 125M, Dow), 1-butanol (Vetec), 1-octanol (Merck), and dimethylformamide (DMF, Vetec) were used as received.

The TPU (Fortiprene TPU 5102/D43, FCC Fornecedora), a polyester-based TPU with nominal Shore D hardness of 43 ± 3, was dried at 90°C for 24 h in a vacuum oven (−650 mm Hg) before use.

*Methods*

**Diurethane Synthesis.** The diurethane additives were obtained by adding approximately 1.8 mol of 1-butanol to 0.8 mol of MDI [Additive 1; dibutyl 4,4’-methylenebis(phenyl carbamate)], or adding approximately 1.8 mol of 1-octanol to 0.8 mol of MDI [Additive 2; dioctyl 4,4’-methylenebis(phenyl carbamate)]. Both additives are cited in the literature [20, 21].

The isocyanate content of the MDI was analyzed according to ASTM D5155B-96 [22]. A value of 32.9% of free isocyanate (NCO) was determined (the expected value being 33.6%).

Diurethane synthesis was carried out in 0.4 L of DMF solution under vacuum, at 55 ± 3°C and 600 rpm, in a 1-L three-way reaction flask. In these syntheses, MDI and DMF were first added to the flask; temperature, vacuum, and mixer speed were controlled. Next, 1-butanol or 1-octanol was slowly added. After addition of the alcohol, the reaction was controlled for 1 h. The solutions obtained were maintained in closed flasks overnight. The solutions were then washed with distilled water, promoting precipitation of the additives. These were filtered and dried at 60°C for 48 h in a conventional oven, and 24 h in a vacuum oven at the same temperature. Diurethanes were characterized by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA).

**Blends.** Blends of 1, 2, 5, and 10% by weight of each additive with TPU were obtained. The blend procedure was carried out in a torque rheometer (an instrumented batch mixer) made in our laboratory, using roller rotors, at 200°C and 60 rpm for 600 s. The mixing chamber had a free volume of approximately 75 cm³; the total mass of each batch was 50 g.

**FTIR.** FTIR (Nicolet is10, Thermo Scientific) analysis was performed in attenuated total reflection mode; the diurethanes were directly analyzed from the powder, and the TPU samples were first molded (210°C, approximately 20 s) into thin films before analysis.

**DSC.** Analysis of diurethanes by DSC (Shimadzu DSC-50) was carried out as follows: the samples were first heated under N₂ at a flux of 50 mL·min⁻¹ and at a rate of 40°C·min⁻¹ up to 200°C and maintained at this temperature for 120 s. The additives were cooled at −20°C·min⁻¹ until −100°C and heated again at 20°C·min⁻¹ until 200°C. The samples analyzed had a mass of approximately 10 mg.

DSC analysis for TPU and the blends with additives was performed at a heating rate of 20°C·min⁻¹, in the range of −100–250°C. Atmosphere and mass were the same as those used for the additives. The DSC was calibrated with indium and zinc standards, before analysis; the estimated error was verified to be less than 1% of the theoretical values of the standards used.

**TGA.** TGA (Shimadzu TGA-50) for diurethanes and TPU were performed at a heating rate of 10°C·min⁻¹, in the range of 20–730°C, in a nitrogen atmosphere at a flow of 50 mL·min⁻¹. The mass of each sample was approximately 15 mg.

**Dynamic Mechanical Thermal Analysis.** Dynamic Mechanical Thermal Analysis (DMTA) (TA Instruments
DMA 2980) was performed on bars of approximately 17.0 × 12.0 × 3.3 mm, cut from molded plates (200°C, 5 min.). To carry out the analysis, the single cantilever mode was used, at a heating rate of 5°C·min⁻¹, in the range of −100°C to 100°C. The frequency was 1 Hz and the amplitude 10 μm.

Through the DMTA analysis, the glass transition temperature (T_g) of the rubber phase was obtained at the temperature where the loss modulus (E″) showed a maximum value.

**Shore D Hardness.** The Shore D hardness analysis (GS-720G, Teclock) was carried out according to ASTM D 2240-97 [23], at 23 ± 2°C, in molded plates of approximately 155 × 145 × 3 mm. These plates were molded at 200°C for 5 min, under a pressure of approximately 5 MPa.

**Stress-Strain.** Stress-strain analysis was carried out according to ASTM D638-99 [24], at 23 ± 2°C, at a strain rate of 500 mm·min⁻¹. The samples (type IV, ASTM D638-99) were cut from sheets (155 × 145 × 3 mm) molded in a hot press (200°C, 5 min, pressure of approximately 5 MPa). The elastic modulus, tensile stress at break, and elongation at break were analyzed.

**Scanning Electron Microscopy.** Scanning Electron Microscopy (SEM) (Jeol, JSM-5800) micrographs were obtained for samples fractured cryogenically in liquid nitrogen; these samples were maintained for approximately 10 weeks at 23 ± 2°C under atmospheric pressure and then metalized with gold and analyzed at 10 kV. The micrographs were analyzed to verify migration of additives.

**RESULTS**

**DSC**

DSC analysis of diurethanes showed that both diurethanes had crystalline structures. Additive 1 had a melting temperature (T_m) of 106.3°C, with a melting enthalpy (ΔH) of 49.5 J·g⁻¹; Additive 2 presented a T_m of 117.2°C, with ΔH of 71.8 J·g⁻¹.

BLENDS OF ADDITIVES AND TPU, AS WELL AS PROCESSED IN THE INSTRUMENTED BATCH MIXER AND “AS RECEIVED” TPU, SHOWED DIFFERENT EVENTS IN THE DSC THERMOGRAMS. THESE EVENTS ARE RELATED TO THE GLASS TRANSITION TEMPERATURE (T_g) OF THE RUBBER PHASE (APPROXIMATELY [−]20°C), THE SHORT-RANGE INTERACTIONS BETWEEN RIGID PHASE CRYSTALLINES AND INTERACTIONS BETWEEN THE RIGID AND RUBBER PHASES (SECOND TRANSITION, 50–65°C), THE RIGID PHASE T_g (115–150°C), AND THE MELTING OF THE TPU CRYSTALS (180–220°C) [6, 7, 10, 16].

The DSC results have been previously discussed in the literature [25]. There were no significant changes in the T_g of the rubber phase with incorporation of either additive because of an expected greater interaction of diurethanes with the rigid phase. Addition of 1% of Additive 1 increased the rigid phase T_g, with a subsequent gradual decrease in rigid phase T_g with an increase in Additive 1 content, probably because of a plasticizer effect. Addition of diurethanes increased the TPU chain mobility during crystallization, which increased the melting enthalpy, and displaced the T_m to higher temperatures. Increasing the amount of Additive 2 caused an increase in the rigid phase T_g.

**FTIR**

Figure 1 shows the FTIR results obtained for the TPU and diurethanes where, for clarity, only the samples containing 1 and 10 wt% of both additives are represented. According to Corish [26], the vibration of NH at around 3300 cm⁻¹, the band of amide I (axial deformation of C=O) present as a shoulder at around 1695 cm⁻¹, and the absorption of amide II (NH angular deformation) at around 1540 cm⁻¹ enable the identification of a polymer as a polyurethane. All of these bands were observed in the samples studied. Diurethanes obtained by reacting diisocyanates with an excess of mono-functional alcohol show two other bands related to urethane groups at approximately 1300 and 1230 cm⁻¹, and are probably related to ketone (CO) and ether (COC) vibrations [26]. These two bands can be clearly observed in the diurethane spectra.

Comparing the unprocessed and processed TPU, similar spectra were observed, indicating that processing of TPU did not lead to significant changes in the chemical structure of the material. It was also observed that the TPU showed a relatively large absorption at 1230 cm⁻¹, indicating that the polyol used in the synthesis was based on polyester [27].

The spectra for the additives showed that the absorption bands at 2960 cm⁻¹ and 2870 cm⁻¹, associated with CH₃ groups [28], were significantly more defined in relation to those observed for the TPU, because no CH₃
groups are expected to be present in the TPU molecules. The absorption at 3045 cm\(^{-1}\), combined with the stretching of CH groups in the aromatic rings, were also more defined in the additives than in the TPU, because of the larger amount of aromatic rings present in the diurethanes.

On comparing the spectra for the additives, one can observe a significant difference in the 1050–1100 cm\(^{-1}\) region (mainly related to CO absorption [28]). This behavior is probably due to a higher mobility of the hydrocarbon tails encountered in Additive 2, which modifies the deformation of urethane linkages and the CO absorption region of the spectra, and the absorption at 2900 cm\(^{-1}\), associated with CH\(_3\).

On comparing the samples containing Additive 1 to those of unprocessed and processed TPU, no significant changes can be observed, regardless of the quantity of this additive. However, samples containing Additive 2 showed more distinct absorption peaks close to 2900 (related to CH\(_2\), CH\(_3\), and CH) and at 1700 cm\(^{-1}\) (C=O linked by hydrogen bond) [29]. The addition and increase of Additive 2 probably caused a significantly higher increase in the chain mobility than that promoted by Additive 1, and may also promote a higher phase separation, inducing an increase in hydrogen bond formation (a distinct peak at 1700 cm\(^{-1}\) was observed for the sample with 10% of Additive 2). Furthermore, it can be observed that the FTIR spectra did not clearly show the formation of new chemical structures, possible because of reactions between the TPU and the additives.

TGA

Figure 2 shows the TGA thermograms for the samples studied. It was observed that both additives presented two distinct weight loss steps and also that the degradation behavior is dependent on the alcohol used in the diurethane synthesis. The increase in molar mass of the alcohol shifted the onset temperature of the degradation steps to higher temperatures, because of an increase in thermal stability. However, the increase in molar mass caused a significant increase in the first stage of weight loss. According to Herrera et al. [18], the first degradation stage of TPU is associated with the degradation of rigid segments containing the urethane groups, and the second stage is related to the degradation of soft segments formed by the polyol. The former may be related to the release of substances derived from the degradation of alcohol and isocyanate (NCO) groups, and the latter to degradation of the aromatic rings and consequent elimination of compounds containing carbon and hydrogen.

A small amount of additive (1–5 wt%) had minimal effect on the weight loss behavior, and a greater weight loss was observed only with a 10 wt% concentration, because of the lower weight loss temperature of the additives compared with the TPU.

The weight loss of the first stage of degradation for Additive 2 was higher than that observed for Additive 1, probably due to the elimination of not only products derived from alcohol and isocyanate groups, but also compounds derived from the polyl aromatic rings of MDI. The weight loss of the second stage of degradation for Additive 2 was lower than that observed for Additive 1 and is related to the degradation of aromatic rings, because Additive 2 has a lower percentage (by weight) of MDI than Additive 1. The lower weight loss of Additive 1 may be related to the formation of more thermally stable compounds during degradation, which changed the weight loss characteristics of the diurethanes studied.

Lu et al. [20] observed that diurethanes of lower molar mass showed higher reactivity of the NCO groups derived from the dissociation of urethane groups at temperatures lower than those found for higher molar mass diurethanes. Hence, the displacement of the mass loss curves to lower temperatures with an increase in additive content, as observed in Fig. 2, may be related to elimination of compounds derived from diurethane degradation because of a reduction in the dissociation temperature of the urethane groups. Also, the detail in Fig. 2 shows that, with the exception of the sample with 10% of Additive 1, samples containing Additive 1 showed higher degradation temperatures than those containing the same content of Additive 2. As Additive 1 has a lower molar mass than Additive 2, this may indicate urethane dissociation at a lower temperature than for Additive 2, leading to a faster equilibrium between the isocyanate and hydroxyl groups derived from urethane dissociation. This could stabilize the urethane groups of the TPU chains, and increase the thermal stability. Also, as Additive 2 had longer hydrocarbon tails, there may have been an increase in the free volume in the melt, increasing the molecular mobility and reducing the degradation temperatures.

DMTA

Figure 3 shows the storage modulus (\(E'\)) and loss modulus (\(E''\)) obtained for the TPU and diurethane from the
DMTA analysis. Table 1 shows the glass transition temperature \(T_g\) of the rubber phase of the samples, obtained from the DMTA results.

Figure 3 and Table 1 show that the processing of TPU led to a reduction in the rubber phase \(T_g\). This phenomenon is probably related to the lowering of the molar mass with processing; also, the lowering of \(T_g\) values may be associated with an increase in phase separation. The incorporation and increase of either additive did not significantly change the \(T_g\), probably because of a combined effect of a lowering of the average molar mass with an increase in additive and reduction of TPU chain degradation because of a lubricant effect of the additive.

In Fig. 3, one can observe that unprocessed TPU and the 10% Additive 2 sample showed the lowest and highest values for the storage and loss moduli after the rubber phase \(T_g\), respectively. This behavior may be related to the lowest crystallinity degree and phase separation found in the unprocessed TPU [25], which can induce a higher mobility of the rigid segments of TPU chains, lowering the modulus values. In contrast, the highest phase separation encountered for the sample with 10% Additive 2 reduced the mobility of the rigid segments, increasing the storage and loss moduli.

From the DMTA analysis, a second relaxation was observed at approximately \(-80^\circ C\), related to movements of the ester groups of the soft segments [30]. This relaxation did not lead to significant modifications with processing and incorporation of diurethanes.

**Shore D Hardness**

Figure 4 shows the results of Shore D hardness for the samples studied. It was observed that the processing of TPU promoted an increase in the hardness compared with that of unprocessed TPU. This increase may be related to the greater crystallinity degree found for processed TPU (melting enthalpy, \(\Delta H = 11.1 \text{ J g}^{-1}\)), compared with that of unprocessed TPU (\(\Delta H = 3.8 \text{ J g}^{-1}\)), as observed in the DSC analysis [25]. According to Meier [31], with the incorporation of small quantities of plasticizer (4–15%), some polymers become harder and more brittle. This behavior is due to an increase in the chain mobility, promoting an increase in the crystallinity degree. Also, the incorporation and increase of additive did not significantly change the hardness, compared with that of processed TPU, because the melting enthalpy of these samples was similar.

**Stress-Strain Analysis**

From the stress-strain results, it was observed that the processing of TPU led to a significant reduction in tensile stress at break, compared with unprocessed TPU (from approximately 44 MPa to near 20 MPa, respectively). This behavior is due to the higher molar mass of unprocessed TPU, and may be because of orientation of the chains of unprocessed TPU during deformation. According to Callister [32], the predeformation technique by drawing consists of plastically deforming a polymer under tension, making the chains slip past one another and become highly oriented. The unprocessed TPU showed a lower degree of crystallinity than the processed TPU, and the chains of the unprocessed TPU showed a greater orientation toward deformation, which led to an increase in the tensile stress at break. Incorporation of either additive resulted in stress at break values similar to that found for

**TABLE 1. Rubber phase \(T_g\) obtained by DMTA.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unprocessed TPU</td>
<td>-7.1</td>
</tr>
<tr>
<td>Processed TPU</td>
<td>-13.8</td>
</tr>
<tr>
<td>1% Additive 1</td>
<td>-13.4</td>
</tr>
<tr>
<td>2% Additive 1</td>
<td>-11.8</td>
</tr>
<tr>
<td>5% Additive 1</td>
<td>-11.8</td>
</tr>
<tr>
<td>10% Additive 1</td>
<td>-12.1</td>
</tr>
<tr>
<td>1% Additive 2</td>
<td>-13.6</td>
</tr>
<tr>
<td>2% Additive 2</td>
<td>-14.1</td>
</tr>
<tr>
<td>5% Additive 2</td>
<td>-14.3</td>
</tr>
<tr>
<td>10% Additive 2</td>
<td>-14.4</td>
</tr>
</tbody>
</table>

**FIG. 4. Hardness (Shore D) for TPU and blends containing different wt% of each additive.**
the processed TPU (approximately 20 MPa). A small reduction in tensile stress at break was observed with an increase in additive content, probably related to a gradual reduction in the average molar mass of the blends [25]; also, this phenomenon may be associated with the poor compatibility of the additives with TPU chains, reducing the tensile stress and elongation at break with an increase in additive content (additives may act as external lubricants).

Figure 5 shows the median curves of the stress-strain tests for unprocessed and processed TPU. It was observed that at strains greater than 200%, the unprocessed TPU presented a deviation from linearity in the stress-strain ratio, whereas processed TPU maintained a certain linearity. The deviation from linearity of the unprocessed TPU could have been caused by orientation of the chains during stretching. The stress-strain behaviors for blends of TPU with either additive were similar to that presented by processed TPU.

Figure 6 shows the results for elongation at break for the samples studied. It was observed that the processing of TPU did not cause a significant change in the elongation at break, compared with unprocessed TPU. With the increase in the amount of either diurethane, there was a reduction in the elongation at break, because of a reduction in the average molar mass of the systems [25]. As Additive 1 has a lower molar mass, the reduction in the elongation at break was greater for the blend with 10% of Additive 1 compared with that presented by the mixture with 10% of Additive 2.

Figure 7 shows the elastic modulus results for the samples studied. It was observed that the processed TPU had a greater elastic modulus than the unprocessed TPU, which may be related to the higher degree of crystallinity of the former. The incorporation of additives to the TPU did not significantly modify the elastic modulus values, because the crystallinity degree found for the blends was similar to that of processed TPU for both additives. Also, the values of the elastic moduli corroborate the results observed by DMTA, at approximately 23°C.

**Final Properties**

Approximately 10 weeks after the molding of the plates for the mechanical tests migration of additives was observed, with the release of a white powder on the surface of the samples.

SEM analysis showed that samples containing either additive released a significant amount of a white powder, related to the migration of diurethanes, probably because of a diffusion process. This behavior indicates that both additives probably acted as processing aids, and do not have strong interactions with the segments presents in the structure of TPU. Figure 8 shows the SEM micrographs for unprocessed TPU and blends of TPU and Additive 2. Visually, blends with Additive 1 showed a similar behavior. Samples with 1 wt% of both additives did not show a considerable migration (Fig. 8c); an increase in the diurethane content led to an increase in migration. From Fig. 8g and h, one can see that the migrated additives formed crystal-like structures on the surface of the molded plates. Migration is related to the low-molecular weight of the additives, which facilitates the diurethane diffusion proc-
theses; the poor compatibility observed between the diurethanes and TPU may also promote migration.

CONCLUSIONS

In this study, two low-molecular-weight diurethanes were incorporated into TPU; the addition of either additive had little effect on the properties studied, except on tensile stress and elongation at break probably because of the modest compatibility with both soft and hard segments.

Increasing the Additive 1 content promoted a decrease in the rigid phase $T_g$, whereas an increase in Additive 2 promoted an increase in this value. This behavior is related to the compatibility of each additive with the rigid phase, i.e., Additive 1 showed higher compatibility than Additive 2.

Infrared spectrometry results showed that the diurethanes were synthesized successfully. The processing of TPU did not promote any significant changes in its FTIR spectrum. Incorporation of Additive 1 did not lead to significant modifications in the FTIR spectra, whereas samples containing Additive 2 showed lower compatibility with TPU, indicating greater hydrogen bond formation, which displaced the C=O and N—H absorption bands.

The results obtained from the TGA showed two main stages of weight loss for the samples studied, related to the degradation of urethane groups and aromatic rings, respectively. The incorporation and increase of the addi-
tive, in both cases, displaced the onset of weight loss to lower temperatures because of an increase in the chain mobility and quantity of low-molecular-weight molecules (diurethanes).

Dynamical-mechanical analysis showed that processing of TPU led to a reduction in the rubber phase $T_g$ because of a reduction in the molecular weight of the polymer. The incorporation and increase of the additive, in both cases, did not significantly change the rubber phase $T_g$, indicating that additives act as a lubricant preventing degradation of TPU chains.

Processing of neat TPU increased the hardness and elastic modulus, because of an increase in the crystallinity degree, but reduced the tensile stress at break, which was related to a decrease in chain flexibility and in the average molecular weight, and an antiplasticizing effect.

Incorporation of diurethanes did not modify the hardness of the blend, because the crystallinity degree was similar for all samples.

Samples containing either diurethane showed migration of the additive, because of the low-molecular weight of the additives and poor compatibility between diurethanes and TPU.

ACKNOWLEDGMENTS

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