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The role of CaO in the Ziegler–Natta catalyst for propylene polymerization

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A certain amount of CaO enhanced the activity of Ziegler–Natta catalyst during propylene polymerization, but decreased isotacticity. The results indicated that CaO accelerated the initial polymerization rates and improved catalyst against deactivation without effects on melting point, crystallinity and morphology of polypropylene. The electron spin resonance (ESR) results revealed that CaO facilitated the reduction of Ti^{4+} species.

KEY WORDS: Ziegler–Natta catalyst; CaO; $MgCl_2$; ESR; polymerization.

1. Introduction

The Ziegler–Natta catalyst, which comprises of $TiCl_4$, $MgCl_2$ and an electron donor, has been widely employed in propylene polymerization [1]. The use of spherical $MgCl_2$ adducts as the catalyst support gives rise to the activity and also controls polymer morphology via a replica phenomenon [2–4]. Increase in stereospecificity is achieved by introducing an electron donor such as monoester, diester and diether compounds to the catalyst [5]. However, the nature of both catalytic activity and stereochemistry of the catalyst have been changed when inorganic particles as fillers are incorporated in the course of *in situ* propylene polymerization, wherein direct addition of fillers during polymerization is conducted instead of using conventional extrusion [6] or injection molding [7]. The former seems to be superior to the latter in several ways including high particle distribution and improved mechanical properties with low filler-particle concentration. However, some drawbacks have been faced. The chemical incompatibility of nonpolar propylene around hydrophilic inorganic metal such as surface silanol functionalities of SiO_2 [8] and the catalyst sensitivity toward these oxophilic species [9] cause the process not facile. In order to overcome these problems, modified SiO_2 with hydrophobic chains is used to increase polymer/filler synergy and prevents catalyst deactivation but the addition of microsized filler particles can cause masking or pore blockage thereby obscuring the active sites in the course of polymerization [10].

The study presented here was intended primarily to perform *in situ* polymerization synthesis of PP/CaO composites using $MgCl_2$/DEP/$TiCl_4$ catalyst in combination with $AlEt_3$ as cocatalyst which has not been reported before. The influence of the Ca/Ti mole ratio on the catalytic activity and kinetics of propylene polymerization, as well as the properties and morphology of the polymer obtained, were investigated and discussed further.

2. Experimental

2.1. Chemicals

Polymerization-grade propylene and $AlEt_3$ (TEA) were donated from National Petrochemical Public Co., Ltd. and Bangkok Polyethylene Co., Ltd., respectively. $TiCl_4$ and CaO were purchased from Merck Ltd. Anhydrous $MgCl_2$ was supplied from Sigma-Aldrich Inc., Phthalic anhydride, diethylphthalate (DEP, used as an internal donor) *n*-heptane, *n*-decane and 2-ethyl-1-hexanol were purchased from Fluka Chemie A.G. Switzerland. *n*-Hexane was donated by Exxon Chemical Thailand Ltd. and was purified by refluxing over sodium/benzophenone under argon atmosphere prior to use. Ultra high purity argon (99.999%) was obtained from Thai Industrial Gas Co., Ltd. and was further purified by passing through molecular sieves 3 Å , BASF catalyst R3-11G, NaOH and phosphorus pentoxide (P_2O_5) in order to remove traces of oxygen and moisture.

All operations were carried out under an inert atmosphere of argon using a vacuum atmosphere glove box and/or standard Schlenk techniques.

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2.2. Catalyst preparation

A catalyst of type $MgCl_2$/DEP/$TiCl_4$ was synthesized in the following manner. About 0.476 g (5 mmol) of anhydrous $MgCl_2$ was added to 2.5 ml of *n*-decane. This suspension was treated with 2.34 ml (15 mmol) of 2-ethyl-1-hexanol and 0.1089 g (0.74 mmol) of phthalic anhydride at 130 °C. It was stirred until the $MgCl_2$ was dissolved. About 20 ml (182.2 mmol) of $TiCl_4$ was added dropwise at −20 °C, subsequent treatment of the solution in the presence of 0.26 ml (1.3 mmol) of diethylphthalate (DEP) at 110 °C for 2 h. The resulting solid product was separated by filtration and the addition of 20 ml of $TiCl_4$ was repeated at room temperature. After heating and keeping the solution at 120 °C for 2 h, this slurry was siphoned off and washed twice with 10 ml of *n*-decane and three times with 10 ml of hexane, respectively. The catalyst was dried under vacuum for 30 min at 40 °C and contained 3% Ti.

2.3. Propylene polymerization

Propylene polymerization was performed in a 100-ml stainless steel autoclave reactor equipped with a magnetic stirrer. The required amounts of hexane (30 ml), TEA, catalyst (Al/Ti molar ratio = 167) and CaO, with the mole ratio of Ca/Ti between 3 and 28, were added into the reactor. The reaction was conducted at 60 °C. Polymerization was started by continuous feeding of propylene at constant pressure of 60 psi for 1 h. After the polymerization, the reaction was then terminated by venting the reactor and the product was washed with acidic methanol. The resulting polymer was then filtered off and dried in an oven at 110 °C for 6 h.

2.4. Characterization

The electron spin resonance (ESR) spectra of catalyst samples were recorded at ambient temperature, with the use of JEOL JES-FE1XG spectrometer under N_2 atmosphere. The values of the *g* factor were determined against the Mn^{2+} standard. The stereoregularity of the obtained polymer was determined by measuring the isotactic index (I.I., wt% of polymer insoluble in boiling *n*-haptane) through Soxhlet extraction with *n*-heptane for 6 h. Scanning electron microscopy (SEM) measurements were scanned with a JSM-5800LV to obtain morphologies of polypropylene. The samples were prepared by coating with gold and general technique in SEM task has been performed. Melting temperatures and crystallinities of polymers were determined using differential scanning calorimetry, DSC (Perkin-Elmer DSC7), at a ramping rate of 10 °C min^{-1} in temperature range of 30–200 °C. Gel permeation chromatography (GPC) of polymers was performed on a three Shodex AT type columns (AT-803, AT-805 and AT-807) for determining the molecular weight (M_W) and molecular weight distribution (MWD). The columns were calibrated with standard narrow molar mass distribution polystyrenes and the measurements were conducted at 135 °C employing *o*-dichlorobenzene as solvent. The microsize particle was measured with a particle size distribution analyzer (PSD) on a Malvern Model Mastersizer S using laser light scattering technique.

3. Results and discussion

It is well known that three various titanium valences; Ti^{4+}, Ti^{3+} and Ti^{2+} are formed by reacting $TiCl_4$ with an alkylaluminium such as AlR_3 (R = alkyl group). Ti^{3+} species is considerably active for the polymerization of both ethylene and propylene while over-reduction of Ti^{3+} to Ti^{2+} leads to ethylene polymerization only [11,12]. These transition metal oxidation states have been widely investigated through electron spin resonance (ESR) spectroscopy which is useful in detecting free radicals from paramagnetic solid materials. The ESR spectra of the catalyst solution with different addition of CaO are shown in figure 1. It was noted that the amount of Ti^{3+} species could be obtained from relative intensity of a signal with a *g*-factor of 1.970 which was presented in all cases [13,14]. Increasing the Ca/Ti mole ratio was found to result in a gradual increase in the Ti^{3+} species, reaching a maximum value at the mole ratio of 6, and then the content of Ti^{3+} started to decrease. Although it is generally believed that the organoaluminium cocatalyst plays an important role in active site formation by alkylation and reduction of the titanium species, the results obviously demonstrated that small amounts of CaO addition could have some

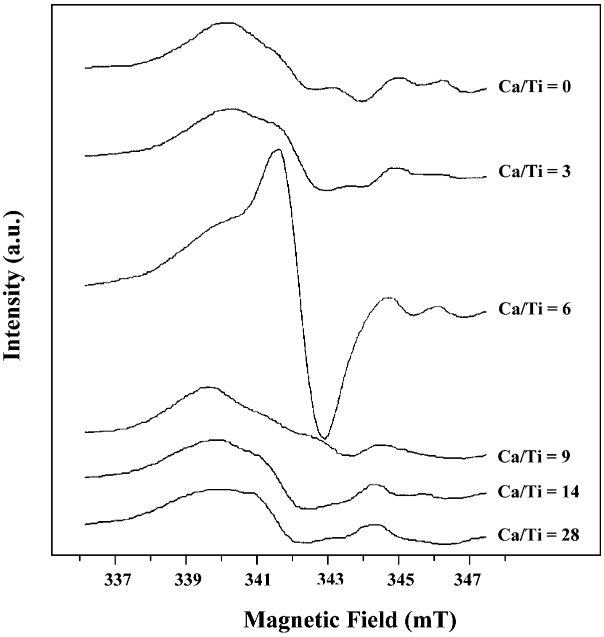


Figure 1. ESR spectra of the catalyst $MgCl_2$/DEP/$TiCl_4$–$AlEt_3$ treated with various Ca/Ti mole ratios.

effect on the induction of Ti^{3+} species as well. In order to develop a better understanding of the effect on CaO addition, the polymerization of propylene was carried out in the semi-batch type autoclave reactor under different reaction conditions of Ca/Ti mole ratio varying from 3 to 28. The propylene consumption was measured by a mass flow meter in order to obtain the activity profiles as shown in figure 2. The activity of all these catalysts exhibited a decay profile. Interestingly, without CaO addition the polymerization proceeded at low reaction rate while the incorporation of which could activate most of the active center in a first few minutes and then followed a fast decay but in higher level. To provide explanations for the aforementioned results, the catalyst activities during the ethylene polymerization were additionally determined and compared with those obtained from the propylene polymerization as shown in figure 3. Only a slight increase in the value of polymerization activity of ethylene was observed while that of propylene was enhanced to attain a maximum value, in which the highest intensity of Ti^{3+} was detected, and then decreased. It was apparent that the addition of a small amount of CaO had an influence on both ethylene and propylene polymerization by increasing the values of active centers leading to monomer insertion acceleration. However, in excess amount CaO can induce over-reduction of titanium to its lower oxidation states, i.e. Ti^{3+} to Ti^{2+}, resulting in poisoning of the catalytic sites for propylene polymerization without a decrease in ethylene polymerization. It should be noted that as reported by Kashiwa *et al.* [11], the presence of Ti^{2+} was more preferred for polymerization of ethylene.

Nitta *et al.* [15] and Liu *et al.* [16] reported that even in the existence of internal electron donor, the alkyl aluminium can transform the monometallic active sites (aspecific or less isospecific) into bimetallic active sites (highly isospecific) by coordinating with the catalyst. Taking this phenomenon into account, the effect of CaO on the active site formation may be attributed to the vacancy occupation by the O^{2-} anions from CaO on the titanium species after its alkylation by cocatalyst as shown in Scheme 1. These O^{2-} provide an increase in the electron density of cationic metal center to form active polymerization site and may stabilize the interaction between this metal and coordinated olefin which could be the main reason for improving resistance of the catalyst to deactivation. However, it may be expected that excess amount of O^{2-} may convert the active center to an inactive one by occupying all vacancies on active species. The other reason to explain this behavior can be attributed to the influence of microparticle size of fillers used on catalyst deactivation. As seen from figure 4, the particle size of CaO determined by the laser light scattering analysis exhibited a very broad uni-modal particle size distribution ranging from 0.3 to 60 μm with an average particle size of 5 μm. García *et al.* [10] studied the *in situ* polymerization of propylene incorporation with silica employing the forth generation Ziegler–Natta catalyst and observed that SiO_2 had some implications on the catalyst deactivation by its physical deposition on the outer surface of the catalyst.

The polymers obtained were characterized and the results are illustrated in table 1, consisting of yield, overall activity, isotacticity index (I.I.), isotactic weight, atactic weight, melting point (T_m), percentage of crystalline polymer (X_c), molecular weight (M_W) and molecular weight distribution (MWD). It was evident that the optimum Ca/Ti mole ratio was reached at 6 in which the highest yield was obtained. In contrast, the isotacticity of polypropylene decreased with an increase in CaO content. Although a number of active sites including aspecific sites and isospecific sites were enhanced, it was obvious that CaO had more significant effect on increasing of the atactic part while high concentrations of the doping treatment led to poisoning the isotactic sites more than the atactic sites.

It is generally accepted that in the presence of internal donor as a Lewis base, it competes with the $TiCl_4$ to

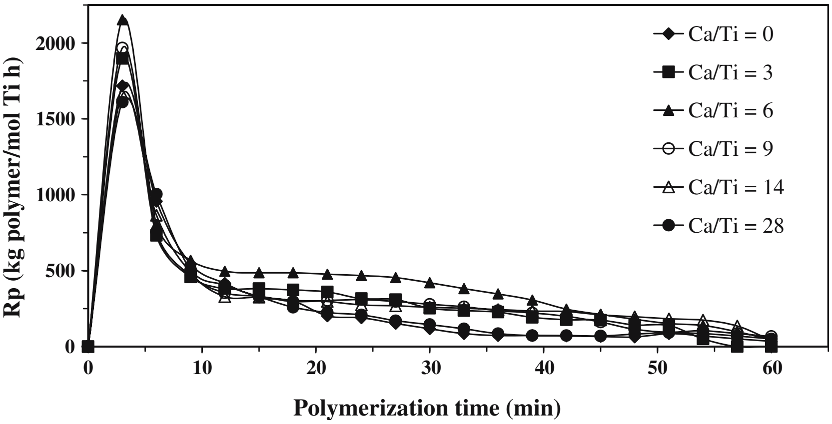
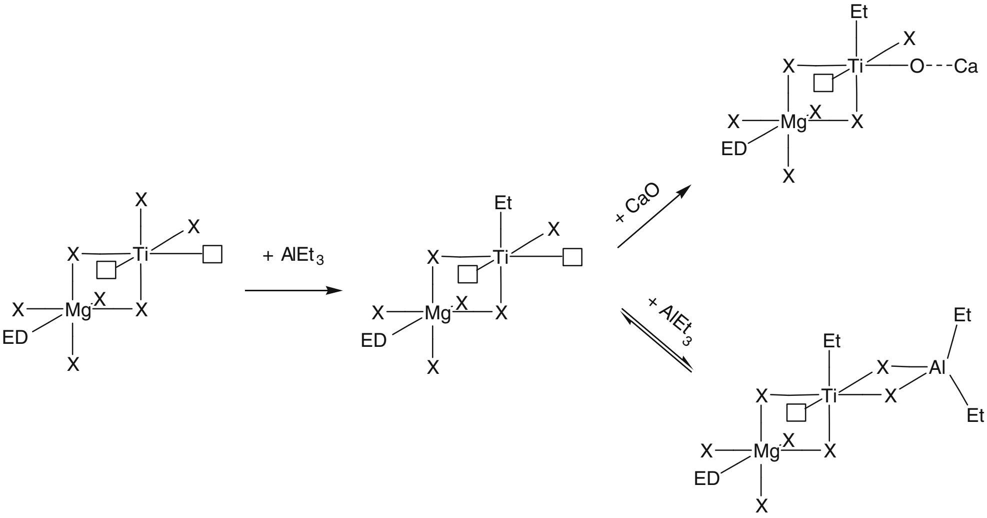


Figure 2. The influence of Ca/Ti mole ratio on *in situ* propylene polymerization kinetics; catalyst: 10 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 167, solvent: *n*-hexane (30 ml), *P*: 60 psi, *T*: 60 °C, *t*: 60 min.



Scheme 1. Suggested mechanism of active site formation catalyzed by CaO in the presence of internal electron donor (ED) (X: –Cl or –Et; □: coordination vacancy).

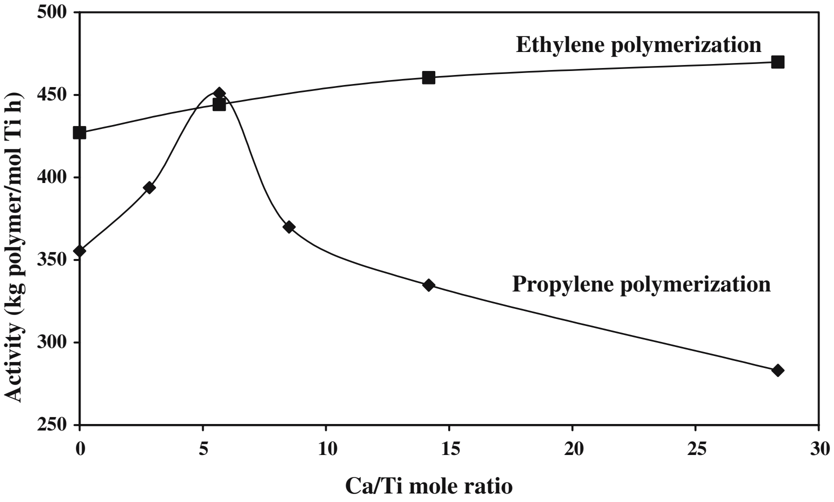


Figure 3. Comparison of the activity of propylene and ethylene polymerization; catalyst: 10 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 167, solvent: *n*-hexane (30 ml), *P*: 60 psi, *T*: 60 °C, *t*: 60 min.

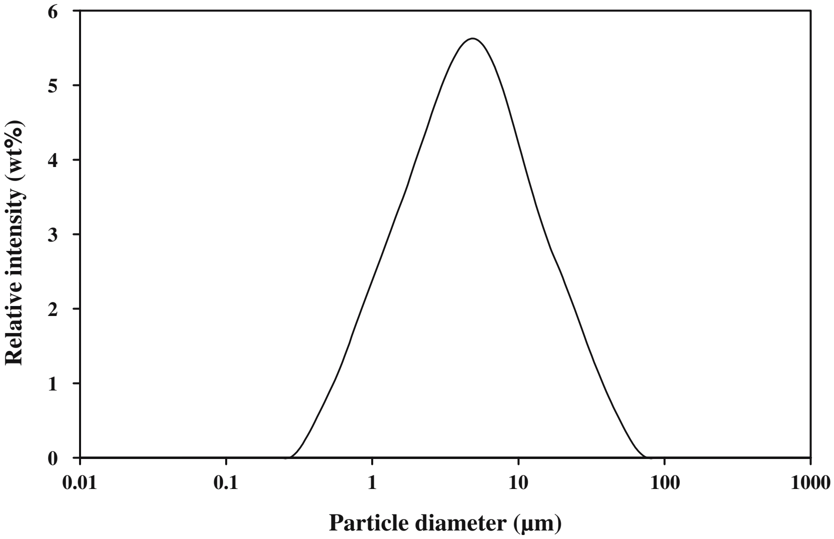


Figure 4. Particle size distribution for microsized calcium oxide.

Table 1
Characterization of polypropylene obtained by catalysts with different Ca/Ti mole ratios

Ca/Ti mole ratio	Yield (g)	Activity (kg polymer/mol Ti h)	I.I.(%)[a]	isotactic PP (g)	atactic PP (g)	T_m (°C)[b]	X_c[b]	M_w[c]	MWD[c]
0	2.2390	355	87.3	1.9536	0.2854	155.3	25.2	309387	15.7
3	2.4810	394	78.6	1.9500	0.5310	156.9	26.8	–[d]	–[d]
6	2.8406	451	76.1	2.1629	0.6777	153.3	27.3	291819	15.9
9	2.3310	370	73.6	1.7165	0.6145	153.4	29.0	–[d]	–[d]
14	2.1087	335	71.7	1.5118	0.5969	158.0	27.9	–[d]	–[d]
28	1.7833	283	71.1	1.2686	0.5147	157.8	27.2	281688	16.3

[a] I.I. = isotactic index, determined by Soxhlet extraction with *n*-heptane for 6 h.
[b] Obtained from DSC.
[c] Obtained from GPC.
[d] Not determined.

coordinate with the vacant coordination sites especially on (110) faces of $MgCl_2$ which in turn higher acidic properties and non-stereospecific active centers. Consequently, Ti species can adsorb on the $MgCl_2$ (100) face instead to form stereospecific sites [17,18]. However, it is important to note in this work that the DEP coordinates much more weakly with the catalyst surface, so it can be easily extracted by TEA from catalyst surface during polymerization resulting in poor stereo selectivity of polymer received.

As can be seen from Scheme 1, it is interesting that the addition of CaO may convert nonstereospecific site to isospecific one by occupying vacancies with O^{2-} anions. On the contrary, this interaction could block the bimetallic active site formation which gives highly isospecific polypropylene. However, it is unclear that how

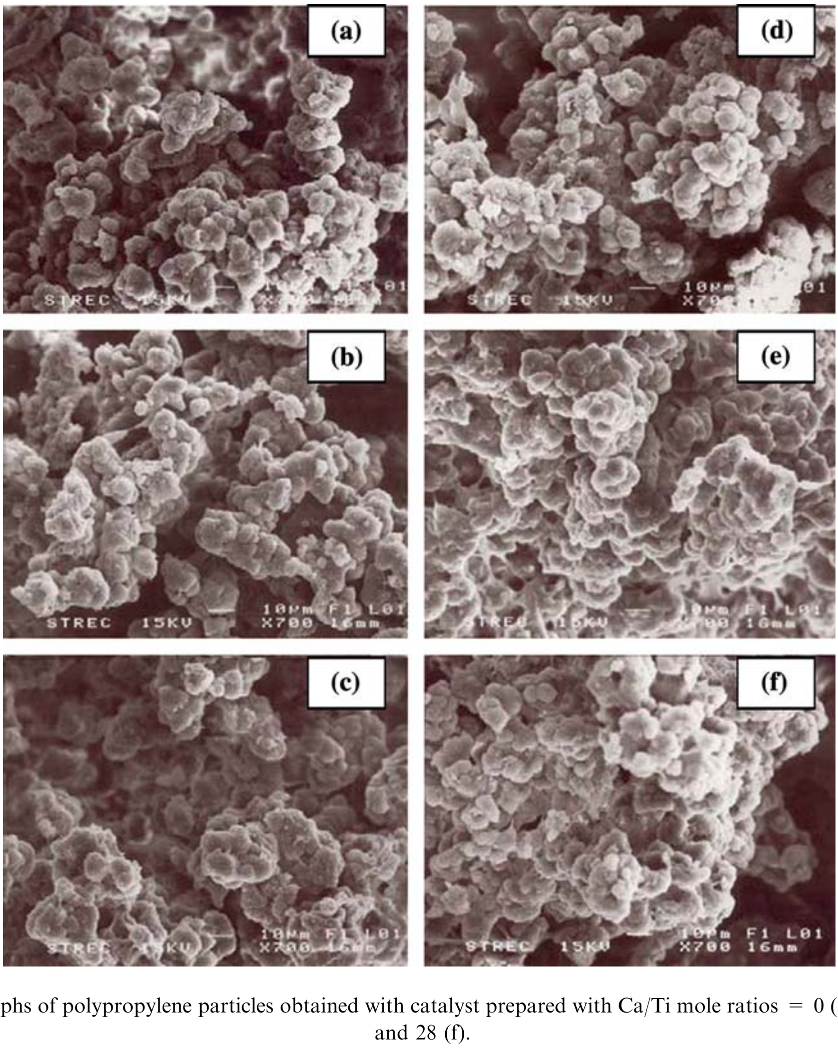


Figure 5. SEM micrographs of polypropylene particles obtained with catalyst prepared with Ca/Ti mole ratios = 0 (a), 3 (b), 6 (c), 9 (d), 14 (e) and 28 (f).

CaO can have a strong decrease in the tacticity of the polymer. By considering the M_w, X_c and T_m of the product (table 1), its crystallinity and melting point remained high while the M_w slightly decreased. One possible explanation is that in the presence of CaO the low molecular weight isotactic polypropylene was produced and could be dissolved in boiling *n*-heptane during Soxhlet extraction resulted in low I.I. detected. It can, moreover, be noted that the addition of small amount of fillers did not affect the melting behavior and crystallinity of the resulting polymer. In addition, SEM micrographs (figure 5) demonstrated that the morphology of all polymers produced with different Ca/Ti addition were virtually similar.

4. Conclusions

Incorporation of CaO during *in situ* polymerization of propylene employing the Ziegler–Natta catalyst showed activity enhancement during the initial stage of polymerization through the reduction of Ti^{4+} to Ti^{3+} which was verified by ESR results. The effect was maximum at Ca/Ti mole ratio = 6. The results also suggested that the presence of inorganic filler even in smaller amounts could improve catalyst against deactivation. However, while the overall catalytic activity increased the stereo selectivity apparently decreased. The properties of the resulting polymer such as T_m, X_c and morphology did not change with varying the mole fractions of Ca/Ti.

Acknowledgments

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