Modification of Preparation Method for Polymer Inclusion Membrane (PIM) to Produce Hollow Fiber PIM

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ABSTRACT: A new preparation method for polymer inclusion membrane (PIM) was developed. The preparation method—called post-treatment method—is very convenient to prepare a hollow fiber PIM. Using this method, a commercial cellulose triacetate (CTA) hollow fiber membrane can be easily converted into a hollow fiber PIM. Thus, a CTA hollow fiber membrane was allowed to swell in 2-nitrophenyl-*n*-octyl ether (NPOE) in the presence of chloroform as a solvent for CTA and *N*,*N*,*N*′,*N*′-tetraoctyl-3-oxapentane diamide (TODGA) as a carrier. After evaporating chloroform, a hollow fiber PIM containing NPOE and TODGA was obtained. The result of the transport experiment of cerium(III) ions using the hollow fiber PIM showed that cerium ions were effectively transported from the feed solution to the strip solution through the hollow fiber PIM, indicating that the hollow fiber PIM was successfully prepared using the post-treatment method. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4372–4377, 2006

Key words: carrier-mediated transport; polymer inclusion membrane (PIM); hollow fiber membrane; post-treatment method; cellulose triacetate

INTRODUCTION

Carrier-mediated transport using supported liquid membrane (SLM) has been known as a promising method for various separation processes such as separation of isomers,[1,2] gases,[3–5] metal ions,[6,7] etc. In SLM, the solvent and carrier are impregnated in the pores of a supporting porous membrane, and the carrier is mobile in the solvent to selectively transport the target molecules. The main drawback of the SLM is the loss of solvent and carrier to the surrounding solutions because of dissolution, formation of emulsion droplets, or differential pressure across the membrane. This instability problem makes SLM unattractive for industrial separation processes.

To obtain a stable membrane, Sugiura et al. have proposed a plasticized cellulose triacetate (CTA) membrane.[8,9] Here, the liquid plasticizer acts simultaneously as an organic solvent similar to that used in SLMs, and the carrier is incorporated in this membrane. This type of carrier-mediated transport membrane is called polymer inclusion membrane (PIM). Several works confirmed the high stability and durability of PIMs.[10–13]

In our previous work,[14] we have developed flat-sheet polymer inclusion membranes consisting of CTA as a matrix polymer, 2-nitrophenyl-*n*-octyl ether (NPOE) as a solvent, and octyl(phenyl)-*N*,*N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO) or *N*,*N*,*N*′,*N*′-tetraoctyl-3-oxapentane diamide (TODGA) as a carrier. We have shown that these PIMs are very effective to transport cerium(III) ions from an acidic aqueous solution to a stripping solution. Since CMPO and TODGA are known as excellent extractants for actinides,[15,16] the PIMs containing these carriers are promising an effective method for the treatment of low level radioactive wastewater. In nuclear industries such as nuclear power plants, the large amount of radioactive wastewater must be concentrated to a smallest possible volume before the storage. Here, the PIMs would be very advantageous because the required amounts of extractants (carriers) and solvents are much smaller than those used in the conventional solvent extraction method.

For the industrial applications, a PIM in hollow-fiber configuration is desired. Nonetheless, to the best of our knowledge, no work has been done to develop hollow fiber PIM, possibly because of the difficulty of the membrane preparation. As described in our previous study,[14] using the conventional method for membrane preparation, a flat-sheet PIM can be prepared by casting a solution of CTA in chloroform containing NPOE and carrier. After drying for 1 day for evaporation of chloroform, a flat-sheet PIM is obtained. Unfortu-

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nately, the preparation of a hollow fiber PIM from the same solution above is very difficult and inconvenient. The spinning of the fibers from the solution would be very difficult because the solution contains a large amount of chloroform, which must be slowly evaporated for at least 1 day. Thus, we suggest that the simplest way to prepare a hollow fiber PIM is the conversion of a CTA hollow fiber membrane into a hollow fiber PIM by a certain post-treatment. Here, the CTA hollow fiber membrane can be easily prepared using the conventional spinning method, and a treatment method has to be explored to convert the CTA membrane into a PIM.

In this work, we have developed a new preparation method called post-treatment method, and applied the method to prepare a hollow fiber PIM. To the best of our knowledge, this is the first PIM developed in hollow fiber configuration. The detail of the method and the condition for the membrane preparation are described. The results of the transport experiment using the PIM are reported.

EXPERIMENTAL

Chemicals

Cellulose triacetate (CTA, 43.6% acetyl content, product no.: CAT 114 4476) was obtained from Eastman Kodak, USA. Chloroform ($CHCl_3$), 2-nitrophenyl-*n*-octyl ether (NPOE, produced by Dojindo Laboratories, Japan), cerium(III) nitrate ($Ce(NO_3)_3$), nitric acid (HNO_3), and sodium nitrate ($NaNO_3$) were all purchased from Wako Pure Chemical Industries, Japan. All chemicals were used as received. *N*,*N*,*N*′,*N*′-tetraoctyl-3-oxapentane diamide (TODGA) was synthesized by ourselves. The detail of the synthesis is described elsewhere.[14]

Determination of swelling ratio of CTA membrane

Preliminary experiments were carried out to determine the swelling ratio of flat-sheet CTA membrane in NPOE. The flat-sheet CTA membrane was prepared as follows. A CTA solution (2 wt %) was prepared by dissolving 2 g of CTA in 98 g of chloroform at room temperature for about 5 h. After filtration using a filter paper, 2 g of the solution was cast onto a glass petri dish (64 mm of diameter), and chloroform was allowed to evaporate slowly in a dry box at a room temperature. After 1 day, the membrane was carefully peeled off the dish. Membrane samples were cut in a size of 1 cm $\times$ 1 cm, and weighed. Then, they were immersed in NPOE or in mixtures containing chloroform and NPOE. The volume ratio of chloroform and NPOE was varied between 1 and 5. The immersing time was varied from 3 to 96 h, and the immersing temperature was varied from 23 to 50°C, which was controlled using a water bath. After immersing, the membrane surface was wiped using tissue paper, and the weight of the swollen membrane was measured as quickly as possible. Then, the membrane was dried at a room temperature in a fume hood to evaporate chloroform. After drying for 1 day, it can be assumed that chloroform was completely removed from the membrane, and the weight of the membrane was measured again. The swelling ratio S was then calculated from the weight of the dry membrane, m_{dry}, and that of the swollen membrane, $m_{swollen}$:

$$S = (m_{swollen} - m_{dry})/m_{dry}$$

Preparation of flat-sheet PIM by post-treatment method and evaluation by transport experiment

A flat-sheet CTA membrane was prepared using a procedure as described in the previous section. To prepare a flat-sheet PIM, the CTA membrane was treated by immersing it in a solution containing chloroform, NPOE, and TODGA. The total volume of chloroform and NPOE was 30 mL, and the conditions for the treatment such as the volume ratio of chloroform/NPOE, the immersing temperature, and the immersing time were chosen based on the result of the swelling experiment as described above. The thickness of the membrane before the post-treatment was 20 μm and increased to 30 μm after the post-treatment.

The transport performance of the flat-sheet PIM was investigated by performing a transport experiment using cerium(III) ion as a model for the radioactive ion. The membrane was clamped between two compartments of a permeation cell. The feed compartment contained 20 mL aqueous feed solution containing 200 ppm $Ce(NO_3)_3$, 0.05*M* HNO_3, and 2.95*M* $NaNO_3$. The strip compartment was filled with 20 mL distilled and deionized water. Both compartments were stirred at 600 rpm, and the temperature was kept constant at 40°C. Very small amounts of samples of the feed and strip solutions were periodically taken and analyzed by inductively coupled plasma (ICP) spectroscopy (ICPS-7500, Shimadzu, Japan). The detail of the transport apparatus for the flat-sheet PIM has been described elsewhere.[14]

Preparation of hollow fiber PIM by post-treatment method and evaluation by transport experiment

Figure 1 shows the post-treatment method of hollow fiber CTA membranes for the preparation of hollow fiber PIMs. The hollow fiber CTA membranes were cut off from a hemodialyzer (Nipro FB-110EGA, Japan; inner diameter: 200 μm, membrane thickness: 15 μm), and immersed in a solution containing chloroform, NPOE, and TODGA. The total volume of chloroform and NPOE was 30 mL, and the conditions for the treatment were chosen based on the result of the post-treated flat PIM as described above.

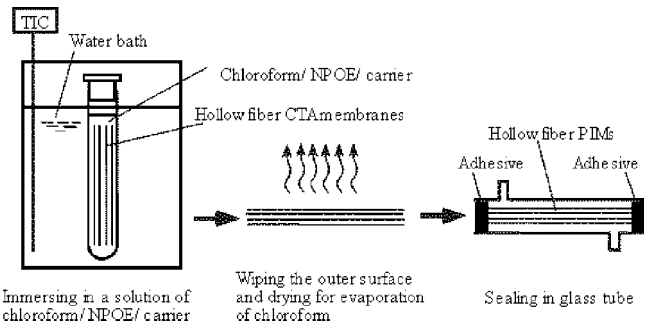

Figure 1 Post-treatment of hollow fiber CTA membrane for preparation of PIM.

The concentration of TODGA in NPOE was adjusted to 15 wt %. The fibers were then taken from the solution, and the outer surfaces were wiped using tissue paper. Finally, the fibers were dried in a fume hood at a room temperature for 1 day to evaporate chloroform.

For the transport experiment, 40 fibers were put in a glass tube (inner diameter: 4 mm, length: 110 mm), and both edges were sealed using epoxy adhesive. Figure 2 shows the experimental setup for the transport experiment using the hollow fiber PIMs. The feed solution was 20 mL aqueous solution containing 200 ppm $Ce(NO_3)_3$, 0.05*M* HNO_3, and 2.95*M* $NaNO_3$. The stripping solution was 20 mL distilled and deionized water. The solutions were circulated using a roller pump at a flow rate of 1 mL/min. Very small amounts of samples of the feed and strip solutions were periodically taken and analyzed using ICP spectroscopy to determine the cerium concentration in the solutions.

RESULTS AND DISCUSSION

Swelling behavior of CTA membrane in NPOE

The result of the swelling experiment showed that the dense flat-sheet CTA membrane almost did not swell after immersing in NPOE even for several days. This result indicates that it is impossible to prepare a PIM by immersing a CTA membrane into NPOE and carrier. The immersing of a base membrane in an organic solvent (such as NPOE) and carrier is a common procedure used for the preparation of supported liquid membrane (SLM). In the case of SLM, the base membrane is a porous membrane, thus the organic solvent can easily penetrate into the pores of the membrane. On the other hand, the base membrane to prepare the PIM is a dense CTA membrane, into which NPOE and carrier shall penetrate. Since NPOE can not penetrate into the dense CTA membrane, an addition of another solvent, in which CTA is soluble, is expected to open a way for NPOE to penetrate into the CTA matrix. Thus, the membrane was immersed in a mixture of NPOE and chloroform. Here, chloroform acts as a solvent for the CTA membrane. Figure 3 shows the effect of volume ratio of chloroform ($CHCl_3$) : NPOE on the swelling ratio of the CTA membrane before and after drying (evaporating chloroform). As expected, the addition of a small amount of chloroform resulted in a highly swollen CTA membrane. The higher the volume ratio of $CHCl_3$: NPOE, the more chloroform and NPOE penetrated into the CTA membrane. Further, as shown in Figure 3, the swelling ratio of CTA membrane after drying was lower than that before drying, indicating that chloroform vaporized from the membrane, and only NPOE remained in the membrane. Similar to the swelling behavior before drying, the swelling ratio after drying (after evaporation of chloroform) increased with increasing volume ratio of $CHCl_3$: NPOE. This means more NPOE penetrates into the CTA membrane when the ratio of $CHCl_3$: NPOE is high. When the volume ratio of $CHCl_3$: NPOE was 4 : 1, a swelling ratio of about 1 was obtained.

According to the results of our previous work,[14] in the case of PIM prepared by the conventional

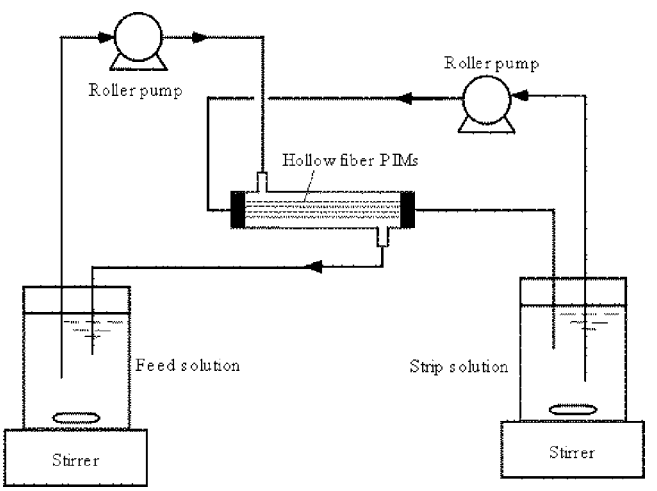

Figure 2 Transport experiment using hollow fiber PIM.

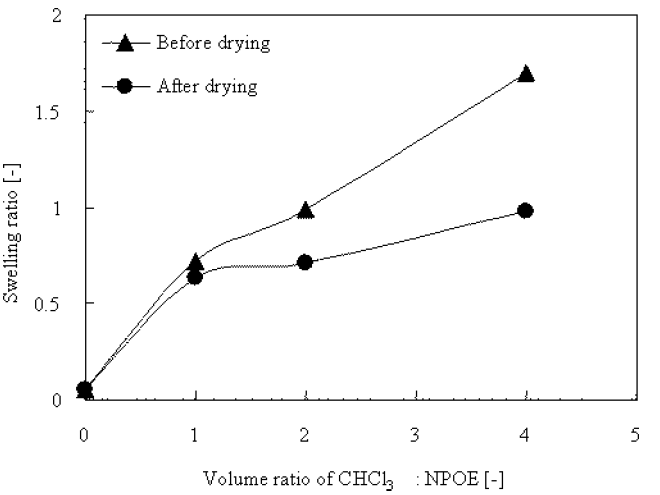

Figure 3 Effect of chloroform addition on swelling ratio of CTA membrane before and after drying (immersing time: 1 day, immersing temperature: room temperature).

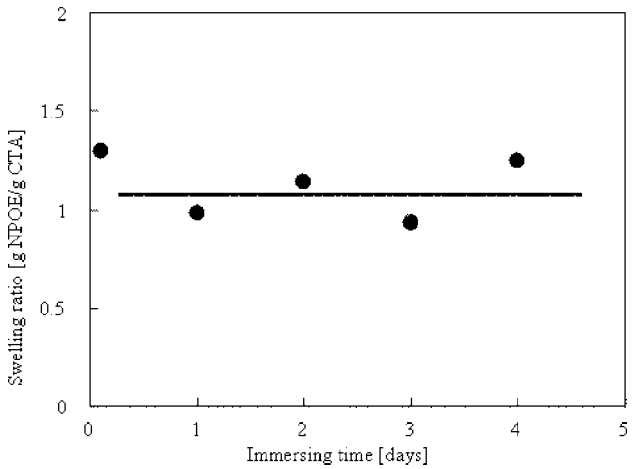

Figure 4 Effect of immersing time on swelling ratio of CTA membrane after drying (volume ratio of $CHCl_3$: NPOE = 4 : 1, immersing temperature: room temperature).

method (casting method), a higher NPOE content is favorable, because it leads to a higher transport rate of cerium ions through the PIM. Thus, the attempt to increase the swelling ratio was done by increasing the volume ratio of $CHCl_3$: NPOE above 4 : 1, however this resulted in a highly swollen, almost soluble gel, and after the evaporation of chloroform, a mechanically weak membrane was obtained.

To obtain a further increase in the swelling ratio, we investigated the influence of the immersing time on the swelling ratio of the CTA membrane. Figure 4 shows the result of the swelling experiment for various immersing times. The data were taken after drying of the membrane (after evaporation of chloroform). As seen, the swelling ratios of the CTA membrane did not almost change by immersing the membrane from several hours to several days, indicating that the equilibrium sorption condition was attained within several hours.

Further, the CTA membrane was immersed in a solution of chloroform and NPOE (4 : 1 v/v) at elevated immersing temperatures. Figure 5 shows the influence of the immersing temperature on the swelling ratio measured after drying. As can be seen, the swelling ratio increased markedly with the increase in immersing temperature. An elevated immersing temperature up to 50°C is suitable to improve the penetration of NPOE into the CTA matrix. Immersing temperatures above 50°C may result in a further increase in swelling ratio, however a possible change of the physical structure of the membrane must be taken into account.

Flat-sheet PIM prepared by post-treatment method

Based on the results of the swelling experiments above, a flat-sheet PIM was prepared by immersing a flat-sheet CTA membrane in a mixture containing chloroform, NPOE, and carrier for 1 day, and then drying the membrane for evaporation of chloroform. To prepare the PIM, a volume ratio of $CHCl_3$: NPOE of 4 : 1 was used, and an elevated immersing temperature of 40°C was applied, since this condition resulted in a membrane with a high swelling ratio combined with a good mechanical strength as described above.

In the preparation of the solution for the post-treatment, the weight of TODGA dissolved in NPOE was adjusted to be 15 wt %. Assuming that the uptake of TODGA and NPOE into the membrane occurs at the same rate, the TODGA concentration in the PIM should be equal to the concentration of TODGA in NPOE before penetrating into the membrane. After drying (chloroform evaporation), a clear PIM having a good mechanical strength was obtained. The physical appearance of the post-treated PIM was almost the same as that of the PIM prepared by the conventional casting method.

Figure 6 shows the result of the transport experiment using the post-treated PIM containing 15 wt % TODGA. Here, the feed solution was an aqueous solution containing 200 ppm $Ce(NO_3)_3$, 0.05*M* HNO_3, and 2.95*M* $NaNO_3$. The ordinate in Figure 6 is the dimensionless concentrations of cerium in the feed and the strip solutions, where $[Ce]_{F,0}$ is the initial cerium concentration in the feed solution. As can be seen, the cerium concentration in the strip solution increased with time, whereas that in the feed solution decreased and became almost zero after 5 h, indicating that cerium ions were effectively transported from the feed solution through the PIM to the strip solution.

The normalized permeate flux of cerium ions through the post-treated PIM was calculated to be

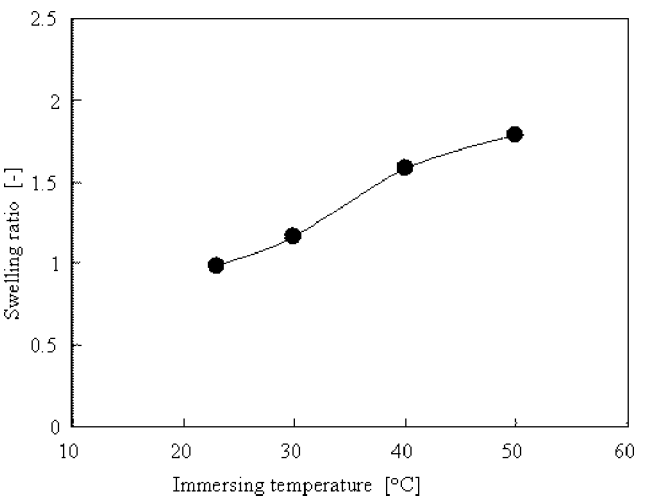

Figure 5 Effect of immersing temperature on swelling ratio of CTA membrane after drying ($CHCl_3$: NPOE ratio = 4 : 1, immersing time: 1 day).

2.3 mol μm m^{-2} h^{-1}. In the case of the PIM prepared by the conventional method with a high ratio of NPOE : CTA of 3 : 1, a normalized permeate flux of 2.9 mol μm m^{-2} h^{-1} was obtained. This means, the permeate flux through the post-treated PIM is about 80% of permeate flux through the conventional PIM. This is reasonable since the ratio of NPOE : CTA of the post-treated PIM is about 1.8 : 1. In the future work, further efforts to increase the swelling ratio have to be done.

Hollow fiber PIM prepared by post-treatment method

Based on the results of the transport experiment using the post-treated PIM in flat-sheet configuration, the post-treatment of a hollow fiber CTA membrane under the same treatment condition is expected to result in a hollow fiber PIM. Thus, the hollow fiber CTA membranes were immersed in a solution of $CHCl_3$: NPOE (4 : 1 v/v) containing TODGA at 40°C for 1 day. After drying for 1 day for the evaporation of chloroform, it can be assumed that chloroform was completely evaporated from the fibers. It was observed that after the treatment, the fibers exhibited a higher flexibility compared to the original CTA fibers, because NPOE acted simultaneously as a plasticizer for the CTA matrix.

Using the conventional method, about 2 mL of chloroform/NPOE containing 0.14 g of TODGA was needed to prepare a flat membrane. In the case of the post-treatment method, we used 30 mL solution of chloroform/NPOE containing 1.06 g TODGA for the preparation of a flat PIM of the same size. Although the quantity of TODGA for the post-treatment method is much higher than that of the conventional method, in the future industrial application we can reuse the solution to prepare a lot of membranes.

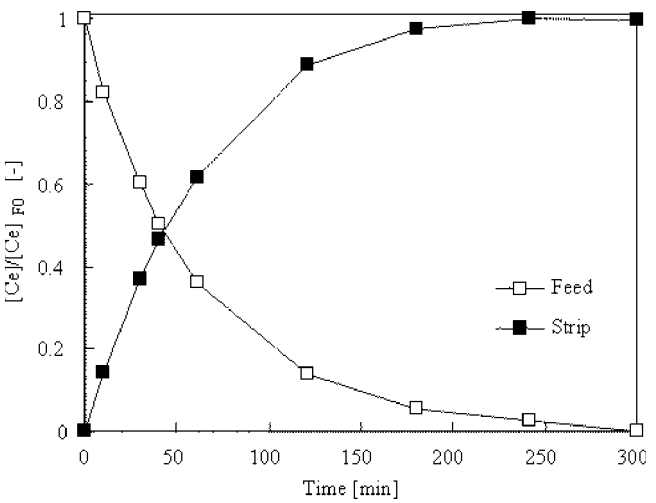

Figure 6 Result of transport experiment using post-treated flat-sheet PIM containing TODGA as carrier.

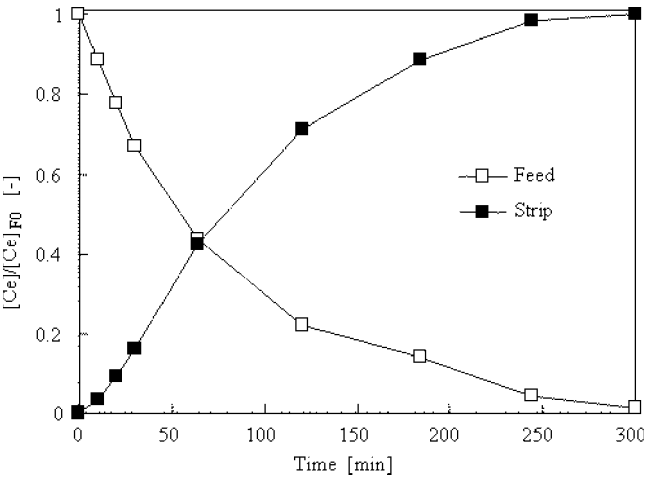

Figure 7 Result of transport experiment using post-treated hollow-fiber PIM containing TODGA as carrier.

Figure 7 shows the result of the transport experiment using the post-treated hollow fiber PIM containing TODGA. The feed solution was an aqueous solution containing 200 ppm $Ce(NO_3)_3$, 0.05*M* HNO_3, and 2.95*M* $NaNO_3$. The concentration profiles are similar to those using the flat-sheet PIM. The increase in the strip concentration and the decrease in the feed concentration with time indicate the transport of cerium ions from the feed phase to the strip phase through the hollow fiber PIM. This result shows that the PIM has been successfully prepared using the post-treatment method. Thus, a hollow fiber CTA membrane can be easily converted into a hollow fiber PIM using the post-treatment method.

CONCLUSIONS

A new method—called post-treatment method—for the preparation of PIM was developed. We showed that the addition of chloroform as a solvent of CTA was very effective to make a CTA membrane swollen in NPOE. The swelling ratio depended on the experimental conditions such as the ratio of chloroform : NPOE and the immersing temperature. Using this method, a hollow fiber CTA membrane was successfully converted into a hollow fiber PIM. The hollow fiber PIM containing TODGA as a carrier was effective to transport cerium ions from the feed phase to the strip phase. To the best of our knowledge, this is the first PIM developed in hollow fiber configuration.

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