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# Schiff's bases of polyallylamine
## Synthesis and membrane properties for reverse osmosis

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## Summary

Schiff's bases of polyallylamine were synthesized by the reaction with four aldehydes. Salicylaldehyde (S)- and 2-pyridinecarboxaldehyde (P)-Schiff's base could be used as reverse osmosis membranes when crosslinked with divinyl sulfone, diacetyl or ethylene glycol diglycidyl ether. S-base membrane had a high mechanical strength but poor water permeability ($K_1$), while P-base membrane showed a high rejection, particularly against $CoCl_2$, and a high $K_1$ because of chlate formation, but poor strength. The membranes of P-base and a hybrid PS-base exhibited a possibility of separating alkali metal salts and transition metal salts from each other.

## Introduction

Primary amino groups-containing polymers are highly reactive and useful as a functional raw material. Hitherto known simple polymers which contain primary amino groups are polyethylenimine and polyvinylamine (PVAm). The former is commercially available as a water solution but the latter can not be readily produced. Recently, polyallylamine (PAAm) which is one of aliphatic polyamines similar to PVAm has been synthesized from an inorganic acid salt of allyamine and now commercially produced via radical polymerization (1,2). PAAm has already been utilized as the starting material for the synthesis of its derivatives and resins (3) and its chelating ability has been examined (4,5).

We have demonstrated that when polymers containing functional groups of complex-forming ability are applied for a reverse osmosis membrane, the separation of transition metal ions from other metal ions is possible because the functional groups take up the metal ions by the complex formation (6). Those functional groups include Schiff's base which can also form complexes with many heavy metal ions. Schiff's bases of PVAm were prepared (7) and the thermal stability of their coordination polymers were examined (8). However, neither synthesis of Schiff's bases of PAAm nor their application to membranes has been reported. Thus, we have prepared Schiff's bases of PAAm and applied them for reverse osmotic separation of metal ions.

## Experimental

### Synthesis of Schiff's bases of PAAm

PAAm-hydrogen chloride (PAAm-HCl) of Mw = 60,000 supplied by Nitto Boseki Co.(Japan) was freed from HCl by passing its 10% aq. solution through a column of anion exchanger Amberlite IRA-402. The free polyamine solution combined with column washings (3~5% PAAm) was concentrated under reduced pressure to 80~90%, and methanol was added so as to obtain 10% solution. To this solution was added dropwise methanol or dimethylformamide (DMF) solution (6~12%) of a required amount of aldehyde (10% total solid) with stirring in a stream of nitrogen, and the mixture was heated at 40 or 80℃ for 2 or 3 h. When PS-type Schiff's base was prepared, a distilled sample of 2-pyridinecarboxaldehyde (P) of Tokyo Kasei Kogyo Co.(Japan) was reacted first and then a distilled sample of salicylaldehyde (S) of Wako Pure Chemical Industries, Ltd.(Japan) reacted. After the reaction,the mixture was concentrated by evaporating methanol under reduced pressure (S- and P-type Schiff's base from S and P, respectively). The solution of P-type Schiff's base was poured into diethyl ether to precipitate the product which was then filtered, washed with diethyl ether and dried in vacuo. The solution of S-type Schiff's base was used without precipitation as the casting solution. The concentration of the solid was determined by precipitating an aliquot of the solution. Addition of β-resorcylaldehyde (2,4-dihydroxybenzaldehyde, guaranteed grade)(Re) of Nakarai Chemicals, Ltd.(Japan) immediately gave a yellow precipitate which stayed unchanged during the reaction time. The precipitate was filtered and washed with methanol (Re-type Schiff's base).

## Membrane preparation

The general procedure is the same as described before (9,10). On a glass plate which was wetted with 1% aq. solution of polyacrylamide and dried, 10% benzyl alcohol (BzOH) solution of P-type Schiff's base (18% DMF solution of S-type, 6% dimethyl sulfoxide (DMSO) solution of Re-type, and 10% DMSO solution of PS-type) containing a required amount of crosslinking agent was cast and dried at 80℃ for a required time. The peeled membrane was immersed in water overnight and used for reverse osmosis at 25℃ with a batch-type apparatus similarly as described in previous papers (6,9). NaCl feed was supplied first, membranes were washed with water under pressure overnight and then $CoCl_2$ feed was supplied. Relative strength based on a cellulose acetate membrane and water content of membranes were measured also similarly as before (6,9). Salt rejection R and hydraulic water permeability $K_1$ were obtained from the following equations, respectively.

$$R = 100(c - c')/c \quad (1)$$

$$Jv = K_1(\Delta P - \Delta\pi)/\Delta x \quad (2)$$

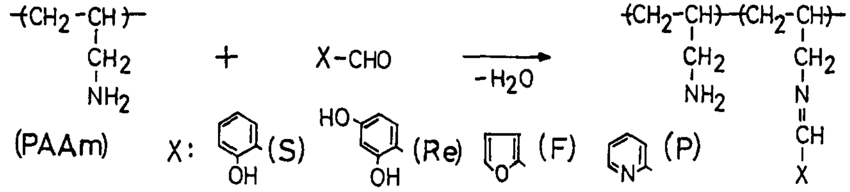
where c (0.06M) and c' are feed and product concentrations determined by measuring electric conductance, respectively, Jv is volumetric flux, $\Delta P$ pressure difference (80 kg/cm$^2$ or 7.85 MPa), $\Delta\pi$ osmotic pressure difference between feed and product solution, and $\Delta x$ membrane thickness.

## Analysis

The composition of Schiff's bases were determined by NMR. S-type base was also subjected to ultraviolet analysis at 314 nm in DMF solution and the composition was determined by comparing with a model Schiff's base 2-n-butyliminomethylphenol prepared from salicylaldehyde and n-butylamine.

## Results and Discussion

The results of the synthesis of Schiff's bases are shown in Table 1. A less than equimolar amount of aldehyde was initially charged to the system as expressed in the following equation in order to use the amino groups for crosslinking in the preparation of membranes.



Most of the Schiff's bases were obtained in a high yield at a relatively low temperature of 40℃ within 3 h in the absence of any acid catalyst. In P-type base methanol was a good solvent for both PAAm and its product, but in other cases the addition of DMF or DMSO was necessary to prevent the product from precipitating except for the case of Re-type base where immediate

Table 1 Synthesis of Schiff's bases of PAAm[a]

| Code[b] | [Aldehyde]/[PAAm] (mol%) | | Solvent[c] | Time (h) | Yield (%) | Composition[d] and Remarks (mol% Schiff's base) |
|---|---|---|---|---|---|---|
| S3 | 90.1 | | M+F | 2 | 97.0 | 86.4 by UV |
| S6 | 63.5 | | M+F | 2 | 89.3 | 67.4 by UV for soluble part |
| S8 | 63.6 | | M+F | 2 | 99.9 | $\overline{Mw}$ of PAAm = 10,000 |
| S9 | 63.5 | | M+F | 3 | 93.6 | |
| Re2 | 100 | | M+SO | 3 | 100 | Hardly soluble in SO |
| F1 | 75.1 | | M+F | 1 | 97.9 | Insoluble in org. solvents |
| P1 | 100 | | M | 2 | 88.1 | 80.5 by NMR(P1$\sim$8) |
| P2 | 80.1 | | M | 2 | $\sim$100 | 71.2 |
| P3 | 80.3 | | M | 2 | 90.8 | 83.4, $\overline{Mw}$ of PAAm = 10,000 |
| P5 | 80.0 | | M | 2 | 96.5 | 79.5 |
| P7 | 75.0 | | M | 2 | 99.1 | 73.8 |
| P8 | 75.0 | | M | 2 | 97.3 | 72.4 |
| | [P]/[PAAm] | [S]/[PAAm] | | | | $[NH_2]/[P]/[S]$ by NMR |
| PS1 | 40 | 40 | M+F | 3 | 92.3 | 15.2/42.8/42.0 |
| PS2 | 40 | 40 | M+F | 3 | 94.0 | 3.6/43.5/52.9 |
| PS3 | 56 | 24 | M+F | 3 | 100 | 18.6/59.0/22.4 |

a) Reaction temperature was 40℃ except for S3 and S6 (80℃).

b) S: salicylaldehyde, Re: β-resorcylaldehyde, F: furfural, P: 2-pyridinecarboxaldehyde, PS: a hybrid of P and S.

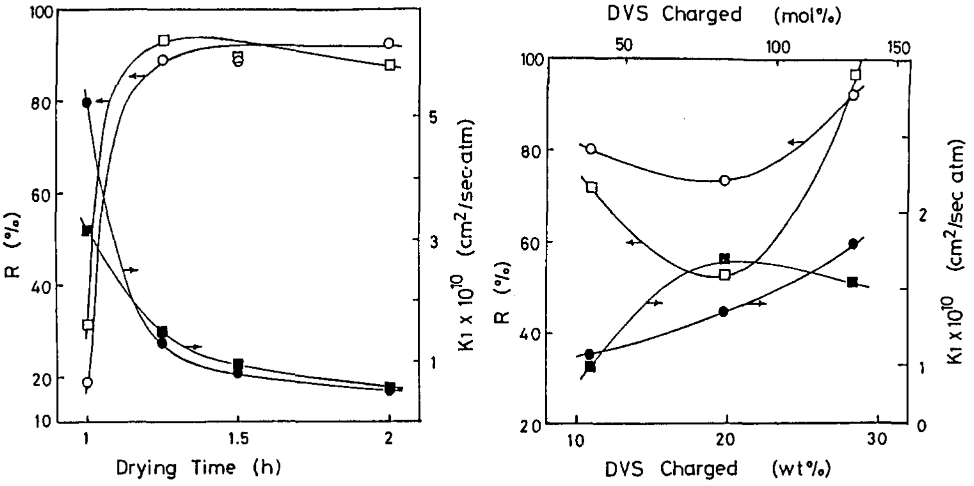
c) M: methanol, F: DMF, SO: DMSO. F and SO were used for the solvent of aldehydes and the resulting polymer as well.

d) Schiff's bases from S contained more or less insoluble fraction and NMR of the soluble part showed a higher content of S than that added in most cases, probably because the insoluble part consists of free amino groups-rich fractions of the polymer.

precipitation occurred upon adding Re.

S-type base of a high substitution like S3 was soluble in organic solvents even after isolation from a solution by precipitation. However, low substituted S-type bases such as S6, S8 and S9 turned partly insoluble after the isolation by precipitation. Therefore, the low substituted S-type bases were used for membrane preparation without precipitation after the reaction, since composition analysis of S3 showed that the added aldehydes nearly quantitatively reacted. NMR spectra of their soluble parts lacked the signal at $\delta$ 13.4 due to OH proton which appeared in S3, and the calculation of peak areas in the spectra always brought a higher ratio of S than initially charged. These results allows one to consider that the insolubilization is caused by a certain interaction between acidic OH and amino groups-rich fractions of the resulting Schiff's base. This can be supported by the fact that in the reaction of two acidic OH-containing Re a precipitate was formed most of which was insoluble. F-type base also gave a precititate which appeared gel-like when concentrated by evaporating methanol after the reaction. The dry polymer was insoluble in common solvents including conc. $H_2SO_4$. A higher substitution of F by adding more amount of F may improve the solubility, but the decrease of residual amino groups will make it unable to prepare a crosslinked membrane.

Those Schiff's bases were used for preparing membranes and their reverse osmosis properties were examined. Since the molecular weight of the starting PAAm was rather low, the membrane prepared without any cross-linking agent was not strong enough to endure the applied pressure of 80 $kg/cm^2$. Hence, an attempt was made to employ an adequate crosslinking agent which is presumed to react with amino groups during drying at 80℃. The most successful agent for S-type base was DVS and the performance of S6 membranes reinforced by DVS is shown in Figs. 1 and 2. The crosslinking reaction involves hydrogen-transfer reaction as reported previously (10).

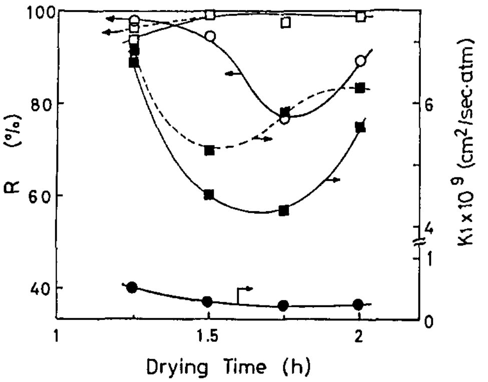


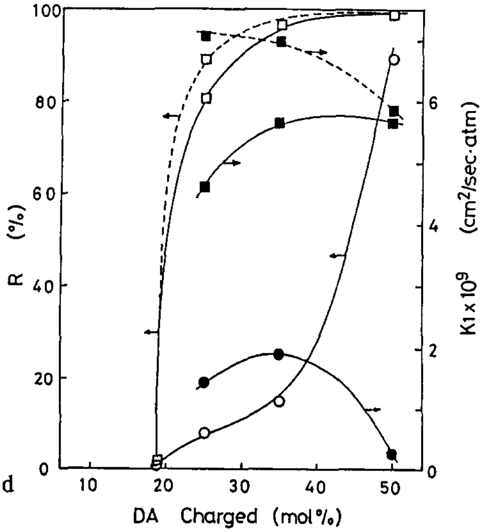
R and $K_1$ vs. drying time for S6 membranes cross-linked with 30 wt% DVS (Fig. 1, left) and vs. DVS charged based on $NH_2$ groups of S6, dried for 1.5 h (Fig. 2, right). ○,●: NaCl; □,■: $CoCl_2$ feed.

These membranes were about 1.7 times as strong as cellulose acetate membrane. Fig. 1 indicates that 1.25 h is critical for rejection and 1.25~2 h is needed to exhibit a stable rejection. In Fig. 2, therefore, the depencence of DVS on the performance is examined at a drying time of 1.5 h. R and $K_1$ were prone to increase along with DVS content. Re-type base was difficult to be transformed into a membrane because of their low solubility and they only brought about a fragile membrane of low performance even when cross-linked with DVS.

For crosslinking agents for P-type bases, several compounds were examined as is shown in Table 2. In the reaction of DA not only dehydration but also an addition of $NH_2$ to C=O of DA are possible. That the crosslinking reaction of P-type bases with DA occurred was readily demonstrated by the fact that on heating a solution containing free PAAm and DA it soon turned viscous and gelation took place. The reaction of DIB involves crosslinking quaternization of pyridine rings as described before (11). The DIB-crosslinked P1 membrane had high rejections and was more water permeable than most of the others. However, the membrane was so soft that a porous support like cellophane had to be used on casting. The effect of DIB on the increase in the performance is apparent when compared with the results in the absence of DIB where the membrane degraded by swelling, giving a very poor rejection of $CoCl_2$. TD and DA gave stronger membranes which could be used without any support, but the membrane cross-linked with TD was weaker and more fragile than that with DA.

DA-crosslinked membranes showed a higher performance than TD-, PDA- and TPA-crosslinked membranes. In all of them including PS membranes, $K_1$ of $CoCl_2$ and also both R and $K_1$ of the second product from $CoCl_2$ feed had a tendency to show higher values than those of NaCl, as is shown in parentheses in Table 2 as several examples. This is accounted for by the complex- or chlate-formation of those membranes with $Co^{2+}$ in contact with $CoCl_2$ feed, changing them into charged membranes which increase R by Donnan



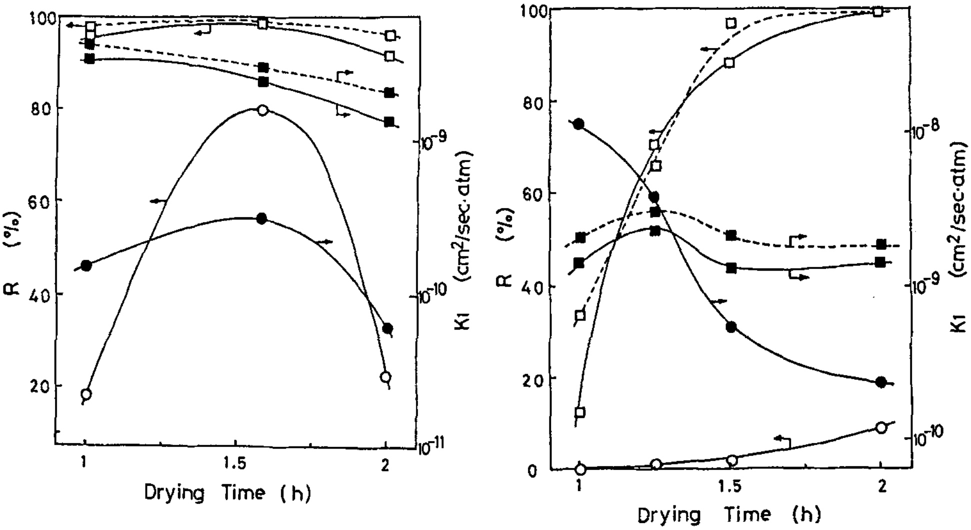


R and $K_1$ of P7 membranes cast from 10 wt% BzOH solution, vs. drying time (Fig. 3, left) and vs. DA charged based on $NH_2$ groups, dried for 2 h (Fig. 4, right). See Figs. 1 and 2 for symbols. ··· : for the second 10 ml product.

exclusion and swell due to increased hydrophilicity (9,10). No such phenomenon was observed in NaCl feed. The swelling was so extensive as to degrade membranes, so that the thickness could not be measured after the test. The strength of P7 was not high, as is shown in Table 2, even before the test, but R and $K_1$ were quite high. On the contrary, S-type membranes had a higher strength, whereas R and $K_1$ were poor. Thus, hybridized membranes of PS-type were prepared and their performance was examined. As is shown in PS1 and PS2 in Table 2 the membranes could hold their structure even though the strength decreased drastically after the test. Swelling after the test is apparent from the increase in water content as well as that in membrane thickness. The improving effect of a crosslinking agent is remarkable in comparison with the results in the absence of the agent. The most successful and reproducible crosslinking agents were DA and EGE. However, the performances of the membranes crosslinked with them could not surpass those of P-type membranes, particularly in $K_1$ in case of a high R value. Thus, it can be emphasized that pyridine rings are effective for increasing water permeability.

All of the above results reveal that S-type Schiff's base gives a strong membrane when crosslinked with DVS but its water permeability is poor, while P-type Schiff's base gives a membrane of excellent water permeability together with a high value of R when crosslinked with DA and other dialdehydes though the membrane swells to a great extent, and that a membrane from PS-type Schiff's base shows an intermediate performance.

Since DA and EGE brought a membrane of a reproducible and considerably high performance in P- and PS-type base, respectively, the influence of more detailed conditions of membrane fabrication on the performance was examined. Figs. 3 and 4 show the dependence of R and $K_1$ on drying time and DA charged



R and $K_1$ vs. drying time for PS3 membrane cast from 10 wt% DMSO solution charged with 50 mol% DA (Fig. 5, left) and EGE (Fig. 6, right) based on $NH_2$ groups. See Figs. 1 and 2 for symbols and Figs. 3 and 4 for dotted line.

Table 2 Results of reverse osmosis for the membranes prepared with various crosslinking agents a)

| Polymer Code | Conc.(%) of casting soln.(solv) | Crosslinking agent b) (mol%) | Drying time (h) | Membr. thickness (μm) c) | | R, % d) (%) | | $K_1 \times 10^{10}$ d) ($cm^2$/sec・atm) | | Water content (%) c) | | Relative strength c) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | B | A | NaCl | $CoCl_2$ | NaCl | $CoCl_2$ | B | A | B | A |
| S6 | 18(DMF) | DVS,116 | 2 | 32.5 | 33.5 | 92.5 | 87.6 | 0.50 | 0.56 | - | 31.5 | - | 1.70 |
| Re2 | 8(DMSO) | none | 1 | 17.7 | - | 13.7 | - | 10.8 | - | | | | broken |
| P1 | 12(DMF) | DIB,22.4 e) | 2 | 52 | 104 | 85.3 | 96.6(96.8) | 68 | 112 (117) | | | | |
| | 12(DMF) | none | 2 | 54 | s | 96.6 | 16.8 | 18 | 182 | | | | |
| P2 | 10(DMSO) | TD,26.0 | 2 | 33.3 | s | 95.3 | 87.6(96.6) | 4.1 | 23.2 (28.0) | | | | |
| | 10(BzOH) | DA,51.0 | 1.5 | 39.1 | s | 93.3 | 99.2 | 24.9 | 42.9 | | | | |
| P3 | 15.1(DMSO) | DA,51.4 | 1 | 35.6 | s | 43.0 | 98.0 | 3.6 | 43.9 | | | | |
| | 5(DMSO) | PDA,50.2 e) | 5.5 | 48.1 | s | 95.7 | 90.0 | 2.7 | 85.8 | | | | |
| | 5(DMSO) | TPA,50.3 e) | 5.5 | 63.2 | s | 78.7 | 25.0(88.1) | 4.7 | 84.1 (72.2) | | | | |
| P7 | 10(BzOH) | DA,50.2 | 2 | 35.9 | s | 89.2 | 98.8(98.3) | 2.5 | 56.2 (62.5) | 57.9 | | 0.2 | |
| PS1 | 8(DMSO) | DVS,53.6 | 2 | 24.6 | 31.0 | 2.0 | 5.4 | 606 | 161 | 16.7 | 31.7 | 1.3 | 0.24 |
| | 8(DMSO) | DA,55.3 | 2 | 26.8 | 42.8 | 78.4 | 85.7(92.5) | 3.5 | 9.1 (11.2) | 18.8 | 37.8 | 2.6 | 0.15 |
| | 10(DMSO) | none | 1 | 22.2 | 25.2 | 0.8 | 1.0 | 52.5 | 796 | | | | |
| PS2 | 10(DMSO) | EGE,31.0 | 2 | 25.0 | 41.9 | 83.6 | 95.3(97.7) | 2.3 | 9.7 (13.2) | 25.9 | 52.9 | 1.6 | 0.40 |
| | | | | | | 90.6 | 95.6(96.7) | 19.5 | 21.8 (23.1) | | | | |

a) Dried at 80℃.

b) DVS: divinyl sulfone, DIB: 1,4-diiodobutane, TD: Tetrad D, a commercial name of a diepoxy compound, DA: diacetyl, PDA: pyridine-2,6-dialdehyde, *TPA*: terephthalaldehyde, *EGE*: *ethylene glycol* diglycidyl ether. Mol% was based on unreacted amino groups.

c) B: before the test, A: after the test. s: too swollen and degraded for the thickness to be measured.

d) The figures in parentheses denote the values for the second 10 ml product from $CoCl_2$ feed. In PS2 two cycles were conducted.

e) Cast on cellophane sheet because the membranes were very soft without the sheet. Cellophane itself had an R value of 10% and corrected values of R are listed.

in P7, respectively. $K_1$'s of $CoCl_2$ were always higher than those of NaCl because of complexation of $CoCl_2$. Initial decreases in $K_1$ in Fig. 3 are explained in terms of the reduction of pore size of the membrane by solvent evaporation, but an increase in $K_1$ of $CoCl_2$ at 2 h may be due to local void formation along with shrinkage by increased crosslinking. A prolonged drying exhibited a tendency to decrease R of NaCl and to increase the difference in R between NaCl and $CoCl_2$. The difference in R is enlarged in Fig. 4 at an addition of about 35 mol% DA. The membrane prepared under those fabrication conditions may be applicable to the separation between alkali and transition matals. Fig. 4 clearly indicates the effect of DA on the enhancement of membrane performance.

The performances of hybrid membranes of PS3 are depicted in Figs. 5 and 6. The performance of PS3 is lower than that of P7 when compared with the results of very similar conditions, e.g., at 2 h in Figs. 3 and 5, most probably because of hydrophobicity of S. The effect of the casting solvent has not been clarified. The comparison between Figs. 5 and 6 reveals that EGE is less reactive than DA, requiring a longer time for displaying a high rejection of $CoCl_2$. The very low rejections of NaCl in Fig. 6 are characteristic and those membranes prepared by drying at 1.5~2 h with EGE-crosslinking appear to be useful for the separation of the two metal salts from each other, as well as the membrane dried at 2 h and crosslinked with DA in Fig. 5.

The membranes described above include those of a high value in both rejection and water permeability. The only drawback is mechanical strength in P-type membranes. However, it seems to be overcome by preparing a composite membrane by using a tough and porous support. A preliminary experiment of preparing such a membrane on a commercial membrane filter of 3 $\mu$m pore diameter has given encouraging results, showing no apparent degradative change in the membrane appearance after the test. The details about the performance of the composite membranes and the separation of a mixture feed of NaCl and $CoCl_2$ will be reported in a future paper.

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