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Shusen Wang[a]; Ming Fang[b]; Meiyun Zeng[c]; Zhizhong Wang[c]; Xiaoqing Zhang[c]
[a] DEPARTMENT OF CHEMISTRY AND ENVIRONMENT ENGINEERING, BEIJING POLYTECHNIC UNIVERSITY, BEIJING, PEOPLES REPUBLIC OF CHINA [b] THE HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY, HONG KONG [c] DEPARTMENT OF CHEMISTRY AND ENVIRONMENT ENGINEERING, BEIJING POLYTECHNIC UNIVERSITY, BEIJING, PEOPLE'S REPUBLIC OF CHINA

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A Selective Silicon-Based Membrane Formed by Pyrolysis of Silicon Resin

SHUSEN WANG*
DEPARTMENT OF CHEMISTRY AND ENVIRONMENT ENGINEERING
BEIJING POLYTECHNIC UNIVERSITY
BEIJING, PEOPLES REPUBLIC OF CHINA 100022

MING FANG
THE HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY
HONG KONG

MEIYUN ZENG, ZHIZHONG WANG, and XIAOQING ZHANG
DEPARTMENT OF CHEMISTRY AND ENVIRONMENT ENGINEERING
BEIJING POLYTECHNIC UNIVERSITY
BEIJING, PEOPLE'S REPUBLIC OF CHINA 100022

ABSTRACT

A new, highly selective silicon-based membrane was developed by pyrolyzing a thermosetting silicon resin precursor in two steps. The pyrolysis step was performed under an inert gas in the range of 800 to 950°C. The activation step was conducted at the same temperature as the first step. Oxygen content in the activation gas was located between 0.5 and 1.0%. The crosslinking density and the matrix structure of the polymeric precursor were important factors for the permeable characteristics of the resulting pyrolysis membrane. The average selectivity was 5 to 10 times those of a pyrolysis membrane from silicon rubber. Additives in the precursor had significant effects on toughness and stability of the resulting membrane. By varying the additive content in the precursor, silicon-based pyrolysis membranes with different stabilities in air were obtained.

Key Words. Pyrolysis; Silicon resin; Membrane; Gas separation; Selectivity

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* To whom correspondence should be addressed.

INTRODUCTION

Inorganic membranes are widely used for the separation of various high temperature gases and many industrially important gas reactions due to their good thermal and chemical stabilities. Typical inorganic membranes are Vycor glass and silica or alumina membranes, which are prepared by chemical leaching or sol–gel processes (1–3). However, the applications of these membranes are often limited by their low selectivity. For this reason there is great interest in finding highly selective and permeable membranes that can withstand harsh environments.

A suitable candidate to meet such requirements may be a molecular sieve carbon membrane prepared by pyrolysis of organic polymers (4, 5). The molecular sieve carbon membrane is supposed to have much higher selectivity than typical inorganic membranes, and it can withstand higher working temperatures. However, due to its carbon-based structure, the membrane is not suitable for hot oxygen environments.

Lee and Khang prepared a hot oxygen-resistant membrane by pyrolyzing silicon rubber, poly(dimethylsiloxane) (6), while Li and Hwang developed a silicon-based membrane by a polymerization–pyrolysis process (7, 8). Because of their silicon-based structures, the resulting membranes are stable in a highly oxidizing environment and are suitable for hot oxygen gas separation processes. However, silicon-based membranes have relatively large average pore sizes and show relatively lower selectivities than molecular sieve carbon membranes.

There are two possible reasons for the difference in selectivity between the silicon-based membranes and the molecular sieve carbon membranes. One possibility lies in a difference in composition or structure of their polymeric precursors. Another is their different preparation conditions. The present research is concentrated on finding a suitable organic silicon precursor and optimum preparation conditions to obtain a highly selective silicon-based pyrolysis membrane. Preliminary experimental results show that a thermosetting silicon resin is an ideal candidate for the precursor. In this paper, research results are reported concerning the preparation method for the highly selective silicon-based pyrolysis membrane, and the effects of composition or structure of the precursor and preparation conditions on the characteristics of the pyrolysis membrane.

EXPERIMENTS

Preparation of Silicon Resin Precursor

Highly crosslinked poly(methylsiloxane) was chosen as the polymeric precursor. The thermosetting polysiloxane was produced by adding a trifunctional monomer, trichloromethylsilane, to dichlorodimethylsilane. Through hydrolysis and polymerization steps, a 3-D network structure in the final product was formed.

For the sake of convenience, a silicon resin prepolymer with the reactive group Si—OH was used as the raw material of the precursor in this study. In order to improve the toughness of the final pyrolysis membrane, it was found necessary to add some additives to the silicon resin. We chose a thermosetting phenolic resin with the reactive group C—OH as the modifying additive.

The silicon resin prepolymer and the additives were mixed in the specified proportion, ground together, and sieved. Then a molding powder was obtained. A mold pressing process was used to shape the precursor. The shaping conditions are shown in Table 1. The resulting silicon resin precursor was a flat membrane. Its thickness could be controlled in the range of 0.05 to 0.10 mm.

Preparation of Pyrolysis Membrane

Figure 1 is a schematic view of the experimental pyrolysis setup. The pyrolysis reactor is a quartz tube with a diameter of 10 cm and is 105 cm in length. The sources of the inert gas and the activation gas were both connected to the pyrolysis tube that was positioned in a high temperature tubular furnace equipped with a temperature controller. Several pieces of silicon resin precursor with a diameter of 50 mm were positioned in the center of the pyrolysis tube. The end of the pyrolysis tube was connected to a three-way valve connected to a vacuum pump or the atmosphere.

Before the pyrolysis step, the vacuum pump was connected to the pyrolysis tube and the air in the tube was drawn off. After that, the vacuum pump was shut down. Simultaneously, the three-way valve was turned to the atmosphere and the valve for the supply of inert gas was opened for the pyrolysis step. The pyrolysis temperature range was set between 800 and 950°C, and pyrolysis was carried out for 150–180 minutes. After the pyrolysis step, the supply of inert gas was switched off and the valve for the activation gas was opened for the activation step which was con-

TABLE 1
Shaping Conditions of Precursor

Shaping temperature	200–250°C
Shaping pressure	30–50 MPa
Solidification time	20–30 minutes

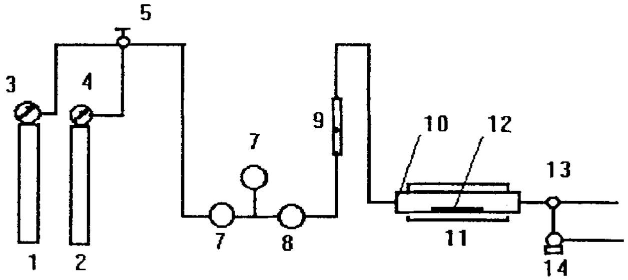

FIG. 1 Experimental setup for pyrolysis. (1) Inert gas, (2) activated gas, (3, 4) pressure regulator, (5, 13) three-way valve, (6) pressure meter, (7) pressure stabilizer, (8) flow stabilizer, (9) flowmeter, (10) quartz reactor, (11) temperature-controlled furnace, (12) silicon resin sample, (14) vacuum pump.

ducted for 20–60 minutes at the same temperature as the first step. The oxygen content in the activation gas was set between 0.5 and 1.0%. Finally, the pyrolyzed samples were cooled to room temperature in an inert gas environment.

Measurements for Gas Permeability and Thermooxidation Resistance of the Pyrolysis Membranes

The schematic diagram of the gas permeation experimental setup is shown in Fig. 2. The test gas flowed through a pressure stabilizer, a flow stabilizer, and was fed into the membrane cell. The flow rate of permeated gas was measured by a soap bubble meter. The permeability of the mem-

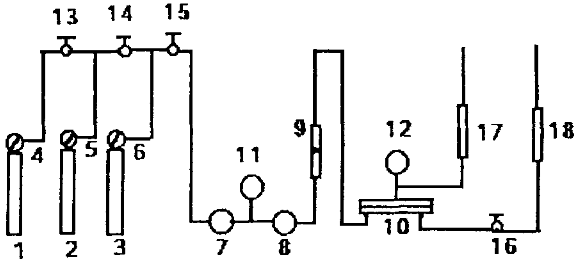

FIG. 2 Experimental setup for permeability measurement. (1–3) Feed gases, (4–6) pressure regulator, (7) pressure stabilizer, (8) flow stabilizer, (9) flowmeter, (10) membrane cell, (11, 12) pressure meter, (13–16) valve, (17, 18) bubble flowmeter.

brane sample was determined from steady-state permeation rates at constant temperature and pressure.

At room temperature the permeabilities of H_2, O_2, and N_2 through the pyrolysis silicon resin membrane were measured by the following equation:

$$Q(i) = (q(i)\delta)/(F\Delta p) \tag{1}$$

where $Q(i)$ = permeability of gas i through the membrane, $cm^3 \cdot cm/cm^2 \cdot s \cdot MPa$

$q(i)$ = volumetric flow rate of permeate gas, cm^3/s

δ = thickness of the membrane, cm

F = effective area of the membrane, cm^2

Δp = pressure difference across the membrane, MPa

The selective factor α was calculated based on the permeability of the pure gases:

$$\alpha(i/j) = Q(i)/Q(j) \tag{2}$$

In order to observe the thermooxidation resistance of the pyrolysis membrane, it was positioned within a high temperature furnace. The membrane was heated to a specified temperature in air and kept for 300 minutes. After cooling to room temperature, the weight loss of the membrane was measured and the change of permeable characteristics with the heating temperature was determined.

RESULTS AND DISCUSSION

Permeable Characteristics of the Pyrolysis Membranes

The permeability and selectivity of several different membranes are listed in Table 2. The permeability of the molecular sieve carbon membrane, the pyrolysis silicon rubber membrane, and the silicon-based membrane by the polymerization–pyrolysis process are quoted from Refs. 4 and 6–8. By comparing the permeability and selective factors of these membranes, several trends appear.

The permeability of the pyrolysis silicon resin membrane in this experiment is lower than that of the pyrolysis silicon rubber membrane. However, the selectivity of the former is much higher than that of the latter. The silicon-based membrane created by the polymerization–pyrolysis process shows a much higher selectivity in comparision to the pyrolysis silicon rubber membrane, but still lower than the pyrolysis silicon resin membrane. The permselective property of the pyrolysis silicon resin mem-

TABLE 2
Permeability and Selectivity of Various Membranes

Membrane	Permeability Q (barrer)[a]			Selectivity α	
	H_2	O_2	N_2	H_2/N_2	O_2/N_2
Pyrolysis membrane from silicon resin	1.55×10^3	2.10×10^2	0.50×10^2	30.92	4.20
Molecular sieve carbon membrane	5.20×10^3 [b]	1.71×10^3	2.40×10^2	21.67[b]	7.13
Silicon-based membrane by polymerization–pyrolysis process	5.10×10^3	1.74×10^3	5.87×10^2	8.69	2.96
Pyrolysis membrane from silicon rubber	7.20×10^6	1.85×10^6	1.93×10^6	3.73	0.96

[a] 1 barrer = 10^{-10} (cm^3·cm/cm^2·s·cmHg).
[b] Data for helium gas.

brane seems to be similar to the molecular sieve carbon membrane because both of them show relatively high selectivity but low permeability.

Effects of Temperature on Permselectivity of Pyrolysis Membranes

A pyrolysis silicon resin membrane was heated in air for 300 minutes at a specified temperature. After cooling to room temperature, the membrane permeability was measured. Figures 3 and 4 describe the change of permeable characteristics with the heating temperature: the permeability decreases for both oxygen and hydrogen, but the selective factors of O_2/N_2 and H_2/N_2 increase with temperature.

When considering the mechanisms of mass transferring through microporous membranes, pore size will play a key role in determining the permeability and selectivity of a membrane if molecular sieving and surface diffusion are important. The heating treatment in air is a reaming process, and a higher heating treatment temperature leads to enlargement of the membrane pore size. An increase of the pore size will lead to an increase of gas-phase transport and a decrease of surface transport. For a single gas, if gas-phase transport and surface transport are assumed to be additive, the results in Figs. 3 and 4 should be the total sum of gas-phase and surface flows (1). Figure 5 gives the pore size distribution of the pyrolysis membrane by the nitrogen adsorption/desorption method based on BET theory.

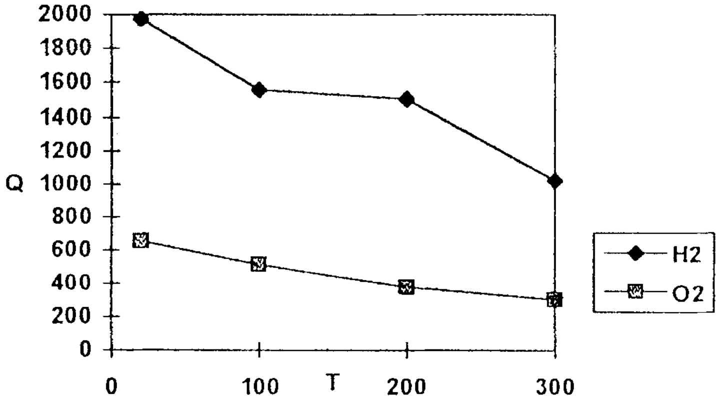

FIG. 3 Effect of temperature (*T*, °C) on membrane permeability (*Q*, barrer). Content of silicon resin in the membrane precursor: 40%. Pressure: 0.1 MPa.

Effects of Additives on Stability of Pyrolysis Membrane

In order to improve the characteristics of the final pyrolysis membranes, it was necessary to add various additives to their polymeric precursors. Generally, two kinds of additives were chosen: organic and inorganic compounds. Inorganic additives (for example, SiO_2 powder in common use

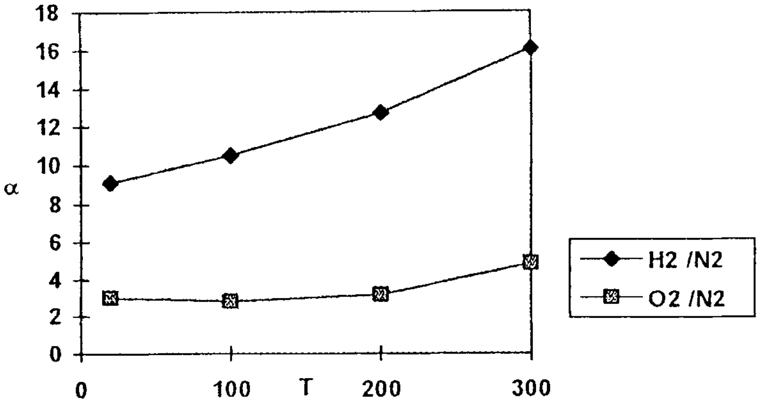

FIG. 4 Effect of temperature (*T*, °C) on membrane selective factor ($\alpha = Q_i/Q_j$). Content of silicon resin in the membrane precursor: 40%. Pressure: 0.1 MPa.

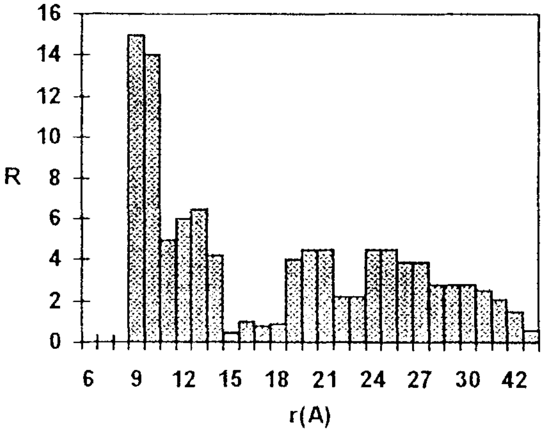

FIG. 5 Membrane pore size distribution (R = *dV/dr*). Content of silicon resin in the membrane precursor: 20%.

in silicon rubber) can improve the thermal and chemical stability of the final pyrolysis membranes. However, a simultaneous unfavorable effect is that the pyrolysis membranes become more brittle. Organic additives show the opposite effects: increasing membrane toughness and a decrease in their thermooxidative stability.

In order to improve the toughness of the pyrolysis silicon resin membrane, we chose an organic compound as the additive in its precursor, even though the additive would cause a decrease of thermal stability of the pyrolysis membrane. In this study a thermosetting phenolic resin was chosen as the additive in the polymeric precursor.

Figure 6 shows the relationship between heating temperature and loss of weight for various membrane samples whose precursors contain different additives. The heating time was 300 minutes for all samples. It is obvious that an increase of organic additive content in the precursor will lead to deterioration of thermostability for the resulting pyrolysis membrane. Figure 7 gives the change of selectivity with heating temperature. The selectivity of the membrane gradually increases with temperature, and then sharply declines after a maximum point. The temperature corresponding to the maximal selectivity should be a limit of applied temperature. Figure 7 shows that the pyrolysis membrane will be stable at 300°C in air if the silicon resin content in its precursor is more than 40%.

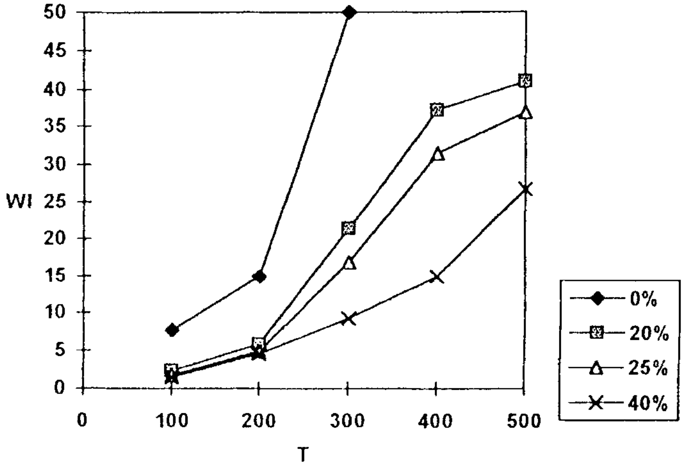

FIG. 6 Relation between heating temperature (*T*, °C) and loss of membrane weight (*WI*, %). Contents of silicon resin in the membrane precursors are 0, 20, 25, and 40%.

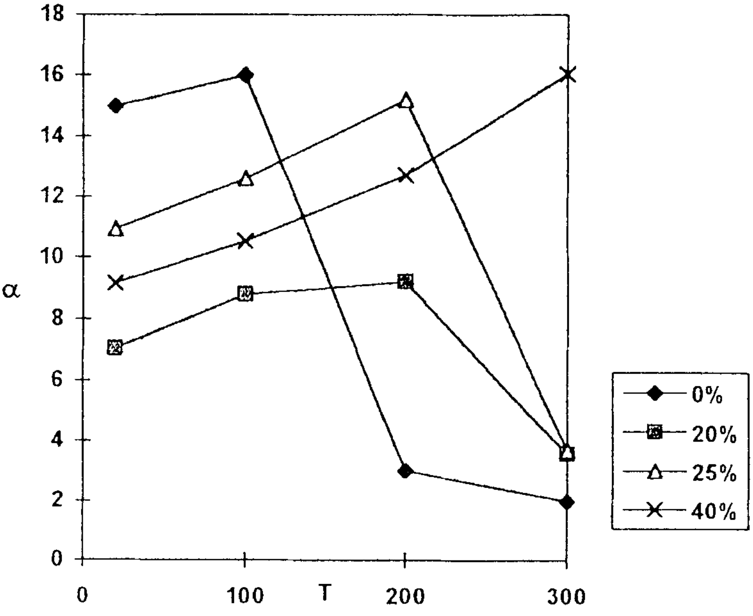

FIG. 7 Relation between heating temperature (*T*, °C) and membrane selective factor ($\alpha = Q_i/Q_j$), $i = H_2, j = N_2$. Pressure: 0.1 MPa.

Effects of Precursor Structure on Permselectivity of Pyrolysis Membrane

Although silicon rubber and silicon resin are thermosetting silicon-based polymers, they are prepared by different crosslinking processes. An important reason leading to the different selectivities of their pyrolysis membranes may be differences in the structures and crosslinking densities of the polymeric precursors (7).

Normally, silicon rubber is crosslinked using vulcanization. Linear poly(dimethylsiloxane) is mixed with peroxides, such as benzoyl peroxide. This mixture is then heated. The peroxides decompose and produce free radicals. The free radicals attack the methyl groups in poly(dimethylsiloxane) and transfer the free radicals to the polymer. Crosslinking occurs by coupling of polymer radicals. The crosslinking bond of poly(dimethylsiloxane) is $Si—CH_2—CH_2—Si$ for the vulcanization of silicon rubber, which has a low crosslinking density in general.

In this study the thermosetting silicon resin is produced by adding a trifunctional monomer to a difunctional monomer. The monomer mixture will polymerize and form a 3-D network with a much higher crosslinking density compared to silicon rubber. In the final product of this process, the crosslinking bond is Si—O—Si instead of $Si—CH_2—CH_2—Si$. From the bond energy data it is easy to find that the —Si—C— bond has a lower energy than the —Si—O— bond. In other words, the lower energy bond is broken before the higher energy bond.

The formation of micropores in pyrolysis membranes is the result of small gaseous molecules channeling their way out of the solid matrix of the polymer during pyrolysis. The breaking of $Si—CH_2—CH_2—Si$ bonds will lead to the destruction of the solid matrix structure during pyrolysis of silicon rubber. In this way, some larger pores will be formed. Therefore, the pyrolysis silicon rubber membrane shows a much higher permeability and lower selectivity. The situation is different for silicon resin. Because the crosslinking bond and main chain bond are all Si—O—Si in the silicon resin structure, its matrix structure will be preserved. Silicon resin has such a high crosslinking density that tiny pores will be formed in the pyrolysis procedure.

Effects of Preparation Condition on Permselectivity of Pyrolysis Membrane

The selectivity of a given inorganic membrane is governed by the pore size, and that can be controlled by the pyrolysis conditions. The pyrolysis temperature and atmosphere are especially important. For the pyrolysis process of silicon resin as investigated in this study, the optimum pyrolysis temperature in nitrogen gas was found to be between 800 and 950°C. A lower pyrolysis temperature will lead to higher permeability but lower selectivity because of insufficient shrinkage of the membrane pore size. The difference in preparation conditions may be one of the causes of the difference in selectivity between the pyrolysis silicon resin membrane and the silicon membrane by the polymerization–pyrolysis process.

CONCLUSIONS

A silicon-based membrane with a relatively high selectivity was obtained by pyrolysis of a thermosetting silicon resin precursor. The matrix structure and composition of the precursor have an important effect on the permselectivity and thermostability of the resulting pyrolysis membrane. A phenolic resin can be used as an additive to improve the toughness of the pyrolysis membrane. The new membrane has good potential for oxygen-containing gas separation at higher temperatures.

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REFERENCES

1. R. R. Bhave, *Inorganic Membranes: Synthesis, Characteristics and Applications*, Van Nostrand Reinhold, New York, NY, 1991.
2. T. Okubu, M. Watanabe, K. Kusakabe, and S. Morooka, "Preparation of γ-Alumina Thin Membrane by Sol-Gel Processing and Its Characterization by Gas Permeation," *J. Mater. Sci.*, *25*, 4822 (1990).
3. A. Julbe, C. Guizard, A. Larbot, L. Cot, and A. G. Fendler, "The Sol-Gel Approach to Prepare Candidate Microporous Inorganic Membranes for Membrane Reactors, *Ibid.*, *77*, 137 (1993).
4. J. E. Koresh and A. Soffer, "The Molecular Sieve Permselective Membrane. Part I. Presentation of a New Device for Gas Mixture Separation," *Sep. Sci. Technol.*, *18*, 723 (1983).
5. J. E. Koresh and A. Soffer, "The Carbon Molecular Sieve Membranes. General Properties and the Permeability of CH_4/H_2 Mixture,"*Ibid.*, *22*, 973 (1987).
6. K. H. Lee and S. J. Khang, " New Silicon-Based Material Formed by Pyrolysis of Silicon Rubber and Its Properties as a Membrane," *Chem. Eng. Commun*, *44*, 121 (1986)
7. D. Li and S. T. Hwang, "Preparation and Characterization of Silicon Based Inorganic Membrane for Gas Separation," *J. Membr. Sci.*, *59*, 331 (1991)
8. D. Li and S. T. Hwang, "Gas Separation by Silicon Based Inorganic Membrane at High Temperature," *Ibid.*, *66*, 119 (1992).

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