



# The effect of water and acidity of the clay for ethylene polymerization over $\text{Cp}_2\text{ZrCl}_2$ supported on TMA-modified clay materials

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Received 20 March 2003; received in revised form 14 June 2003; accepted 14 June 2003

## Abstract

The organic aluminum compounds (OACs) have been prepared on the surface of clay such as montmorillonite K-10 (MMT-10) and Kunipia by reaction of partial hydrolysis of trimethylaluminum (TMA). The effect of the water and acidity of the clay in ethylene polymerization was investigated over  $\text{Cp}_2\text{ZrCl}_2$  supported on the TMA-modified clay. Irrespective of whether water was present or not in the clay,  $\text{Cp}_2\text{ZrCl}_2$  supported on the TMA-modified clay showed catalytic activity for ethylene polymerization when acidic MMT-10 was used. However, in the case of basic Kunipia, no catalytic activity for ethylene polymerization was obtained. When Kunipia was changed to acidic by intercalation of an inorganic compound,  $\text{Cp}_2\text{ZrCl}_2$  showed the catalytic activity for ethylene polymerization in combination with the products of the partial hydrolysis of TMA on acidified Kunipia without methylaluminoxane (MAO).

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*Keywords:* Acidity; Clay minerals; Metallocene catalysts; Polyethylene

## 1. Introduction

Methylaluminoxane (MAO) is the product of the partial hydrolysis of trimethylaluminum (TMA) with water and an excessive amount of MAO was needed for activation of metallocene catalysts for ethylene polymerization. Nowadays, this problem has been solved by means of immobilization of soluble metallocene catalyst on solid support in several ways [1]. The main methods are: direct adsorption of the metallocene compound on inorganic supports such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , zeolite,  $\text{MgCl}_2$ , etc. adsorption of metallocene

compounds on support modified by  $\text{AlR}_3$ , MAO, or other compounds; adsorption of the complexes of metallocene with MAO on silica or other carriers. All these methods require the use of the MAO to activate the supported catalyst for olefin polymerization. Smectite clay minerals have layer lattice structures in which two dimensional oxyanions are separated by layers of hydrated cations. It has the oxygen framework of a 2:1 layered silicate. The idealized structural formula for dioctahedral and trioctahedral 2:1 phyllosilicates is  $\text{M}_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$ , where M is the metal cation for neutralization of the clay material and  $x$  is between 0.5 and 1.3. To balance the charge deficiency, hydrated cations are located between the silicate layers. Normally, the cations are alkaline earth ions such as  $\text{Na}^+$ ,  $\text{Ca}^+$ , etc. [2]

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Woo et al. [3] impregnated MAO-treated zeolite with  $\text{Cp}_2\text{ZrCl}_2$ , but this system needs MAO for the ethylene polymerization. However, Novokshonova and co-workers [4] synthesized the aluminoxane on zeolite by partial hydrolysis of TMA with inside zeolite water and then formed the heterogenized complexes with  $\text{Cp}_2\text{ZrCl}_2$ . Using these catalysts they carried out the ethylene polymerization without addition of supplementary MAO. Suga et al. [5] and Weiss et al. [6] prepared the metallocene supported catalysts based on fixed MAO as the product of TMA partial hydrolysis with clay and  $\text{Cp}_2\text{ZrCl}_2$ .

In this work, we prepared the fixed organoaluminum compounds as the product of partial hydrolysis of TMA with clays and used the compound for ethylene polymerization. The effect of the water and the acidity of the clay were investigated in ethylene polymerization on the clay/TMA– $\text{Cp}_2\text{ZrCl}_2$  systems.

## 2. Experimental

### 2.1. Materials

Montmorillonite K-10 (MMT-10), which has surface area of 220–240  $\text{m}^2/\text{g}$ , was purchased from Aldrich, and Kunipia, which has surface area of 750  $\text{m}^2/\text{g}$ , was donated by Kunimine Co.,  $\text{Cp}_2\text{ZrCl}_2$  and trimethylaluminum and zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) was used as received from Aldrich. Toluene (from Baker Chemicals) was used as a solvent after distillation. Nitrogen and polymerization purity grade ethylene, which was donated by Daerim Petroleum Company, were used after passing the oxy trap and molecular sieve trap to remove oxygen and water.

### 2.2. Intercalation of $\text{ZrOCl}_2$ in the layer of the Kunipia (Zr-Kunipia)

Intercalation of  $\text{ZrOCl}_2$  in the layer of the Kunipia was conducted [7]. Zirconyl oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) was the salt to be hydrolyzed and used as the treatment agent. The oligomeric solution was prepared from  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  by dissolving the equivalent amount of the salt in deionized and distilled water to produce a 0.1 M solution. This solution was aged at room temperature for 10 days at a pH of

1.30 in the synthesis of zirconium intercalated Kunipia; the stoichiometry should be at least 2.5 mmol of Zr/1.0 g clay. Normally, 25 cc of the oligomeric solution was added dropwise to 1.0 g of clay suspension while vigorous stirring was maintained. The reaction took place at 50 °C in a constant temperature bath shaker over a period of 3 days. The sample was then separated and washed by vacuum filtration.

### 2.3. Preparation of organic aluminum compounds on the clay

MMT-10 was used after dried under vacuum at 160 °C or used as received in a hydrated form that contained 4.9 wt.% of water. Kunipia and Zr-Kunipia contained the water content of 10.0 and 7.4 wt.%, respectively. The synthesis of organic aluminum compounds on the clay was carried out in a 250 ml glass reactor at 25 °C with intensive stirring of components. The amount of  $\text{CH}_4$  evolved was determined by a burette. The general method of the treatment of clay by TMA was as follows.

Clays such as hydrated MMT-10, dehydrated MMT-10, Kunipia, and Zr-Kunipia were suspended in toluene, respectively. TMA was injected dropwise into the bottle was allowed to react with water or hydroxyl group in clay. The consumption of the TMA in the reaction was checked by the evolution of the methane gas. When the evolution of the methane gas was stopped, the introduction of the TMA was completed.

### 2.4. IR spectrum

The MMT-10 or Kunipia was pelletized under 250  $\text{kg}/\text{cm}^2$  (3.6  $\text{mg}/\text{cm}^2$ ). The pellet was installed in the in situ IR cell. The clay pellet was allowed to react with TMA in the in situ IR cell for over 3 h at 25 °C. The excess TMA was evacuated under  $1.3 \times 10^{-4}$  Pa and then analysed by Nicolet Magna-IR 560.

### 2.5. Polymerization of ethylene

The ethylene polymerization was carried out in the 1L Parr reactor or 500 ml glass reactor. Toluene, clay slurry and  $\text{Cp}_2\text{ZrCl}_2$  were introduced into the reactor and stirred for 1 h at 50 °C. The polymerization was started as the ethylene was introduced into the reactor.

The ethylene pressure in the reaction zone and the polymerization temperature were held constant. After 1 h, the reaction was terminated with methanol. The molecular weight of PE samples was measured by the viscosity method [8]. The melting point ( $T_m$ ) of PE was determined on a TA2000 differential scanning calorimeter at a heating rate of 10 K/min from 313 to 453 K.

### 3. Results and discussion

Kaminsky and Hahnsen [9] synthesized the methylaluminumoxane (MAO) at moderate conditions by partial hydrolysis of TMA with hydrated water in  $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ . The MMT-10 contains water of approximately 4.9 wt.% measured by TGA. When the MMT-10 was dried at 160 °C for 15 h in vacuum, the adsorbed water on the surface of the MMT-10 would be removed. The peaks for the water in MMT-10 and Kunipia at 3430 and 1640  $\text{cm}^{-1}$  were not observed for the dried MMT-10 and Kunipia as shown in Figs. 1 and 2, respectively. This shows that all of the water in the clay was removed.

In the case of dehydrated MMT-10, 1 g of clay reacted with only 1.0 mmol of TMA and 1.14 mmol of  $\text{CH}_4$  was evolved. However, in the case of hydrated MMT-10, 1 g of clay reacted with 2.8 mmol of

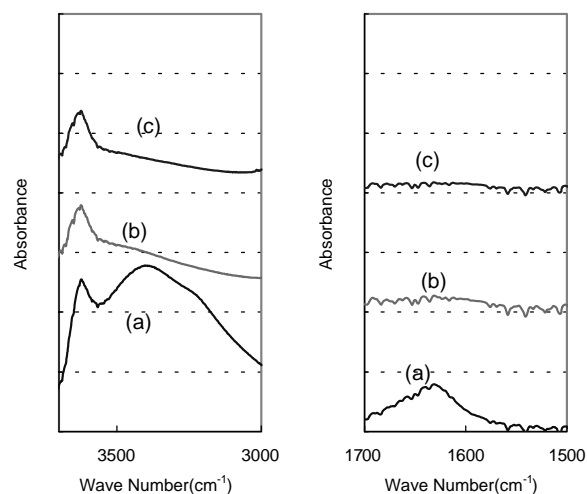


Fig. 1. IR spectra of the MMT-10. (a) Hydrate MMT-10, (b) dehydrate MMT-10, (c) MMT-10 treated with TMA.

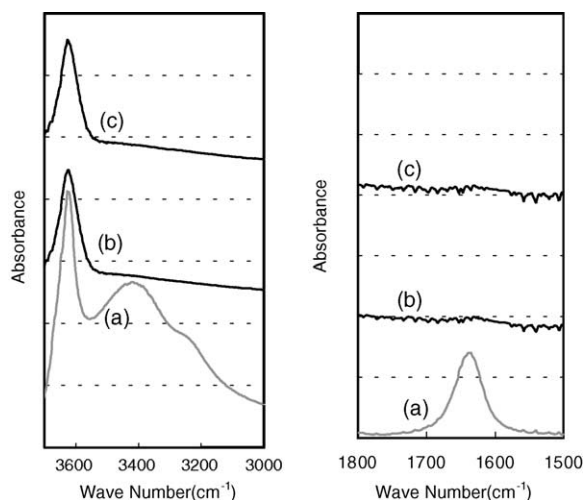


Fig. 2. IR spectra of the Kunipia. (a) Hydrated Kunipia, (b) dehydrated Kunipia, (c) Kunipia treated with TMA.

TMA and 5.72 mmol of  $\text{CH}_4$  was evolved, as shown in Table 1. From these results, we supposed that the 1 mol of TMA reacted with 1 mol of water in hydrated MMT-10 and 1 mol of hydroxyl group in dehydrated MMT-10, respectively. The amount of the water in the hydrated MMT-10 calculated from the reaction of TMA was 5.04 wt.%, which was similar to the value estimated by the TGA. However, the amount of the hydroxyl group reacted with TMA, calculated from the reaction of TMA, is 1.70 wt.%, which was smaller than the amount of the hydroxyl group calculated from its chemical composition in the dehydrated MMT-10. That is, when TMA reacted with dehydrated MMT-10, the hydroxyl group in the dehydrated MMT-10 remained. Thus TMA reacted with all of the water in the hydrated MMT-10 and reacted with a part of the hydroxyl group in the dehydrated MMT-10. The peak, at 3640  $\text{cm}^{-1}$  for the hydroxyl groups in MMT-10 and Kunipia, did not disappear after the reaction with TMA, as shown in Figs. 1 and 2. This indicates that the hydroxyl groups inside the octahedral structure of the clay could not react with TMA, because TMA is too large to migrate to the hydroxyl groups.

The aluminum compounds were attached to the surface of MMT-10 by reacting with TMA. The amount of organic aluminum compounds on the hydrated MMT-10 surfaces was 2.8 times that on the dehydrated MMT-10, as shown in Table 1. The resulting

Table 1

The consumption of TMA and generation of CH<sub>4</sub> in preparation of catalyst

Clay	TMA consumption (mmol Al/g clay)	Amount of CH <sub>4</sub> (mmol CH <sub>4</sub> /g clay)	CH <sub>4</sub> /TMA (mole ratio)	(H <sub>2</sub> O or OH)/g clay (wt.%) <sup>a</sup>
Hydrated MMT-10	2.8	5.72	2.04	5.04 <sup>b</sup>
Dehydrated MMT-10	1.0	1.14	1.14	1.70 <sup>c</sup>

<sup>a</sup> The content be calculated from the amount of the H<sub>2</sub>O or OH reacting with TMA.<sup>b</sup> The content of H<sub>2</sub>O in clay.<sup>c</sup> The content of OH in clay calculated by the consumption of TMA.

Table 2

Effect of dehydration of montmorillonite on ethylene polymerization

Clay	Zr (μmol)	Al <sup>a</sup> /Zr ratio	Al <sup>b</sup> /Zr (TMA)	Activity	M <sub>u</sub> (g/mol)	T <sub>m</sub> (°C)
Hydrated MMT-10	20	300	150	519	274533	135.4
Dehydrated MMT-10	20	300	220	217	307028	134.5

Activity, kg PE/mol Zr h atm. Polymerization conditions: clay, 1 g; temperature, 50 °C; pressure, 50 psi; time, 1 h.

<sup>a</sup> Total aluminum injected to the reactor with the form of clay slurry.<sup>b</sup> Al as TMA form.

organic aluminum compounds on MMT-10 can be used for ethylene polymerization over Cp<sub>2</sub>ZrCl<sub>2</sub> instead of MAO.

Because the excess amount of TMA was used in preparation of the MMT-10 slurry, the reacted TMA and unreacted TMA existed in the MMT-10 slurry. TMA-modified MMT-10 was impregnated with Cp<sub>2</sub>ZrCl<sub>2</sub>. When hydrated MMT-10 was used, the activity for the ethylene polymerization was higher than that of dehydrated MMT-10 at the same Al/Zr ratio, as shown in Table 2. This may be due to the larger amount of the organic aluminum compounds supported on hydrated MMT-10 than on dehydrated MMT-10 because the metallocene catalyst activated by organic aluminum compounds on MMT-10 [6]. There are also free TMA in MMT-10 slurry, while the amount of TMA in dehydrated MMT-10 slurry was smaller than in hydrated MMT-10. Therefore, low activity of dehydrated MMT-10 was due to the larger amount of free TMA on it than that on the hydrated one. Deactivation of Cp<sub>2</sub>ZrCl<sub>2</sub> in olefin polymerization occurs when the active species reacts with one molecule of TMA to form a bimetallic complex. The polymerization activity should decrease with an increase in the TMA concentration [10].

The polymerization curves are shown in Fig. 3. MMT-10 showed very high activity at the initial stage of the polymerization, but the activity was decreased

sharply. The catalytic activity of dehydrated MMT-10 reached the maximum and maintained the level, as shown in Fig. 3.

Tables 3 and 4 show the effect of the Al/Zr ratio and TMA on polymerization performance. When the total amount of aluminum on MMT-10 was increased, the activity was increased as shown in Tables 3 and 4. However, without free TMA, the activity was very low and the catalytic activity was deactivated very rapidly

Table 3

Effect of Al/Zr ratio and TMA on ethylene polymerization by dehydrated MMT-10

Al/Zr	340	340	340	340	680	1000 (MAO)
TMA (Al/Zr)	0	250	500	1000	500	–
Activity	170	305	395	125	1090	880

Activity, kg PE/mol Zr h atm. Polymerization conditions: Zr, 2 μmol; temperature, 50 °C; pressure, 1 atm; time, 1 h; clay, 0.5 g.

Table 4

Effect of Al/Zr ratio and TMA on ethylene polymerization by hydrated MMT-10

Al/Zr	760	760	760	1520	1000 (MAO)
TMA (Al/Zr)	0 <sup>a</sup>	500	1000	500	–
Activity	185	835	465	1365	880

Activity, kg PE/mol Zr h atm. Polymerization conditions: Zr, 2 μmol; temperature, 50 °C; pressure, 1 atm; time, 1 h; clay, 0.5 g.

<sup>a</sup> Polymerization time was 20 min.

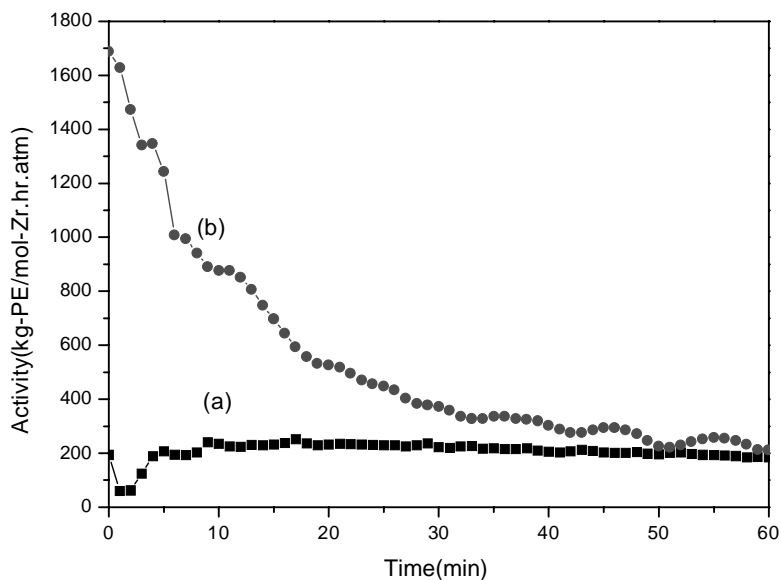


Fig. 3. Polymerization curves for ethylene polymerization over  $\text{Cp}_2\text{ZrCl}_2$  impregnated on clay. (a) Dehydrated MMT-10, (b) hydrated MMT-10. Polymerization conditions are same as Table 2.

as shown in Fig. 4. As the amount of TMA was increased, the maximum activity was obtained at the TMA/Zr molar ratio of 500. These phenomena showed the same trend for both cases. This reveals that organic

aluminum compounds anchored on MMT-10 worked as an activator of  $\text{Cp}_2\text{ZrCl}_2$  for ethylene polymerization, but that it is insufficient to maintain the catalytic activity as shown in Fig. 4(a). This was due to the

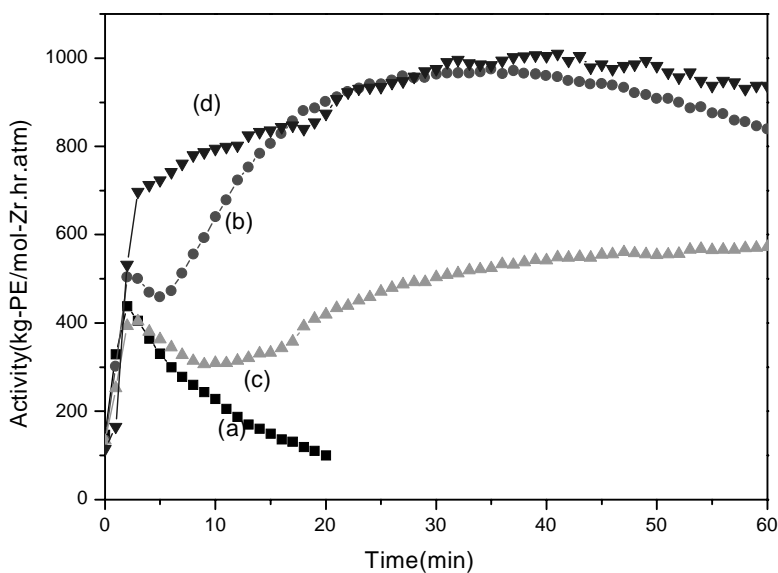


Fig. 4. Polymerization curves for ethylene polymerization over  $\text{Cp}_2\text{ZrCl}_2$  catalyst impregnated TMA-treated hydrated MMT-10. TMA/Zr: (a) 0, (b) 500, (c) 1000 and (d) MAO. Polymerization conditions are same as Table 4.

Table 5  
The relationship between pH of the clay and catalytic activity

	Kunipia/TMA	ZrOCl <sub>2</sub> /Kunipia/TMA	Kunipia/MAO	MMT-10/TMA
pH	10.0	1.2	–	3.2
Activity	Trace	2300	125	1000

Activity, kg PE/mol Zr h atm. Polymerization conditions: Zr, 2 μmol; temperature, 50 °C; pressure, 1 atm; time, 1 h; clay, 0.5 g.

unreacted hydroxyl group exposed to the Cp<sub>2</sub>ZrCl<sub>2</sub> as the polymerization took place in MMT-10. When the polymerization proceeded, the clay was break down to smaller particles, so the unreacted hydroxyl groups can be exposed to the surfaces of the clay. This hydroxyl group can react with Cp<sub>2</sub>ZrCl<sub>2</sub>, resulting in the deactivation.

As shown in Table 2, irrespective of whether there was water or not in MMT-10, the products of the partial hydrolysis of TMA with MMT-10 activated metallocene precursors for ethylene polymerization. In order to survey the effect of acidity on the polymerization, we investigated the basic montmorillonite Kunipia, which has the pH 10.0 in aqueous solution. As shown in Table 5, the catalyst system loaded on Kunipia, which was treated with TMA, did not show any catalytic activity for the ethylene polymerization even though Kunipia contained 10 wt.% of the water. In contrast, Cp<sub>2</sub>ZrCl<sub>2</sub> supported on Kunipia showed catalytic activity for ethylene polymerization when Kunipia was impregnated with MAO. Anchoring of aluminoxane onto the mesoporous host was accomplished by controlled in situ hydrolysis of TMA [11]. It is understood that the aluminoxane compounds work as a Lewis acid to extract anionic ligands such as chloride (Cl<sup>-</sup>) anion from metallocene [12]. Therefore, if the MAO was synthesized and loaded by partial hydrolysis of TMA with water on Kunipia, the Cp<sub>2</sub>ZrCl<sub>2</sub> should show the catalytic activity for the ethylene polymerization.

When Kunipia was acidified via intercalation of ZrOCl<sub>2</sub> in the interlayer of Kunipia, the acidity of Kunipia was changed from pH 10.0 to 1.2 in aqueous phase. Cp<sub>2</sub>ZrCl<sub>2</sub> activated by the product of partial hydrolysis of TMA with acidified Kunipia showed high catalytic activity unlike unmodified Kunipia, as shown in Table 5. Therefore, we were not convinced that the MAO was synthesized in Kunipia as a result of partial hydrolysis of TMA with water.

Chemisorption of metallocene on superacidic solid Bronsted acids have been utilized to activate metallocene precatalysts via metal–carbon bond protonolysis to generate highly electrophilic supported cationic metallocene polymerization catalysts [13].

Sano et al. [14] tried to apply the Al-MCM-41 to the metallocene catalyst system in order to clarify the nature of Lewis acidity of the Al-MCM-41. The polymerization of propylene carried out by rac-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and Al-MCM-41 evacuated at 500–800 °C using triisobutylaluminum (TIBA) as the alkylating agent. They reported that the Lewis acid sites on the Al-MCM-41 were able to effectively activate the metallocene catalyst and acted as counteranions. TMA was supported on the clay to react with OH groups or physisorbed water regardless of the acidity of the clay. However, MAO-like oligomeric aluminum compounds were not produced in the case of basic clay due to the suppression of oligomerization activity.

#### 4. Conclusions

The use of the heterogenized zirconocene catalysts based on fixed organic aluminum compounds as products of partial hydrolysis of TMA with montmorillonite eliminated the requirement of the addition of MAO. The products of partial hydrolysis of TMA with MMT-10 gave the catalytic activity for the ethylene polymerization over Cp<sub>2</sub>ZrCl<sub>2</sub>. Regardless of the presence of water in the montmorillonite, the metallocene catalyst showed catalytic activity when supported on the acidic montmorillonite treated with TMA, while in the case of basic montmorillonite the metallocene catalyst did not show the catalytic activity. As the acidity of the basic montmorillonite changed to acidic by intercalation of inorganic material, Cp<sub>2</sub>ZrCl<sub>2</sub> showed the catalytic activity when

supported on the modified montmorillonite treated with TMA. Therefore, the main factor for the activation of  $\text{Cp}_2\text{ZrCl}_2$  for ethylene polymerization is not the presence of water but the acidity of the montmorillonite.

### Acknowledgements

This research was funded by The Center for Ultra-microchemical Process Systems (CUPS) sponsored by KOSEF (2001–2002).

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