EFFECT OF SODIUM SILICATE MODIFICATION BY NANO-SiO_2 ON COATING PROPERTIES USED IN INVESTMENT CASTING

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ARTICLE INFO

Received: 29/4/2025
Revised: 30/5/2025
Published: 30/5/2025

KEYWORDS

Investment casting
Sodium silicate
Binder modification
Nano-SiO_2
Binder-to-powder ratio

ABSTRACT

Sodium silicate is widely used as a binder in coating slurry in investment casting technology to produce components with high dimensional accuracy and good surface smoothness. However, this slurry still presents several limitations, including low permeability, high residual strength, and a propensity for surface cracking. The aim of this study is to introduce a sodium silicate modification method to overcome these disadvantages. The nano-SiO_2 modifier, which was synthesized by the sol-gel method, consists of spherical SiO_2 with low tendency to agglomerate and an average diameter of approximately 20 nm. Sodium silicate was modified by nano-SiO_2 at concentrations of 2.5%, 5.0%, and 7.5% by weight relative to the unmodified binder. Each modified binder formulation was subsequently mixed with zircon powder at binder-to-powder ratios of 60:40; 57.5:42.5, and 55:45, was evaluated based on properties such as viscosity, adhesion performance, and permeability. The optimum parameters for the coating slurry are as follows: the sodium silicate with a modulus of 2.9 modified by 2.5% nano-SiO_2; a binder-to-powder ratio of 55/45; and 0.5% Carboxymethyl cellulose used as an additive. According to theory of investment casting, the sample was cast in a vacuum chamber, using a pumps to maintain the low-pressure environment. In this study, the applied pressure is 0.4 kg/cm^2 which can improve the casting quality.

ẢNH HƯỞNG CỦA BIẾN TÍNH THỦY TINH LỎNG BẰNG NANO-SiO_2 ĐẾN TÍNH CHẤT CỦA LỚP SƠN ĐÚC MẪU CHẢY

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THÔNG TIN BÀI BÁO

Ngày nhận bài: 29/4/2025
Ngày hoàn thiện: 30/5/2025
Ngày đăng: 30/5/2025

TỪ KHÓA

Đúc mẫu chảy
Nước thủy tinh lỏng
Biến tính
Nano-SiO_2
Tỉ phần chất dính/bột

TÓM TẮT

Chất dính thủy tinh lỏng vẫn được sử dụng rộng rãi trong công nghệ đúc mẫu chảy để sản xuất các chi tiết có độ nhẵn bóng bề mặt cao, kích thước chính xác. Tuy nhiên, huyền phù thủy tinh lỏng vẫn còn một số hạn chế, thí dụ, độ thông khí kém, độ bền còn lại cao, dễ bị nứt bề mặt. Bài báo này giới thiệu một phương pháp biến tính thủy tinh lỏng nhằm khắc phục các nhược điểm trên. Chất biến tính nano-SiO_2 được tổng hợp bằng phương pháp sol-gel, với kích thước hạt trung bình là 20 nm. Các mẫu thử gồm nước thủy tinh lỏng được biến tính lần lượt bằng 2,5%, 5,0%, và 7,5% theo khối lượng, sau đó trộn từng mẫu với bột Zircon để đạt được tỉ lệ chất dính/bột là 60:40; 57,5:42,5; 55:45, chất phụ gia là Carboxymethyl cellulose. Các đặc tính của sơn khuôn mẫu chảy được đánh giá bao gồm độ nhớt, khả năng bám dính và độ thông khí. Thông số tối ưu đạt được là thủy tinh lỏng có mô-đun 2,9, được biến tính bởi 2,5% nano-SiO_2, sử dụng 0,5% chất phụ gia. Theo lý thuyết về đúc mẫu chảy, sản phẩm được đúc trong buồng chân không, sử dụng bơm để đạt được môi trường áp suất thấp. Trong nghiên cứu này, áp suất được áp dụng là 0,4 kg/cm^2 có thể cải thiện chất lượng vật đúc.

DOI: https://doi.org/10.34238/tnu-jst.12699

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1. Introduction

In traditional investment casting, ceramic shells are fabricated using two methods: clay molding and ceramic shell molding. Among these, ceramic shell molding remains the dominant technology in current industrial applications [1]. Within this process, the preparation of the first coating layer plays a critical role in determining the quality of the castings. Refractory materials used as powder grains (typically various oxides) exhibit significantly different interactions with both the binder and the paraffin pattern. Zircon powder has been shown to produce minimal interfacial reactions between the shell and the casting, resulting in fewer pores in the ceramic shell, and yield the shallowest metal penetration depth into the mold [2].

The composition and fabrication of the primary coating layer are considered among the most fundamental factors in ceramic shell mold production for investment casting. The quality of the ceramic shell can be enhanced by modifying the nature of the refractory materials and adjusting the binder-to-powder ratio (B/P ratio) [3] – [6]. The quality of the ceramic shell is entirely dependent on the binder, the proportion of additives, and the density of the slurry. Modifying the binder to improve the coating properties has been actively studied. Sodium silicate modified with sodium polyacrylate as a binder has demonstrated good stability. The decomposition of carbon element from the modifier creates a reducing environment, enhancing the surface quality of casting product [7]. Glucose has been used as both a modifier and a hardening agent for sodium silicate. The viscosity of sodium silicate increases with applied stress. The wettability and stability of the coating are significantly improved. Additionally, glucose promotes the gelation and hardening processes of the sodium silicate [8]. Microwave hardening of sodium silicate has proven to be more efficient and productive, significantly reducing curing time compared to conventional methods [9]. Modification using nano-ZnO particles has enhanced the adhesion and stability of coatings that utilize sodium silicate. Employing ultrafine nanoparticles also enhances residual strength, reduces the required amount of modifiers, improves moisture resistance, and minimizes defects such as porosity in the binder system [10] – [13]. The most attention was paid to binders containing nano- SiO_2 for model layers of shell casting molds. Nanoparticales contained in the binders were characterized by a near-spherical shape and average particle size of 16-25 nm [14]. The Stöber process, which is an example of a sol-gel process, could be used to prepare silica (SiO_2) particles of controllable and uniform size for applications in materials science. The results showed that, SiO_2 particles have spherical shape, uniform size, monodisper, stability in the solvent, amorphous phase structure [15].

This paper focuses on investigating the effects of nano-SiO_2 powder on certain properties of the coating used in investment casting. The core methodology involves modifying sodium silicate with nano-SiO_2 to improve the adhesion and strength of the ceramic shell. A foaming agent (Carboxymethyl cellulose - CMC) and vacuum-assisted mold cavity treatment are also employed to enhance the mold's filling capability of the investment casting process.

2. Materials and method

Silicon dioxide (SiO_2) nanoparticles were synthesized by sol-gel method. All reagents used were of analytical purity. In this synthesis procedure, tetraethyl orthosilicate (TEOS) was used as a precursor material, (99.9% purity). The rest of the reagents were ammonia (NH_4OH) used as catalyst and solvents as ethanol and deionized water from Merck Chemical, (99.9% purity).

Commercially available liquid glass used in this study has the following specifications: a modulus of 2.9 and a density of 1.39 g/cm³. Quartz powder used as a refractory material contains more than 99.5% SiO_2, with particle sizes smaller than 45 µm accounting for 95% of the total. According to the supplier's data, the particle size distribution is as follows: 1–10 µm (12%), 10–30 µm (40%), 30–44 µm (43%), and 44–60 µm (5%). Carboxymethyl cellulose (CMC), with the chemical formula $[C_6H_7O_2(OH)_x(OCH_2COONa)_y]_n$, is a derivative of natural cellulose, sourced from China. It has a density of 1.59 g/cm³ and is slightly soluble in cold water.

The viscosity of the slurry was measured using a Zahn cup No. B4 according to ASTM D4212. The Engle viscosity (E_o) is defined as the ratio of the flow time of the slurry to that of distilled water for an equal volume. The Engle viscosity can be converted into other standard viscosity units.

The permeability of the ceramic shell was determined using a permeability measurement device (Figure 1). The principle of the permeability measuring instrument is based on Darcy's law, and the permeability coefficient K is calculated using the following formula:

$$\mathrm{K} = \frac{V.d}{F.\Delta p.t} \qquad (1)$$

Where *K*: permeability of the coating (m^2/Pa.s), *V*: volume of air passing through the ceramic shell (m^3), *d*: thickness of the ceramic shell (m), *F*: surface area through which the air flows (m^2), *Δp*: pressure difference across the sample (Pa), *t*: time for the air volume *V* to pass through the shell (s).

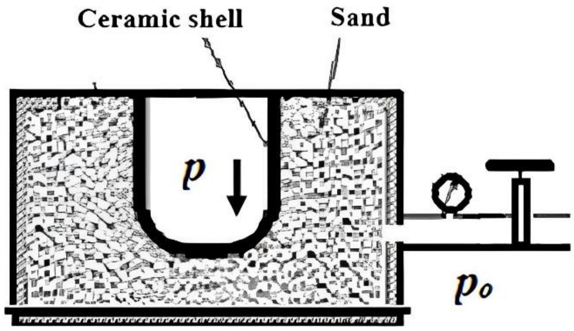

Figure 1. *Schematic diagram of the ceramic shell permeability measurement setup*

To evaluate the adhesion strength of the ceramic shell to the wax pattern, a paraffin pattern in the form of a rectangular bar with dimensions D × R × H = 1.0 × 0.5 × 7.5 cm was prepared. The initial mass of the pattern was recorded as G_0 (in milligrams). The pattern was then fully immersed in the prepared slurry for 5 seconds to ensure complete surface coverage. After immersion, the pattern was gently removed and held vertically for a few seconds to allow excess slurry to drain off.

Immediately following this, the coated pattern was subjected to a CO_2 gas stream for hardening, simulating the gelling and setting process of the slurry under actual shell-forming conditions. Once the coating had fully solidified, the pattern was weighed again to determine its mass G. The adhesion strength R, representing the amount of coating retained per unit surface area of the wax pattern, was calculated using the formula:

$$\mathrm{R} = \frac{G - G_0}{S} \qquad (2)$$

Where G: mass of the pattern after the coating solidified (mg), G_0: initial mass of the uncoated pattern (mg), S: total surface area of the pattern (cm²). This method provides a quantitative assessment of the coating's adhesion ability, which is critical for ensuring the structural integrity of the ceramic shell during the subsequent drying and casting processes.

The ceramic shell was fabricated through a multi-layer coating process using the prepared slurry. The wax patterns were first dipped into the slurry mixture to ensure uniform coverage. Immediately after dipping, fine refractory sand with a particle size ranging from 0.1 to 0.2 mm was uniformly sprinkled onto the wet surface. This first layer was then hardened using CO_2 gas and left to cure under ambient conditions for 2 hours. After the initial layer had fully set, a second coating of slurry was applied using the same dipping technique. This time, medium-grade refractory sand with a particle size of 0.45–0.63 mm was used for the stuccoing step. Similar to the first layer, the second layer was also cured in ambient air for 2 hours to ensure proper bonding and hardening.

The third and final slurry layer was then applied, followed by stuccoing with coarse sand of particle size 0.8–1.0 mm. The shell was once again cured in air for 2 hours. The increasing coarseness of sand in successive layers contributes to mechanical strength and permeability of the final shell structure. Following the completion of all ceramic layers, the wax pattern was removed by steam dewaxing at a temperature of approximately 90–100 °C. The dewaxed ceramic shell was then subjected to a high-temperature firing process at 850–900 °C. The shell was held at this temperature for approximately 2.5 hours to achieve sufficient sintering and structural integrity. After sintering, the shell was allowed to cool naturally in ambient air.

3. Results and discussion

3.1. Morphology of nano-SiO_2

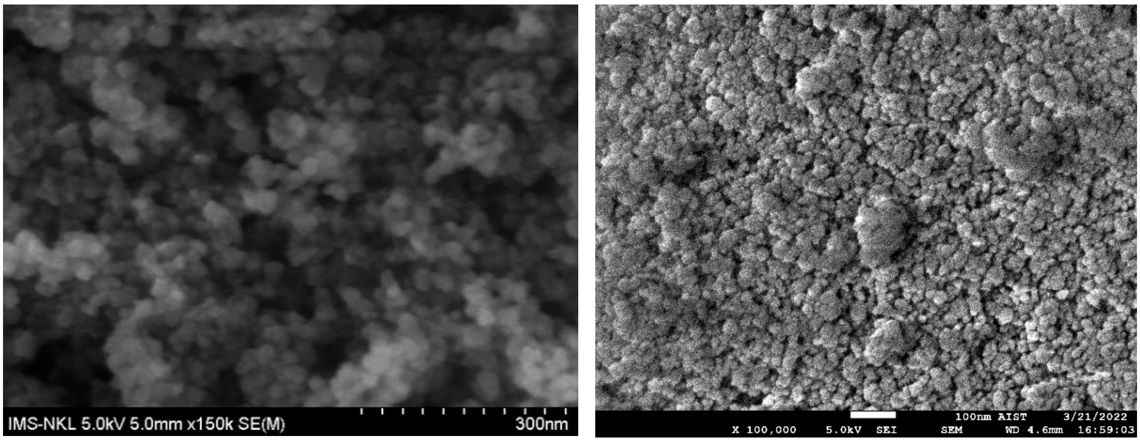

Figure 2. *SEM image of SiO_2 sample*

The sample of SiO_2 was prepared by sol-gel method, SEM was used to study the morphology of the powder sample. Figure 2 indicates that prepared SiO_2 powder consists of spherical SiO_2 with low tendency to agglomerate. SEM analysis also confirmed the average diameter of SiO_2 particles is approximately 20 nm. Sodium silicate with a modulus of 2.9 was modified by nano-SiO_2 at concentrations of 2.5%, 5.0%, and 7.5% by weight relative to the unmodified binder. Each modified binder formulation was subsequently mixed with zircon powder at binder-to-powder ratios (B/P ratio) of 60:40; 57.5:42.5, and 55:45, was evaluated based on properties such as viscosity, adhesion performance, and permeability.

3.2. Viscosity of sodium silicate modified by nano-SiO_2

The viscosity of the slurry depends on two primary factors: (1) the intrinsic viscosity of the binder (governed by internal friction between liquid layers), and (2) the interaction between solid particles in the slurry and the binder medium. The sodium silicate system modified with nano-SiO_2 can be regarded as a colloidal system, since both the inherent silicate particles and the added nano-SiO_2 have particle sizes within the colloidal range.

The relationship between slurry viscosity and nano-SiO_2 content is presented in Figure 3. The results indicate that the addition of nano-SiO_2 initially leads to a reduction in binder viscosity, reaching a minimum at approximately 2% nano-SiO_2. Beyond this point, the viscosity increases and reaches a peak at 5% nano-SiO_2, before decreasing again at higher concentrations.

This non-linear behavior is consistent with the characteristics of colloidal systems. Sodium silicate with a modulus of 2.9 behaves as a colloidal dispersion, where interparticle interactions can alternate between attractive and repulsive forces as particle spacing changes (Figure 4). Increasing the concentration of nano-SiO_2 effectively reduces the average interparticle distance, similar to increasing particle density in a colloidal system. At an optimal dispersion density, particles repel one another sufficiently to remain suspended, leading to a stable and low-viscosity system. However, when the concentration of nano-SiO_2 exceeds the saturation threshold, the system becomes overloaded with ultrafine particles. This results in increasing mobility of the dispersion medium and diminishing intermolecular interactions, thereby reducing the overall viscosity.

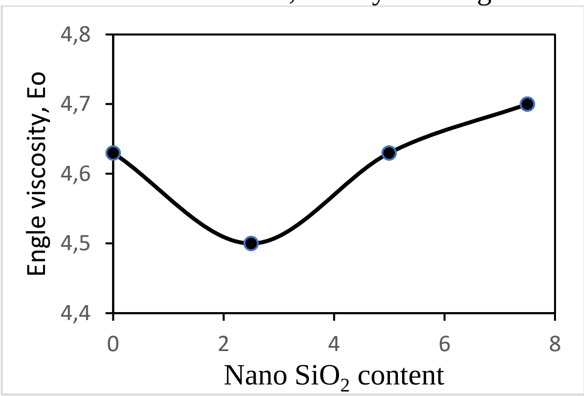

Figure 3. *Viscosity of the slurry as a function of nano-SiO_2 content*

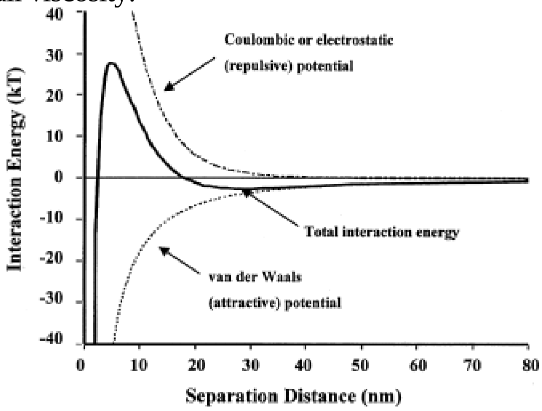

Figure 4. *Schematic interaction energy versus distance profiles of the colloidal system [16]*

These findings highlight the critical role of nano-SiO_2 content in controlling the rheological behavior of the binder system and optimizing slurry performance for ceramic shell fabrication. When using sodium silicate as a binder in investment casting, the uniform distribution of the binder on the surface of the paraffin pattern and the thickness of the adhered layer depends entirely on the viscosity of the slurry. Controlling slurry viscosity is therefore critical to the formation of the initial coating layer as well as the subsequent backup layers in the ceramic shell. Based on viscosity measurements, all subsequent experiments in this study were considered using nano-SiO_2 contents in a range of 2-2.5%, in order to ensure that the slurry maintained a suitably low viscosity.

3.3. Adhesion of the coating to the surface of pattern

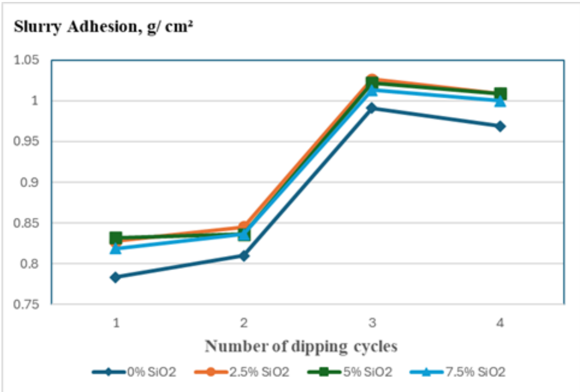

Figure 5. *Slurry adhesion as a function of nano-SiO_2 content and number of dipping cycles*

Figure 6. *Ceramic shell showing swelling and delamination defects*

The adhesion of the first coating layer and subsequent layers is shown in Figure 5. The adhesion of the first coating layer to the surface of the paraffin pattern plays a critical role in determining the overall quality of the ceramic shell. This first coating layer not only provides a smooth surface that is "inherited" by the later mold but also creates sufficient permeability for the application of the vacuum process in the shell formation, similar to the lost foam casting method. All experiments were conducted using liquid glass with a modulus of 2.9.

Figure 5 shows that the adhesion of the first coating layer is very low, corresponding to a thickness of only about 0.5–0.7 mm. This phenomenon can be explained by the poor wettability and adhesion of the slurry to the paraffin surface. Therefore, prior to forming the ceramic shell, it is essential to treat the surface of the paraffin pattern with special solutions. An effective cleaning solution for the paraffin surface was used in this study. The adhesion, and hence the thickness of the coating layer on the wax surface, stabilized after the second dip. Thus, for investment casting, the focus should be on studying the treatment of the wax pattern surface and the composition of the first coating layer to ensure good and uniform adhesion of the coating to the wax surface. With its special surface characteristics, nano-SiO_2 significantly improved the adhesion of the coating. The optimal nano-SiO_2 content, approximately 2 to 2.5%, ensures the best adhesion. Higher nano-SiO_2 concentrations result in uneven shell layer thickness.

3.4. Permeability of the ceramic shell

To investigate the influence of the B/P ratio on the permeability of ceramic shells, a series of samples were prepared using sodium silicate modified with nano-SiO_2 at concentrations of 2.5%, 5.0%, and 7.5% by weight relative to the unmodified binder. Each modified binder formulation was subsequently mixed with zircon powder at B/P ratios of 60:40, 57.5:42.5 and 55:45. Figure 7 illustrates the correlation between permeability and the nano-SiO_2 content, while Figure 8 highlights the effect of the B/P ratio on this property.

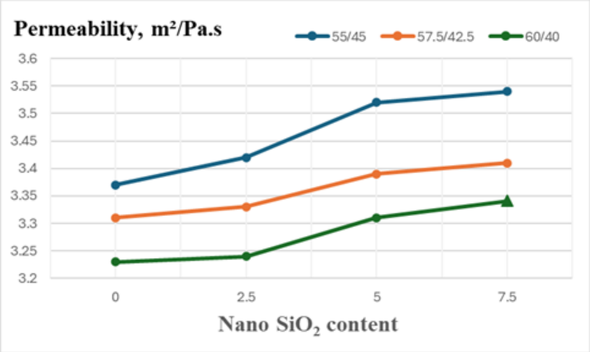

Figure 7. *Effect of nano-SiO_2 content on shell permeability*

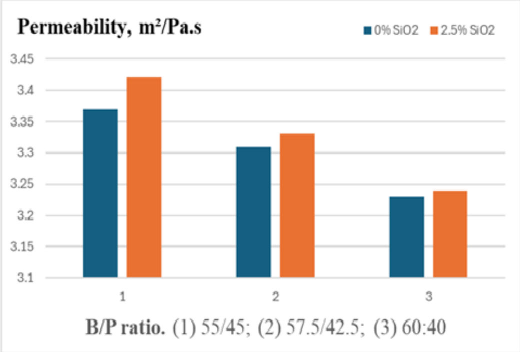

Figure 8. *Effect of B/P ratio on shell permeability*

At lower concentrations, the addition of nano-SiO_2 leads to a decrease in slurry viscosity (Figure 3), which enhances the fluidity of the suspension and thereby improves its ability to uniformly adhere to the surface of the wax pattern (Figure 5). Both reducing the B/P ratio and increasing the nano-SiO_2 content increases the permeability of the ceramic shell. The permeability of the ceramic shell increases with the nano-SiO_2 content in the range of 2.5 to 5%, reaching approximately (3.3–3.5) × 10^{-7} m²/Pa.s, after which it tends to stabilization. However, it is not possible to continuously reduce the B/P ratio, as this would significantly raise the viscosity of the slurry, making it difficult to manufacture the shell after each dipping. A binder-to-powder ratio in the range of 57.5/42.5 to 55/45 is considered ideal for the dipping process. When the B/P ratio was reduced less than 55/45, the adhesion continued to increase after additional dips. However, the slurry becomes too viscous, resulting in a relatively thick coating layer after each dip, leading the ceramic shell exhibited several defects, including swelling and delamination (Figure 6).

Figure 9. *Experimental casting product*

Based on the results from the basic experiments on viscosity, strength, and permeability of the ceramic shell, a set of basic parameters for the slurry was used to cast a tiger-product with complex surface. The sodium silicate with a modulus of 2.9 modified by 2.5% nano-SiO_2; a B/P ratio of 55/45 and 0.5% CMC used as an additive. The system was vacuum treated with a pressure of 0.4 kg/cm² to enhance the filling ability without the need to heat the mold to high temperatures. The cast details showed clear, distinct patterns and designs as seen in Figure 9. Hence proved the permeability of the ceramic shell helps to absorb any gas including paraffin decomposition products if paraffin residue remains on the surface of the mold cavity. Cleaning of the cast parts was easy, with no sand adhering to the surface of the cast objects.

4. Conclusion

The experimental results demonstrate that the modification of sodium silicate with nano-SiO_2 has a significant influence on the key properties of the ceramic shell coating, including viscosity, adhesion, and wettability. When the nano-SiO_2 content exceeds approximately 2.5%, the viscosity of the slurry prepared with sodium silicate (modulus 2.9) increases noticeably, indicating changes in colloidal interactions within the binder system. The adhesion of the coating to paraffin patterns is strongly affected by both the surface treatment of the paraffin and the quality of the initial coating layer. The incorporation of nano-SiO_2 in the binder formulation was found to enhance adhesion performance, particularly at concentrations of approximately 2.5%. Moreover, the use of nano-SiO_2 enables better control of slurry viscosity, with B/P ratios ranging from 57.5/42.5 to 55/45 yielding the most favorable results in terms of workability and shell quality. The optimized slurry composition proved to be highly suitable for improved investment casting applications, yielding defect-free, well-defined cast surfaces and facilitating efficient shell removal.

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