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The Character of Acid Sites on the Gypsum Surface

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The maximum value in the number of acid sites per unit of surface area of the gypsum formed in the reaction between $Ca(NO_3)_2$ and H_2SO_4 was observed at the heat-treatment temperature of 200 °C, corresponding to the dehydration temperature for the change from its hemihydrate form to soluble anhydrite. The IR-absorption spectra of the gypsum showed no bands assignable to isolated OH groups or Ca–OH species. The IR spectra of the pyridine adsorbed on the gypsum showed only the bands due to Lewis-acid sites. The gypsum heat-treated at temperatures lower than 500 °C showed catalytic activities for the double-bond isomerization of 1-butene. The *cis-/trans-* ratio of 2-butene was 2—2.5, showing that the catalytic activity was due to Lewis acid, not to Brönsted acid. The isomerization of cyclopropane to propene was scarcely promoted by the gypsum at 250 °C. This fact is another indication of the absence of Brönsted acid sites on the heat-treated gypsum. Most of the weak Lewis acid sites ($H_0 \leqq +4.8$) were ascribable to exposed Ca^{2+} ions surrounded by monodentate sulfate ions on the surface of metastable anhydrite III-$CaSO_4$.

In recent years, gypsum has been obtained in great quantities as a by-product in the SO_2-recovery process from exhaust gases. Accordingly, the development of a new method of utilizing the recovered gypsum is desirable. Use as a filler or a reinforcement agent in composite materials seems to be promising. Because of the polar nature of the gypsum surface, however, surface modification or an increase of lipophilicity is necessary for the two uses mentioned above. As has been shown in the previous study[1)] dealing with the increase in lipophilicity of the gypsum surface upon interaction with butylamine, acid sites on the surface may be used for the surface modification.

The presence of acid sites on the calcium-sulfate surface was first reported about thirty years ago.[2)] The surface acidity of gypsum has been investigated by subsequent workers.[3–6)] Although the acid sites have been assumed to be the Lewis type,[7)] the Lewis acidity has not beed substantiated. The absence of Brönsted sites has not yet been examined. Furthermore, the relation between the surface acidity and the catalytic activities for the acid-catalyzed reaction has scarcely been investigated.

In the present work, the character of acid sites on the surface of precipitated gypsum was investigated mainly by means of IR-spectroscopic measurements and by the determination of catalytic activities for the isomerization of 1-butene and the conversion of cyclopropane to propene.

Experimental

Materials. The precipitated gypsum used was prepared by the addition of concentrated sulfuric acid to an aqueous solution of $Ca(NO_3)_2$, followed by aging and completely washing with deionized water. The nitrate ions remaining in the precipitate could be removed with ease by the heat-treatment of the product, as evidenced by the trace amounts of NO_2 gas evolved during the heat-treatment. The carbonate content was determined to be 0.09 wt% by the gas-chromatographic analysis of the gas evolved during the heat-treatment of the sample up to 900 °C.

IR Spectra. Except for the study relating to the coordinations of $SO_4{}^{2-}$ ions, which was carried out by using KBr pellets, the IR spectra were measured using a self-supporting disc in an *in situ* cell. The samples were compressed into thin discs and were evacuated at different temperatures.

X-Ray Diffraction and Surface Area. The X-ray powder diffraction patterns were recorded using Cu $K\alpha$ as the radiation source. The specific surface area was determined by applying the BET method to the adsorption of N_2 at −196 °C.

Acid Properties. The acid properties of samples were examined by titrating with butylamine in benzene according to Johnson's method.[8)] The Brönsted and Lewis acidities were determined by observing the IR spectra of pyridine adsorbed on the samples.

1-Butene Isomerization. The 1-butene isomerization was carried out in a closed gas-circulation reactor having a volume of 0.43 l. Above 0.7 g of the sample was placed in the reactor and degassed for 2 h at various temperatures. After the sample has then been cooled to room temperature, 1-butene of 110 Torr was introduced and circulated for 0.5 h at 200 °C. The products were analyzed by gas chromatography using a 7-m column packed with VZ-7.

The catalytic activity was expressed by the mole percentage of the product per unit of weight of the catalyst (g^{-1}) per unit of time (min^{-1}) determined at the reaction time of 30 min. As an indication of the acid character, the mole ratio of *cis*-2-butene to *trans*-2-butene (abbreviated as *cis-/trans-*) at zero conversion in the isomerization was determined by extrapolation.

Conversion of Cyclopropane to Propene. The conversion was carried out in a glass reactor containing 0.05 g of gypsum which had been heat-treated at various temperatures. Pulses of cyclopropane were injected into the helium-carrier stream from a calibrated, 1.09-ml doser and were passed through the gypsum at a total pressure of 1 atm. The product gas was analyzed by gas chromatography using a 3-m column packed with Porapack N. The conversion of cyclopropane to propene in the first pulse was taken as a measure of the catalytic activity.

Results and Discussion

Changes in Structures and Surface Areas of Gypsum with Increase in Treatment Temperature. As is shown in Table 1, the results of the X-ray diffraction analysis for the sample show that the monoclinic structure of the dihydrate changed into the hexagonal structure of the hemihydrated gypsum (β-$CaSO_4 1/2H_2O$) or soluble anhydrite (III-$CaSO_4$) at about 100 °C, and then into the orthorhombic structure of the insoluble anhydrite (II-$CaSO_4$) at about 400 °C. The changes in the

Table 1. Crystal structure and specific surface area of gypsum heat-treated at different temperatures

Treatment temp °C	Crystal structure	Specific surface area/m² g⁻¹
Room temperature	$CaSO_42H_2O$	3.3
100	$CaSO_41/2H_2O$ or III-$CaSO_4$	13.5
200	$CaSO_41/2H_2O$ or III-$CaSO_4$	7.3
300	$CaSO_41/2H_2O$ or III-$CaSO_4$	21.8
400	II-$CaSO_4$	26.8
500	II-$CaSO_4$	26.7
600	—	21.3
700	—	4.3

crystal structure of the sample with the increase in the temperature almost coincided with that reported for gypsum ($CaSO_42H_2O$).9) However, the change of β-$CaSO_41/2H_2O$ into III-$CaSO_4$ at 190—210 °C9) could not be observed, since these two forms are very similar or the almost isomorphous with each other.10,11)

Table 1 also shows the effect on the surface area of heating up to 700 °C. The specific surface area of the sample depends largely on the heat-treatment temperature. Two maxima are observed at about 100 °C and 400—500 °C. These temperatures are nearly equal to the transition points of the dihydrate to the hemihydrate, and of the soluble anhydrite to the insoluble anhydrite, respectively. These facts suggest that the change in crystal structure may increase the surface area. Because of the similarity in crystal form, the transformation of β-$CaSO_41/2H_2O$ to III-$CaSO_4$ may not cause the increase in the surface area.

Surface Acidity Determined by Amine Titration. Figure 1 shows the surface acidities of the sample heat-treated at different temperatures. The sample has no acid sites stronger than those corresponding to an H_0 value (indicator, pK_a) of 3.0, but it does display some weak acidity in the range of H_0 from 4.8 to 3.0. The acid amount per unit of weight showed a maximum value at a heat-treatment temperature of 300 °C.

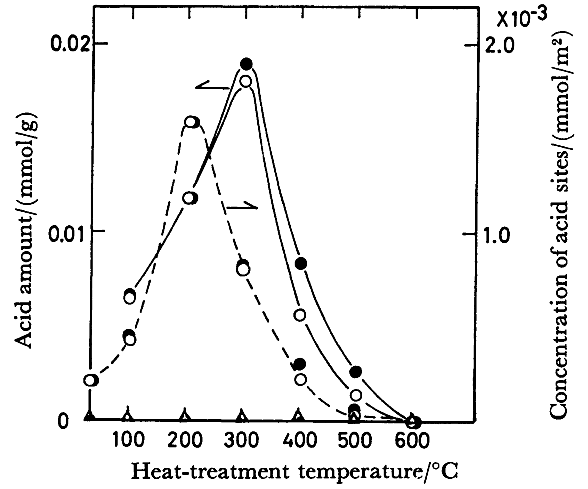

Fig. 1. Effect of treatment temperature on acid amount and acid site concentration.
△: $H_0 \leqq 3.0$, ○: $H_0 \leqq 4.8$, ●: $H_0 \leqq 6.8$.

To discuss the acid-site concentration on the surface, the acid amounts per unit of surface were calculated, as is shown by the dotted line in Fig. 1. A maximum in the acid-site concentration is shown at about 200 °C. From a structural point of view, the temperature at which the maximum acid concentration was obtained (200 °C) corresponds to the transition temperature of the hemihydrated gypsum to the soluble anhydrite form.9) The soluble anhydrite has a crystal structure almost isomorphous with that of hemihydrated gypsum and has an active cleavage plane, on which Ca^{2+} and SO_4^{2-} ions are unevenly distributed.7) It is well known that the soluble anhydrite is metastable and tends to be converted to the hemihydrated gypsum with the absorption of water. It is probable that the acid sites are formed on the metastable, or soluble, anhydrite.

Infrared Spectroscopy. The Ca^{2+} ions on the plane of the hemihydrated gypsum may be the sites of Lewis acidity (in a general sense). However, it is also possible that the ions may polarize adjacent OH groups or the O–H bonds in H_2O molecules adsorbed on the surface and produce Brönsted acid sites. Hence, the elucidation of the characteristics and behavior of OH groups and H_2O molecules on/in gypsum was attempted by means of IR spectroscopy.

Previously, the presence of a small amount of water in the so-called soluble anhydrite gypsum has been detected in the IR studies using the KBr12) or Nujol13) method. However, since the anhydrous form is very hygroscopic, these methods are inadequate for the confirmation of the presence and behavior of H_2O and related OH groups in the course of heat-treatment. Accordingly, the IR absorption analysis was carried out using a self-supporting disc in an *in situ* cell. As is shown in Fig. 2, the broad bands due to OH stretching

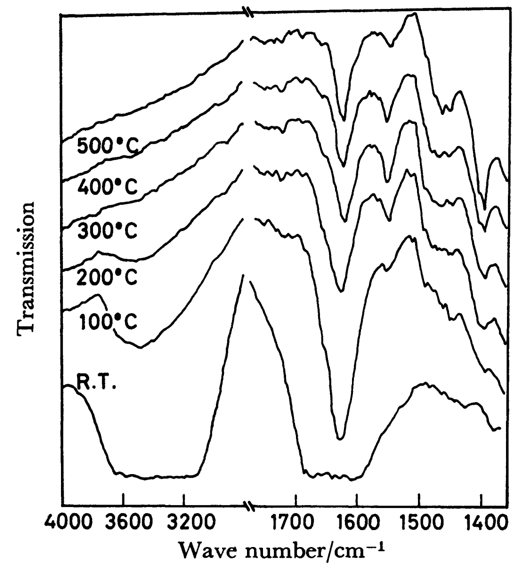

Fig. 2. Infrared spectra for precipitated gypsum evacuated at various temperatures.

and H_2O bending were observed at 3200—3600 cm^{-1} and 1600—1700 cm^{-1} respectively for the evacuation at room temperature. The band at 1600—1700 cm^{-1} was converted into a sharp 1627 cm^{-1} band at 100 °C, and this band still remained at higher temperatures such as 500 °C. Even though this band is ascribable to H_2O bending vibrations, the band assignable to OH stretching disappeared above 300 °C, as is shown in Fig. 2. Therefore, the absorption band which survived above 300 °C may be assigned not to H_2O but to bidentate carbonate, which gives the absorption at 1630 cm^{-1}.[14] Thus, the band at about 1620 cm^{-1} in the spectra observed for the gypsum heat-treated below 300 °C is probably due to both H_2O and carbonate. The bands at 1396 and 1405 cm^{-1} might be due to the asymmetric stretching vibration of the N–O bond belonging to the NO_3^- ion,[15] which could not be completely removed during the preparation. Other bands at 1430—1500 cm^{-1} might be assigned to carbonate or hydrogen carbonate ions.[16]

In general, the bands at 3600—3700 cm^{-1} due to isolated OH groups are observed for many heat-treated metal oxides. As has been shown in the discussion with respect to the surface acidities of Al_2O_3 and SiO_2–Al_2O_3,[17] the isolated OH groups may be acidic, for they are surrounded by three metal atoms, and so would be affected by the greatest induction due to metal atoms. In the case of gypsum, there are no distinct bands due to isolated OH groups in the region of 3600—3700 cm^{-1}. Thus, the existence of Brönsted acid sites due to the isolated OH groups on the gypsum surface seems impossible.

Infrared Spectra of Pyridine on the Surface of Gypsum. Infrared spectroscopic studies of pyridine adsorbed on a solid surface have made it possible to distinguish between Brönsted and Lewis acids.[18] The IR spectra of pyridine on gypsum evacuated at different temperatures were measured in order to elucidate the character of the acid sites. As is shown in Fig. 3, a strong absorption band at 1445 cm^{-1} was observed in the case of gypsum which had been dried in the air at 200 °C for 2 h and then evacuated in a cell at 200 °C for 2 h. As the evacuation temperature was raised, the band at 1445 cm^{-1} became weaker. This band is attributable to hydrogen-bonded (at 1440—1447 cm^{-1} [19]). The band at about 1445 cm^{-1} is not so sharp, as is shown in Fig. 3, the bands due to hydrogen bonding and to coordinative bonding are close to each other. Therefore, it is difficult to determine the character of the active sites merely by the inspection of the IR spectrum of pyridine on the surface. However, the shoulder at 1605 cm^{-1} is more readily attributable to the coordinatively bonded pyridine (at 1600—1663 cm^{-1} [19]) than to the hydrogen-bonded pyridine (at 1580—1600 cm^{-1} [19]). The finding that the absorption band at 1445 cm^{-1} remained after evacuation at 200 °C also supports the presence of Lewis acid sites rather than that of hydrogen-bonding sites, which may be weak with respect to retaining the pyridine molecules.

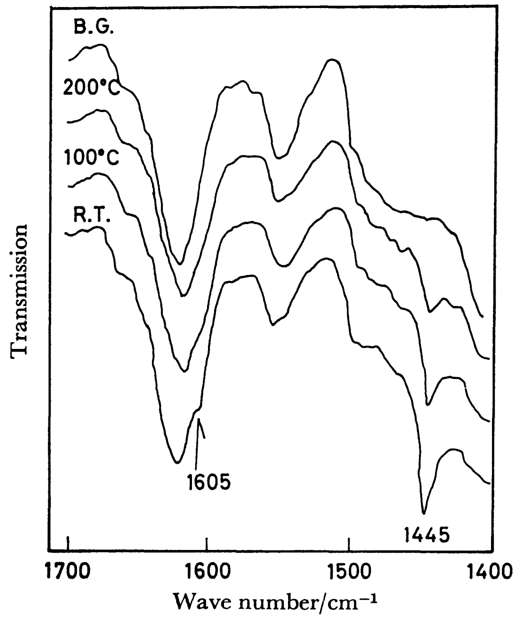

Fig. 3. Infrared spectra for pyridine adsorbed on precipitated gypsum.
B.G.: Background; Precipitated gypsum treated in the air at 200 °C for 3 h and evacuated for 2 h. R.T., 100 and 200 denote the evacuation temperature of samples treated with 10 Torr of pyridine for 10 min.

The absorption bands at 1540 cm^{-1} and about 1640 cm^{-1} are characteristic of pyridinium ions and are generally used for finding of Brönsted-acid sites.[19] The band at about 1540 cm^{-1} is indistinguishable from the bands of gypsum (as shown in the spectrum (B. G.) in Fig. 3). However, the absence of the band at 1640 cm^{-1} suggests that there are no Brönsted-acid sites on gypsum.

TABLE 2. CONVERSION OF CYCLOPROPANE TO PROPENE[a]

Catalyst	Heat-treatment temperature[b] °C	Conversion %
Gypsum	300	0.7
	400	0.8
	500	0.3
	600	0.4
SiO_2–Al_2O_3	500	100
TiO_2	500	100
None		0.4

a) The reaction condition were as follows; temperature: 250 °C, catalyst weight: 50 mg, carrier and its velocity: He, 10 ml/min. b) All the catalysts had been heat-treated for 3 h.

Catalytic Activities for Conversion of Cyclopropane and for the Double-bond Isomerization of 1-Butene. The catalytic activity of heat-treated gypsum in the conversion of cyclopropane was examined at 250 °C. As is shown in Table 2, the conversion of cyclopropane to propene, which should be catalyzed by Brönsted acids,[20] were all less than 1%, irrespective of the heat-treatment temperature, and were close to those obtained in the absence of the gypsum. The conversion of the reaction catalyzed by the commercial SiO_2–Al_2O_3 catalyst, named N 631 (Nikki Chem. Co.), which is a typical Brönsted-acid catalyst, was 65% at such a low

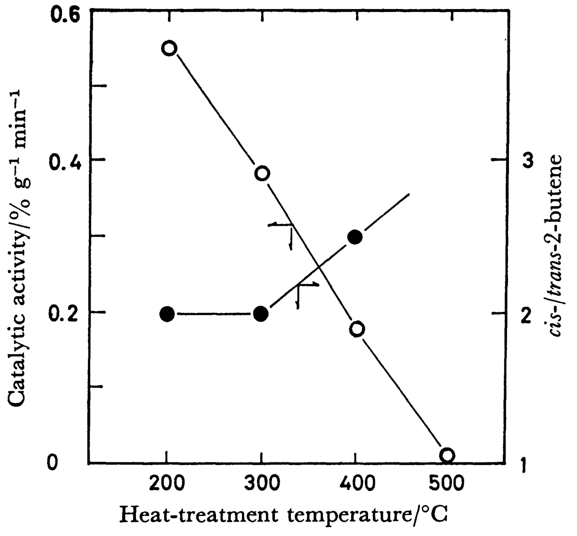

Fig. 4. Catalytic activity and selectivity *vs.* treatment temperature.
Reaction temperature : 200 °C, Pressure of 1-butene : 110 Torr.
Evacuation was carried out for 2 h at each tretment temperature.

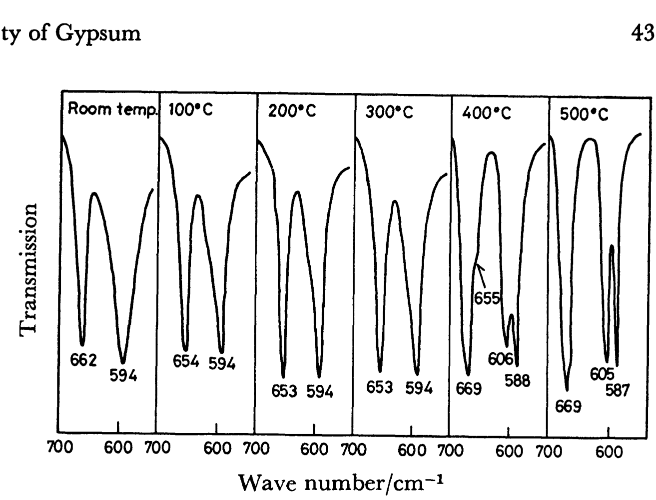

Fig. 5. Infrared spectra for sulfate ions on precipitated gypsum heat-treated at different temperatures

temperature as 150 °C for the same contact time. In addition, the conversion of the reaction at 250 °C catalyzed by TiO_2, which had been prepared from $TiOSO_4$ and which had a considerable quantity of Brönsted-acid sites,[21] was nearly 100%. These contrasted results indicate that there are no Brönsted-acid sites on the gypsum surface.

In order to further investigate the acid character of the gypsum, the isomerization of 1-butene was carried out at 200 °C in the presence of the heat-treated gypsum. The catalytic activity and *cis-/trans-* ratio at zero conversion are plotted as functions of the evacuation temperature in Fig. 4. When the gypsum was evacuated at 200 °C, its catalytic activity was relatively high. The activity decreased with an increase in the evacuation temperature, and almost disappeared when the gypsum was treated at 500 °C under evacuation. For lower evacuation temperatures, such as 200 °C and 300 °C, the initial *cis-/trans-* ratio was 2; this was elevated to 2.5 as the evacuation temperature was raised to 400 °C. It is already known that the *cis-/trans-* ratio in the products of the reaction of 2-butenes is determined by the nature of the active site; that is, if the active site is the Brönsted type, the ratio should be about 1, while if the active site is the Lewis type, the ratio should be about 2.[22] Since the value in Fig. 4 is 2—2.5 throughout the evacuation-temperature range, the acid must be the Lewis type.

Coordination of Sulfate Ions to Calcium Ions. In order to discuss the coordinations of SO_4^{2-} ions to Ca^{2+} ions, the IR spectra due to SO_4^{2-} ions were observed in the wave-number region of about 400 to 1400 cm^{-1}. The IR spectra showed the absorption band (ν_3) due to the stretching vibration of S–O, S=O at 1100—1200 cm^{-1} and that (ν_4) due to the bending vibration of –O–S–O– in the region of 580—680 cm^{-1}. In a previous report,[12] the splitting of ν_3 and ν_4 has already been observed for gypsum heat-treated at 337—390 °C and 358—375 °C respectively; it was there ascribed to the transition from III-$CaSO_4$ to II-$CaSO_4$.

The splitting of ν_3 could also be found in this study. However, the details of the splitting could not be made clear, because the bands are essentially broad. Therefore, the splitting of the sharp band due to –O–S–O– bending was examined. Fig. 5 shows the IR absorption spectra of gypsum heat-treated at different temperatures in the 550—700 region. As is shown in this figure, the spectra gave bands at 594 cm^{-1} and near 653 cm^{-1} which were specific to the monodentate SO_4^{2-} ions.[23] With increases in the heat-treatment temperature, these bands gradually disappeared, while bands appeared at 588, 606, and 669 cm^{-1} when the sample was heat-treated at a temperature higher than 300 °C. According to the study of Nakamoto *et al.*, these bands are ascribable to bidentate SO_4^{2-} ions.[23] Since the X-ray diffraction analysis (shown in Table 1) of the sample showed that soluble anhydrite (III-$CaSO_4$) was transformed into insoluble anhydrite (II-$CaSO_4$) between 300 °C and 400 °C, the monodentate and bidentate ions are considered to be present in soluble and insoluble anhydrite respectively.

Thus, when gypsum was heat-treated at temperatures higher than 300 °C, the metastable anhydrite (III-$CaSO_4$) was converted into stable anhydrous form (II- or I-$CaSO_4$) and Ca^{2+} ions on the surface became closely surrounded by bidentate sulfate ions. In such a configuration, the Ca^{2+} ions on the surface cannot interact with other molecules as electron acceptors. This is possibly the reason why the Ca^{2+} ions on the insoluble, or stable, anhydrite do not function as Lewis-acid sites. On the other hand, the Ca^{2+} ions on the soluble anhydrite, which are less closely surrounded by monodentate sulfate ions, are able to accept electron pairs of other molecules. Thus, the Lewis-acid center may be formed by an empty orbital of the Ca^{2+} ions on the surface of III-$CaSO_4$. A similar phenomenon has also been observed in the dehydration of $NiSO_4xH_2O$, in which strong acid sites ($H_0 \leqq -3.0$) have been found.[24] However, the electronegativity of the Ca^{2+} ion is smaller than that of the Ni^{2+} ion;[25] hence, the Lewis acidity due to the Ca^{2+} ion should not be so strong. In fact, the acid function (H_0) was determined to be mostly 3.0—4.8, as has been described previously.

The maximum acid-site concentration of heat-treated gypsum (shown in Fig. 1) is about twice that reported for alumina, which is a typical Lewis acid, heat-treated at 500 °C (0.0008 mmol/m^2 at $H_0 \leqq +1.5$).26) However, the amount is considerably less than that for heat-treated nickel sulfate (0.011 mmol/m^2 at $H_0 \leqq +4.8$ and 0.005 mmol/m^2 at $H_0 \leqq -3.0$).24) The concentration of Ca^{2+} ions on the surface is much more than that of acid sites. For example, the former concentration on the (001) plane is calculated to be 0.0034 mmol/m^2 on the basis of the lattice constant ($a,b=6.99$ Å, $c=6.34$ Å).11) As suggested by the comparison between the concentration of the acid sites and Ca^{2+} ions, not all the Ca^{2+} ions on the III-$CaSO_4$ surface can be Lewis-acid sites. The details of the active-site formation must be studied further.

Even if a small amount of water should be occluded in the III-$CaSO_4$ formed at temperatures lower than 300 °C, as has been shown in previous studies,12,13) the polarization of the surface OH groups and/or H_2O molecules by Ca^{2+} ions must be impossible because Ca^{2+} ions have only a low electrostatic potential (ion valency/radius). Therefore, the weak solid acidity should be of the Lewis type ascribable to the Ca^{2+} ions on the unstable crystal surface.

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