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Some filtration parameters of diluted TiO_2/water suspensions and the cake microstructure after sintering

O. Şan *

Dumlupinar University, Department of Ceramic Engineering, 43100 Kütahya, Turkey

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Abstract

Some filtration parameters (filter medium and average specific cake resistance) of dilute TiO_2/water suspensions and the cake microstructure after sintering were investigated through the experiments conducted with and without binder at two concentrations (0.3 and 0.6 wt.% relative to the solids) and using coarse and fine pore size of filter medium (average pore size: 3 and 0.2 μm). Clogging and non-clogging filtration conditions were observed due to the particle–filter medium interaction. Medium clogging phenomena was observed with the particles without polymerization using coarse pore size filter medium and polymerized particles (0.6 wt.%) filtered with fine pore size filter medium. The cakes obtained from the clogging and non-clogging filtration conditions were dried and sintered at 950–1100 °C. The water adsorption tests and SEM studies showed an adequate relation between the clogging and non-clogging filtration conditions and microstructure of the cakes after sintering. The sintered products obtained from the non-clogging filtration condition had promising engineering properties in which fine and uniform grains with connected pores could be obtained.

Keywords: A. Suspensions; B. Microstructure; D. TiO_2

1. Introduction

The filtration is a major solid–liquid separation process in mineral, chemical and ceramic industries. The solid particles in the suspension form a growing filter cake on the filter medium and the liquid flows through interstices of the cake and filter medium. The liquid flow is affected by the size and shape of particles and their compaction properties. It is obvious that the formed cake microstructure greatly determines the filtration parameters. The second part of filtration system is the filter medium. Its influence on the cake filterability greatly depends on the particle–filter medium interactions. There is no problem with coarse particles filtered through both the fine-pore and coarse-pore filter media. However, in the case of fine particle filtration, it is required to correct the selection of the filter medium; otherwise, clogging phenomena appear and the filter medium resistance constitutes a substantial portion of the overall filtration resistance [1–9]. Medium clogging phenomena have been also observed with the application of additional operation to the suspension such as polymer conditioning. In that case, the problem is complex. Once the polymer is introduced into the suspension, it can adsorb not only on the particles but also on the walls of the membrane pores and thereby reduce the pore size available for filtration. This leads to medium clogging phenomena. Thus, only an appropriately small amount of polymer is to be used to gain an advantage [10–12].

Filtration of the water suspensions was the aim of a number of experimental work concentrating on the practical filtration problems as well as on the model studies devoted to the fundamental questions of microfiltration [13]. Dilute TiO_2/water suspensions have been found useful and adequate for the investigation of filtration fundamentals for the following reasons: (i) TiO_2 is a refractory oxide and insoluble in water. Aqueous suspensions of TiO_2 are very difficult to settle even when centrifuged. These properties provide filtration without sedimentation effect. (ii) In dilute

* Tel.: +90 274 265 2031/4302; fax: +90 274 265 2066.
E-mail address: osmansan@dumlupinar.edu.tr.

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suspension filtration, each particle moves separately from the others and tends to follow streamlines of the flow directed towards the filter medium pores, resulting in high compaction. The dispersion of untreated and polymerized particles in liquid media plays an important role in determining the resulting particle packing efficiency, final structure integrity and microstructure homogenity after sintering.

2. Filtration resistances

In cake filtration, medium resistance (R_m) could be obtained directly by measuring pressure drop across the filter medium (P_m)

$$R_m = \frac{P_m}{\mu q} \tag{1}$$

where q is the instantaneous superficial filtrate rate (m^3/m^2s), μ is the filtrate viscosity (Ns/m^2). The pressure drop on the filter medium is measured by a sensor located at cake–filter medium interface. Hosten and San [6] reported that the sensing probe at cake–filter medium interface is placed approximately 0.4 mm above the filter medium. The measured pressure is a composite value comprising of the pressure drop of the filter medium itself and a cake layer-adjacent to the medium.

Conventional theory of cake filtration is based on a two-resistance-in-series (the filter medium resistance and the cake resistance) model [14].

$$R = R_c + R_m = \frac{P}{\mu q} = \left(\frac{\langle\alpha\rangle c}{A}\right)V + R_m \tag{2}$$

where R is the instantaneous total filtration resistance (1/m), R_c the cake resistance, P the applied pressure of filtration (N/m^2), $\langle\alpha\rangle$ the average specific cake resistance (m/kg), c the mass of solids filtered per unit volume of filtrate (kg/m^3), A the filter area (m^2) and V the cumulative filtrate volume (m^3).

Eq. (2) has been derived by assuming that the medium resistance (R_m) is constant and the average specific cake resistance ($\langle\alpha\rangle$) depends primarily on the particle size of the material and the pressure drop across the cake. When filtration data are plotted as filtration resistance (R) versus filtrate volume (V), a straight line is obtained with a slope proportional to the average specific cake resistance ($\langle\alpha\rangle$) and the intercept gives the filter medium resistance (R_m).

The analysis of filtration data using the classical approach provides good fitting for non-clogging filter medium or slightly medium clogging phenomena [6,15]. The intercept of the filtration resistance (R) versus filtrate volume (V) plot shows a positive value for non-clogging medium. If the medium clogging is serious and continues throughout the course of filtration, this theory indicates erroneous implication in which the plotting of filtration resistance (R) versus (V) yields negative intercepts.

In filtration, the filter medium has two functions: transmitting the filtrate and providing a support for the formed cake. During the process, the migrating fine particles through the cake pores fill the voids near the bottom of the cake leading to non-uniform variations in the density across the thickness of cake. The fine particles at cake–filter medium interface have a great importance for controlling the filtration rate. A high resistance to the liquid flow is expected due to the skin-layer formed on the filter medium. An alternative filtration theory, namely multiphase continuum theory, dictates that the least permeable part of the filtration system occurs at the cake–filter medium interface and controls the filtration system [16,17]. The permeability at cake–filter medium interface is determined by keeping the cake pressure drop at a constant value. In that case, the sensor is located at the cake–filter medium interface and it measures the cake pressure drop. A constant cake pressure can only be done after a thin layer of a powder formed on the filter medium. Thus, the measured permeability at the cake–filter medium interface is the indication of a composite value comprising of the permeability of filter medium itself and a cake layer-adjacent to the medium.

The medium clogging decreases the filtration efficiency of solid–liquid separation schemes in the mining and chemical industries. The other important consequence of the medium clogging in the ceramic industry is the uniform-particle-compaction; it could not be obtained with the clogged-medium. The following are the possible compaction phenomena with a clogged-medium: (i) the filtering time is too long and segregation of particles produced gradient compaction; (ii) deposited particles on the medium may be oriented and/or rearranged; and (iii) local densification may be formed at the cake–filter medium interface. Uniform ceramic compaction has great significance for the subsequent stages of processing such as drying and sintering. Information on the medium clogging by a simple filtration data analyzing is thought to be useful for the prediction of the ceramic-microstructure. Şan and Tuncer [18] observed that the clogging and non-clogging filter medium through the filtration compaction influenced the cake uniformity and thus the cake microstructure after sintering. Under non-clogging-medium filtration conditions, cakes are thinner and more homogeneously compacted to yield finer grain growth and homogeneous, microstructures in sintered cakes. The clogged filter showed inferior microstructure of a sintered sample.

In this study, some filtration parameters (average specific cake and medium resistances) of dilute TiO_2/water suspensions were determined by altering the filter medium (two different pore sizes) and particle pretreatment using a polymer (Na-carboxymethyl cellulose: acted as a binder and an effective deflocculant) at two different concentrations. The filter cakes were sintered and then the microstructures were investigated with respect to the cake obtained under clogging and non-clogging filtration conditions.

3. Experimental

TiO_2 particles (OPEX crystalline 137) were used as the suspended particles. The average particle size was about 0.37 μm. A dilute suspension was prepared by suspending 11.36 wt.% solids in distilled water ($c = 128.2$ kg/m^3) without and with binder agent (Na-carboxymethyl cellulose) at two different concentrations (0.3 and 0.6 wt.% relative to the dry solids). The sample without and with polymer will be referred as "untreated" and "pretreated", respectively. In order to produce a well-mixed feed suspension at room temperature, it was stirred in a beaker using a magnetic stirrer for 30 min. A polymer solution with the desired concentration was subsequently added to the suspension, and the mixture was stirred vigorously for several minutes.

The filtration device was constructed from a transparent plexiglas and consisting of a cylinder with an inner diameter of 70 mm, a cover plate and a base part. The base part holds the perforated supporting brass plate, the brass wire gauze (65-mesh) and the filter medium. The filter media used in the experiments were cellulose acetate type membrane filter having 0.2 μm average pore size (Sato SM 11107), and a conventional filter paper of 3 μm average pore size (Whatman No. 44). The as-prepared suspensions were poured into the cylinder and the cover plate was tightly fixed; then, a pressurized air was applied over the suspension to obtain the desired pressure-difference (150 kPa). The pressure was kept constant by manually adjusting the needle valve fitted to the upper part of experimental unit. The filtrate collected in a beaker was placed on the electronic balance.

The average particle size of the TiO_2 powder was measured by using a laser diffraction particle analyzer. The open porosity of sintered cakes was measured by the capillary water adsorption test. The sintered samples were coated with a thin film of gold–palladium and the microstructure examined using a scanning electron microscopy (CamSan S4).

4. Results and discussion

The comparative filtration resistances for experiments run under various conditions are shown in Figs. 1–3. A comparison of Figs. 1 and 2 reveals that the untreated suspension filtered through the fine medium offers slightly less total resistance to filtration as compared to its filtration through the conventional coarser filter medium. Also, the filtration of the pretreated suspension through the fine membrane medium offers much less resistance if the addition of Na-cmc is at its lower content (0.3 wt.%). At this lower addition of the binder agents, the type of the filter medium does not seem to have any significant effect on the total filtration resistance (see Fig. 3 plot (a) and Fig. 2 plot (b)). However, at the higher addition (0.6 wt.%), the coarser pore size of the conventional medium leads to much lower total resistance (see Fig. 3 plot (b) and Fig. 1 plot (a)). The quite remarkable variation of the total filtration resistance in

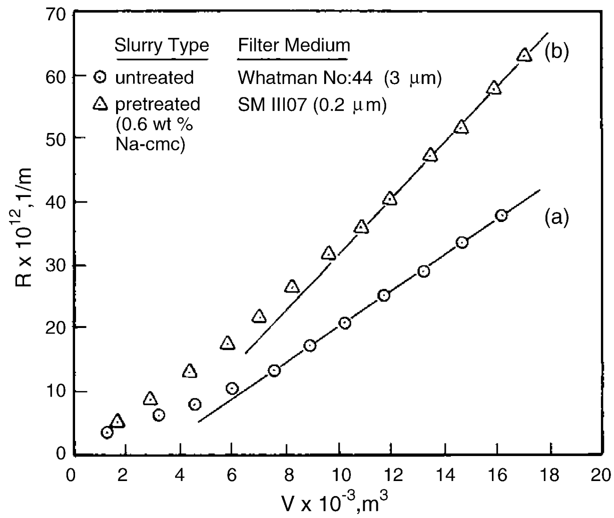

Fig. 1. Plots of filtration resistance vs. filtrate volume: (a) filtration of untreated TiO_2 suspension with coarse pore size filter medium (average pore size: 3 μm); and (b) filtration of pretreated-suspension (0.6 wt.% of Na-cmc) using fine pore size filter medium (average pore size: 0.2 μm).

the experimental runs should be at least partly due to the extent of filter medium clogging. The filter medium resistance (R_m) and the average specific cake resistance $\langle\alpha\rangle$, obtained from the graphically determined intercept and slope of the conventional R versus V plots, are given in Table 1. A peculiar result can be observed from the experimental runs shown in Fig. 1, which corresponds to the cases where the highest total resistances are observed. The intercepts of the linear portions of these plots yield unrealistic negative filter medium resistances.

The false medium resistance values observed in the case of high total filtration resistances, and the initial non-linearity of the plots (see Fig. 1) suggest significant levels of filter medium clogging. The similar phenomenon has been

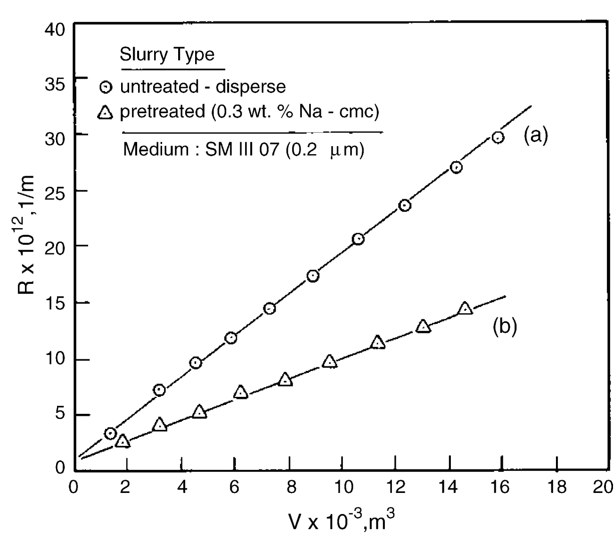

Fig. 2. Plots of filtration resistance vs. filtrate volume: (a) untreated-suspension; and (b) pretreated-suspension (0.3 wt.% of Na-cmc) filtered with fine pore size filter medium (average pore size: 0.2 μm).

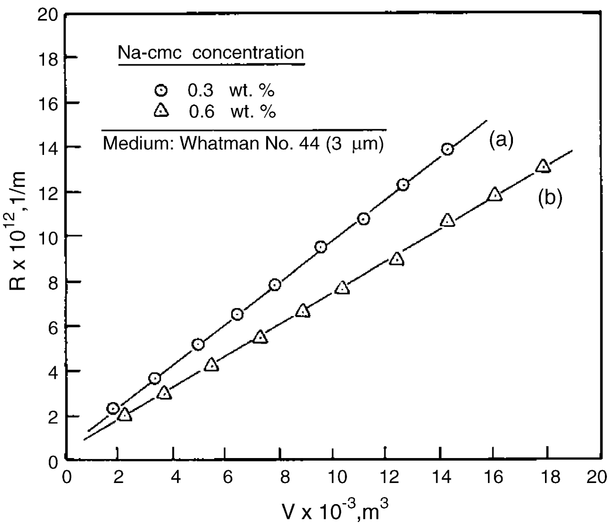

Fig. 3. Plots of filtration resistance vs. filtrate volume: (a) pretreated-suspension at 0.3 wt.% of Na-cmc; and (b) pretreated-suspension at 0.6 wt.% of Na-cmc, filtered with coarse pore size filter medium (average pore size: 3 μm).

reported by Bridger et al. [19], and by our previous study [6]. During the initial non-linear stage of filtration, the medium resistance undergoes a rapid rise while clogging and blocking of medium take place [9]. The initial collection of cloudy filtrates with the coarse pore size of filter medium during filtering of the untreated suspension is the indication of the occurrence of medium clogging. The polymer-pretreated suspensions give clear filtrate even though at the initial stage of filtrations for both coarse and fine pore size of filter medium used in the system. The clogging mechanism during the filtration of polymer-pretreated suspension is different in the sense that the dosage of the polymer and the type of filter medium make the filtration process either clogging or non-clogging type. The high polymer concentration with membrane filter shows such a clogging phenomena (see Fig. 1 plot (b)) as the mechanism proposed by Akay and Wakeman [10], Nguyen and Ripperger [11], Chiu and James [12]. Contrary to the results presented in Fig. 1, the experimental runs plotted in Figs. 2–3, indicating totally linear plots and near-origin positive intercepts, are justifiable as non-clogging filter medium filtrations.

Fig. 2 shows a measurable (non-clogging) medium resistance from the intercept of each R versus V linear plot for the untreated-disperse and low concentration polymer-added suspension filtered through the fine-porosity filter medium. This is a typical result of particle polymerization that is to provide a non-clogging medium by the capture of ultrafines. Furthermore, the same filter medium resistance observed with the untreated disperse suspension supports the suggestion of the occurrence of a non-clogging medium. Similar plots are observed with the pretreated suspension filtration both at low and high polymer concentrations as shown in Fig. 3. These findings reveal: (i) low polymer concentration is enough for increasing of the TiO_2 particle filterability; (ii) the untreated-disperse fines clog the coarse pore size of filter medium (see Fig. 1 plot (a)); however, the fines do not clog the fine pore size membrane (see Fig. 2 plot (a)) because of the differences in the pore size, structure and pore size distribution of the two used filter papers. Noteworthy is the fact that the membrane filter has more uniform continuous structure than the conventional filter paper.

Conceptually, the polymer-added suspension decreases the average specific cake resistance, and its concentration is important for the production of large flow channels, leading to further decrease in the average specific cake resistance. The hypothesis is experimentally verified in the case of non-clogging medium (see Fig. 3). High-resistance filtration in the presence of medium clogging (see Fig. 1) induces an apparently high average specific cake resistance.

The high resistance of average specific cake resistance is thought to be the consequence of non-uniform particle compaction, the observation of high filtration resistances with clogged-filters is the evidence. The clogged-filter pores divert the liquid flow path to the free pores. The elongation on the flow undergoes the particle compaction and increased the formation of skin-layer at cake–filter medium interface. The migrating fine particles or polymer species easily fill the voids near the bottom of the cake. A non-uniform variation in density across the thickness of cake could be obtained.

Table 1
The medium resistances and average specific cake resistances for the untreated or pretreated TiO_2 slurries filtered using coarse (Whatman No. 44; average pore size: 3 μm) or fine pore size (Sato SM11107; average pore size: 0.2 μm) of filter medium

Filter medium	Suspension	$R_m 10^{-12}$ (1/m)	$\langle\alpha\rangle 10^{-10}$ (m/kg)
Whatman No. 44	Untreated-disperse	Erroneous implication	8.34
Conventional filter (average pore size: 3 μm)			
	Pretreated-0.3 wt.%-Na-cmc	0.50	2.85
	Pretreated-0.6 wt.%-Na-cmc	0.50	2.15
Sato SM 11107	Untreated-disperse	1.12	5.59
Membrane filter (average pore size: 0.2 μm)			
	Pretreated-0.3 wt.%-Na-cmc	1.12	2.83
	Pretreated-0.6 wt.%-Na-cmc	Erroneous implication	13.10

Table 2
The water absorption of sintered titanium dioxide cakes formed by coarse (Whatman No. 44; average pore size: 3 μm) or fine pore size (Sato SM11107; average pore size: 0.2 μm) of filter medium

Filter medium	Suspension	Water absorption (wt.%)			
		950 °C (3 h)	1000 °C (3 h)	1000 °C (8 h)	1100 °C (8 h)
Whatman No. 44	Untreated-disperse	18.47	15.50	13.32	7.78
Conventional type (average pore size: 3 μm)					
	Pretreated-0.3 wt.%-Na-cmc	20.97	18.01	15.58	9.12
	Pretreated-0.6 wt.%-Na-cmc	21.65	18.65	16.09	9.41
Sato SM 11107	Untreated-disperse	24.30	21.60	16.55	9.43
Membrane type (average pore size: 0.2 μm)					
	Pretreated-0.3 wt.%-Na-cmc	27.00	24.38	18.79	10.69
	Pretreated-0.6 wt.%-Na-cmc	26.50	24.07	18.48	10.15

It is an inferior microstructure for further ceramic processing. On the other hand, the uniform particles compaction has an isotropic interfacial energy. Thus, the cake microstructure after sintering will be of high quality.

The obtained filter cakes were dried and then sintered at 950–1100 °C. Table 2 shows water adsorption of the sintered cakes formed with untreated and polymer-added type of suspensions by the use of coarse pore size (conventional) and the fine pore size (membrane) filter medium. Irrespective of the type of suspension filtered (untreated or polymer-pretreated), sintering of cakes formed on the membrane filter yields ceramic bodies having higher percentages of water absorption than the ones formed on the conventional filter medium, for the both different sintering temperatures and times. It is noteworthy to mention that the higher dosage of the polymer in the filtration process through the membrane filter does not lead to any increase in water absorption, and in fact, there is a slight but consistent lowering of the water absorption as compared to the filtration cases on the same filter with the lower content of the polymer. This finding can be reasonably explained by the occurrence of severe filter medium clogging that influences the uniformity of particle compaction.

The grain morphology of the filter cakes after sintering has been investigated in our previous study [18] in which the dilute TiO_2 water suspension without polymer filtered using the conventional (clogged) and membrane type (non-clogged) filters. The grain morphology appears to be conceptually consistent with that inferred from the above open porosities. Figs. 4 and 5 show the SEM micrographs of the unpolished surfaces of the fractured edges of the sintered filter cakes at 1000 °C for 8 h. These figures show that the green body compacted with the clogged filter medium having partial pore coalescence and abnormal grain growth with relatively larger and unidirectional, partially-elongated growth (see Fig. 4). However, filtration with the non-clogging filter leads to a well-dispersed structure (see Fig. 5).

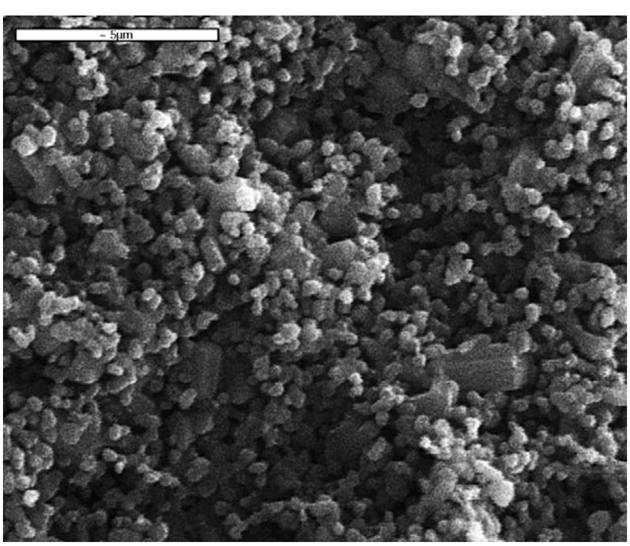

Fig. 4. SEM image of sintered filter cake fracture edge (unpolished) formed by use of conventional types of filter medium (Whatman No. 44; average pore size: 3 μm) through untreated suspension filtration.

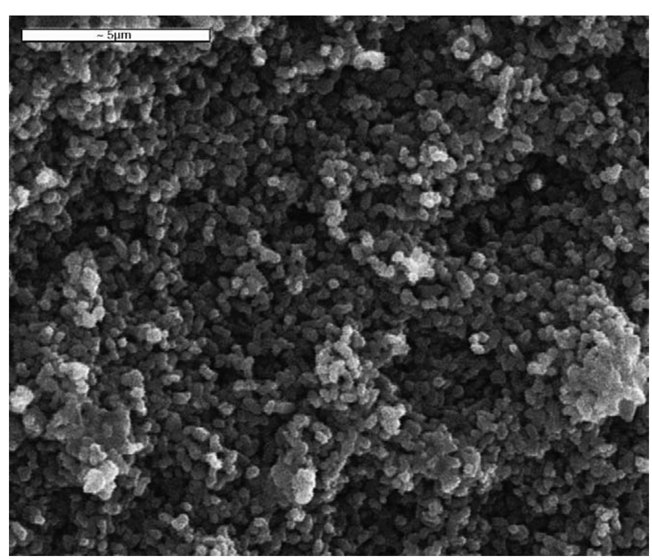

Fig. 5. SEM image of sintered filter cake fracture edge (unpolished) formed by use of membrane type of filter medium (Sato SM11107; average pore size: 0.2 μm) through untreated suspension filtration.

5. Conclusions

The filter cake and medium resistances were determined for the filtration of dilute TiO_2/water suspensions (mean particle size: 0.37 μm and filtration pressure: 150 kPa) without and with two different concentration of Na-cmc binder (0.3 and 0.6 wt.% relative to the solids) and the filter medium used as coarse and fine pore sizes (average pore size: 3 and 0.2 μm). The filtration runs without polymer through the coarse pore size and those with high-concentration-polymer-added suspension through the fine pore size filter medium indicated higher filtration resistances compared to that of experiments with fine and coarse pore size-filters, respectively. These results are attributed to the occurrence of a serious medium clogging phenomena due to the clogging caused by either migrating fines or particle–polymer interaction at cake–filter medium interface. A lower water absorption of sintered samples was obtained with the clogged-medium filtration-conditions. The SEM migrographs showed that a finer grain growth and homogeneous, porous structures were obtained with the non-clogging filtration-condition and the clogging media shows local densification. This work provides a new approach to the study of the filtration through filter medium clogging and non-clogging conditions and their cakes properties after sintering.

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