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Slip-casting properties of Si_3N_4 with Y_2O_3 and Al_2O_3 as sintering additives

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The effects of particle charging and powder–liquid suspension stability on the slip-casting properties of Si_3N_4 powder were examined. Y_2O_3 and Al_2O_3, used as sintering additives, were seen to affect the dispersion stability of the base material (Si_3N_4). The zeta potentials of the three powders and the rheological behaviour of the 55 wt% solids-loaded slips, involving known concentrations of a polymeric deflocculant (Dolapix PC33), showed that the multicomponent system can be dispersed stably within the pH range 9–11. Green compacts, obtained by casting these slips into plaster moulds, were found to give densities in the range 50–61% of the theoretical value. © *1998 Chapman & Hall*

1. Introduction

Processing of silicon nitride, like other ceramic materials, requires fine powders to be used. Attractive forces, on the other hand, always act between these fine particles because of the presence of the weak van der Waals forces which cause the individual particles to adhere and form a coarse mass called an "agglomerate". It has been recognized that [1–3] inhomogeneities, such as agglomerates, present in the green body may remain or be enhanced during sintering and affect the mechanical properties of the final structure. The trend, therefore, has been concentrated from the firing stage to earlier stages in the processing in order to disperse these coagulates. Colloidal processing routes, such as slip casting, have been suggested as a preferred way for fabricating agglomerate-free high-quality ceramics [4], where a uniformly dense green microstructure that can be sintered with relative ease can be produced from colloidal suspensions if the particles are consolidated in a controlled manner [5].

Slip casting is a process of fabricating complex shapes without expensive machining. The slip is a suspension of powder in a suitable liquid. On pouring into an absorbent mould, usually plaster of Paris, the liquid is drawn off, leaving a solid casting on the inner walls of the mould. A good casting slurry is a highly concentrated particle suspension which is well stabilized [6]. High solids content reduces the amount of liquid sucked away by the mould, whereas the stability against deflocculation gives a dense consolidated layer.

This study examines the influences of the particle potential (zeta potential), pH and slip rheology on the formation of a compact by slip casting. Although the sintering of the slip cast compacts is not considered, Y_2O_3 and Al_2O_3 are used as the sintering additives throughout the experiments in order to monitor their effects on the suspension dispersion. Electrostatic stabilization in combination with steric stabilization mechanisms have been used to develop a stable slip from the triple system Si_3N_4–Y_2O_3–Al_2O_3. Accordingly, an optimum in the pH and the organic deflocculant added has been sought which gives the highest packing.

2. Experimental procedure

2.1. Materials and material handling

Commercial-grade silicon nitride (Si_3N_4) (grade LC12N, HCST, Germany), aluminium oxide (Al_2O_3) (Baikalox, grade CR10, Baikowski Chimie, France) and yttrium oxide (Y_2O_3) (grade Fine, HCST, Germany) powders were used as the starting materials. The specific surface area (Quantasorb, Quantachrome Inc., NY, USA) and its corresponding mean particle size (calculated according to $d = 6/\rho A_S$, where ρ is the density and A_S is the surface area) of the as-received powders are given in Table I.

Aluminium oxide (Al_2O_3) and yttrium oxide powders (Y_2O_3) were mixed in equal quantities to yield a 10 wt% sintering aid for silicon nitride. Weighed batches of $Si_3N_{4+}Y_2O_3 + Al_2O_3$ powder mixtures were attrition milled (Union Process, research model 01-HD, Akron, OH, USA) for 30 min at a shaft speed of 300 rev min^{-1} in a silicon nitride jar with silicon nitride balls of 6 mm diameter. The mill was loaded with a powder-to-ball ratio of 1 to 3, with ethyl alcohol as the milling liquid. After milling, the alcohol of

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TABLE I Surface area and particle size values for the as-received powders

Material	Grade	Brunauer–Emmett–Teller specific surface area ($m^2 g^{-1}$)	Mean particle size (μm)
Si_3N_4 (HCST)	LC12N	18.91	0.1
Y_2O_3 (HCST)	Fine	11.76	0.1
Al_2O_3 (Baikalox)	CR10	8.68	0.17

the mixed slurry was evaporated over a hot-water bath. During the drying process, the slurry was continuously stirred with a propeller. The dried powders were crushed in an agate mortar to break up the agglomerates and subsequently sieved through a 100 mesh sieve.

2.2. Zeta potential measurements

The charge characteristics of Si_3N_4, Y_2O_3 and Al_2O_3 powders were determined, separately, using a Zeta-Meter system 3.0+ (Zeta-Meter Inc., Long Island City, NY, USA) which operates according to the electrophoresis technique. Measurements were made with the powder brought into a suspension in double-distilled water. The slurry concentration in each determination was kept at 0.05 g of powder per litre of water. The pH values of these suspensions were adjusted by using either 37 M HCl or 1 M NaOH solutions. NaCl was added to impart a constant ionic strength $I = 0.001$ M. The stabilized suspensions were ultrasonicated (Ultrasonik model 250, The J. M. Ney Co., CT, USA) to disperse any agglomerates present before the measurement. Zeta potentials were determined from the average mobility measurements conducted on 50 different particles in the same suspension.

2.3. Slip rheology determination and slip-casting test

Slips were prepared from the attrition-milled powder mixtures at solids loadings of 55, 60 and 65 wt%. Double-distilled water was used as the suspending medium for the powders. The necessary amounts of HCl and NaOH solutions were added to adjust the pH. In order to enhance stability, a commercial organic deflocculant, Dolapix PC33 (Zschimmer & Schwarz GmbH, Germany), was introduced in amounts of 0.5, 1.0 and 1.5 wt%, based on the weight of the slip. The slips were mixed in a polyethylene bottle including silicon nitride balls of 6 mm diameter, in equal weight of the slip, for 20 h. Ultrasonic agitation was used before casting and viscosity measurements to break up the weak agglomerates of powder.

The rheological characteristics of slips were measured using a rotating-spindle Brookfield RV digital viscometer (Brookfield Engineering, Stoughton, MA, USA). The flow properties were determined in accordance with the procedure specified in the ASTM standard D 2196 test [7]. The shear rate in these measurements were varied in the range 0–100 rev min^{-1} of the spindle rotation.

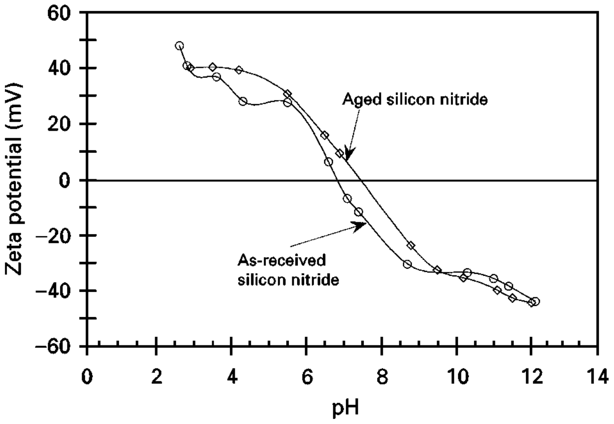

Figure 1 Zeta potentials of as-received and aged silicon nitride as functions of pH ($I = 0.001$ M NaCl).

Slip-casting experiments were made by pouring the slips into Teflon rings set on absorbent plaster blocks (Baldudak Alci Fab., Cankiri, Turkey). A constant casting time of 30 min was allowed for every casting. The resultant cakes were dried at room temperature for one night and then heated at 150 °C for 12 h. Green densities of the cast samples were determined by the liquid displacement technique using xylene. An average of three to four cast specimens were measured for every slip condition to get a representative value. The relative density was based on a 3.2721 $g cm^{-3}$ theoretical density, which was calculated from the theoretical densities of individual constituents (α-Si_3N_4, 3.18 $g cm^{-3}$; Y_2O_3, 5.03 $g cm^{-3}$; Al_2O_3, 3.96 $g cm^{-3}$).

3. Results

3.1. Zeta potentials

The zeta potentials of the as-received and aged (attrition milled for 30 min in ethyl alcohol medium and then ball milled for 20 h in double-distilled water using Si_3N_4 balls) silicon nitride powders at various pH values are plotted in Fig. 1. The curves show an absolute maximum in the zeta potential at the highly acidic (pH 2) and basic (pH 12) side. Zero-point charge (ZPC) occurs at about pH 6.75 for as-received silicon nitride and at about pH 7.45 for aged silicon nitride. Above pH 12 and below pH 2, where the potentials are at their highest absolute value, flocculation was observed and therefore no measurement could be made.

Fig. 2 gives the zeta potential results of the Y_2O_3, Al_2O_3 and aged Si_3N_4 powders. It can be observed

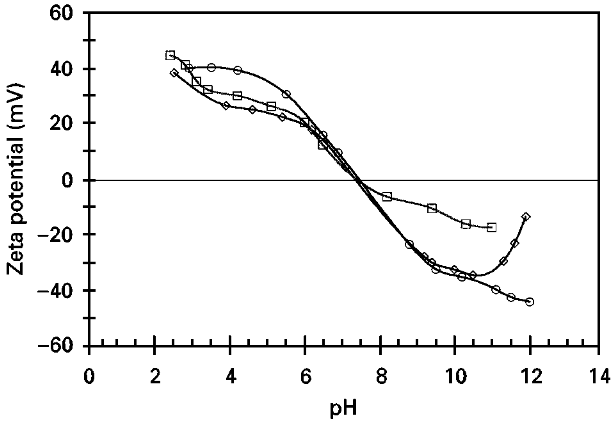

Figure 2 Zeta potentials of aged silicon nitride (○), yttrium oxide (□) and aluminium oxide (◇) as functions of pH ($I = 0.001$ M NaCl).

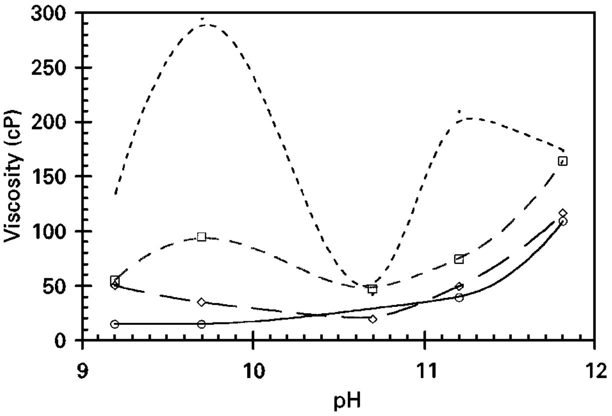

Figure 4 Viscosity (at a constant shear rate of 9.3 s^{-1}) versus pH for the 55 wt% solids-loaded slips with Dolapix PC33 additions. (—⊖—), no PC33; (—◇—), 0.5 wt% PC33; (—⊟—), 1 wt% PC33; (-----), 1.5 wt% PC33.

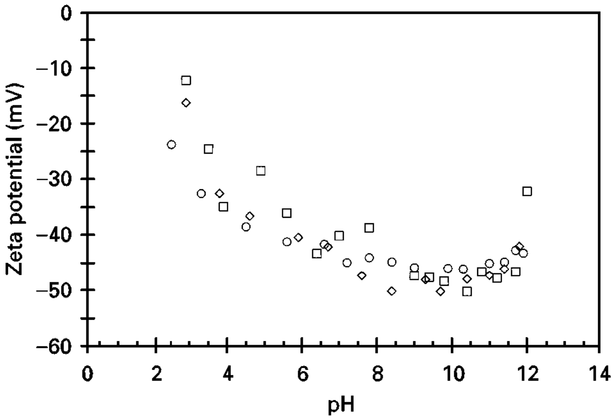

Figure 3 Zeta potentials of aged silicon nitride (□), yttrium oxide (◇) and aluminium oxide (○) with 1 g of Dolapix PC33 per litre as functions of pH ($I = 0.001$ M NaCl).

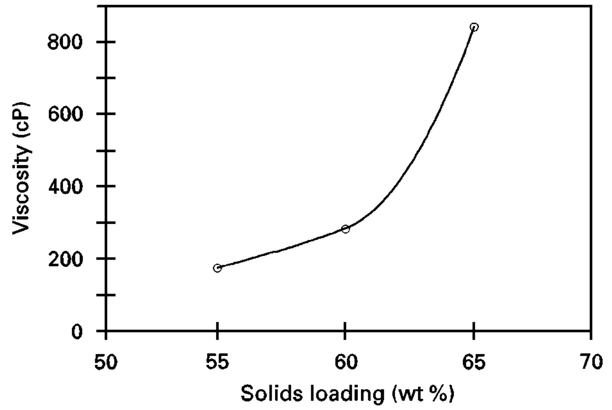

Figure 5 Effect of solids loading on the viscosity (at constant shear rate of 9.3 s^{-1}) of slips at pH 10.7 with 1.5 wt% Dolapix PC33 addition.

that Y_2O_3 and Al_2O_3 powders have different absolute maximum potentials; Al_2O_3 has a higher potential for basic conditions compared with Y_2O_3. The two powders have approximately the same maximum for acidic conditions.

The effects of Dolapix PC33 on the zeta potentials of the three powders, determined separately at several pH values, is given in Fig. 3. It is observed that the addition of the deflocculant resulted in a higher negative value of the zeta potential in a wide pH range. This shows that the surface-active deflocculant is strongly adsorbed onto the particle surfaces, charging them electrically in such a way that the ZPC is shifted towards approximately pH 2.5.

3.2. Rheology of Slips

3.2.1. Viscosity

Fig. 4 shows the plots of the apparent viscosities of the slips, at a constant shear rate of 9.3 s^{-1} (10 rev min^{-1}), for different pH levels and deflocculant additions. The curves illustrate an increase in the viscosity, with fluctuations occurring (unexpected decrease in the viscosity at pH 9.2 and pH 11.8 can be seen) as the amount of Dolapix PC33 is increased. The general trend observed is that all go curves through a minimum viscosity. This reflects the stability of the slip, concerning viscosity only, which is achieved in a wider pH range (pH 9–11) for 0.5 wt% PC33 stabilized slips, and has been limited to narrower regions for increased deflocculant additions. Fig. 5 shows the effect of solids content on the viscosity of the slip at pH 10.7 with 1.5 wt% Dolapix PC33 addition.

3.2.2. Flow behaviour

Fig. 6 gives the shear stress versus shear rate plots for the slips at various pH values and deflocculant additions. Curves illustrate near-Newtonian and pseudoplastic flow characteristics. Various levels of yield in the shear stress are recognized for the pseudoplastic slips.

3.3. Green-body characterization

Fig. 7 gives the green density results of the specimens formed from the slips experimented in this study. The green density values show that all the samples formed

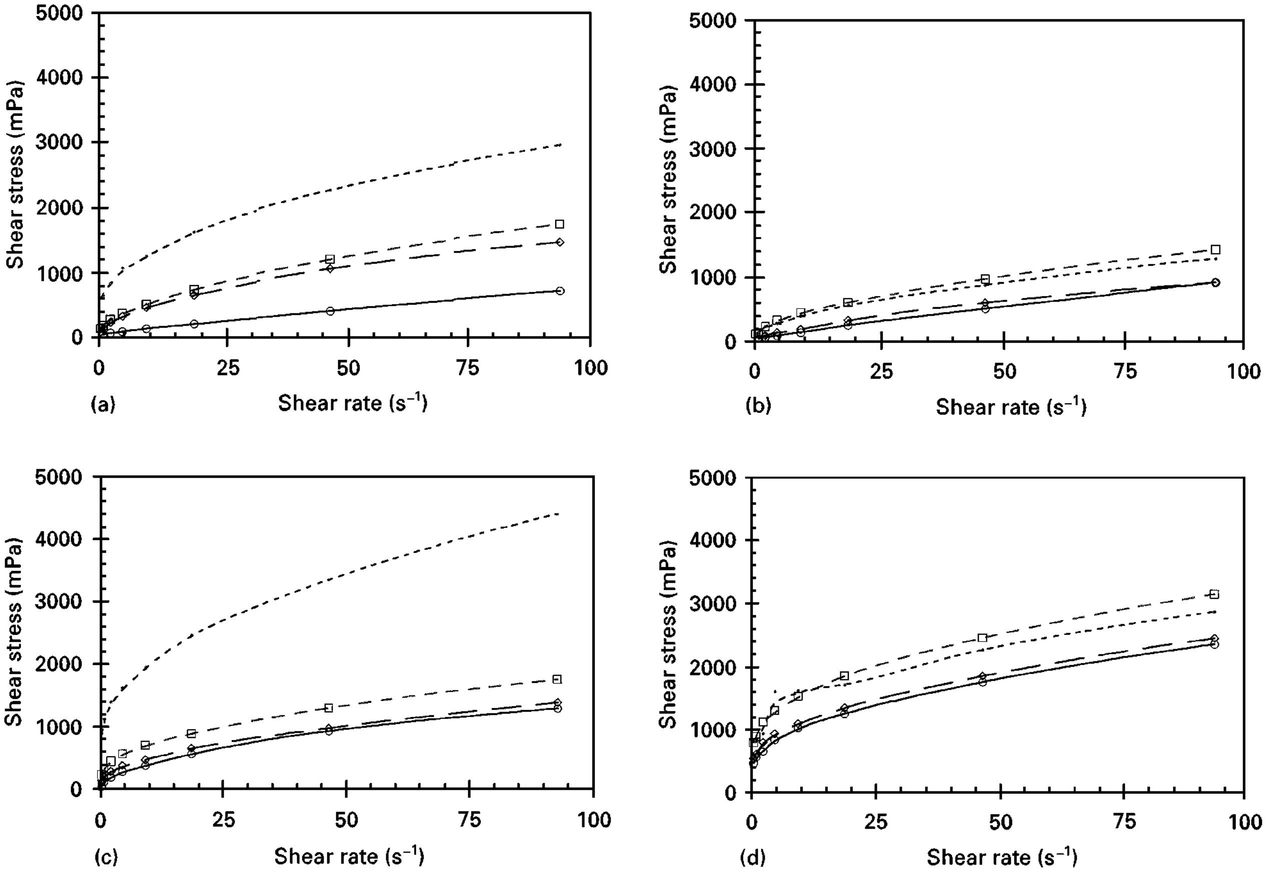

Figure 6 Shear stress versus shear rate behaviour of the slips for various Dolapix PC33 additions at (a) pH 9.2, (b) pH 10.7, (c) pH 11.2 and (d) pH 11.8. (—⊖—), no PC33; (—◇—), 0.5 wt% PC33; (—⊟—), 1.0 wt% PC33; (-----), 1.5 wt% PC33.

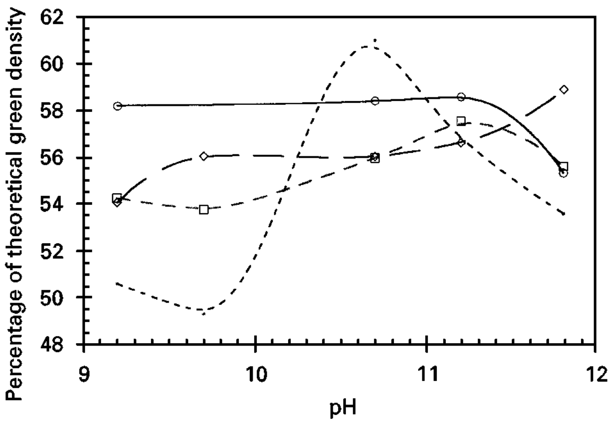

Figure 7 Green density of the compacts as a function of pH and different Dolapix PC33 additions. (—⊖—), no PC33; (—◇—), 0.5 wt% PC33; (—⊟—), 1 wt% PC33; (-----), 1.5 wt% PC33.

from the 55 wt% solids-loaded slips have a density above 50% of the theoretical density. The highest green density among the specimens tested has been found for the pH 10.7 condition with 1.5 wt% Dolapix addition. The lowest green density measured was at pH 9.7 with 1.5 wt% Dolapix. The addition of more solids in the slip caused the density to decrease significantly to 48% and 46% of the theoretical value for 60 wt% and 65 wt% solids loading, respectively.

4. Discussion

4.1. Zeta potential

The value of the ZPC for the as-received silicon nitride has been explained [8] by the dominance of amino-derived surface groups, silazane (Si–NH$_2$) and silylamine Si$_2$–NH, which is also interpreted as the equilibrium ZPC for silicon nitride in aqueous suspensions. The increase in the ZPC value, from about pH 6.75 to about pH 7.45 is suggested [9] to be due to the possibility of the formation of amino groups on the surface by simple hydrolysis. Zeta potentials of the three powders were found to be very sensitive to the presence of the polymeric deflocculant which is observed to have resulted in a higher negative value of the zeta potential in a wide pH range. This shows that the surface-active deflocculant is strongly adsorbed onto the particle surfaces, charging them electrically in such a way that the ZPC is shifted towards approximately pH 2.5. This makes it possible to prepare castable slips at pH values closer to neutrality, which is desirable regarding the lifetime of plaster moulds.

Considering that 30 mV is a limit for dispersion [10], above about pH 10 on the basic side and below about pH 4 on the acidic side would be the best conditions to prepare stable dispersed suspensions of Si$_3$N$_4$ powder. On the other hand, the zeta potential data for the three powders, measured individually, suggests a dispersion at approximately pH 9–11 for alkaline conditions and approximately pH 2–4 for acidic conditions. The addition of Dolapix PC33 promotes the preparation of stable dispersions of the individual powders in the approximate range pH 4–12.3. On the other hand, it can also be observed that Dolapix PC33 is not suitable for use in acidic environments since the potentials for these dropped to low values, indicating that this deflocculant has basic anchoring groups.

4.2. Rheology of slips

When the three constituents are placed in the same medium, successful deflocculation for pH 9–11 was achieved, whereas suspensions were strongly unstable for below pH 9. In relation to the zeta potential results, slip stability could not be achieved for acidic conditions, with the addition of Dolapix PC33. The unstability was observed by an extremely pseudoplastic flow behaviour of the high solids-loaded (55–65 wt%) slips with high viscosities. It has been shown [10, 11] that oxide additive containing slurries restricts stability by forming positive counter-ions of high valency owing to the dissociation of their hydrates in water. These cations, which have an opposite charge to the particle surface, strongly decrease the zeta potential and, hence, the repulsive forces between the particles, by decreasing the double-layer thickness. For the Y_2O_3 and Al_2O_3 system, the critical concentrations of dissolved Y^{+3} and Al^{+3} ions necessary for flocculation were determined [11] to be at pH 8. It was found that the measured yttrium ion concentration at this pH, which corresponds to the critical concentration calculated, causes flocculation of the slips. The aluminium ion concentration was found to be too low to cause coagulation in this case. As the pH of the slip is increased, the Y^{3+} concentration decreased, making stable slip preparation possible.

The flow characteristics of the slips were found to correlate well with the viscosity and zeta potential data. A near-Newtonian flow was observed for the low-viscosity slips because of the effective deflocculation process. Unstable suspensions showed a pseudoplastic behaviour with a certain yield value in the shear stress. This indicates a highly flocculated mixture with the plasticity property required to break up these large numbers of agglomerates.

The addition of more solids to the slip, having approximately pH 10.7 with 1.5 wt% Dolapix PC33 addition, increased the viscosity, producing a pseudoplastic suspension with a high yield point. This can be attributed to the decreased amount of liquid left in the suspension which is necessary to wet all the particles and to create stability due to electrostatic, steric or electrosteric mechanisms.

4.3. Green-body characterization

The packing efficiency is governed by the slip preparation steps. The increases in the viscosity and the deviation from non-Newtonian flow behaviour are reflected as decreases in the green density. Thus, the green density results for the higher solids-loaded suspensions has resulted in a low green density. This poor packing is a reflection of its rheology. On the other hand, the slips having a low viscosity and ideal-like rheology showed higher green densities. The green body prepared from the slip having pH 10.7 with 1.5 wt% Dolapix addition has given the best density; this could be due to the polymer film adsorbed at the surface of the particles. This layer probably behaved like a lubricant, during the consolidation of the particles, improving the packing efficiency.

5. Conclusions

Using the individual zeta potential results for the Si_3N_4, Y_2O_3 and Al_2O_3 powders, maximum surface charging was found to occur for pH 9–11 and pH 2–4. The role of the polymeric deflocculant was to shift the ZPC to more acidic conditions. Rheological properties of the slips have shown that castable slips having low viscosities with near-Newtonian flow could be prepared in the alkaline media, within the range pH 9–11. The presence of the dissolved Al^{3+} and Y^{3+} ions for the electrostatically stabilized slips and the basic anchoring groups of the polymeric deflocculant for the electrosterically dispersed suspensions were effective in producing very unstable slips below pH 9.

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