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Preparation and characterization of palladium-plated porous glass for hydrogen enrichment

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Abstract

In this study, cylindrical porous glass tablets were plated by palladium using electroless plating technique. Hypophosphite and Co(II) complexes were used as reducing agents in the prepared plating baths. Experiments were carried out in an especially designed glass vessel in which helium gas was continuously bubbled through the solution to create uniform concentration and to remove hydrogen gas from the surface for the case of hypophosphite-based procedure. XRF analysis of the upper layer of the composite membrane prepared by the hypophosphite-based bath showed a Pd/Si ratio of 4.6. SEM photographs indicated impregnation of Pd into the substrate upto 200 μm. However, the thickness of the dense Pd layer was only about 15 μm. SEM photographs and XRF results showed that hypophosphite-based bath was much more successful than the Co(II) complex-bath in Pd plating. Permeation experiments carried out at different temperatures showed that the contribution of surface diffusion to the permeation was significant at low temperatures and solution–diffusion mechanism was not important in the 40–200 °C temperature range for these membranes. The selectivity ratio for H_2/N_2 was found to be about 7 at 200 °C.

Keywords: Hydrogen; Composite membrane; Palladium; Electroless plating

1. Introduction

Palladium–alumina or palladium–silica composite membranes and Pd-impregnated porous substrates have potential applications in the improvement of the yield in hydrogen production in conventional steam reforming and shift conversion reactors. In our recent studies, enhancement of hydrogen diffusivity and permeability in alumina pellets due to impregnated palladium were illustrated [1,2]. Flow and diffusion characteristics of hydrogen in such Pd-impregnated pellets were investigated using a dynamic technique.

Dense palladium membranes have high selectivities but low permeabilities. In order to increase the mechanical strength of a membrane, palladium may be supported on a porous substrate. There are various preparation techniques, such as electroless plating, sputtering, electrochemical and chemical vapor deposition, etc. for the preparation of supported palladium membranes. Electroless plating is the most popular technique for the preparation of such composite palladium membranes. Major advantages of this technique include the ease of coating on materials having any shape, low cost and the use of very simple equipment.

The mechanism of the electroless plating technique is based on the autocatalytic reduction of metallic salt complexes on the substrate surface. Plated metal on the surface acts as a catalyst for further reaction. The activation step is necessary to initiate the reaction. The traditional activation procedure consists of two steps, namely immersion into the acidic tin chloride and acidic palladium chloride solutions. Number of other procedures were also proposed for the activation step in the literature [3,4]. The reducing agents containing hydrogen atoms bonded with phosphorus (hypophosphite ion), carbon (formaldehyde), boron (borohydride ion) or nitrogen (hydrazine) are generally used in the electroless plating processes [5]. Microporous alumina membranes were coated with a thin palladium film using electroless plating by Ilias et al. [6]. The plating chemistry has very important role in coating of Pd using electroless plating technique. Cheng and Yeung [7]

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a	mean pore radius (m)
D_K	Knudsen diffusivity (m^2/s)
D_s	surface diffusivity (m^2/s)
K	adsorption equilibrium constant
L	length of the membrane (m)
ΔP	pressure drop across the membrane (Pa)
ε	porosity
γ	defined by Eq. (1) (m/s)
μ	viscosity (Pa s)
τ	tortuosity factor corresponding to viscous flow and Knudsen flow
τ_s	tortuosity factor corresponding to surface diffusion flow

investigated the effect of plating chemistry on palladium deposition, plating efficiency and membrane structure. Their results showed that the hypophosphite-based plating bath had a slower plating rate, but it had better plating efficiency than the hydrazine-based plating bath. Number of different methods (electroless plating, electroplating, chemical vapor deposition and high-velocity oxy-fuel spraying) were reported in the recent literature for the preparation of palladium composite membranes [8–12]. In the work of Zheng and Wu [11], it was shown that pore size shrinkage of palladium layer is promoted by the increase in systemic pressure.

A novel deposition process involving reduction of cobalt(II) complexes in the electroless plating of copper, silver and gold was reported by Vaskelis et al. [13]. The cobalt(II) complexes, which are used in this plating process can be regenerated. This is considered as a major advantage of this technique.

In the present study, porous glass tablets were plated by palladium using the electroless plating technique. Hypophosphite-based plating bath was used in the preparation of Pd/glass composite membranes. Then, possible application of the Co(II) complex-based plating bath for Pd plating over the porous glass support was also tested. Characterization studies were performed using SEM and XRF and then membranes were tested for the permeation rates of hydrogen and nitrogen.

2. Experimental

2.1. Membrane preparation and characterization

In this work, porous glass tablets were used as substrates for the preparation of the palladium composite membranes. Tablets, 2.5 cm in diameter and 0.3 cm in length, were supplied by Robu Glassfilter. The porous glass tablets were tested for thermal stability in a temperature range of 100–500 °C. The surface area values of the pretreated tablets were measured using the BET technique. The surface area of the original porous glass tablet was 13.2 m^2/g. After 6 h of heat treatment, surface area reduced to 8.8 m^2/g. Further heat treatment at temperatures upto 500 °C did not cause any further change in the surface area. Porous tablets, which were pretreated at 500 °C for 18 h were used as the substrate in this study. Using a mercury porosimeter, the porosity and the average pore radius (based on intrusion volume) of this substrate were determined as 0.46 and 1.3×10^3 nm, respectively. Differential pore size distribution of the porous glass support is given in Fig. 1. This substrate was first cleaned with sodium hydroxide solution and then with hydrochloric acid solution. Then, it was immersed into a distilled water bath. Before the activation step, one face and the edges of the substrate were tightly wrapped with Teflon tape. One face of the porous glass substrate was then activated by immersing it into an acidic $SnCl_2$ (pH was about 1.2) solution, which was followed by immersing it into an acidic $PdCl_2$ (pH was about 1.3) solution. The activation steps were repeated 10 times to deposit Pd nuclei onto the surface. Activated support was dried at 100 °C. This tablet was then immersed into the plating solution for 3 h.

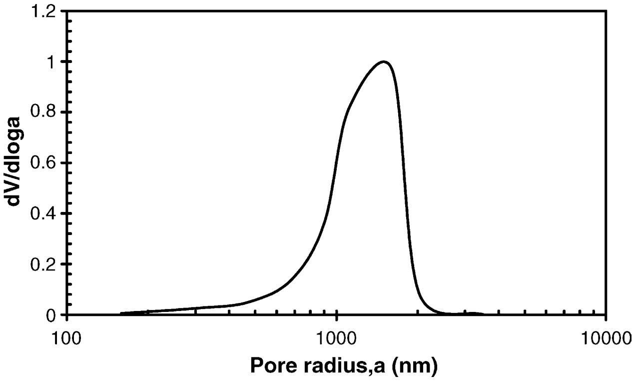


Fig. 1. Differential pore size distribution of the porous glass support.

The compositions of the plating solutions used in the hypophosphite-based and Co(II) complex-based plating baths are listed in Table 1. The plating baths were kept at 45 °C and the pH range of baths were adjusted to 10–11 for both plating baths. Ammonia solution (28%) was used for adjusting the pH of the baths. For the Co(II) complex-bath, $Co(NH_3)_6^{2+}$ and $Co(NH_3)_5^{2+}$ are expected to be the major complexes present in the solution [5].

Plating studies were carried out in an especially designed glass vessel (Fig. 2). Helium gas was continuously bubbled

Table 1
Compositions of (a) hypophosphite-based and (b) Co(II) complex-based baths (in g/l)

Component	
Part (a)	
$PdCl_2$	2.0
NH_4Cl	30.0
$Na_2H_2PO_2$	12.0
Part (b)	
$PdCl_2$	2.0
NH_4Cl	30.0
$CoSO_4$	2.5
$(NH_4)_2SO_4$	37.5

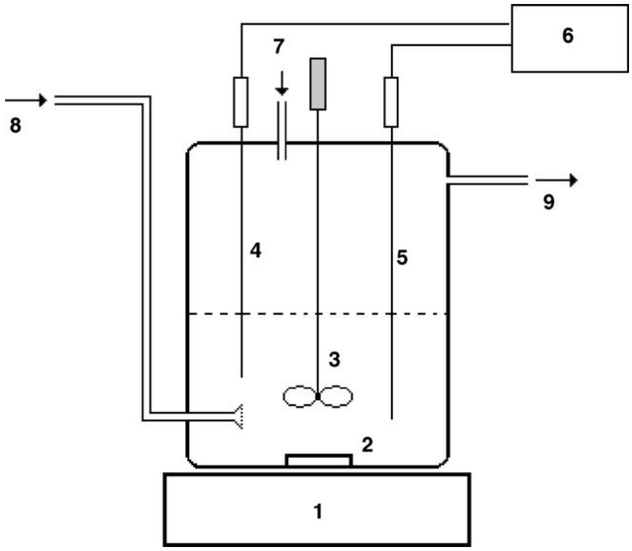


Fig. 2. Glass vessel used in plating studies: (1) heating plate; (2) tablet; (3) stirrer; (4) temperature probe; (5) pH probe; (6) temperature and pH meter; (7) solution inlet; (8) He gas inlet; (9) He gas outlet.

through the solution to create uniform concentration and to remove the produced hydrogen gas from the surface, in the case of hypophosphite-based electroless plating procedure. Hydrogen gas generated in this process is a cause of crack formation during the plating process [7]. The bath loading was 3 mm^2/ml. Plating steps of 3 h were repeated four times in both cases. The morphologies of the coating were analyzed using SEM photographs and the composition of the membrane layer were analyzed using XRF (Rigaku RIX 3000).

2.2. Permeation rate measurements

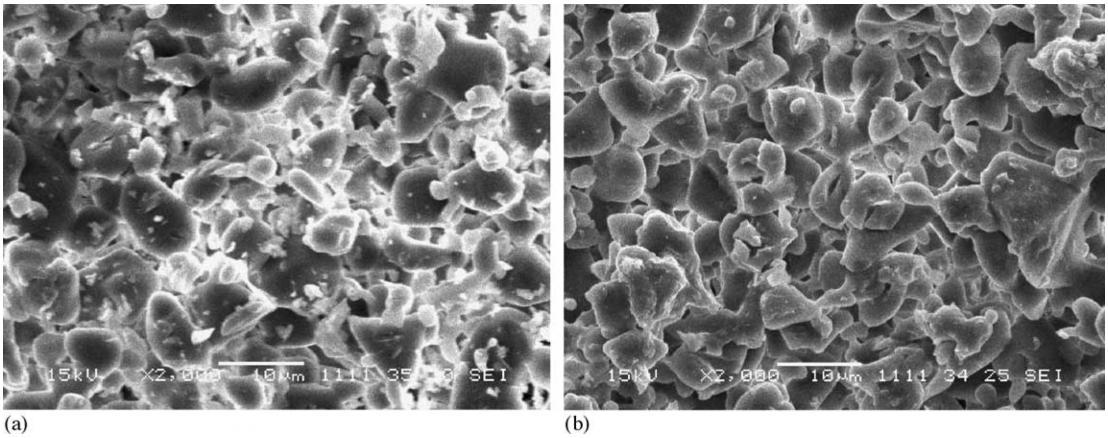
Permeation rates of hydrogen and nitrogen through the substrate and composite membranes were determined under steady-state conditions using a Wicke–Kallenbach-type diffusion cell. Pressure difference across the tablets were adjusted using the valves placed at the exit of the streams. Permeation experiments were carried out in a temperature range between 40 and 200 °C and with pressure differences up to 12 kPa. Either hydrogen or nitrogen was passed over both faces of the membranes. Calibrated rotameters and mass flow meters were used to measure the flow rates of each stream. Pressure difference across the pellet was measured using a manometer. The flow rates of the exit streams were also measured at atmospheric pressure. Permeation rates were then evaluated from the differences of flow rates of inlet and outlet lower streams.

3. Results and discussions

3.1. Membrane characterization

The surface morphologies of the substrate, activated substrate and prepared composite membranes were examined by the scanning electron microscope (SEM). SEM photographs are given in Fig. 3, for substrate and activated substrate surfaces. As it is seen from Fig. 3, the surface morphology did not change significantly after the activation step. Almost the same surface compositions (about 96% Si, 3.5% Al, other species) were determined from the XRF analysis for the original substrate and the activated substrate.

The SEM photographs of the surface and the cross-section of the coated layer of the composite membrane obtained using the hypophosphite-based bath are given in Fig. 4. Some nonuniformities of the palladium layer and presence of some cracks were observed in the SEM photograph. The SEM photograph of the cross-section showed that palladium was impregnated into the porous substrate upto a thickness of about 200 μm. However, the thickness of the dense palladium layer was only about 15 μm. The XRF results obtained for the composite membrane are tabulated in Table 2. Pd to Si ratio in the upper layer of the composite membrane was found as 4.6. As shown in Table 2, there is also significant amount of phosphorous on the coated surface. Cheng and Yeung [7] also reported presence of phosphorous in such membranes. The metaphosphorous acid [PO_2^-] is expected to be formed during the oxidation of hypophosphite and then it may react



(a) (b)

Fig. 3. SEM photographs of: (a) substrate and (b) activated substrate.

Table 2
Surface composition of coated in hypophosphite-based bath onto porous glass (XRF analysis)

Component	%
Si	12.4
P	28.7
Zr	1.4
Pd	57.5

with hydride ions and water. Phosphorous deposits on the coating according to the following reaction:

$$PO_2^- + 3H^- + 2H_2O \rightarrow P + 4OH^- + 1.5H_2$$

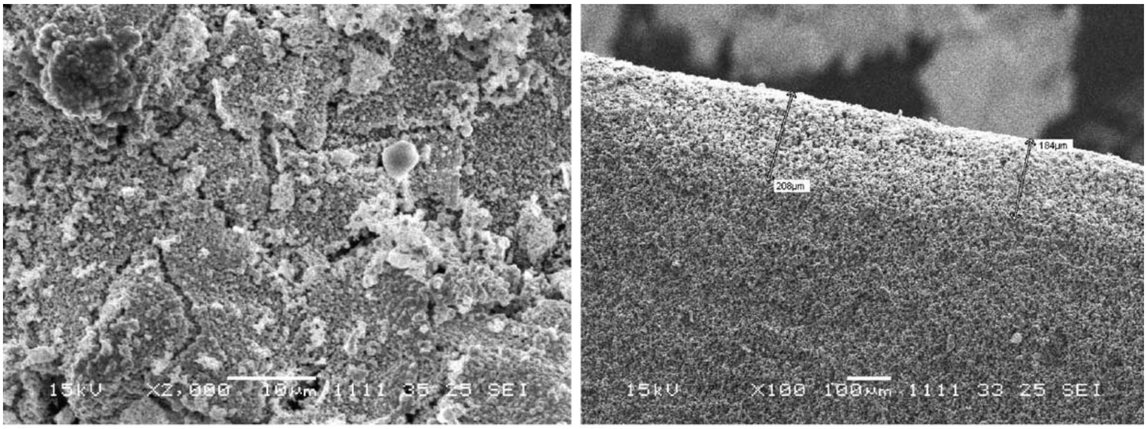
Cheng and Yeung [7] reported that phosphorous formation was eliminated at high pH values. However, in this study, significant amount of phosphorous was still detected in spite of high pH values.

As mentioned before, helium gas continuously bubbled through the solution to create uniform concentration and for fast removal of hydrogen gas from the surface in the case of hypophosphite-based procedure. For comparison purposes, another composite membrane was prepared without the He flow. SEM photographs of the coated surfaces obtained with and without He flow are given in Fig. 5. The size of palladium grains on the coated substrate in hypophosphite-based bath using helium flow is more uniform than the surface of composite membrane obtained without He flow.

The SEM photograph of the coated surface obtained in the Co(II) complex-based bath (Fig. 6) showed a similar structure with the activated surface (Fig. 3b), indicating poor deposition of Pd with this bath. In Fig. 6, pores having diameters in the range of 1–5 μm are clearly seen. XRF results also confirmed a very low Pd/Si ratio for this sample (less than 0.01). Results showed that Co(II) complex-based procedure was not successful for the plating of palladium on the porous substrate, under the conditions studied in this work.

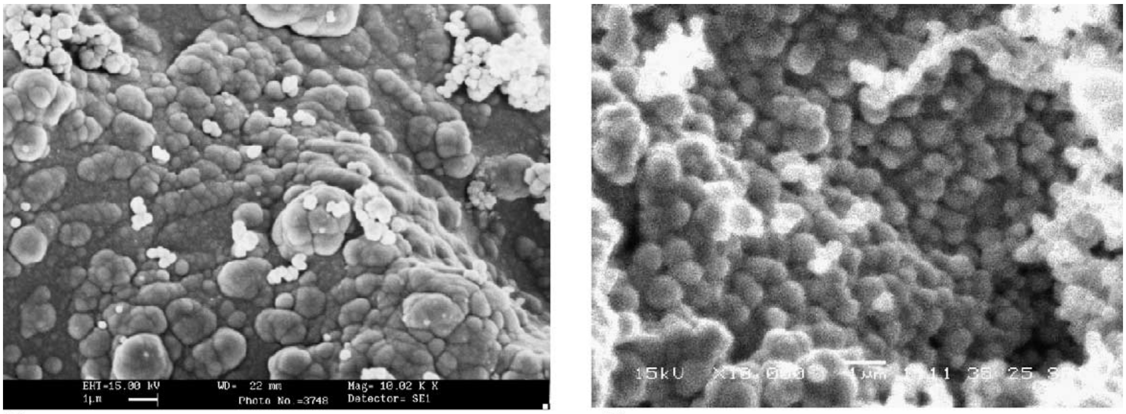
3.2. Permeation rate measurements

Permeation rate measurements were carried out with hydrogen and nitrogen gases using the composite membrane prepared in the hypophosphite-based bath. Permeation rates obtained at 200 °C are shown in Fig. 7. The selectivity (permeation rate ratio of hydrogen to nitrogen) was about 7 from Fig. 7. Previously [14], the selectivity values of H_2/N_2



(a) (b)

Fig. 4. SEM photographs of coated layer in hypophosphite-based bath with helium flow: (a) surface and (b) cross-section.



(a) (b)

Fig. 5. Coated surface in hypophosphite-based bath: (a) without helium flow [14] and (b) with helium flow.

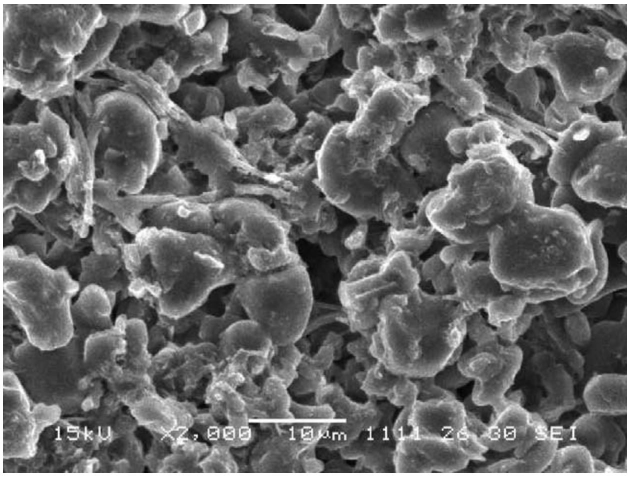


Fig. 6. SEM photographs of coated surface in Co(II) complex-based bath.

for the composite membrane prepared using hydrazine-based bath was determined as 2.7 at 200 °C. It can be said that better selectivity values were obtained in this study with the hypophosphite-based bath. However, further improvements are needed in the selectivities.

Although the selectivity of H_2/N_2 was relatively high, the permeation rate value for nitrogen was still significant. This result indicated the presence of the pores and defects in the Pd layer of the composite membrane. Some of these nonuniformities were also seen in the SEM photograph (Fig. 4).

Fig. 8 shows the hydrogen permeation rates obtained at different temperatures through the membrane. The effect of temperature on the permeation rate of hydrogen through the membrane is small in the temperature range between 40 and 200 °C. In fact, some decrease was observed with an increase in temperature. These results indicated that contribution of surface flow to the permeation of hydrogen through the composite membrane was significant at low temperatures and the solution–diffusion mechanism was not controlling the transport of hydrogen through the membrane in the temperature range studied. The mechanism called solution–diffusion of hydrogen transport through a palladium film (metallic layer) is complex and generally has three steps: reversible dissociation of hydrogen molecule, reversible dissolution of surface atomic hydrogen into the palladium metal and diffusion of atomic hydrogen in the membrane [8]. For this mechanism, the permeability constant is expected to increase with temperature exponentially. However, for surface diffusion and surface flow, a decrease of diffusivity and permeability were expected with an increase in temperature [1,2].

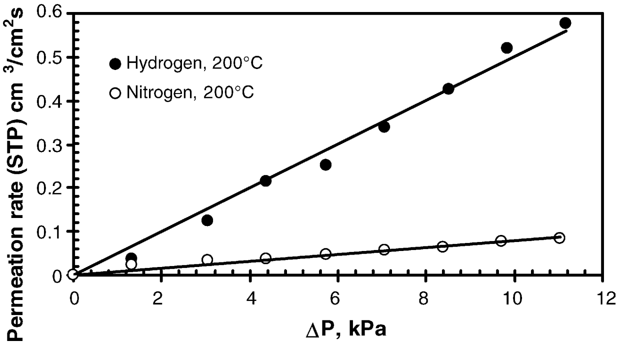


Fig. 7. Permeation rates of hydrogen and nitrogen through membrane prepared with helium flow ($T = 200$ °C).

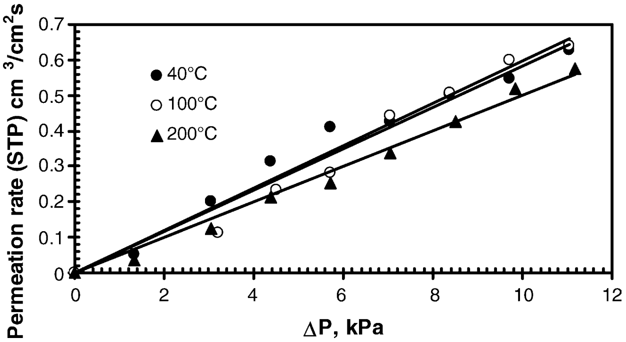


Fig. 8. Permeation rates of hydrogen through membrane prepared with helium flow.

As it was shown in our previous work [1], the permeation flux through a porous pellet (γ) may contain the contributions of viscous flow, Knudsen flow and surface flow.

$$\gamma = \frac{-\Delta P}{L}\left[\frac{\varepsilon}{\tau}\left(\underbrace{\frac{a^2}{8\mu}}_{\text{viscous flow}} + \underbrace{\frac{D_K}{P}}_{\text{Knudsen flow}}\right) + \underbrace{\frac{D_s K}{P\tau_s}}_{\text{Surface diffusion flow}}\right] \quad (1)$$

Surface diffusion term involves adsorption equilibrium constant of hydrogen on palladium and adsorption equilibrium constant decreases with an increase in temperature. From Fig. 4, some pores smaller than 100 nm were observed in the palladium-coated layer of the substrate. Due to these defects, some contribution of Knudsen flow is also possible. However, Knudsen diffusivity is also expected to increase with an increase in temperature. The decrease of the permeation rate of hydrogen with an increase in temperature can only be explained by the significant contribution of surface diffusion flow. The order of magnitude of viscous flow term of Eq. (1) was estimated (by taking pore radius as 100 nm) to be at least an order of magnitude smaller than the order of magnitude of the Knudsen flow term. In the case of Knudsen flow, the permeation rate ratio of H_2 to N_2 is expected to be inversely proportional with the square root of the molecular weights, which is about 3.7. The higher experimental value of permeation rate ratio of hydrogen to nitrogen (about 7) is another indication of surface diffusion contribution. The behaviour of temperature dependence of prepared membrane is similar to that in the palladium-impregnated alumina tablets investigated in our previous studies [1,2]. The reasons of the invalidity of the solution–diffusion mechanism in the prepared membrane can be sequenced as studying at low temperatures and failure in coating studies to obtain a dense palladium layer. Goto et al. [15] also showed that solution–diffusion mechanism gained importance above 200 °C.

4. Concluding remarks

Hypophosphite-based procedure for the electroless plating of porous glass by palladium was shown to be quite successful. Crack formation due to hydrogen gas deposition on the surface was reduced by continuous flow of helium gas over the surface in the especially designed electroless plating vessel. Pd/Si ratio in the upper layer of the composite membrane was determined as 4.6. Permeation rate ratio of hydrogen to nitrogen was found to be about 7 for this membrane. Surface flow contribution to the permeability of hydrogen was found to be significant under the experimental conditions of this work.

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