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Optical CO_2 sensor of the combination of colorimetric change of α-naphtholphthalein in poly(isobutyl methacrylate) and fluorescent porphyrin in polystyrene

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Abstract

An optical CO_2 sensor based on the overlay of the CO_2 induced absorbance change of pH indicator dye α-naphtholphthalein in poly(isobutyl methacrylate) (polyIBM) layer with the fluorescence of tetraphenylporphyrin (TPP) in polystyrene layer is developed. The observed luminescence intensity from TPP at 655 nm increased with increasing the CO_2 concentration. The ratio I_{100}/I_0 value of the sensing film consisting of α-naphtholphthalein in polyIBM and TPP in polystyrene layer, where I_0 and I_{100} represent the detected luminescence intensities from a layer exposed to argon and CO_2 saturated conditions, respectively, that the sensitivity of the sensor, is estimated to be 192. The response and recovery times of the sensing film are less than 6.0 s for switching from argon to CO_2, and for switching from CO_2 to argon. The signal changes are fully reversible and no hysterisis is observed during the measurements. The highly sensitive optical CO_2 sensor based on fluorescence intensity changes of TPP due to the absorption change of α-naphtholphthalein in polyIBM layer with CO_2 is achieved.

Keywords: Optical CO_2 sensor; Poly(isobutyl methacrylate); α-Naphtholphthalein; Fluorescence; Colorimetric change

1. Introduction

In the chemical, clinical analysis and environmental monitoring fields, CO_2 sensing techniques are widely used. The CO_2 in gaseous phase has been measured by infrared (IR) absorptiometry [1,2] and electrochemically using Severinghaus electrode [3]. Optical CO_2 sensor based on the strong IR absorption of CO_2 has been developed. However, sensitive IR absorptiometry sensor is subject to strong interference from water vapour and is an expensive system. In contrast, CO_2 sensor using Severinghaus glass electrode, which detects the changes in the pH of surrounding bicarbonate ion solution brought about by permeation and subsequent hydration of CO_2 through a thin silicone film. Thus, highly sensitive and simple CO_2 sensor is desired. Recently, the optical CO_2 sensors based on the CO_2 induced absorbance or fluorescence change of pH indicator have been developed. The optical CO_2 sensors are classified into two types. One is the sensor based on the colorimetric change of pH indicator dye, such as thymolsulfonphthalein (thymol blue), α-naphtholphthalein and so on [4–8]. The other sensor is the basis of the CO_2 induced fluorescence change of fluorescent dye such as 1-hydroxypyrene trisulfonate [8–13]. For the fluorescent phenol and hydroxypyrene based CO_2 sensor, the fluorescence intensity change with the shift of fluorescent dye from its fluorescent form (phenolate anion) into the non-fluorescent form (phenol neutral form) is used. In contrast, Walt et al., reported the optical CO_2 sensor based on the pH dependent fluorescence and energy transfer between luminescence dye to pH indicator [14–16]. However, the number of compound, which fluorescence intensity is changed by CO_2, is extremely limited. The optical CO_2 sensor with the combination of colorimetric change of pH indicator dye and luminescent dye (internal reference dye) will be developed. In principle, the CO_2 sensor based on the luminescence change will be devel-

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oped by the wavelength overlap between the luminescence band of internal reference dye and the absorption band, which is changed by CO_2, of pH indicator dye. The study on the CO_2 sensor using two dyes with reference dye has been reported [17]. In this report, the fluorescent ruthenium complex is used as a reference dye. In the optical sensor, the effect of surrounding humidity on the response and sensitivity is serious problem. Thus, the hydrophobic polymer film is desirable for the dye immobilization media. As the fluorescent ruthenium complexes are ionic molecules, the preparation of homogenous dye layer is difficult. Porphyrin molecules are suitable for the hydrophobic fluorescent dye. Tetraphenylporphryin (TPP), which is the hydrophobic molecules, is useful fluorescent dye for the immobilized to hydrophobic polymer media. We previously reported the optical gaseous CO_2 sensors using various pH indicators in ethyl cellulose layer and red-luminescent europium(III) complex or TPP in polystyrene layer as an internal reference dye [18–21]. Especially, α-naphtholphthalein has a large A_0/A_{100} value compared with the other pH indicators, where A_0 and A_{100} are absorbance in the 100% argon and 100% CO_2 gaseous, respectively. α-Naphtholphthalein has the absorption band at 600 nm and this band decreases with increasing of CO_2 concentrations. On the other hand, TPP has the emission band at 655 nm with excitation of 350 nm and this emission is not affected by CO_2. Thus, α-naphtholphthalein and TPP are useful for pH indicator and internal reference dye, respectively. Moreover the conventional optical CO_2 sensor using cheep black light will be developed by device consisting of α-naphtholphthalein and TPP. In the sensing film consisting of two dyes immobilized in same polymer film, pH indicator indicates with internal reference dye in polymer film. Thus, we suggest the two separate polymeric films, pH indicator and internal reference layers, via the glass substrate. As the pH indicators are surrounded with polymer molecules, on the other hand, the optical sensing performance strongly depends on the properties of polymer matrices of pH indicator layer. A CO_2 permeable polymer with a low diffusion barrier for CO_2 is desired. Poly(isobutyl methacrylate) (polyIBM) film has a highly CO_2 permeability and a low diffusion barrier for CO_2 [22]. Thus, polyIBM is a suitable matrix for optical CO_2 sensing of pH indicator layer.

In this work, polyIBM is applied to the polymer matrix for pH indicator layer of optical CO_2 sensor based on the colorimetric change of α-naphtholphthalein and the fluorescence of TPP and its sensing properties for CO_2 is developed.

2. Experimental

2.1. Materials

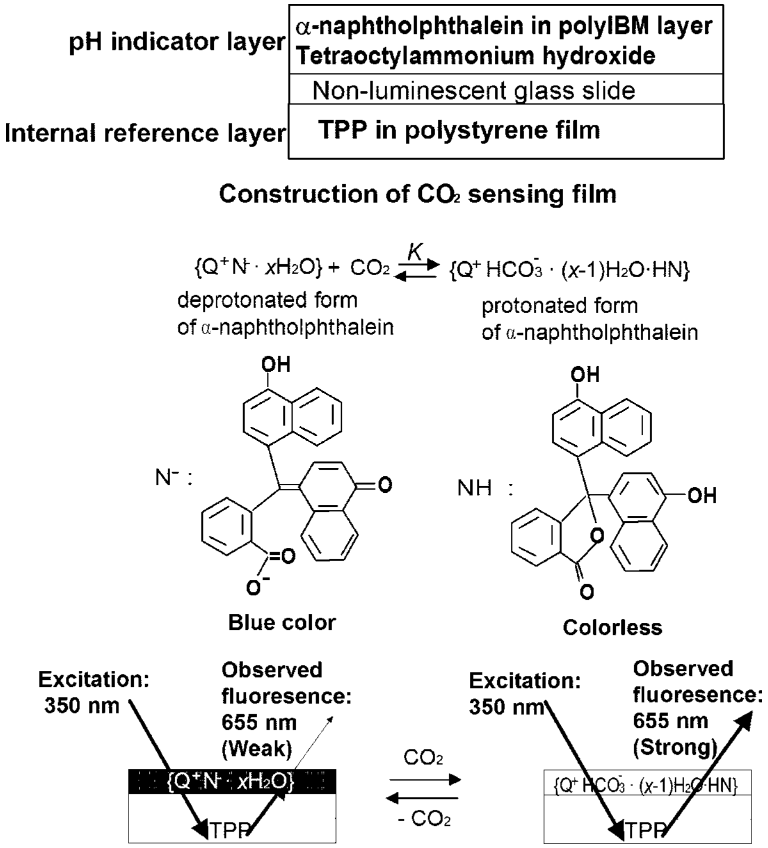
Tributyl phosphate and α-naphtholphthalein are obtained from Wako Pure Chemical Co. Ltd. Poly(isobutyl methacrylate) (polyIBM; average M_W 100,000, GPC grade), TPP and tetraoctylammonium hydroxide are obtained from Tokyo Chemical Industry Co., Ltd. Polystyrene (average M_W 280,000, GPC grade) is purchased from Aldrich. Non-luminescence glass slides are obtained from Mitsubishi Chemical Co., Ltd. The other reagents are of the highest grade available.

2.2. Preparation of CO_2 sensing film

The CO_2 sensing film had composition CO_2 indicator dye/phase-transfer agent/polymer/plasticizer/solid support/reference luminescence dye/polymer, i.e., α-naphtholphthalein/tetraoctyl ammonium hydroxide/polyIBM/tributyl phosphate/non-luminescent glass slide/TPP/polystyrene as shown in Scheme 1. To improve the response and recovery times, and sensitivity of the sensor based on the pH indicator immobilized polymer film, tributyl phosphate is used as a plasticizer [4–6]. At first, α-naphtholphthalein immobilized in polyIBM film is prepared onto the one side of non-luminescent glass slides (1.4 cm × 5.0 cm) according to the previous reported method [6]. Component solution (1) is prepared by adding 3.7 nmol α-naphtholphthalein to 2 ml of a 0.7 mol dm^{-3} tetraoctylammonium hydroxide in methanol solution. Component solution (2) is 0.025 g of polyIBM in 2.5 ml toluene. The solution for α-naphtholphthalein film consisted of 1.5 ml of solution (1), 2.5 ml of solution (2), 0.5 ml of tributyl phosphate and 7.0 ml of toluene. Tributyl phosphate is used to form the plasticized film. The α-naphtholphthalein film is formed by casting 0.2 ml of the above solution onto one side of a non-luminescent glass slide (1.4 cm × 5.0 cm). The film is dried at room temperature and then TPP immobilized in polystyrene film is formed by casting 0.2 ml of a mixture of 1.0 μmol of TPP in toluene solution onto the opposite side of the glass slides. The thickness of α-naphtholphthalein in polyIBM layer is 10 μm. The prepared film is defined as CO_2 sensing film.

2.3. Properties of CO_2 sensing film

The sensing properties of CO_2 sensing film are studied using fluorescence spectra changes. Fluorescence spectra of the CO_2 sensor film are measured using a Shimadzu RF5300-PC fluorescence spectrometer with a 150 W xenon lamp as an excitation light source. Excitation and emission bandpasses are 3.0 nm. The sample substrate is mounted at a 45° angle in the quartz cell to minimize the light scattering from the sample and substrate. The excitation light is irradiated from the α-naphtholphthalein film side and the reflectance light is also detected from the α-naphtholphthalein film side. Different CO_2 standards (in the range 0–100%) in a gas stream are produced by controlling the flow rates of CO_2 and argon gases entering a mixing chamber. The total pressure is maintained at 760 Torr (1 Torr = 133.322 Pa). All the experiments are carried out at room temperature. The properties of CO_2 sensing film are studied. The reaction process between α-naphtholphthalein and CO_2 can be described as shown in Scheme 1; where $\{Q^+N^-\cdot xH_2O\}$ is the ion pair



Scheme 1. The construction of CO_2 sensing film, the reaction process between α-naphtholphthalein and CO_2, and the principle of optical CO_2 sensing.

formed between the tetraoctylammonium cation Q^+ and the deprotonated form of α-naphtholphthalein N^-. The ratio of the concentrations of the α-naphtholphthalein in its protonated and deprotonated forms is proportional to the concentration of CO_2. In Scheme 1, K is the equilibrium constant. The schematic representation of sensing principle is shown in Scheme 1. As deprotonated form of α-naphtholphthalein (N^-) is blue color in the absence of CO_2, the fluorescence at 655 nm from TPP layer is absorbed by N^- layer. Thus, the observed fluorescence intensity decreases. In contrast, the protonated form of α-naphtholphthalein (NH) is colorless in the presence of CO_2. Thus, the observed fluorescence intensity increases. The observed luminescence intensity at 655 nm increased in proportion to the transmittance (T) of the deprotonated form of α-naphtholphthalein (N^-). The T of the deprotonated form of α-naphtholphthalein is expressed as follows:

$$T = 10^{-\varepsilon d[\{Q{+}N^- \cdot\, xH_2O\}]} \tag{1}$$

where ε and d are the molar extinction coefficient and thickness of sensor film, respectively. Thus, $-\varepsilon d$ is constant and can be replaced by A. The relationship between I and T is expressed as follows:

$$I = BT = B10^{A[\{Q{+}N^- \cdot xH_2O\}]} \tag{2}$$

where B is a constant. The concentration of $\{Q^+N^- \cdot xH_2O\}$ is expressed as Eq. (3):

$$[\{Q^+N^- \cdot xH_2O\}] = -KA[\{Q^+N^- \cdot xH_2O\}]_0/(K + [CO_2]) \tag{3}$$

Here, $-KA[\{Q^+N^- \cdot xH_2O\}]_0$ is replaced by a constant C. Then Eq. (2) is re-written to Eq. (4).

$$I = B\ 10_{\{-C/(K+[CO_2])\}} \tag{4}$$

The observed luminescence intensity change by CO_2 is expressed to be I/I_0. I_0 is the luminescence intensity at 655 nm of CO_2 sensor film in 100% argon gas. Thus, the relationship between observed luminescence intensity at 655 nm and CO_2 concentration is following the Eq. (5).

$$I/I_0 = 10_{\{-C(1/(K+[CO_2])-1/K)\}} \tag{5}$$

3. Results and discussion

3.1. Spectral properties of CO_2 sensing film

The luminescence spectrum change of CO_2 sensing film when excited at 350 nm under various CO_2 concentrations as shown in Fig. 1. The excitation light is irradiated from the α-naphtholphthalein film side. As the absorption band at 350 nm

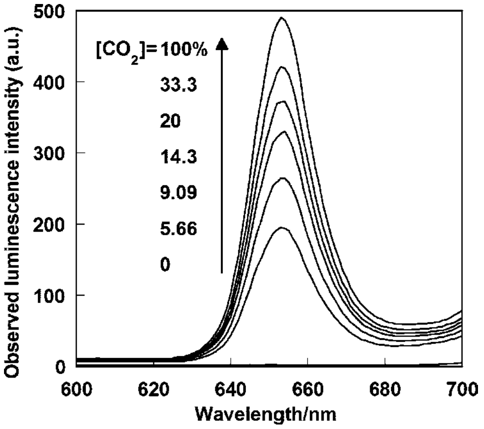


Fig. 1. Luminescence spectrum change of CO_2 sensing film under various CO_2 concentrations. The excitation wavelength is 350 nm.

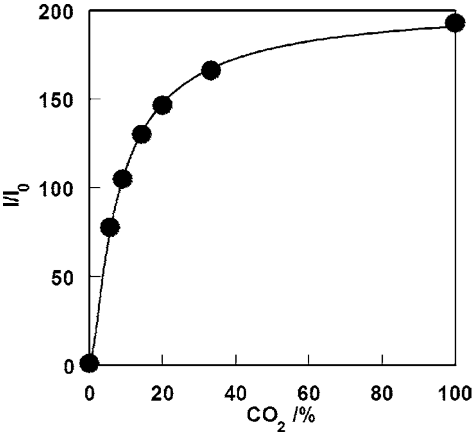


Fig. 2. The I/I_0 value of CO_2 sensing film under various CO_2 concentrations. The excitation and emission wavelengths are 350 and 655 nm, respectively. The solid line is the best-fit using Eq. (5).

of α-naphtholphthalein did not change in the presence and in the absence of CO_2, the excitation light penetrated to TPP film without loss. As the absorption band abound 655 nm of α-naphtholphthalein decreased with increasing the CO_2 concentrations, the observed luminescence intensity from TPP at 655 nm increased. On the other hand, little change of fluorescence of TPP in polystyrene film is observed by CO_2 gas, indicating that the fluorescence of TPP is not affected by the CO_2.

3.2. CO_2 sensing properties

The ratio I_0/I_{100} is used to represent the sensitivity of the sensing film, where I_0 and I_{100} represent the detected fluorescence intensities from a sensor film exposed to 100% argon and 100% CO_2, respectively. In general, the sensor having the ratio I_0/I_{100} more than 3.0 is a suitable sensing device [23]. The I_0/I_{100} value of CO_2 sensing film is estimated to be 192. In contrast, we previously reported that the I_0/I_{100} value of CO_2 sensing film consisting of thymol blue in ethyl cellulose layer and $[Eu(tta)_3]$ in polystyrene layer is estimated to be 16.0 [15,16]. Thus, highly sensitive optical CO_2 sensor is developed using α-naphtholphthalein immobilized in polyIBM layer. Fig. 2 shows the plot of I/I_0 versus the CO_2 concentration. In Fig. 2, the solid line is the best-fit using Eq. (5). This result indicates that CO_2 sensor film can be calibrated by Eq. (5).

Next, the interference from other gaseous species to performance of CO_2 sensing film is investigated. For oxygen, rare gas, and carbon monoxide, no change of sensitivity of CO_2 sensing film is observed. When CO_2 sensing film is exposed acid gas such as HCl, in contrast, the observed luminescence from CO_2 sensing film increased the same as CO_2 gas. However, no observed luminescence change of CO_2 sensing film is observed when the film is exposed to argon gas. Thus, the present CO_2 sensor is interfered from the acid gas such as HCl. In contrast, no change of sensitivity of CO_2 sensing film is observed by basic gas such as NH_3 gas. As this CO_2 sensing film contains the excess OH^-, this film shows no sensitivity for basic gas. The improvement of interference from acidic and basic gaseous to CO_2 sensing film is being studied in detail.

3.3. Response and recovery properties

An operational stability test of CO_2 sensing film is studied. At first, the response and recovery properties of CO_2 sensing film is conducted by reading the luminescence intensity signal while CO_2 saturated and argon saturated are investigated. Fig. 3 shows the response and recovery properties of CO_2 sensing film for 600 s. The response times for sensing film are defined the 90% response and recovery times, exhibited by the sensors when they are exposed to an alternating atmosphere of CO_2 and argon, respectively. The response time

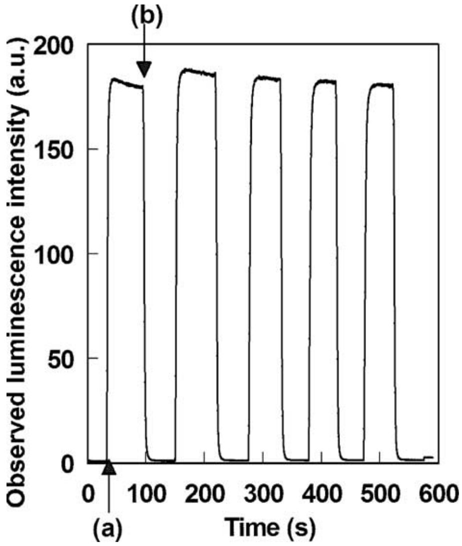


Fig. 3. Response and recovery characteristic of CO_2 sensing film on switching between 100% argon (1) and 100% CO_2 (2). The excitation and emission wavelengths are 350 and 655 nm, respectively.

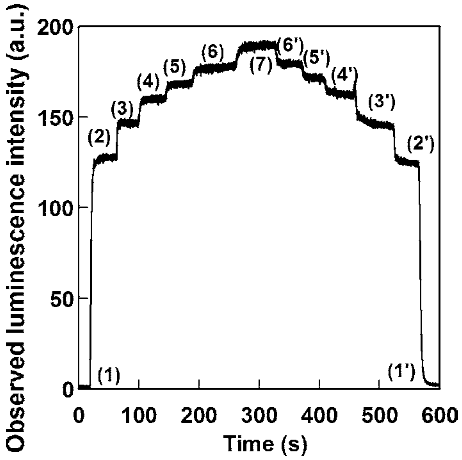


Fig. 4. Response and recovery characteristic of CO_2 sensing film when increasing and decreasing CO_2 concentrations change. The excitation and emission wavelengths are 350 and 655 nm, respectively. (1), (1′) 0; (2), (2′) 12.0;(3), (3′) 16.0; (4), (4′) 25.0; (5), (5′) 30.0; (6), (6′) 33.3; (7) 100% CO_2.

for switching from argon to CO_2 of the CO_2 sensing film is 5.6 ± 1.3 s. The recovery time for switching from CO_2 to argon of the film is 4.7 ± 0.2 s. These results indicate that the CO_2 sensing film especially shows a rapid recovery for switching from CO_2 to argon.

Next let us focus on the measurement hysterisis of CO_2 sensing film. At first, the response and recovery characteristic of CO_2 sensing film is shown in Fig. 4 when increasing and decreasing CO_2 concentrations change. The signal changes are fully reversible and measurement hysterisis is not observed. Next, dynamic response of the CO_2 sensing film under various CO_2 concentrations is shown in Fig. 5. This test is repeated and signal changes are monitored when increasing and decreasing CO_2 concentrations change randomly. The signal changes also are fully reversible and measurement hysterisis is not observed. From the response and recovery times of CO_2 sensing film are less than 6.0 s as shown in Fig. 3. From Figs. 4 and 5, however, the realistic response time of CO_2 sensing film under various CO_2 gas concentration changes is less than 30 s.

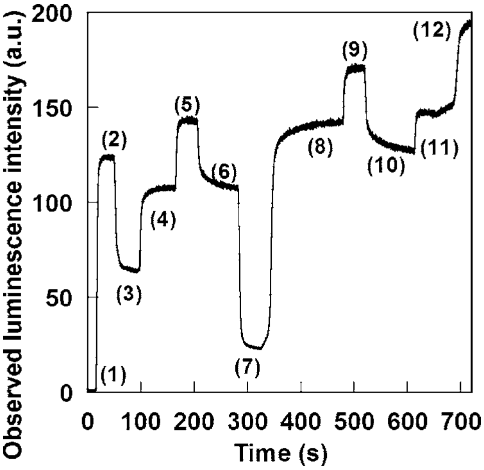


Fig. 5. Dynamic response of CO_2 sensing film when CO_2 concentrations are changed randomly. (1) 0; (2) 12.0; (3) 5.0; (4) 9.09; (5) 16.0; (6) 9.09; (7) 3.0; (8) 14.3; (9) 33.3; (10) 28.0; (11) 33.3; (12) 100% CO_2.

The important problem for the application to an optical CO_2 sensing is photostability of CO_2 sensing film. After continuously the light with 350 nm is irradiation to CO_2 sensing film for 24 h, little charge of CO_2 sensing properties is observed. This result indicates that this CO_2 sensing film is stable against irradiation.

This CO_2 sensing film is applied for the CO_2 measurement using fluorescence spectral change in water media. The sample substrate is mounted at 45° angle in the quartz cell with pure water. Different CO_2 standards (in the range 0–100%) in a gas stream are produced by controlling the flow rates of CO_2 and argon gases entering the quartz cell with pure water and sample substrate. The I_0/I_{100} value of CO_2 sensing film is estimated to be 204. However, the response and recovery times are 38 and 87 s, respectively. The diffusion of CO_2 and argon gas in water is lower than that in gas phase. Thus, the response properties of CO_2 sensing film in water media are lower than that in gas phase measurements.

The thickness effect of α-naphtholphthalein in polyIBM layer of CO_2 sensing film on the CO_2 sensing and response properties is studied. The I_0/I_{100} values of α-naphtholphthalein in polyIBM layer with the thickness of 10, 20 and 30 μm are 192, 73.8 and 25.0, respectively. The response times of α-naphtholphthalein in polyIBM layer with the thickness of 10, 20 and 30 μm are 5.6 ± 1.3, 8.8 ± 1.2 and 10.1 ± 1.3 s, respectively. The recovery times of the films with the thickness of 10, 20 and 30 μm are 4.7 ± 0.2, 7.7 ± 1.2 and 12.2 ± 1.3 s, respectively. The diffusion of CO_2 and argon gaseous is more rapid with decrease the thickness of α-naphtholphthalein in polyIBM layer. Thus, the sensitivity and response properties of CO_2 sensing film are improved using the thinner α-naphtholphthalein in polyIBM layer.

4. Conclusion

An optical sensor for CO_2 based on fluorescence intensity changes of TPP due to the absorption change of α-naphtholphthalein in polyIBM layer with CO_2 is developed. The observed fluorescence intensity from TPP at 655 nm increased with increasing the CO_2 concentrations. The I_{100}/I_0 value of the CO_2 sensor is 192. The CO_2 sensing film can be calibrated by the plot of I/I_0 versus the CO_2 concentration. The response and recovery times of the sensing film are less than 6.0 s for switching from argon to CO_2, and for switching from CO_2 to argon. The signal changes are fully reversible and no hysterisis is observed during the measurements. The highly sensitive optical CO_2 sensor based on fluorescence intensity changes of TPP due to the absorption change of α-naphtholphthalein in polyIBM layer with CO_2 is achieved.

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