

Study of Blend Membranes Consisting of Nafion[®] and Vinylidene Fluoride–Hexafluoropropylene Copolymer

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ABSTRACT: An attempt to modify membranes for direct methanol fuel cells by blending Nafion[®] with a (vinylidene fluoride)–hexafluoropropylene copolymer (VDF–HFP copolymer) from their solutions is reported. The purpose of this work was to reduce the methanol transport while still retaining the essential proton conductivity in a water-containing environment. The apparent conductivity, methanol barrier property, and equilibrium contact angle as a function of the membrane compositions are discussed. The blend membranes were also investigated using X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Compared with the pure Nafion[®] membrane, the Nafion[®]/VDF–HFP copolymer blend membrane with 62.5 vol % of the VDF–HFP copolymer shows a decrease in the apparent conductivity by about 2 orders of magnitude, and the methanol barrier properties increase substantially when only 25 vol % of the VDF–HFP-copolymer is incorporated. The equilibrium contact angles of water drops on the Nafion[®]/VDF–HFP copolymer blend membranes as a function of the VDF–HFP copolymer content are rather similar to the plot of the advancing angle versus the percentage of the lower-surface-energy phase. X-ray diffraction studies indicate that these two polymers crystallize separately when blended and cast from their solutions, and the crystallization behavior is equivalent to that of the unblended state. DSC reveals that when the VDF–HFP copolymer is mixed with Nafion[®] in their solution forms, an interdiffusion or other interaction takes place at the interfaces between their noncrystalline regions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 121–127, 1998

Key words: membrane; blend; Nafion[®]; conductivity; vinylidene fluoride–hexafluoropropylene copolymer

INTRODUCTION

Nafion[®], a perfluoropolymer containing sulfonic acid groups, is currently the most frequently used polymeric electrolyte in membranes for many fuel cell applications. This material has good hydrothermal stability, proton conductivity, and struc-

tural strength and also results in relatively good kinetics for the electrochemical reduction of oxygen on a platinum catalyst.^{1–6} Direct methanol fuel cells using this electrolyte are currently being considered as a desirable electrochemical power source in vehicular applications.^{7–10} One of the difficulties with the direct oxidation of methanol at the anode of such a polymeric electrolyte membrane fuel cell is the transport of methanol through the membrane from the anode to the air electrode (cathode). This cross-transport results in some of the methanol being oxidized by air without generating electrical power. The metha-

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nol also has an adverse effect on the performance of the cathode. This report describes an attempt to modify the membranes for direct methanol fuel cells by solution blending Nafion[®] with a (vinylidene fluoride)-hexafluoropropylene copolymer (VDF-HFP copolymer) in order to reduce the methanol transport while still retaining the essential proton conductivity in the water-containing environment.

Insulating polymers can be changed into an electronically conducting material by mixing with an electronically conductive filler such as a metal powder, carbon black, or an intrinsically conducting polymer powder. Therefore, in the present study, a cocontinuous morphology of the ionomer phase and the polymer filler phase is required to obtain the desirable ionic conductivity while still preserving other typical properties of the polymer matrix.¹¹⁻¹³ The transport properties of the Nafion[®]/VDF-HFP copolymer blend membranes for methanol, water, and protons can also be expected to be governed by the nature, ratio, and phase morphology feature of both polymers. Up to now, little attention has been given to the Nafion[®]/VDF-HFP copolymer blend system.

EXPERIMENTAL

A VDF-HFP copolymer with a vinylidene fluoride content of 90 mol % ($M_n = 350,000$, Kynar Flex 2801-00, Elf Atochem America, Inc., Philadelphia, PA) was used as-received in powder form. A VDF-HFP copolymer solution was prepared by dissolving the powder in dimethylformamide. A Nafion[®] (1100 E.W.) solution, 5 wt %, in isopropanol and a water mixture was supplied by Solution Technology, Mendenhall, PA. The two polymer solutions were mixed by magnetic stirring at room temperature. The resulting solution was cast onto a flat glass surface in a membrane fabrication cell and then heated in an oven at 100°C for about 3 h to remove the solvents. To prevent the gelation of the VDF-HFP copolymer when blended with a high volume of the Nafion[®] solution (isopropanol and water mixture), extra dimethylformamide was added into the solution mixture. The resultant membranes were peeled from the fabrication cell and then kept in distilled deionized water before testing.

For a comparison, Kaolin clay-filled Nafion[®] membranes were prepared by casting the Nafion[®] solution containing fine powders (0.4 μm) obtained from J. M. Huber Corp., Atlanta, GA. The powders were first mixed with 40 mL isopropanol and then

sonified for 1 h. After an uniform suspension formed, the 5% Nafion[®] solution and dimethyl sulfoxide (3 : 1 ratio) were added to the solution and sonified for another hour. The resulting solution was cast in a membrane fabrication cell and then heated in an oven at 90°C to remove the isopropanol. After the isopropanol was evaporated, the oven temperature was increased to 180°C for another hour in order to remove the dimethyl sulfoxide solvent. The deposited membranes could be easily peeled from the flat glass by wetting the membrane with a 1 : 1 ethanol/water solution.

The AC impedance of membranes at room temperature was measured using a Solartron SI 1250 frequency response analyzer with an SI 1287 electrochemical interface. To obtain good contact of the membrane surfaces with two electrodes, a 25-cm² membrane sample (thickness 0.005 cm) was pressed between two flexible electrodes made of Teflon-bonded conductive carbon black and then held tightly between two pieces of graphite plate. The AC impedance was measured using a two-electrode method. To distinguish membrane resistance from interfacial resistance, a high scanning frequency is needed. For this experiment, the scanning frequency ranges from 64,000 to 0.1 Hz.

The schematic diagram of the setup for the measurement of methanol transport rates through membranes is shown in Figure 1. Typically, liquid methanol and water mixtures were fed to one side of the single cell. Nitrogen and water-vapor mixtures were introduced to the other side of the cell. To eliminate the effect of diffusional resistance in the gas phase and to obtain a uniform methanol concentration over the entire channel, a recycle pump was used on the gas side.

The equilibrium contact angle was measured using a contact angle goniometer (Ramehart, Inc.) at room temperature in air with deionized water as the probe liquid. A Scintag XDS 2000TM diffractometer with a CuK α radiation source (45 kV, 40 mA) was used to collect the X-ray diffraction data for the blend membranes. DSC measurements were carried out using a differential scanning calorimeter (DSC 2920, AT Instruments) at a heating rate of 15°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Apparent Conductivity

Figure 2 shows the apparent conductivity of the Nafion[®]/VDF-HFP copolymer blend membranes

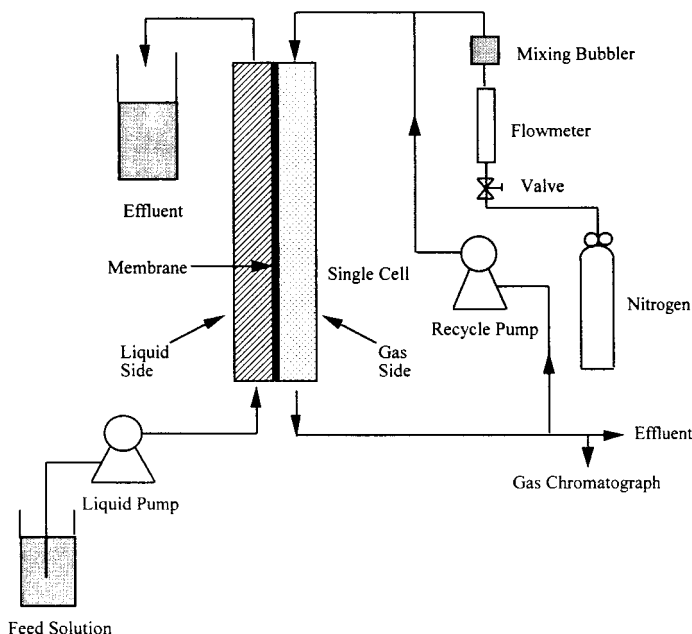


Figure 1 Schematic diagram of the setup for measurement of methanol transport rates through membranes.

as a function of the VDF-HFP copolymer content. The apparent conductivity decreases but retains a significant value with increasing VDF-HFP copolymer content until a Nafion®/VDF-HFP copolymer volume composition reaches 37.5/62.5. Compared with the pure Nafion® membrane, the blend membrane with 62.5 vol % of the VDF-HFP

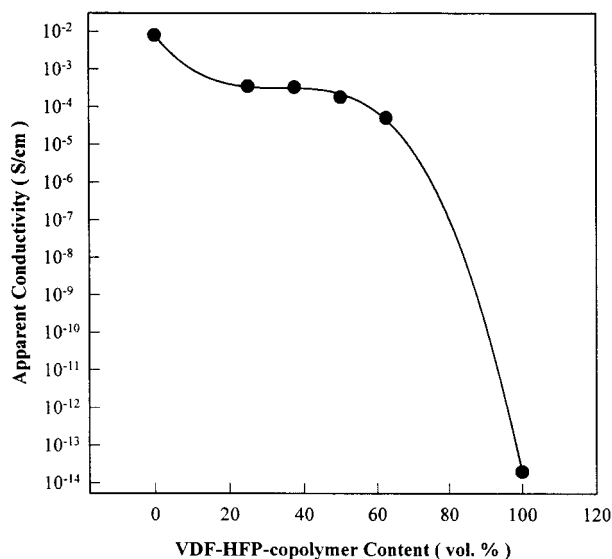


Figure 2 Apparent conductivity of the Nafion®/VDF-HFP copolymer blend membranes as a function of the VDF-HFP copolymer content.

copolymer shows a decrease in the apparent conductivity by about 2 orders of magnitude. Unlike pure Nafion® or the pure VDF-HFP copolymer membrane, the blend membranes are translucent rather than transparent and present a whitish color. This suggests that a phase-separation process takes place and the Nafion®/VDF-HFP copolymer blends are nonequilibrium two-phase systems. When Nafion® is blended with a lower volume fraction of the VDF-HFP copolymer component, the Nafion® phase is expected to remain a continuous conductive network morphology with the VDF-HFP copolymer phase dispersed throughout the Nafion® matrix phase. It is evident that incorporation of the insulating VDF-HFP copolymer causes the loss of the apparent conductivity. A cocontinuous blend morphology, based on a connected path within another connected path, of the Nafion®/VDF-HFP copolymer system is probably obtained in some range of component ratio variation.^{14,15}

If Nafion® is blended with a higher volume fraction of the VDF-HFP copolymer component, a phase-inversion process can take place. The VDF-HFP copolymer phase becomes continuous and the Nafion® forms a dispersed phase. As a result, the continuous conductive network morphology no longer exists, as indicated by the abrupt decrease in the apparent conductivity when the VD-

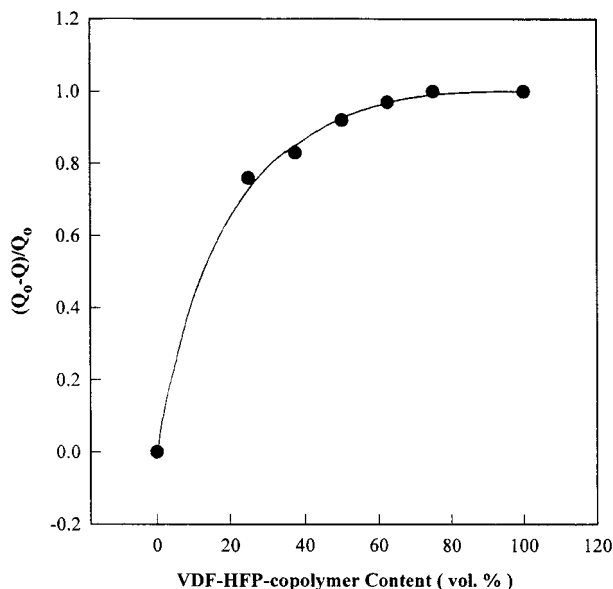


Figure 3 The methanol barrier property of the Nafion[®]/VDF-HFP copolymer blend membranes as a function of the VDF-HFP copolymer content at 45°C using a 0.8M methanol solution with 300 mL/min N₂ in the gas side.

F-HFP copolymer content exceeds 62.5 vol % (see Fig. 2). A loss in the number or a reduction in the size of the ionic clusters considered to be present in the Nafion[®] phase¹⁶ could also be a factor in decreasing ionic conductivity as the Nafion[®] content is reduced.¹⁷

Methanol Barrier Property

A parameter, $(Q_0 - Q)/Q_0$, is defined to characterize the changes in the methanol barrier properties for the test membrane systems, where Q_0 is the steady-state methanol transport rate for the pure Nafion[®] membranes and Q is that for the Nafion[®]/VDF-HFP copolymer blend membranes. Figure 3 shows the methanol barrier property of the blend membranes as a function of the VDF-HFP copolymer content. Compared with the pure Nafion[®] membrane, the methanol barrier properties increase substantially when only 25 vol % of the VDF-HFP copolymer is incorporated. It should be noted that this fact can not be explained by the inversion blend morphology as discussed above. For comparative purposes, the apparent conductivity data and methanol flux reduction for the Kaolin-filled membranes are shown in Table I. To achieve the same methanol barrier property in this inorganic powder-filled Nafion[®] membrane, a much higher volume fraction of the filler

than that of the VDF-HFP copolymer needs to be incorporated. Therefore, these results suggest that a cocontinuous blend morphology is formed or the so-called double percolation limit is reached in the Nafion[®]/VDF-HFP copolymer system even at a Nafion[®]/VDF-HFP copolymer volume composition of 75/25.^{14,15} The methanol barrier capacity increases gradually as the VDF-HFP copolymer content increases. No methanol crossover occurs through the membrane when the Nafion[®]/VDF-HFP copolymer volume composition reaches 25/75, at which the phase morphology changes. Consequently, the Nafion[®] becomes the dispersed phase while the VDF-HFP copolymer still remains continuous.

Equilibrium Contact Angle

Since a liquid makes contact with the outermost molecular layer of a surface, contact angles are sensitive to chemical and structural changes which occur at the surface. It is reasonable to consider that the surfaces of the multiphase polymer blends are heterogeneous and comprise different types of domains. Some interesting theoretical descriptions and experimental research on a surface consisting of high- and low-surface-energy domains have been done.^{18,19} Figure 4 shows the equilibrium contact angles of water drops on the Nafion[®]/VDF-HFP copolymer blend membranes as a function of the VDF-HFP copolymer content. The contact angle increases rapidly with increase of the VDF-HFP copolymer content (the lower-surface-energy phase) and then gradually leveled off when the VDF-HFP copolymer phase reaches a certain coverage. This behavior is rather similar to the plot of the advancing angle, which is a measure of the wettability of the low-surface-energy phase of the heterogeneous surface versus the percentage of the lower-surface-energy phase.¹⁹ The surface may be all VDF-HFP copolymer at a high VDF-HFP copolymer content

Table I Properties of the Kaolin Clay-filled Nafion[®] Membranes

Kaolin Clay Content (vol %)	Apparent Conductivity (S/cm)	$(Q_0 - Q)/Q_0$ ^a
30	7.4×10^{-3}	0.13
45	1.0×10^{-3}	0.33

^a Membrane thickness is about 0.018 cm.

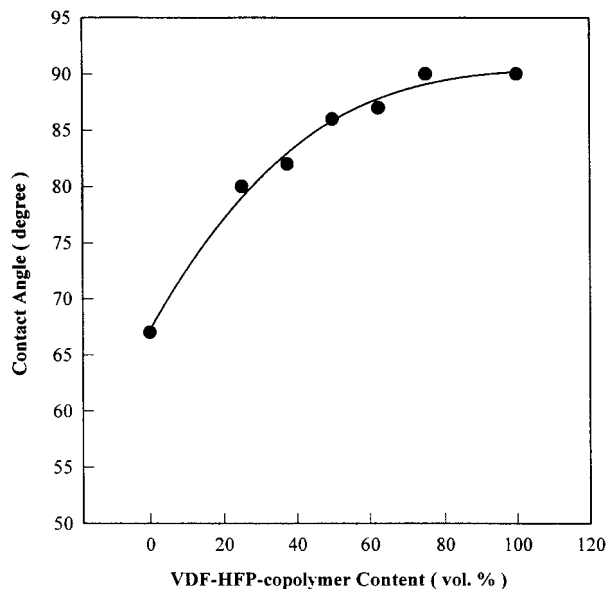


Figure 4 Plot of the equilibrium contact angles of water drops on the Nafion®/VDF-HFP copolymer blend membranes versus the VDF-HFP copolymer content.

since it appears to be breaking up the Nafion® regions. These results are consistent with increase of the methanol barrier property and decrease of the apparent conductivity with the increasing VDF-HFP copolymer.

X-ray Diffraction

It is known that both Nafion® and the VDF-HFP copolymer are semi-crystalline polymers. The X-ray diffraction studies indicate that the Nafion®/VDF-HFP copolymer blend membranes with different volume fractions prepared by solution casting also present a detectable crystallinity (Fig. 5). The pure VDF-HFP copolymer membrane presents a strong and sharp diffraction peak near $2\theta = 20^\circ$ as shown in Figure 5(a), which is assigned to the crystals of form II.^{20,22} For the pure Nafion membrane, a strong and broad diffraction peak occurs near $2\theta = 18^\circ$ as shown in Figure 5(f). Both the diffraction peak for the VDF-HFP copolymer membrane and the one for the Nafion® membrane are observed in the blend membranes as shown in Figure 5(b–e). The relative intensities of both peaks vary in proportion to their volume fractions in the blend membranes. This fact suggests that these two polymers crystallize separately when blended and cast from their solutions and that the crystallization behavior is equivalent to that of the unblended state. This result offers evidence for the incompatibility of the two polymers.²³

Differential Scanning Calorimetry

Figure 6 shows the DSC curves for the Nafion®/VDF-HFP copolymer blend membranes with different volume compositions. The pure VDF-HFP copolymer membrane presents two endothermic peaks centered at 50 and 152°C, respectively. It is obvious that the strong peak at 152°C is responsible for the melting point of the VDF-HFP copolymer. The weak peak at 50°C probably results from relaxations taking place in an amorphous region of the VDF-HFP copolymer.^{22,24} No significant change in the melting point for the blend membranes is shown in Figure 6(b–f). However, the relaxation occurring at 50°C for the VDF-HFP copolymer is substantially affected by the incorporation of Nafion®. The peak gradually shifts to higher temperature with increasing Nafion® content until the Nafion®/VDF-HFP copolymer volume composition reaches 62.5/37.5 and

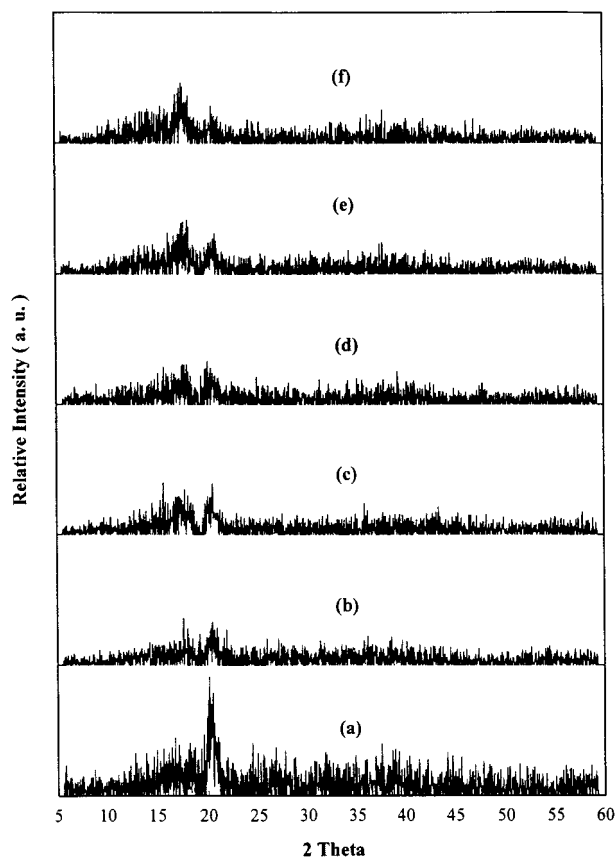


Figure 5 X-ray diffraction data for the Nafion®/VDF-HFP copolymer blend membranes: (a) VDF-HFP copolymer; (b) 25 vol % Nafion®; (c) 37.5 vol % Nafion®; (d) 50 vol % Nafion®; (e) 62.5 vol % Nafion®; (f) 75 vol % Nafion®.

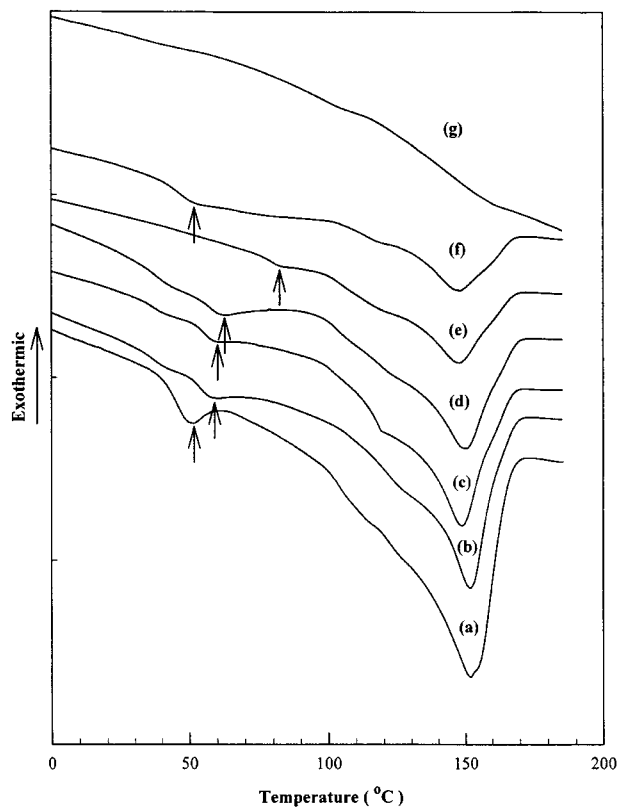


Figure 6 DSC curves for the Nafion[®]/VDF-HFP copolymer blend membranes: (a) VDF-HFP copolymer; (b) 25 vol % Nafion[®]; (c) 37.5 vol % Nafion[®]; (d) 50 vol % Nafion[®]; (e) 62.5 vol % Nafion[®]; (f) 75 vol % Nafion[®]; (g) Nafion[®].

then shifts back to 50°C for extremely high Nafion[®] contents. This behavior suggests that the relaxation occurring at 50°C is probably related to the motions of the chain which is located at the boundaries of the amorphous regions in the VDF-HFP copolymer. When the VDF-HFP copolymer is mixed with Nafion[®] in their solution forms, an interdiffusion or some other interaction between polymers takes place at the interfaces between their amorphous regions, leading to a shift in the relaxation peak. The interfacial area of the two polymers in an immiscible blend depends on the component volume fractions and the morphological features of the blend. The largest shift of the VDF-HFP copolymer relaxation peak is found for the Nafion[®]/VDF-HFP copolymer blend with a volume composition of 62.5/37.5, suggesting that the interfacial area is largest for this composition. Although the glass transition temperature of Nafion[®] has been reported at 109°C,²⁵ it is not detectable with this DSC analysis as shown in Figure 6(g).

CONCLUSIONS

Compared with the pure Nafion[®] membrane, the Nafion[®]/VDF-HFP copolymer blend membrane with 62.5 vol % of the VDF-HFP copolymer shows a decrease in the apparent conductivity by about 2 orders of magnitude. The methanol barrier properties increase substantially when only 25 vol % of the VDF-HFP copolymer is incorporated. These results can be explained by the behavior of a nonequilibrium two-phase system with a cocontinuous morphology feature, based on a connected path within another connected path, of the Nafion[®]/VDF-HFP copolymer blend system. The equilibrium contact angles of water drops on the Nafion[®]/VDF-HFP copolymer blend membranes as a function of the VDF-HFP copolymer content are rather similar to the plot of the advancing angle, which is a measure of the wettability of the low-surface-energy phase of the heterogeneous surface versus the percentage of the lower-surface-energy phase. X-ray diffraction studies indicate that these two polymers crystallize separately when blended and cast from their solutions, and the crystallization behavior is equivalent to that of the unblended state. DSC reveals that when the VDF-HFP copolymer is mixed with Nafion[®] in their solution forms an interdiffusion or other interaction of the both polymer chains takes place at the interfaces between their amorphous regions.

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