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Slip casting of silicon nitride for pressureless sintering

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Properties of aqueous slips of silicon nitride/spinel mixtures were studied. Vanisperse CB was used as deflocculant. It was shown that mixtures previously milled in water form stable slips, while those milled in isopropanol form jelly-like aqueous suspensions unsuitable for casting. A single-stage slip may be prepared by milling and mixing Si_3N_4 powder with spinel and water without a deflocculant. Viscosity, pH and density of the slips were studied and a set of crucibles was cast and fired in nitrogen at 1650° C for 1 h to bulk density 3.1 g cm^{-3}.

1. Introduction

Slip casting of silicon nitride powders has been studied by Soviet workers [1, 2]. Samsonov and Dobrovolskii [1] prepared slips by mixing silicon nitride with a 1.5% aqueous solution of polyvinyl alcohol; the solid-to-liquid ratio was 6:4 and the pH of the slip (adjusted with HCl) was 5. Green density of the cast ware was 55 to 65% of the theoretical density (TD). Pivinskii *et al.* [2] observed optimum rheological and technological properties of aqueous suspensions of Si_3N_4 after wet milling at pH 0.5 to 1.5 and obtained slips with density up to 2.05 g cm^{-3} (the volume content of the solid phase was 48%, corresponding to a solid-to-liquid ratio of about 3:1) which in turn yielded cast ware with green density up to 2.15 g cm^{-3}; i.e. 67% TD. The aqueous suspensions of Si_3N_4 showed a strong thixotropy. However, there is no mention of the addition of sintering aids to silicon nitride by Samsonov and Dobrovskii [1] and Pivinskii *et al.* [2]. Jack [3] refers to slip casting of a mixture of silicon nitride and alumina forming sialon products after firing for 1 h at 1700° C.

Masaki and Kamigaito [4] (and cited in [5]) studied oxide admixtures to silicon nitride and found that spinel $MgO \cdot Al_2O_3$ makes for better sintering than either of its component oxides or their mechanical mixture. Rabinovich *et al.* [6], confirmed their results and found that a 10 to 15% admixture of spinel to the Starck Si_3N_4 powder permits sintering to 90 to 92% TD for ball-milled mixtures and to 95% to 97% TD for attrition-milled ones, at 1600 to 1700° C.

The present work deals with the properties of aqueous slips of silicon nitride mixed with sintering aids. The 85 wt% Si_3N_4/15% spinel mixtures were taken as an example.

2. Experimental procedure

Silicon nitride powder (supplied by the firm of Hermann C. Starck, Berlin), with BET specific surface 10.97 m^2 g^{-1} (HCST-3025) was mainly used throughout the work. Analysis and properties of this material and method of preparation of spinel (fired at 1400° C) are described by Rabinovich *et al.* [6].

For preparation of most of the slips, silicon nitride/spinel mixtures were wet-mixed and milled and then dried in a drying oven at 110° C, after which the slips were prepared by mixing with water in a "Rapido" porcelain mill, with a few ½ inch alumina balls, for 5 to 8 min. A few slips were prepared by direct milling and mixing of all the ingredients in plastic jars (0.3 to 3 × 10^3 cm^3 in volume) for 24 to 92 h, with alumina cylinders and isopropanol or deionized water. Attrition milling was carried out in a type PE 075 Netzsch laboratory apparatus as described by Rabinovich *et al.* [6].

Vanisperse CB (Aktieselskapet Borregaard,

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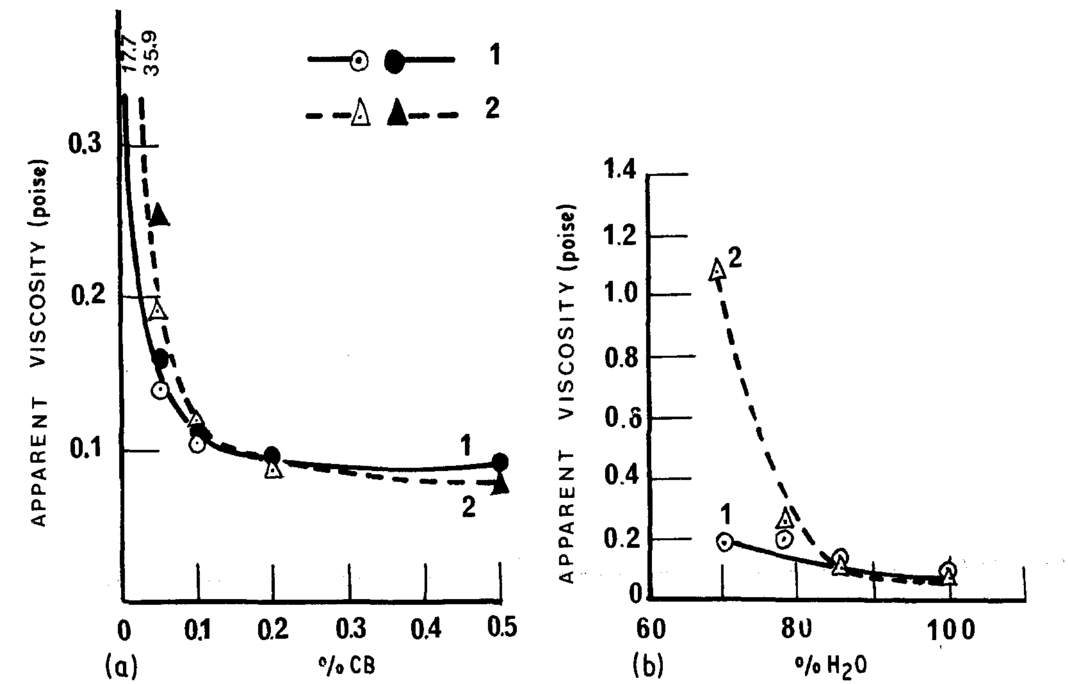

Figure 1 Apparent viscosity of slips as a function of: (a) amount of CB deflocculant at constant solid : water ratio = 1 : 1 (100% water, Series I); (b) amount of water at 0.2% CB (Series II). Rotation speeds of viscometer bob: (1) 486 rpm, (2) 162 rpm; bob MVI (SVI for slip without CB). Measurements taken 48 h (blank symbols) and 72 h (solid symbols) after preparation of slips. 25° C, pH 8 to 9.3.

Norway) was mainly used as deflocculant. As a rule, it was added as an aqueous solution, but in a few cases it was introduced in dry form prior to mixing.

Viscosity, pH and rate of casting were generally determined 48 h after preparation of the slip. Apparent viscosity was measured at different rotation speeds on a "Rotavisko" viscometer (model RV).

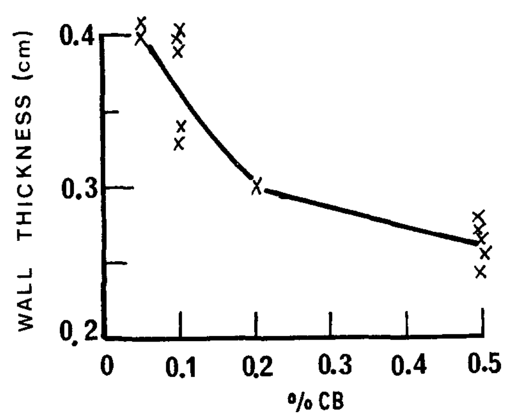

Figure 2 Wall thickness of crucibles, drain-cast in standard plaster moulds, after 1 min, as a function of amount of CB at 100% water (Series I), 25° C.

The slips were cast in moulds of Heliodur 40 alabaster, plaster : water ratio = 1 : 0.6. Standard plaster moulds (30 mm upper and 26.5 mm lower diameters, 17 mm height) were used for measurement of the rate of drain casting (wall thickness) after 1 min.

Cast ware were fired at 1650° C for 1 h in a 250 cm^3 alumina crucible filled with Si_3N_4 powder, under 1 atm of nitrogen, as described by Rabinovich *et al.* [6]. Heating to 1400° C took 90 to 100 min; from 1400 to 1650° C, the heating rate was 5 to 6° C min^{-1}.

3. Results and discussion

Slips of Series I to III were prepared from a dry mixture previously attrition-milled in water for 2 h (specific surface 14.9 m^2 g^{-1}). Results of the apparent viscosity measurements at two rotation speeds of the viscometer bob for samples with a constant solid : water ratio, Series I, are shown in Fig. 1a. As seen, minute admixtures of CB have a significant effect on fluidity and an amount of 0.2% proved optimal. There was no significant difference in fluidity between 2 and 3 days after preparation of the slips, nor between the two speeds of rotation.

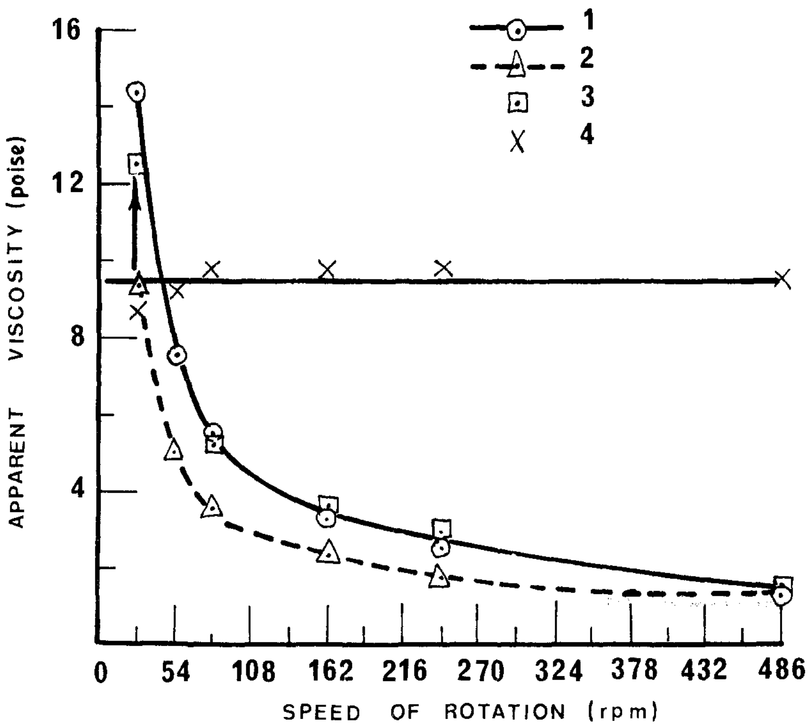

Figure 3 Apparent viscosity of a slip with 70% water and 0.2% CB (from Series III) as a function of rotation speed of viscometer bob SV I; 25° C, pH 9.3: (1) under acceleration; (2) under deleration (arrow shows change in apparent viscosity after 5 min rest); (3) under acceleration after rest (measurements taken on day of preparation of slips); (4) calibration points for glycerol interpolated to 25° C; horizontal line represents tabular [7] value 9.45 poise for 25° C.

Some reduction in the amount of water at a constant CB content (Series II, Fig. 1b) does not affect the viscosity noticeably at the higher speed of rotation, but increases it significantly at the lower speed. Especially high thixotropy was shown by slip with 70% water (solid : water ratio = 10 : 7); in fact, it was very awkward to work with and constant manual shaking of the cup was necessary to prevent it from solidifying.

The rate of drain casting of slips of Series I is shown in Fig. 2. The rate is seen to decrease with increasing CB content; an increase in water has a similar, albeit less pronounced, effect.

Because of loss of slip during measurements, a fresh series (Series III, similar to Series II having constant CB content, 0.2%, and different solid : water ratios) was used to study thixotropy. Higher values of apparent viscosity were obtained compared with Series II; these discrepancies are attributable mainly to use of a newly prepared batch of spinel and in part to use of a different bob. In qualitative terms reproducibility of the results was quite good. Dependence of the apparent viscosity of one of the slips of Series III on speed of rotation of the viscometer bob is shown in Fig. 3. This slip (70% water) showed significant reduction of the viscosity with increasing speed and recovery following reduction of speed and a brief rest. The more fluid slips (77.5 and 100% water) showed rather different behaviour: following reduction of the viscosity at high speeds, the slips remained fluid under repeated reduction of the speed. Thus, the more fluid (high-water) slips show lower thixotropy.

Series IV, V and VI were based on a mixture ball-milled in isopropanol for 24 h (specific surface 9.3 m^2 g^{-1}), which showed a totally different behaviour from those attrition-milled in water. Series IV involved the maximum water amount used in Series I to III (100%), and 0.1 to 0.5% CB, but only slips with 0.4 and 0.5% CB proved sufficiently fluid for casting. Increase of the water content at 0.2% CB (Series V) failed to yield fluid slips. Series VI involved increased amounts of both water (100, 120 and 160%) and CB (0.4%); the curves for this series show low viscosity and rather low thixotropy. These slips were cast in the standard plaster moulds. Some of the casts were cracked on drying; others showed better results, although a few bubbles remained on the surface of the cast ware. Series VII was based on a silicon nitride powder with a lower original specific surface (6.56 $m^2 g^{-1}$), ball-milled for 3 days in isopropanol. The slips were rather fluid on the day of preparation, but next day they acquired a jelly-like consistency and both mixing and vibration failed to restore fluidity.

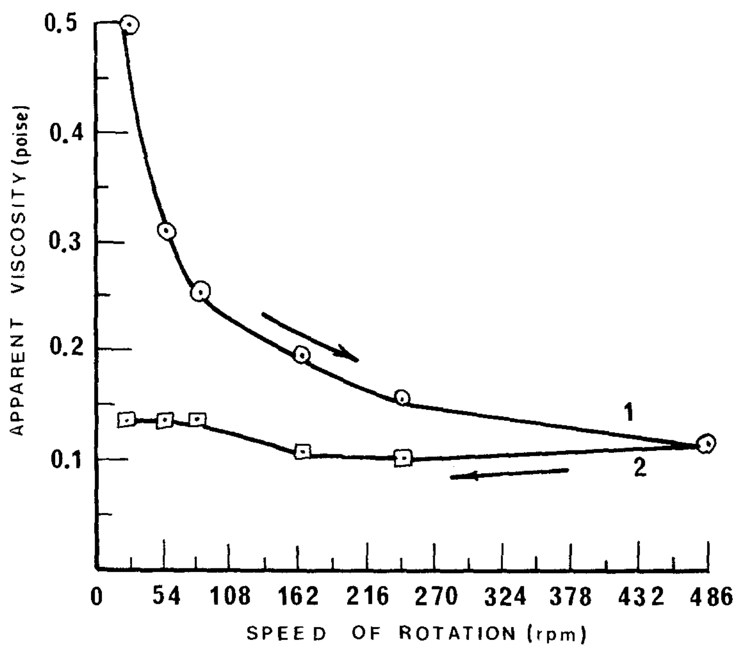

Figure 4 Apparent viscosity of a slip prepared by one-stage process; bob MVI, 19° C. Under acceleration (Curve 1) and deceleration (Curve 2).

Therefore, milling in water yields stable castable slips with lower amounts of water and CB compared with milling in isopropanol, for which slip quality is poorer, the longer the milling time. The positive effect of the water is attributable to the small amounts of silica formed in the reaction $Si_3N_4 + H_2O \rightarrow 3SiO_2 + 4NH_3$, the possibility of which is supported by the smell of ammonia noticed in the process. (The ammonia itself plays no useful role here. This was established by adding it deliberately to some of the slips.)

The best castable slip was obtained by direct ball milling and mixing in water, without a deflocculant, at solid:water ratio 2:3. After 3 days' milling, the slip had a pH of 10.2 (reduced to 9.2 on storage for 4 weeks). The viscosity curve (Fig. 4) showed rather low viscosity and thixotropy.

In an attempt to reproduce a low pH slip described by Pivinskii *et al.* [2] a 600 g batch of Si_3N_4/15% spinel mixture was ball-milled in an aqueous solution of HCl, pH 1.2. The experiment began at a solid:water ratio of 4:1, but the result was completely non-fluid and only on further addition of the solution over a period of 80 h milling to a solid:water ratio of 1:1 and density 1.5 g cm^{-3} (as against 2.05 g cm^{-3} in the work of Pivinskii *et al.* [2]) a relatively fluid but non-castable suspension was obtained, with pH 8.2. Castability was acquired by readjusting to pH 1.2 with concentrated (32%) HCl. The casting rate was 0.26 to 0.28 cm min^{-1} and green density of the dried crucibles near 1.3 g cm^{-3}, close to that of the ware obtained from slips with alkaline pH (up to 1.4 g cm^{-3}, i.e. near 40% TD). The difference between our results and data of Pivinskii *et al.* [2] may be explained by the effect of the sintering aid in our study.

The pH dependence of the apparent viscosity was studied on an identical slip, except that the whole amount (600 cm^3) of the HCl solution was added right at the beginning of milling. After 92 h milling, this slip (pH 8.8, density 1.5 g cm^{-3}) was divided into 6 portions, 75 cm^3 each, and the pH was adjusted in the 0.65 to 9.8 interval with small portions of HCl (32%) and NH_4OH (about 58%). The results are shown in Fig. 5; as seen, minimum viscosity is actually reached at pH near 1.3 and the change in viscosity with speed (thixotropy) is lower at low pH. After 48 h storage, the viscosity of the slip with pH 1.3 dropped by 20% without change in pH; admixture of CB (in dry form, 0.2% on basis of dry mixture) failed to produce an additional change in viscosity but slightly increased the pH (to 1.35). Hence, it is possible to speak of two pH intervals yielding castable slips of the Si_3N_4/spinel mixtures. The slips with low pH, however, were characterized by heavy formation of bubbles on casting.

The casts prepared from slips with alkaline pH are shown in Fig. 6. The largest crucible (green volume 0.5 l) was cast from the slip prepared by the one-stage process (see Fig. 4); attempts to achieve

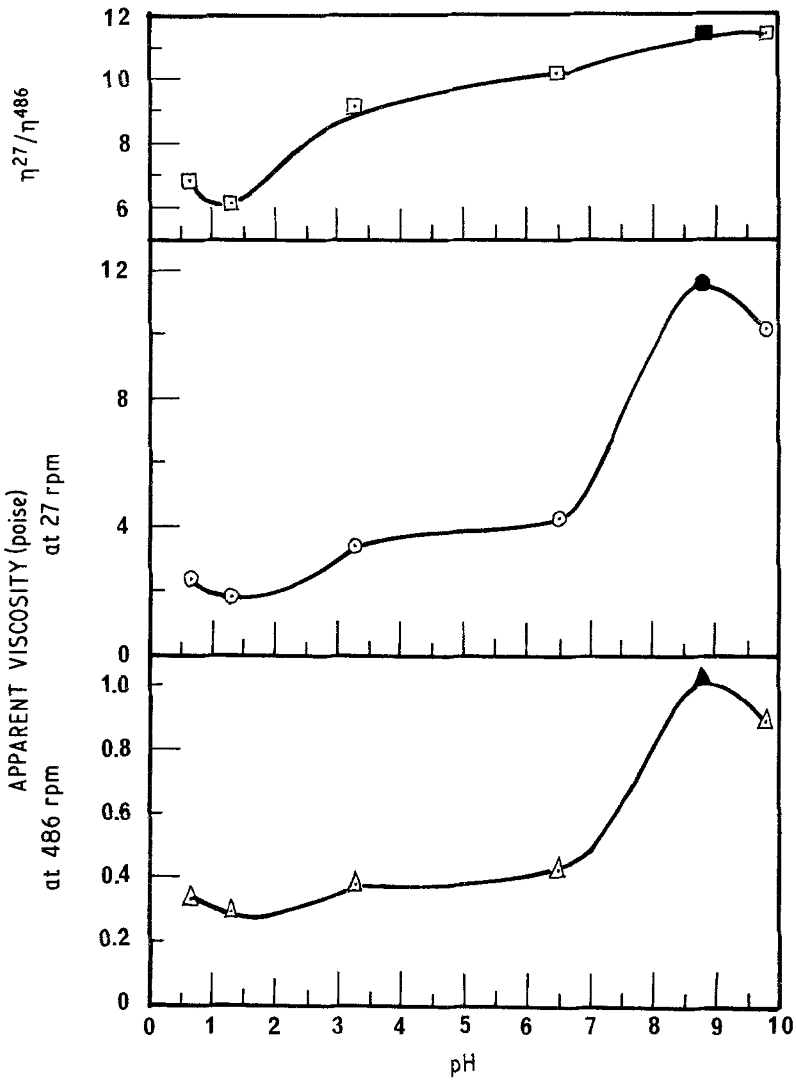

Figure 5 Apparent viscosity η of slips at two rotation speeds, and viscosity ratio for these speeds, as a function of pH (solid : water ratio = 1 : 1); bob MVI, 29° C. Measurements taken on day of preparation of slips. Solid symbols refer to original slip, without HCl and NH_4OH additions.

the same size with other slips were unsuccessful, as the crucibles cracked on drying. (However, the rate of casting of the one-stage slip was noticeably lower compared with the other slips). After sintering, all of this ware showed the same values of bulk density, open porosity and water absorption as the pressed specimens [6]; maximum values of bulk density were 3.1 g cm^{-3} for attrition-milled and near 3.0 g cm^{-3} for ball-milled mixtures. In spite of the fairly heavy shrinkage (20 to

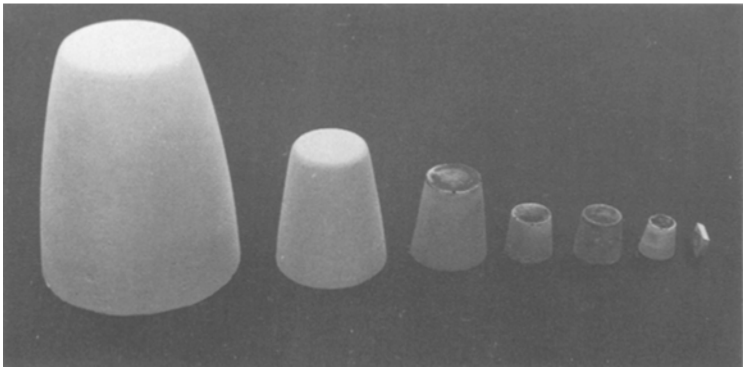

Figure 6 Slip cast ware of silicon nitride/spinel mixtures. Left to right: (1) green ~ 500 cm^3 crucible cast from slip No. 29; (2) green ~ 100 cm^3 crucible; (3) similar crucible after sintering; (4 to 6) sintered crucibles of various sizes; (7) plate tried for cutting of steel. Scale (at bottom): every 2 large divisions = 1 cm.

25% linear, 50 to 57% in volume) the crucibles retained their shape satisfactorily. A limited study of casting of pure Si_3N_4 and of Si_3N_4/MgO mixtures showed that qualitative findings of this work for Si_3N_4/spinel slips were applicable to other mixtures and, therefore, have general character.

4. Summary

(1) Silicon nitride with admixture of spinel ($MgO \cdot Al_2O_3$) yields castable aqueous slips both in the presence of a deflocculant (Vanisperse CB) and without it, as well as on addition of HCl to the milling medium. Stable slips are obtainable from mixtures milled in water, while those milled in isopropanol yield either unstable slips or jelly.

(2) Aqueous silicon nitride/spinel slips show significant thixotropy.

(3) Slip cast Si_3N_4 ware lends itself to sintering to high bulk density (93 to 97% TD) without deformation, in spite of heavy shrinkage (more than 50% in volume).

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References

1. G. V. SAMSONOV and A. G. DOBROVOLSKII, *Refractories* (Translated from Russian) No. 6 (1966) 369.
2. YU. E. PIVINSKII, L. G. PODOBEDA, A. D. BURAVOV and L. P. POLUBATONOVA, *Sov. Powder Metall. Met. Ceram.* **15** (1976) 193.
3. K. H. KACK, *Trans. J. Brit. Ceram. Soc.* **72** (1973) 376.
4. H. MASAKI and O. KAMIGAITO, *Yogyo-Kyokai-Shi* **84** (1976) 508.
5. G. E. GAZZA, in "Ceramics for High Performance Applications-II", edited by J. J. Burke, E. N. Lenoe and R. N. Katz, (Brook Hill Pub. Co., Chestnut Hill, Mass. USA, 1978) pp. 1001–10.
6. E. M. RABINOVICH, L. HAREL and R. FISCHER, "Special Ceramics – 7" edited by D. Taylor and P. Popper (British Ceramic Society, Stoke-on-Trent, 1981) p. 71.
7. "Handbook of Chemistry and Physics", 36th edn. edited by C. D. Hodgman, R. C. Weast, C. W. Wallace and S. M. Selby, (Chemical Rubber Company, Cleveland, Ohio, 1954) p. 2015.

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