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PROPYLENE POLYMERIZATION ACTIVITY AND ACIDIC PROPERTY OF METAL SULFATES

By

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Abstract

The polymerization reaction of propylene catalyzed by solid acids such as nickel sulfate, cupric sulfate, aluminum sulfate, titanium oxide *etc.* was studied. It was found that the polymerization rate calculated from the volume decrease of propylene at the constant pressure best correlates with the acidity at acid strength $H_0 \leqq +1.5$ in both cases of nickel sulfate and cupric sulfate. Aluminum sulfate having the acidity 0.7∼0.8 mmol/g at $H_0 \leqq +1.5$ lost the catalytic activity when it was poisoned with 0.8 mmol of ammonia. No catalytic activity was found for titanium oxide which has only weak acid sites but no strong acid sites of $H_0 \leqq +1.5$. From these results it was concluded that the acid sites having acid strength $H_0 \leqq +1.5$ are catalytically active for the propylene polymerization.

Introduction

We have reported previously that metal sulfates such as nickel sulfate, aluminum sulfate *etc.* showed fairly strong acidic property on the surface and that the acidic property changed remarkably on heat-treatment.[1)][2)] Recently TARAMA *et al.* found that the metal sulfates catalyzed the polymerization of propylene and that the catalytic activity increased with increase of the number of the acid sites having acid strength $H_0 \leqq +3.3$.[3)] However, the range of acid strength of catalytically active site is not clearly shown, since they used the only one indicator of $pKa = +3.3$. More recently we have found that acid sites having various acid strength exist on the surface of nickel sulfate.[4)] In order to test how the catalytic activity correlates with the acid strength of the catalysts as well as their acidity, we have investigated the polymerization of propylene by using nickel sulfate and some other solid acids as catalysts.

Experimental

Materials and Reagents: Nickel sulfate ($NiSO_4 \cdot 7H_2O$, guaranteed reagent of Kanto Chemical Co., Tokyo) was heated in an electric furnace attached

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with a thermocouple for 3 hours at various temperatures ranging from 150 to 600°C and cooled in an evacuated desiccator before use. The powdered catalyst collected between 100 and 200 or 200 and 300 mesh sieves was used. Cupric sulfate ($CuSO_4$ anhydrous, guaranteed reagent of Kanto Chemical Co.) and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, extra pure reagent of Kojima Chemical Co., Tokyo) were heat-treated at 300°C for 3 hours. Aluminum chlorides used were G. R. anhydrous material (Kanto Chemical Co.) heat-treated in vacuum (10^{-2} mmHg) for 15 minutes at 150°C and G. R. hydrate (Kanto Chemical Co.) heat-treated in vacuum (10^{-2} mmHg) for 3 hours at 150°C. Titanium oxide used was G. R. material of Kanto Chemical Co.

Propylene (C. p. grade of Matheson Co., U.S.A.) and ammonia were purified by distillation in vacuum. *n*-butylamine (E. P. reagent of Tokyo Chemical Industry Co.) was used without further purification. All indicators used for the determination of acidic property were of the same preparations as those described in our previous work.[4)5)] Benzene (G. R. of Kanto Chemical Co.) used as a solvent for the indicators was purified by drying over sodium followed by distillation.

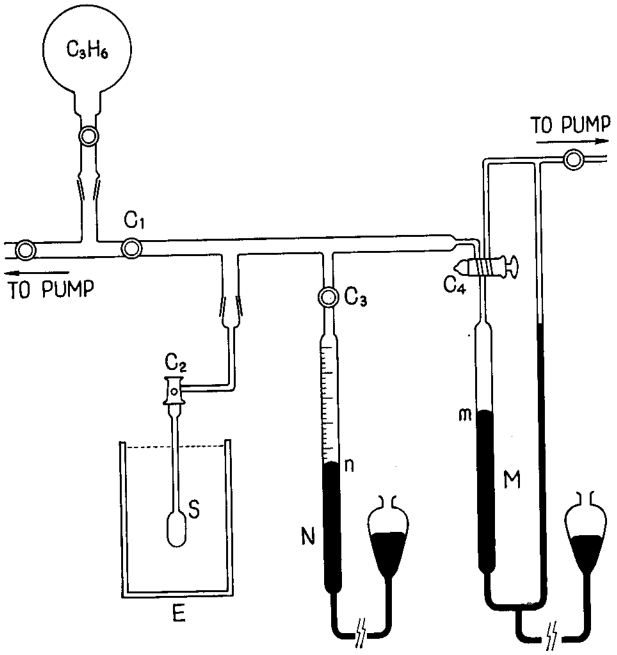

Fig. 1. Apparatus, C_1, C_2 *etc.*: stopcocks, S: sample tube, M: manometer, N: gas burette, E: electric furnace or water bath.

Measurement of Polymerization Rate: The rate of the polymerization of propylene was followed by using the apparatus shown in Fig. 1. After outgassing (10^{-6} mmHg) the catalyst and the apparatus, propylene was allowed to enter the system $C_1 C_2$ n m and then expanded into the sample tube S containing 1 g or 2 g of catalyst maintained at a constant temperature, the pressure of propylene being immediately read by using mercury manometer M. The pressure tends to decrease when propylene is brought in contact with catalyst because of the polymerization and/or the adsorption, but it was kept constant by decreasing the volume of the reaction system by operating gas burette N manually. The volume decrease was rapid in early stage but after 20~30 minutes a slow decrease (ΔV) at constant rate was observed. The inclination of the straight line appeared in later stage ΔV cc (S.T.P.)/min was taken as the rate of polymerization.

Measurement of Acidity and Acid Strength: Surface acidity and acid strength of the catalysts used were measured similarly as in the previous work.[4)]

Poisoning with Basic Compounds: A known amount of ammonia from a gas burette was introduced onto the solid catalyst kept at 50°C. After measuring the pressure, ammonia was evacuated. The amount of the adsorbed ammonia was calculated from the amount of ammonia initially introduced and that remained in the gaseous phase after the adsorption. In the case of *n*-butylamine the catalyst was kept under the vapor of the amine for 15 minutes at its saturated vapor pressure at room temperature followed by the evacuation of the amine. No attempt was made for the determination of the amount of the amine adsorbed.

Results and Discussion

1) Temperature and Pressure Dependence on Polymerization Rate.

Dependence of reaction temperature is shown in Table 1. The polymerization

TABLE 1. Effect of reaction temperature on the polymerization rate.

Propylene pressure: 408 mmHg,
Catalyst: 2 g of $NiSO_4$ heat-treated for 3 hours at 350°C.

Reaction temperature °C	Polymerization rate v cc/min, g
30	0.022
100	0.050
200	0.013

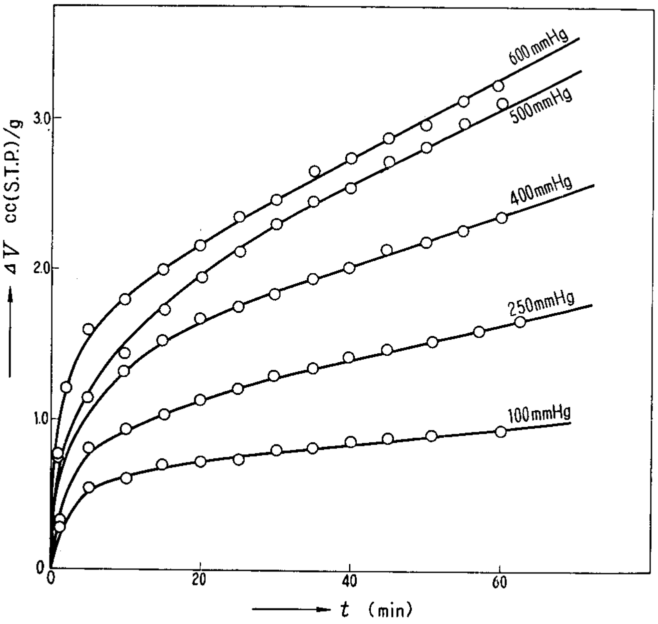

Fig. 2. Volume decrease of propylene at different pressure. Temperature: 100°C, Catalyst: $NiSO_4$ (200~300 mesh) heat-treated at 350°C for 3 hrs.

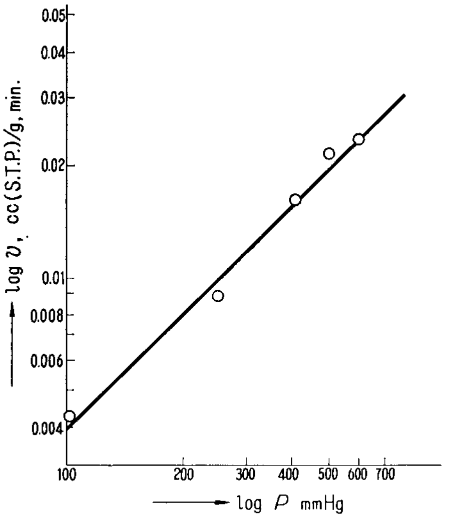

Fig. 3. Polymerization rate *vs.* pressure of propylene. Temperature: 100°C, Catalyst: $NiSO_4$ (200~300 mesh) heat-treated at 350°C for 3 hrs.

rate increases with increase of reaction temperature from 30 to 100°C, but decreases with increase of temperature from 100~200°C. This agrees with the results observed by TARAMA *et al.* that the maximum of the propylene polymerization rate appeared at the reaction temperature of around 110~120°C when silica-alumina[6] or nickel sulfate[3] was used as the catalyst. They interpret the maximum as being due to the increase or decrease of the amount of chemically adsorbed propylene.[6] Dependence of propylene pressure at 100°C is shown in Fig. 3, where the logarithm of the polymerization rate is plotted against the logarithm of propylene pressure. The rate of polymerization was calculated according to the method described in the foregoing section from the plot of the volume decrease of propylene against reaction time as shown in Fig. 2. A straight line with inclination +1 as observed in Fig. 3 represents a reaction of first order in the partial pressure of propylene.

2) Correlation of Polymerization Activity with Acidic Property of Nickel Sulfate: Acidity and acid strength of the nine samples of 100~200 mesh nickel sulfate which were heat-treated at various temperatures ranging 150~600°C for 3 hours are shown in Table 2. The rates of polymerization catalyzed by the nine catalyst samples are given also in the Table, which were calculated from the plot of ΔV *vs.* t as shown in Fig. 4. As seen in Table 2,

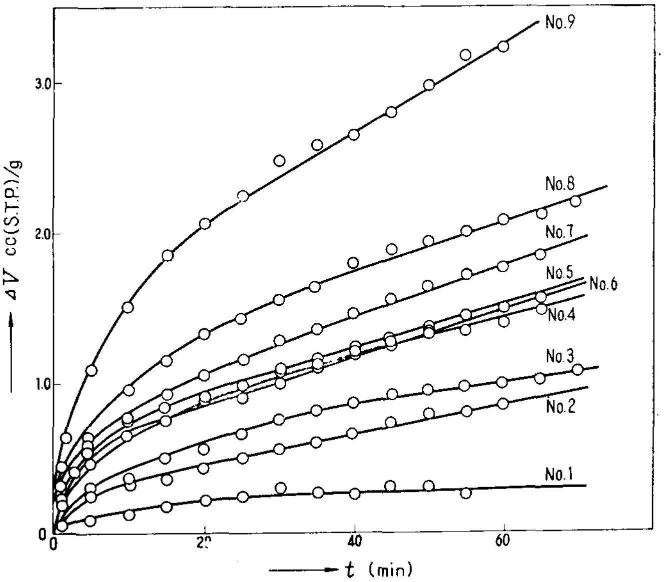

Fig. 4. Volume decrease *vs.* time for nine samples of $NiSO_4$ heat-treated at various temperatures shown in Table 2. Reaction temperature: 100°C, Pressure: 400 mmHg.

TABLE 2. Polymerization rate and acidic property of $NiSO_4$.
Reaction temperature: 100°C, Propylene pressure: 400 mmHg.

No. of Samples	Temperature of heat-treatment °C	Acidity, mmoles/g					Polymerization rate v cc (S.T.P.)/min, g
		Methyl red ($pKa = +4.0$)	Benzene-azo-α-naphthylamine ($pKa = +4.0$)	p-dimethylamino-azobenzene ($pKa = +3.3$)	Benzeneazo-diphenylamine ($pKa = +1.5$)	Dicinnamal-acetone ($pKa = -3.0$)	
1	600	0.032	0.022	<0.004	<0.004	0	0
2	150	0.031	0.027	0.023	0.023	0	0.0091
3	250	0.035	0.036	0.029	0.026	0.011	0.0093
4	350	0.105	0.093	0.073	0.074	0.028	0.013
5	464	0.069	0.067	0.043	0.042	0	0.013
6	367	0.093	0.083	0.065	0.069	0.009	0.015
7	300	0.092	0.081	0.073	0.067	0.034	0.016
8	400	0.085	0.086	0.077	0.071	0.030	0.016
9	325	0.136	0.138	0.120	0.118	0.063	0.028

No. 1 sample which has an appreciable acidity at acid strength $H_0 > +3.3$, but no or little acidity at $H_0 \leqq +3.3$ shows no catalytic activity for the polymerization. Fig. 5 shows that any plots of the polymerization rates against the acidities of nine samples at any acid strength ranges $+4.0 < H_0 \leqq +4.8$, $+3.3 < H_0 \leqq +4.0$ and $+3.3 < H_0 \leqq +4.8$ deviate largely from a straight line with inclination $+1$. These facts indicate that the weak acid sites having acid strength $H_0 > +3.3$ are not catalytically active for the propylene polymerization.

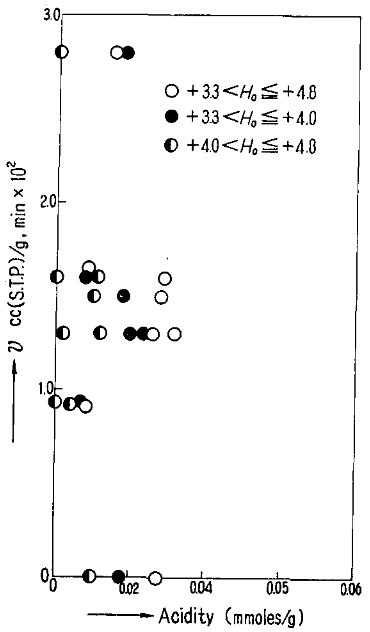

Fig. 5. Polymerization rate *vs.* acidity at weak acid strength range. Catalyst: $NiSO_4$.

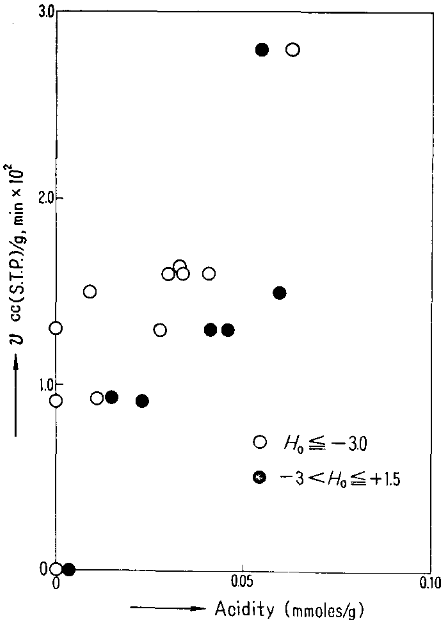

Fig. 6. Polymerization rate *vs.* acidity at strong acid strength range. Catalyst: $NiSO_4$.

Since it is seen in Table 2 that the acidity measured by using *p*-dimethylaminoazobenzene of $pKa = +3.3$ as an indicator is almost the same as that measured by using benzeneazodiphenylamine of $pKa = +1.5$, there exist almost no acid sites having acid strength $+1.5 < H_0 \leqq +3.3$. The polymerization rates in Table 2 are now plotted against the acidities at $-3.0 < H_0 \leqq +1.5$, $H_0 \leqq -3$ and $H_0 \leqq +1.5$. The plots with the acidities at $-3.0 < H_0 \leqq +1.5$ and $H_0 \leqq -3$ deviate largely from a straight line with inclination $+1$ as shown in Fig. 6, while those with the acidity at $H_0 \leqq +1.5$ lie on a comparatively good straight line as shown in Fig. 7.*) Therefore, it seems likely that the acid sites having

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*) The data of Table 3 were also plotted.

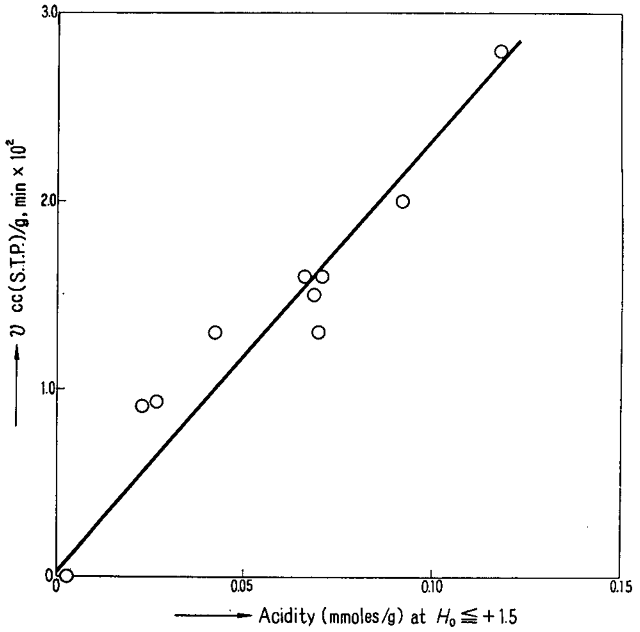

Fig. 7. Polymerization rate *vs.* acidity at acid strength $H_0 \leqq +1.5$.

acid strength $H_0 \leqq +1.5$ are catalytically active. JOHNSON reported that silica-alumina polymerizes propylene and the polymerization activity correlates with the acidity measured by using *p*-dimethylaminoazobenzene of $pKa = +3.3$ as an indicator.[7] Since it was reported by BENESI[8] that silica-alumina has no or little acid sites having weaker acid strength than $H_0 = -8.2$, JOHNSON's observation is in good accord with our conclusion. However, it seems impossible with silica-alumina having only strong acid sites at $H_0 \leqq -8.2$ to investigate the extent of strength of acid site which is active for the polymerization. That the observation by TARAMA *et al.*[3] as mentioned in introduction should be inevitably included in our conclusion, since there are no acid sites having acid strength $+1.5 < H_0 \leqq +3.3$ as shown in Table 2.

3) **Polymerization by Various Solid Acids.** The results of the propylene polymerization catalyzed by titanium oxide, cupric sulfate and aluminum chloride are shown in Table 3. The polymerization rates were calculated from Fig. 8 as described in the foregoing section. Titanium oxide without heat-treatment is known as an solid acid which has only weak acid sites, *i.e.*, whose acidity is 0.01 mmol/g at acid strength $H_0 \leqq +4.8$, but 0 at acid strength $H_0 \leqq +1.5$.[*] The rate of polymerization by this solid acid was found to be

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[*] The acidity at $H_0 \leqq +3.3$ is also zero.

TABLE 3. Polymerization activity and acidity at $H_0 \leqq +1.5$ of various solid acids.

Reaction temperature: 100°C, Propylene pressure: 400 mmHg.

Catalyst			Acidity at $H_0 \leqq +1.5$	Polymerization rate
Chemical form before heat-treatment	Heat-treatment			
	Temp. °C	Time	mmoles/g	v cc (S.T.P.)/g, min
TiO_2			0	0
$CuSO_4$	300	3 hr	0.035	0.0074
$NiSO_4 \cdot 7H_2O$	340	3 hr	0.092	0.020
$AlCl_3 \cdot 6H_2O$	150 in vacuum	3 hr	<0.5	0.080
$AlCl_3$	150 in vacuum	15 min	cannot be measured	very fast

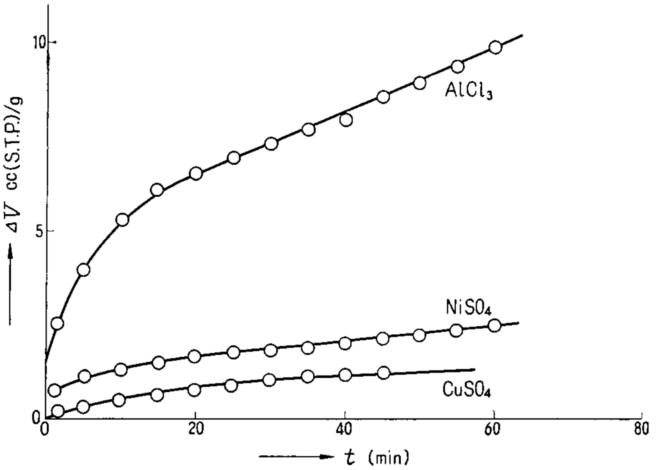

Fig. 8. Volume decrease *vs.* time. Temperature: 100°C, Pressure: 400 mmHg.

zero. This agrees with the conclusion obtained for nickel sulfate that the acid sites having $H_0 \leqq +1.5$ is catalytically active for the polymerization. Cupric sulfate having the acidity at $H_0 \leqq +1.5$ polymerizes propylene. In both cases of cupric sulfate and nickel sulfate, the polymerization rate increases with increasing the acidity at $H_0 \leqq +1.5$ as shown in Fig. 9.[**] Aluminum chloride hydrate heated in vacuum showed a great catalytic activity, though it was unfortunate that the acidity cannot be quantitatively determined according to the present method, since it took long time to resume the color of the basic

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[**] The data were taken from Tables 2 and 3.

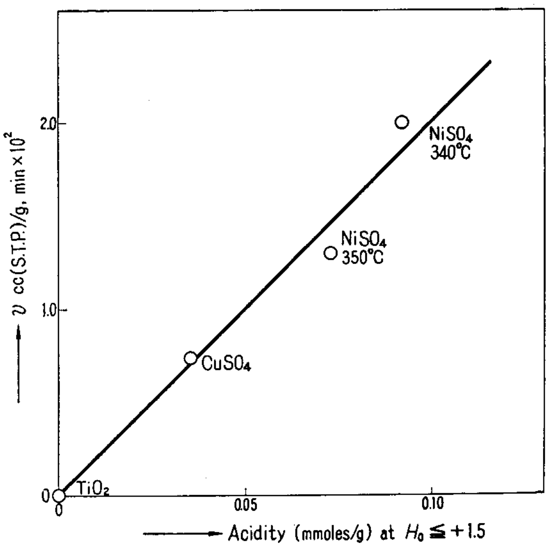

Fig. 9. Correlation of polymerization rate with acidity at $H_0 \leqq +1.5$. Temperature: 100°C; Pressure: 400 mmHg.

form of the indicator by the amine titration, resulting in the poor reproducibility of the data. The rate of polymerization by anhydrous aluminum chloride heated in vacuum was too fast to estimate. The acidity of the anhydrous material could not be measured, since the color of the conjugate acid form of the indicator adsorbed on the chloride did not change to the color of the basic form even with the addition of more than 50 ml of 0.1 N *n*-butylamine per gram of the chloride.

4) **Polymerization by Aluminum Sulfate Poisoned with Basic Compounds.** The results are shown in Table 4. Aluminum sulfate having 0.7~0.8 mmol/g acidity at $H_0 \leqq +1.5$ showed a high catalytic activity, but lost

TABLE 4. Polymerization by $Al_2(SO_4)_3$ poisoned with ammonia and *n*-butylamine.
Reaction temperature: 50°C, Propylene pressure: 400 mmHg.

Catalyst	Acidity at $H_0 \leqq +1.5$ mmoles/g	Polymerization rate v cc (S.T.P.)/g, min
$Al_2(SO_4)_3$	0.7~0.8	0.040
$Al_2(SO_4)_3$ poisoned with *n*-butylamine	expected to be zero	0
$Al_2(SO_4)_3$ poisoned with 0.81 mmol ammonia	expected to be zero	0

entirely the catalytic activity when the all acid sites are poisoned with *n*-butylamine or with 0.81 mmol ammonia per gram of the catalyst. This indicates that the active site of the catalyst is the acid site and more in detail the acid site having acid strength $H_0 \leqq +1.5$ is catalytically active for the polymerization in conformation with the conclusion for nickel sulfate and cupric sulfate.

Acknowledgment

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