CORRELATION BETWEEN GAS AND LIQUID PERMEABILITY IN SOME NANOSILVER-IMPREGNATED AND UNTREATED HARDWOOD

HR Taghiyari

Wood Science and Technology Department, The Faculty of Civil Engineering, Shahid Rajaee Teacher Training University, Lavizan, Shabanloo St, Tehran, Iran. E-mail: htaghiyari@srttu.edu

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TAGHIYARI HR. 2012. Correlation between gas and liquid permeability in some nanosilver-impregnated and untreated hardwood. Permeability is an important physical property of wood as a porous material that determines many of its applications. The present study was therefore aimed at analysing the effects of nanosilver impregnation on specific longitudinal gas permeability as well as two longitudinal liquid permeability, i.e. first drop time and 5-cm lowering time using Rilem tube test method. Relationship between these permeability times were analysed in three native solid wood, *Populus nigra* (poplar), *Fagus orientalis* (beech) and *Carpinus betulus* (hornbeam). Specific longitudinal gas permeability values obtained were 20.77 $\times 10^{-13}$, 8.20 $\times 10^{-13}$, 7.85 $\times 10^{-13}$ and 6.10 $\times 10^{-13}$ $m^3 m^{-1}$ in poplar, beech, hornbeam sapwood and hornbeam heartwood respectively. Empty-cell impregnation process of nanosilver suspension not only washed out part of the extractives but also the pressure might have removed some of the tiny physical tissues and natural obstacles in vessel elements. Consequently, permeability increased by more than 50% in poplar and hornbeam heartwood which had simple perforation plates. However, permeability was decreased by 3.7% in beech. We hypothesised that this was due to first, the settlement of nanosilver particles or extractives that were dissolved in the suspension within scalariform perforation plates, thus, blocking fluid transfer process; and second, collapsing and accumulation of the scalariform perforation plates due to the high pressure in impregnation vessel. Clear direct relation was found between gas and liquid permeabilitiy.

Keywords: Specific gas permeability, microstructure, porosity, Rilem tube, solid wood

TAGHIYARI HR. 2012. Hubungan antara kebolehtelapan gas dan cecair dalam sesetengah kayu keras yang terimpregnat dengan nano perak dan yang tidak dirawat. Kebolehtelapan merupakan ciri fizikal penting kayu sebagai satu bahan berliang. Sifat berliang inilah yang banyak menentukan kegunaan kayu. Kajian ini bertujuan untuk menganalisis kesan impregnasi nano perak terhadap kebolehtelapan gas membujur spesifik serta dua kebolehtelapan cecair membujur iaitu masa jatuh pertama dan masa penurunan 5 cm menggunakan kaedah tiub Rilem. Hubungan antara masa kebolehtelapan dianalisis dalam tiga kayu asli iaitu *Populus nigra* (poplar), *Fagus orientalis* (bic) dan *Carpinus betulus*. Nilai kebolehtelapan gas membujur spesifik ialah 20.77 $\times 10^{-13}$, 8.20 $\times 10^{-13}$, 7.85 $\times 10^{-13}$ dan 6.10 $\times 10^{-13}$ $m^3 m^{-1}$ masing-masing untuk poplar, bic, kayu gubal *C. betulus* dan teras kayu *C. betulus*. Proses impregnasi sel kosong menggunakan ampaian nano perak bukan sahaja menghilangkan sebahagian ekstraktif tetapi tekanan mungkin menghilangkan tisu fizikal halus dan halangan semula jadi di dalam saluran. Akibatnya, kebolehtelapan meningkat melebihi 50% dalam poplar dan teras kayu *C. betulus* yang memiliki plat liangan yang ringkas. Bagaimanapun, kebolehtelapan menurun sebanyak 3.7% dalam bic. Kami membuat hipotesis bahawa ini diakibatkan oleh dua sebab iaitu (1) pemendapan zarah nano perak atau ekstraktif yang larut dalam ampaian di plat liangan skalariform lalu menghalang pemindahan cecair dan (2) tekanan tinggi di dalam salur impregnasi menyebabkan plat liangan skalariform runtuh dan tersumbat. Hubungan langsung yang jelas didapati antara kebolehtelapan gas dengan cecair.

INTRODUCTION

Understanding wood permeability is of vital importance as it has great impact on its utilisation in different industries such as wood preservation, wood drying and pulp and paper (Chen et al. 1998). Gas permeability in solid wood can be measured at 0.001 s precision and thus may be used for scientific and industrial purposes (Taghiyari et al. 2010, Taghiyari & Sarvari-Samadi 2010). Gases usually do not interact with cell wall materials but liquids may have chemical and physical interactions with them, mostly their hydroxyl groups. Permeability is important in industries that deal with impregnation or extraction of liquids from solid wood. Therefore, finding a correlation between gas and liquid permeability is important for industrial decision-making processes.

Effects of nanosilver impregnation have been studied on heat treatment of wood (Taghiyari 2011c), fire-retardant properties (Taghiyari 2011b), water and vapour absorption, and swelling but not much has been reported on the subsequent effects of nanosilver impregnation on gas or liquid permeability in solid wood. The present study was therefore aimed at analysing the effects of nanosilver impregnation of some native hardwood on gas and liquid permeability, as well as any possible relationships between them.

MATERIALS AND METHODS

Specimen procurement

Three hardwood species were chosen based on their importance in various industrial applications in Iran; they were beech (*Fagus orientalis*), poplar (*Populus nigra*) and hornbeam (*Carpinus betulus*). Three discs at breast height were prepared from each species. Discs of the hornbeam were big enough to provide us with sapwood and heartwood specimens separately but not the other two species. Specimens in each species were divided into two main groups, namely, control sample and nanosilver-impregnated specimen (NSIS). In order to minimise variation between control and NSIS specimens, dowel-shape cylinders (12 cm in length and 18 mm in diameter) were procured in longitudinal direction of trees. Two 5-cm long specimens were then cut from each 12-cm long cylinder; the upper specimen was kept as control sample and the lower specimen was measured for gas permeability before being impregnated with nanosilver suspension. For every species, 20 pairs of specimens free from any knots, fissures and checks were prepared. In order to eliminate the effects of surface finish on permeability measurement, both ends of each specimen were trimmed using a sharp cutter blade. Each specimen was covered with silicon adhesive in order to control fluid flow through only the desired longitudinal direction.

Impregnation process

Nanosilver suspension (200 ppm) was applied to the specimens using electrochemical technique. The size range of silver nanoparticles was 20–80 nm. The pH of the suspension was 6–7. Two kinds of surfactants (anionic and cationic) were used in the suspension as stabiliser; the concentrations of the surfactants were three times the nanosilver particles. Empty-cell impregnation process (Rueping method) was carried out in a 3-bar pressure vessel for 20 min. Specimens were weighed just before and after impregnation using a digital scale having 0.0001 g precision to measure the amount of nanosilver absorption, as well as after seasoning to measure the amount of possible weight loss or gain. Moisture content of specimens was 8.5% before nanosilver impregnation and when they were dried. After impregnation, all specimens and control samples were kept at room temperature for 6 months before permeability measurements.

Gas permeability measurement

Longitudinal gas permeability measurement was carried out using an apparatus designed and built by the author with millisecond precision (Taghiyari 2011a, Taghiyari & Efhami 2011) (Figure 1). Falling water volume-displacement method was used to calculate specific longitudinal gas permeability values (Siau 1971, Taghiyari et al. 2010). A total of 20 specimens were cut randomly at scattered locations from each disc for longitudinal permeability. Connection between the specimen and holder of the apparatus was made fully air-tight. A pressure gauge with millibar precision was connected to the whole structure to monitor pressure gradient (ΔP) and vacuum pressure at any particular time as well as height of water column. Moisture content of all specimens was 8.5% at the time of permeability measurement.

Three measurements were taken for each specimen. Superficial permeability coefficient was then calculated using equations 1 and 2 (Siau 1995). The superficial permeability coefficient was then multiplied by viscosity of air (μ = 1.81 × 10^{-5} Pa s) to obtain specific permeability value ($K = k_g \mu$).

$$k_g = \frac{V_d CL\,(P_{atm} - 0.074\,\bar{z})}{tA\,(0.074\bar{z})(P_{atm} - 0.037\bar{z})} \times \frac{0.760\ \text{mHg}}{1.013 \times 10^6\ \text{Pa}} \qquad (1)$$

$$C = 1 + \frac{V_r\,(0.074\,Dz)}{V_d\,(P_{atm} - 0.074\,\bar{z})} \qquad (2)$$

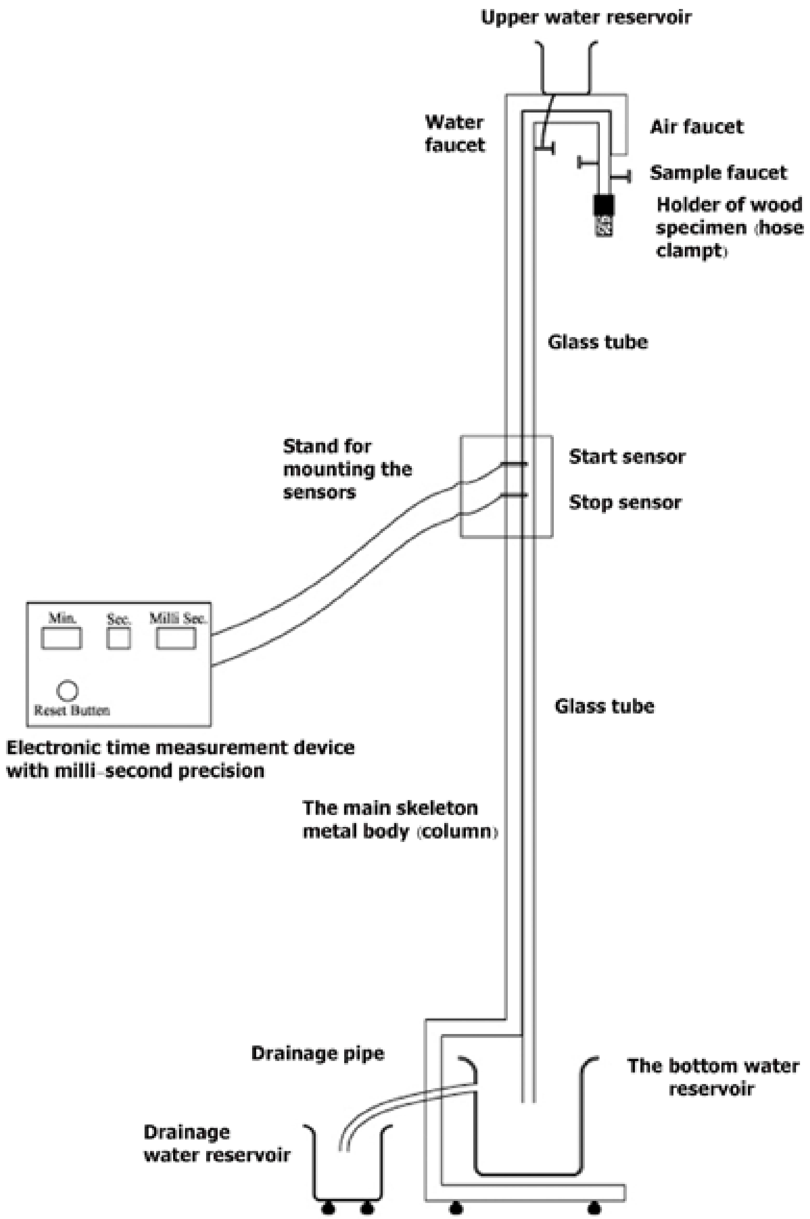

Figure 1 Gas permeability apparatus equipped with millisecond precision electronic time measurement device

where

- k_g = longitudinal specific permeability ($m^3\ m^{-1}$)
- V_d = $\pi\ r^2\ \Delta z$ (m^3); r = radius of measuring tube (m)
- C = correction factor for gas expansion as a result of change in static head and viscosity of water
- L = length of wood specimen (m)
- P_{atm} = atmospheric pressure (m Hg)
- $\bar{z}$ = average height of water over surface of reservoir during period of measurement (m)
- t = time (s)
- A = cross-sectional area of wood specimen (m^2)
- Δz = change in height of water during time t (m)
- V_r = total volume of apparatus above the start sensor (including volume of hoses) (m^3)

Liquid permeability measurement

Liquid permeability was measured using Rilem tube test method II.4 (Figure 2) according to ASTM E-514 (ASTM 2009). Two measurements were taken, the time the first drop of water falls off the bottom surface of the 5-cm long

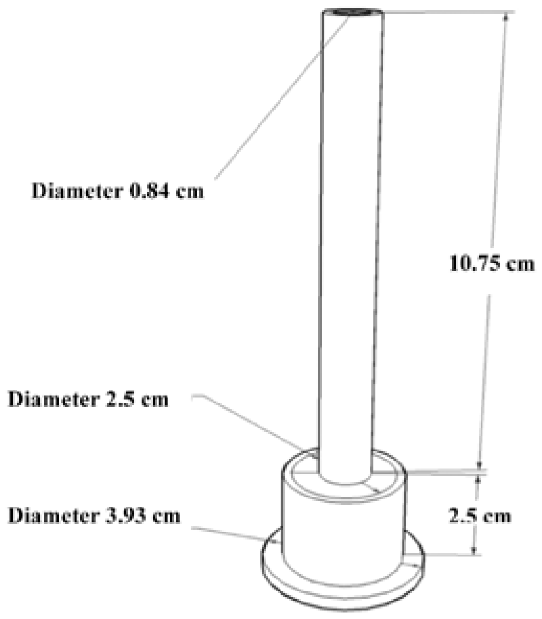

Figure 2 Liquid permeability measurement apparatus (Rilem tube)

specimen and the time the level of water in the Rilem tube reduced by 5 cm (i.e. 6.6 ml). Relationship between gas time and the first-drop time, as well as the 5-cm lowering time was then measured.

Statistical analysis

Statistical analysis was conducted using SAS software program, version 9.1 (2003) at 99% confidence level. Regression analysis and hierarchical cluster, including dendrogram and using Ward methods with squared Euclidean distance intervals, were carried out using SPSS 16 software (2007).

RESULTS AND DISCUSSION

The control specimen was located exactly on top of the NSIS; this way the two specimens had the same longitudinal axis. Therefore, the variation between the permeability of the two specimens in each pair would be theoretically minimised. However, up to 60% variation was observed between specimens in each pair. Concentrations of extractive content and pitch deposits, which block vessel perforations and pits, are not the same in different parts of tree and, therefore, permeability values would also vary significantly (Rice & D'Onofrio 1996, Taghiyari et al. 2010).

Maximum longitudinal gas permeability value in control specimens was found in poplar (20.77×10^{-13} m^3 m^{-1}) and the lowest in hornbeam heartwood (6.1×10^{-13} m^3 m^{-1}) (Figure 3). Gas permeability values in beech and hornbeam sapwood were 8.20×10^{-13} and 7.85×10^{-13} m^3 m^{-1} respectively. Nanosilver impregnation caused gas permeability to increase by 77% in hornbeam heartwood. In poplar and hornbeam sapwood, increase in gas permeability was also observed (73.8 and 45.2% respectively). In beech specimens, however, 3.7% decrease was observed.

Nanosilver absorption values were 0.2964, 0.3592, 0.3483 and 0.3413 g cm^{-3} for poplar, beech, and hornbeam sapwood and heartwood respectively. All species showed decrease in weight after drying (Table 1).

Permeability is influenced by porosity and capillary structure of wood (Flynn 1995). Therefore, perforation plates may be the reason for the increase or decrease in permeability after nanosilver impregnation. Perforation plates in poplar and hornbeam are simple. In beech, however, perforation plates are both simple and scalariform. Gas and liquid permeability will increase in species with only simple perforation plates. Considering the weight loss of specimens in this study (Table 1), it was hypothesised that the empty-cell process might have washed out part of the extractives that had blocked the way of fluid transfer. Furthermore, the pressure used in the process might have also torn apart some of the tiny physical obstacles and small tissues in the vessels. On the contrary, the perforation plates in beech are comprised of both simple and scalariform. A mixture of larger nanosilver particles and dissolved extractives might have settled down or became entangled among the tiny spaces of the plates, blocking fluid transfer process (Perre & Karimi 2002). Some of the perforation plates and tyloses that were abundant in beech had also collapsed (Figure 4) and caused a blockage in some of the active vessels of the specimen and, consequently, caused permeability to decrease.

The increase in permeability of poplar and hornbeam was not so much caused by the degradation of pit membranes but more by the great difference in longitudinal and transversal permeability values in hardwood, as well as the elements involved in the process of fluid transfer.

Table 1 The amount of nanosilver absorption and weight loss in the four treatments

Species	Nanosilver absorption ($g\ cm^{-3}$)	Weight loss (%)
Poplar	0.2964	1.439
Beech	0.3592	2.975
Hornbeam (sapwood)	0.3483	2.258
Hornbeam (heartwood)	0.3413	2.689

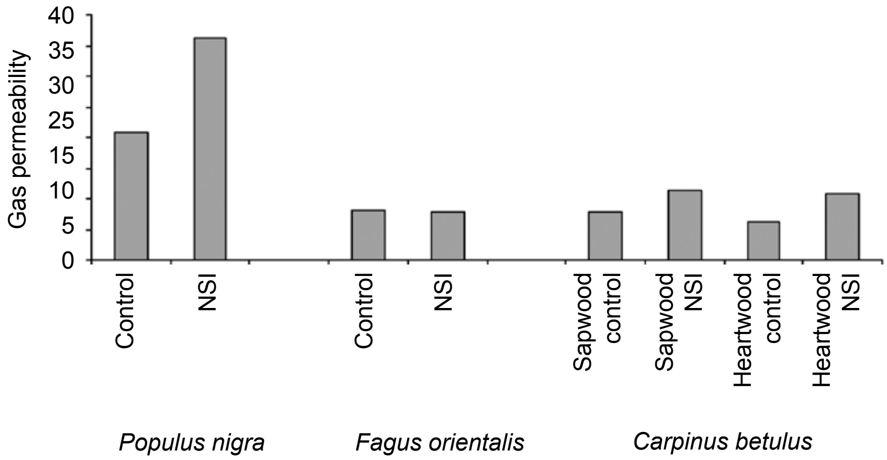

Figure 3 Specific longitudinal gas permeability values ($\times 10^{-13}\ m^3\ m^{-1}$) of different species and treatments; NSI = nanosilver impregnated

Longitudinal gas permeability was reported to be more than 3000 times higher than radial value in *P. nigra* var. *betulifolia* (Taghiyari & Efhami 2011). Moreover, when open vessels are present in hardwood, they behave as open capillaries along the entire length of the wood specimen. The large vessel diameter compared with that of pit openings makes the flow through fibres and longitudinal parenchyma insignificant (Siau 1971). In softwoods however, fluid transfer only occurs through pit membranes; so, any possible chemicals or physical factor such as high pressure that may corrupt or blow up pit membranes will significantly increase permeability (Woo et al. 2005). Future studies should include a variety of species and different impregnation fluids and pressures to arrive at a final conclusion to these hypotheses.

Minimum mean time for the first drop was 1.54 min in nanosilver-impregnated poplar and the maximum time was 42.05 min in control beech specimens (results not shown). The minimum time taken for the water level to reduce 5 cm in the Rilem tube was 53.97 min in nanosilver-impregnated hornbeam heartwood, whereas the maximum was observed in nanosilver-impregnated beech specimens (6,049.35 min).

Regression analysis for first drop and 5-cm lowering times showed significant and rather high r^2 values between gas and liquid permeability times (Table 2). Therefore, both time-measuring methods for liquid permeability may be used as criteria for permeability evaluation with the gas permeability values. Cluster analysis of different species and treatments in the present study, however, clearly showed that gas permeability and liquid permeability (first drop) were closely clustered (Figure 5). The 5-cm liquid permeability was clustered rather differently. It may then be concluded that in 5-cm long specimens of hardwood, whether nanosilver impregnated or not, first drop measuring time would give a better scope of longitudinal gas permeability values.

CONCLUSIONS

Nanosilver impregnation using empty-cell process washed out part of the extractives

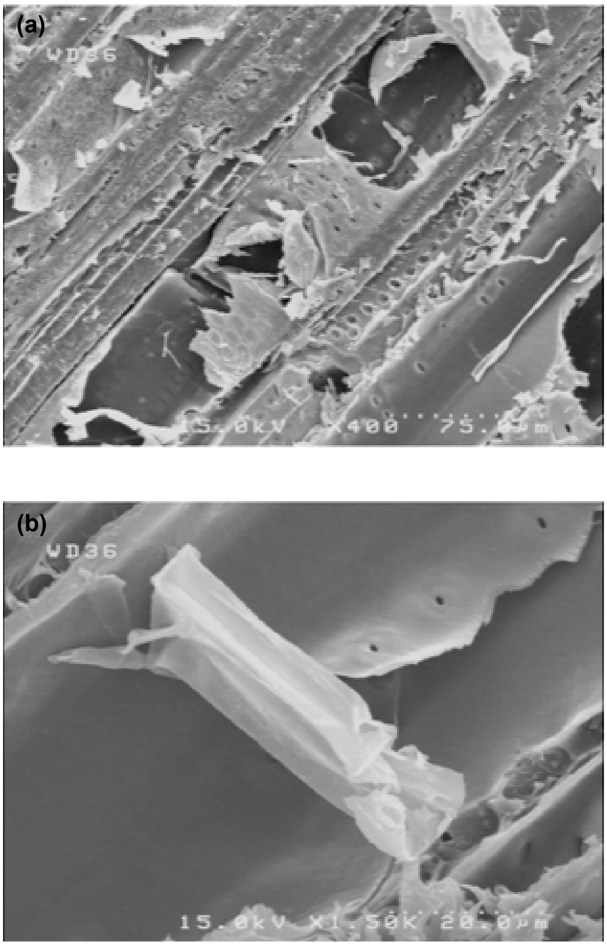

Figure 4 SEM micrographs of (a) tyloses and (b) scalariform perforation plates blocking fluid transfer in vessel elements of beech species

Table 2 Regressions analysis for correlation between times for gas and liquid (first drop and 5-cm lowering times) permeability

Species and treatment	Poplar	Poplar NSI	Beech	Beech NSI	Hornbeam sapwood	Hornbeam sapwood NSI	Hornbeam heartwood	Hornbeam heartwood NSI
r^2 (Gas—first drop)	0.60 ** (+)	0.84 ** (+)	0.75 ** (+)	0.82 * (+)	0.76 ** (+)	0.17 ns	0.99 ** (+)	0.95 ** (+)
r^2 (Gas—5-cm lowering)	0.90 ** (+)	0.95 ** (+)	0.59 ns	0.99 ** (+)	0.51 * (+)	0.15 ns	0.99 ** (+)	0.96 ** (+)

* and ** = statistically significant at 5 and 1 % confidence levels respectively, ns = not significant; NSI = nanosilver impregnated; (+) positive

in the wood, resulting in an increase in gas and liquid permeability. Perforation plates played an important role in the increasing or decreasing effect of nanosilver impregnation on permeability. Collapsing and accumulation of scalariform perforation plates and tyloses in beech due to high pressure in the impregnation vessel blocked fluid transfer and caused permeability to decrease. A high correlation was found between gas and liquid permeability. However, from the cluster analysis, it was concluded that first drop time would give a better criterion for estimation of gas permeability in solid wood.

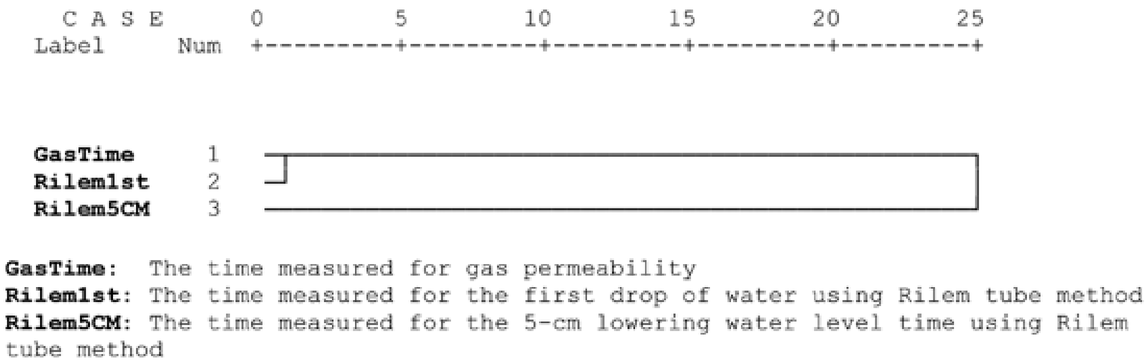

Figure 5 Cluster analysis for gas and liquid (first drop and 5-cm lowering times) permeability based on different species and treatments in the present study

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