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Kolonnenschäumen I: The Technique of Laminae Column Foaming

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Summary

Laminae column foaming is a special type of column foaming (foam separation). The foam is degraded to fast-moving, nearly planar laminae, which are rinsed by reflux. The method is distinguished by a simple technique, quick establishment of the steady state, and the possibility of working even with low-foaming solutions and handling small quantities of substances. The uncomplicated surface formation and laminae/wall system enable the principles of foam separation to be studied. The phenomena of laminae column foaming are described, as are types of laminae producers, countercurrent columns, and laminae destroyers, and a complete apparatus with circulating gas. Column foaming is compared with column distillation and column crystallization, and its place in the system of column separation methods is discussed.

INTRODUCTION

A foaming solution can be separated into foaming fractions and a nonfoaming or only slightly foaming residue in an apparatus based on long-known principles described by, e.g., Wo. Ostwald et al. (*1,2*) in the 1930's.* A gas (compressed air or, better, nitrogen) streaming from a fritted filter, metal net, or capillary produces bubbles in the liquid, which collect on the surface to a more or less stable, more or less fine- or coarse-structured foam. In general, surface-active sub-

* A review of recent investigations and new techniques was published by R. Lemlich during translation of the submitted manuscript [*Ind. Eng. Chem.*, **60**(10), 16 (1968)].

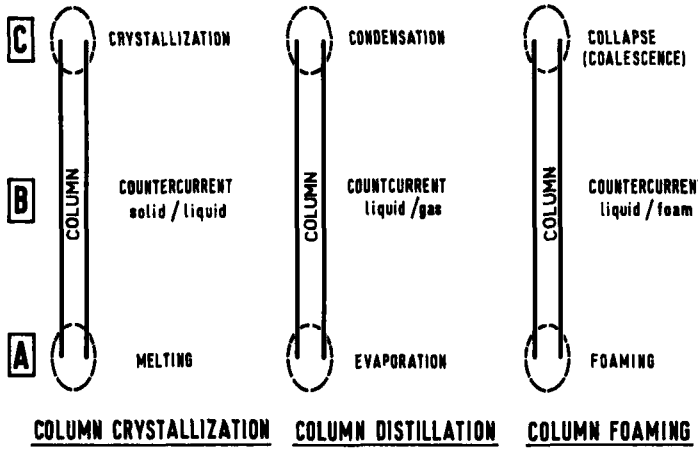

FIG. 1. Column foaming compared with the countercurrent separation processes of column crystallization and column distillation.

stances are concentrated into the foam fractions; the well-formed foam of some substances shows no shift in concentration from that in the aqueous residual solution [e.g., *Säuregrün* (*1*)].

In a wet foam bubbles first carry an excess of liquid with them, which drains back as the foam rises in a tube. If now the foam is completely destroyed at the upper end of this *column* and converted into a reflux, then conditions are produced similar to those in the countercurrent separation processes of column distillation and column crystallization (*3,4*). See Fig. 1.

For comparison one can divide the columns for column crystallization (CC) = *Kolonnenkristallisieren* (KK), column distillation (CD) = *Kolonnendestillieren* (KD), and column foaming (CF) = *Kolonnenschäumen* (KS) into three regions with the functions shown in Table 1.

So much for analogy. In column distillation and column crystallization the characteristic multistage nature of the column processes depends on the interconversion of the phases that move counter to each other and are continuously evaporating and condensing or melting and crystallizing. However, even though in the usual column procedure for foaming some foam is destroyed into the liquid phase, no new foam is created in the column-range (B). Function (B) consists of drainage of the liquid adhering to the foam bubbles—somewhat in analogy to the drainage of mother-liquor from a crystalline solid phase. This

TABLE 1

Function	CC (KK)	CD (KD)	CF (KS)
(A)			
Phase change	Melting	Evaporation	Foaming
Phasenwandel	*Schmelzen*	*Verdampfen*	*Verschäumen*
(B)			
Two phases, countercurrent	Countercurrent flow, solid/liquid	Countercurrent flow, liquid/gas	Countercurrent flow, liquid/foam
Gegenstrom, zweier Phasen	*Gegenstrom, fest/flüssig*	*Gegenstrom, flüssig/gasförmig*	*Gegenstrom, flüssig/schaumförmig*
(C)			
Reverse phase change	Crystallization	Condensation	Collapse (Coalescence)
Phasenrückwandel	*Kristallisieren*	*Kondensieren*	*Kollabieren*

action, however, is supplemented by rinsing, extraction, and exchange effects of the reflux. New foam is created only when the liquid reflux reaches the bottom of the column (A). Separation is thus continuously improved until an equilibrium (steady state) exists. Even modern apparatuses for foam separation functioning under total reflux form practically no new foam at (B) [cf. Harper and Lemlich (*5*) and Karger et al. (*6*)]. Ostwald and Mischke (*7*) indeed carried out their foaming cycle in such a way that most of the liquid draining from the foam was collected outside the column and was only then reintroduced to the frit; strictly speaking, this process is not a *column* process like CD and CC. However, in a stable foam–liquid system the *temporal succession* of separations is finally converted into a *spatial juxtaposition* along the countercurrent stream, provided that continuous foam formation prevents rapid back-mixing. In combination with rinsing effects the expression *Kolonnenschäumen* (*column foaming*) thus seems permissible. Nevertheless, the problem of simultaneous multiple foaming has previously been solved in practice (*7*) and in theory (*8*) in the same way as originally for distillation and crystallization: several units are arranged one behind the other. Attempts to combine the individual steps within a single column, as in CD, and thus to achieve true *column* foaming will be published elsewhere.

The foam separation techniques described generally operate with a

foam of more or less fine bubbles. From observations of a gas-washing flask, a modified technique for separation of surface-active substances was deduced. The foam is degraded to almost planar laminae, which pass to the column tube at a rate of 0.1 to 1 m/sec and collapse at the upper end of the column. With the above limitation this method should be called *Lamellen-Kolonnenschäumen* (*laminae column foaming*). It is characterized by very rapid establishment of the steady state, by surface formation even in solutions that barely foam, and by a simple technique. Conversion to the micro scale is possible (0.1 ml achieved to date).

PHENOMENOLOGY

If a glass tube is pulled out to a narrow orifice at the bottom and is filled with an aqueous solution of a surface-active substance to a height of a few millimeters, and if compressed air or nitrogen is blown in at the lower end or vacuum is laid on at the upper end, then—in a specific pressure region—thin laminae will be formed from the solution. The pressure required depends on, inter alia, the diameter of the column, the concentration, and the viscosity. The laminae are slightly curved toward the region of lower pressure. Visual demonstration of the separation on the rising laminae is best done with a colored test solution. An aqueous solution of surface-active Patent-Blue (PB) and surface-inactive red Neucoccin (NC) may be used; this also permits comparison with the results of earlier foaming methods (*1,7*).

As the difference in pressure at the two ends of the column is increased, surface formation passes through three stages:

1. Laminae rise slowly (a few centimeters per second), separated by a few centimeters, with a broad border of liquid on the tube wall and a relatively short path upward.
2. Very thin laminae rise rapidly (0.1 to 1 m/sec), separated by 3 to 10 mm, with a long upward path.
3. Turbulent mixing of liquid and gas occurs in the lower part of the column, and foam is formed.

The second stage, where the succession of laminae should be dense and as constant as possible, gives the fastest and most complete separation (cf. the column with laminae drawn in, Fig. 5).

The initial violet PB + NC solution is separated into a series of

violet laminae which, proceeding upward, become increasingly bluish-violet and then blue, finally collapsing at the upper end and forming the liquid reflux. The liquid, which is now richer in surface-active Patent Blue, runs down the tube wall, flowing over the rising laminae that it meets in its path and giving its Patent Blue up to them. The reflux thus changes its color through bluish-violet to reddish-violet and is converted at the bottom of the column into new laminae. A slight difference in color between reflux and rising laminae is characteristic of a well-arranged column. Separation is considerably decreased if the liquid phase passes the fronts of the individual laminae too quickly. In the ideal case a pure red solution, completely free from the foaming dyestuff, collects at the lower end of the column. Conversely, in the foam separation of more than one substance the surface-active component enriched in the foam always seems to be accompanied by a certain amount of the surface-inactive substance [compare the enrichment and impoverishment curves in Ref. (7)].

The time required for establishment of equilibrium, i.e., the time until no further separation can be recognized, depends on, inter alia, the foam-forming system, the concentration, and the size and type of the column. With 10^{-5} to 10^{-1}% aqueous solutions of PB/NC in columns of 4 to 30 mm i.d. and 0.5 to 7.5 m length, times ranged from a few tens of seconds to 1 hr. With decreasing volume of starting solution the time required is decreased and the quality of separation increased. The best results have been achieved if, during operation, the height of liquid in the laminator was only about the same as the diameter of the column tube, the remaining parts of the apparatus containing twice to ten times this quantity in the form of laminae and reflux; exact ratios depend on the system and the type of column. Independently of this maximum, very dilute solutions naturally show the effect of enrichment by bubble fractionation (5).

TECHNIQUE

Certain rules, applied to laminae column foaming, should ensure a regular succession of laminae, prevent premature collapse of the laminae and formation of fine bubbles in the columns, and provide a good countercurrent with the reflux flowing slowly downward. The variations studied will be treated according to the three basic elements in Fig. 1.

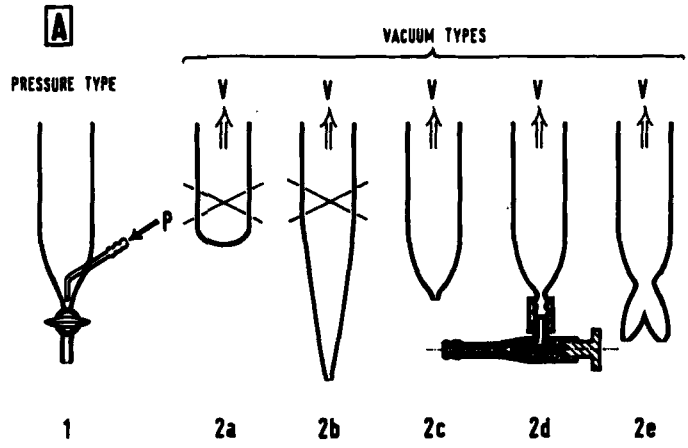

FIG. 2. Laminators for laminae column foaming.

Phase Change: The Laminator

The pressure-type laminator A1 (Fig. 2), operated with compressed air or nitrogen, was used for the first experiments. Its rounded form leads to a largely undisturbed formation of laminae, and it transforms the whole starting solution into laminae. During the separation, new surface is formed immediately from the reflux and without mixing with a long column of liquid.

However, the laminae are often destroyed in the laminator by the high pressure needed for long columns; or, because of the pressure, the gas streams through the liquid without regular formation of laminae. So it became customary to apply a vacuum to the head of the column or to use the gas-circulation technique described below. Type A2c, which corresponds to A1, was devised as a mean between two extremes: type 2a, with its flat end, provides too broad a base for the liquid, and with a medium-sized orifice the liquid is pressed like a fountain; type A2b, with its snout-like end, distributes the gas uncontrollably through the liquid; at high gas velocities a process akin to boiling leads to a foam of fine bubbles.

The pressure or vacuum needed for regular formation of laminae depends on the viscosity and foaming power of the solution and is best controlled by a screw valve with a nozzle 0.2 to 2 mm wide (according to the diameter of the column; type A2d); this device is particularly useful with gas circulation. The special type A2e—with two laminators—provides laminae with both right-handed and left-handed oscil-

lation. Substance can be fed in and fractions can be taken out without interrupting the separation in the column. Type A2d has proved best for general work.

Countercurrent Stream of Two Phases: Types of Columns

In region (B) of the column the rising laminae are to loose liquid and are to be washed by the liquid draining from the surfaces and by the reflux formed in the phase-reverser (C).

The simplest form of column, B1a in Fig. 3, consists of straight, smooth glass tubing whose diameter has been chosen according to the foaming power and viscosity of the solution used (see below). The relatively small surface and the limited quantity of liquid that it can accommodate are disadvantages; if the column is overloaded, the countercurrent of liquid breaks suddenly through the laminar front, depreciating the separation. Better wetting and higher capacity for liquid phase are provided by etching the glass surface or roughening it by sandblasting (types B1a′, B1b′). Angled tubes such as B1b provide long useful length, a rate of reflux reduced by the inclination, and an interesting flooding of the laminae at the corners. The laminator must, of course, be sealed on vertically.

Type B2 can be considered as a simplified Vigreux column with points running in the direction of the current, so as not to destroy the

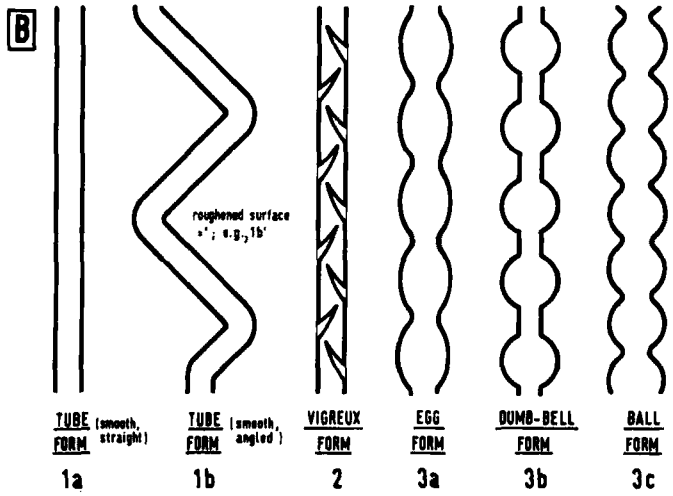

FIG. 3. Types of column for laminae column foaming.

laminae prematurely. Type B2 is suitable only for solutions of medium foaming power; at one extreme laminae burst at once, at the other foam is formed. Columns of type B1a with a few peaks every 10 cm gave particularly good separations.

Columns of type B3a to B3c, with their large surfaces, are known as condensers. When tested, the bulb type B3a with no sharp bends proved advantageous. If, too wide—more than a ratio of about 1:4—it becomes mostly full of useless foam. For large tubes at the limit of laminae stability egg-shaped units are to be preferred. The unsuitable dumbbell type leads to formation of foam in the tube, which then deposits in the bulbs.

Phase Reversal: The Delaminator

Laminators and columns must be free from sharp bends and edges, must have a limited diameter, and should not have a water-repellent surface. However, these properties are desirable at the top of the column in order to provide total reflux without complicated mechanical or thermal arrangements or long delay. Figure 4 shows various delaminators.

The containment of foam in a ring of silicone grease, known from preparative work, contaminates the apparatus; as shown in C1, however, an insert of PTFE or other water-repellent plastic is suitable.

When solutions foam only slightly, the upper end of the column can be closed by a bulb or ellipsoid (C2a). When the foam is more stable a series of 3–10 successive egg-shaped units (C2b, cf. B3a) can be

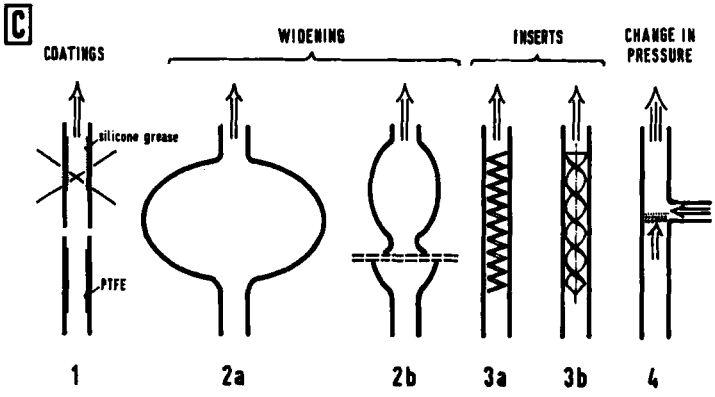

FIG. 4. Delaminators for laminae column foaming.

used, but the narrow parts must be at least twice to three times the diameter of the column; at the beginning of the separation process the hollows fill with foam from the laminae residues, and further laminae come to rest there and are converted into reflux.

The best results have been obtained with inserts. The spiral type C3a is useful only for weakly foaming liquids, since stable laminae break through. Bands of stainless steel, aluminium, or glass, twisted about their axis, as devised originally for another purpose (*9*) fill with foam and provide a break of also stable laminae; while owing to the twin passages they do not hinder removal of the carrier gas. Optimally, form C3b is combined with PTFE coating.

Finally, laminae that are not too stable can be destroyed by a change in pressure in the column. In type C4 the quantity of gas per unit area is suddenly increased at the position shown by dotted lines, and the laminae burst. This principle can be used so as to change the useful length of columns in series of tests, and further production of laminae can be steered as in type A2d.

Apparatus of Type A2d/B1a/C3b for Laminae Column Foaming

The various types within groups (A), (B), and (C) can be combined at will and lead, for example, to the particularly simple type shown in Fig. 5.

The smooth, straight column tube has at its upper end a twisted metal or glass strip as delaminator; the lower end is drawn out to a nozzle of 1 mm internal width. The gas stream is regulated by a small valve or by a screw clip on rubber tubing. The water pump on the chemist's bench makes him independent of compressed air, which usually contains oil (see below for the water-blower drawn instead of a water-pump). The vacuum method incidentally gives more stable laminae and thus better separations. For batchwise working the initial solution is sucked in through the lower stopcock, transformed into laminae and reflux, and sucked off through stopcocks at the upper and lower ends of the column. For small columns glass vessels with screw caps and rubber discs are suitable; the samples can be added and removed by a syringe.

The favorable tube diameters shown in Fig. 6 were determined by means of a series of dilutions made from 0.1% solutions each of Patent Blue and Neucoccin. The largest diameter is limited by the stability of laminae, the smallest by the cohesion of the liquid.

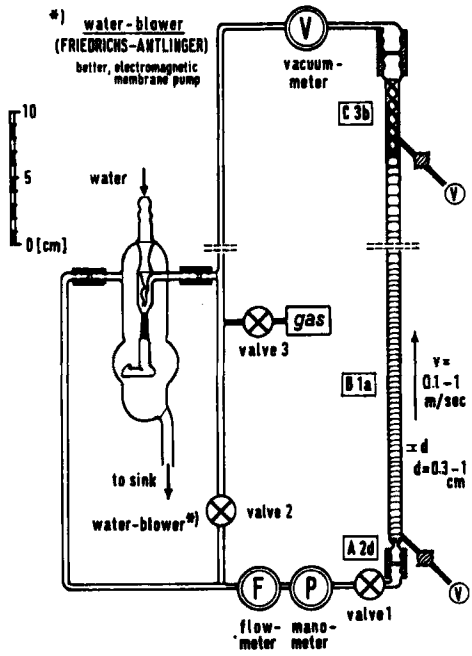

FIG. 5. Apparatus of type A2d/B1a/C3b for laminae column foaming, arranged for gas circulation.

The lower limit of about 4 mm for aqueous systems can be exceeded if the starting solution is added at the bottom carefully and only in an amount sufficing to fill the column space with laminae and to provide reflux on the wetted wall. In this way 0.1 ml of the PB/NC dyestuff solution was freed from PB in a tube of 30 cm length and 2 mm i.d.

Above a minimum length the separation of the colors is visibly proportional to the length of the column. With a tube of 10 mm i.d. the lower limit for satisfactory separation is about 1 m (I), but 2 m (II) is recommended. The 7.5-m column (III) has a correspondingly greater effect. The initial charges were 10–20 ml for II and 50–100 ml for III. The longer column allows greater throughput if starting solution is added continuously in the middle range (the broken part of the column in Fig. 5); the larger volume and the longer separation passage also aid buffering of temporary overloading. Times required for steady state at 10 mm i.d. amount to 1–20 min at II and 10 min to 1 h at III, depending on the system and the amount of filling.

In a run with type III, samples were taken after 1 h and again after 3 h and, after dilution, examined spectroscopically (Fig. 7). In both cases the residue was mostly free from surface-active PB; still faster and relatively greater concentration effects were obtained with greater dilutions. As mentioned previously the top fraction with enriched PB always contains traces of surface-inactive NC. The dyestuffs appeared noticeably more concentrated in the samples used for the second set of spectra, owing to water evaporation. To prevent loss of liquid many workers saturate the gas with water vapor before its introduction into the column [cf., e.g., Ref. (*5*)]. Gas transport and moistening can be elegantly combined by means of the water-blower (Friedrichs–Antlinger; commercially obtainable). Figure 5 shows the closed gas circulation with low losses and constant saturation. For readily water-soluble, dangerous, or expensive gases an oil-free, electromagnetic, membrane pump made of stainless steel and PTFE is recommended. Operation of the water-blower or membrane pump is controlled by a short circuit with valve 2 in parallel with the column; a further valve regulates the vacuum in the column corresponding to A2d. A reservoir provides gas for the whole system via valve 3. Measuring apparatus consists of a pressure and a vacuum manometer and a flow-meter; a photoelectric laminae-counter may be added.

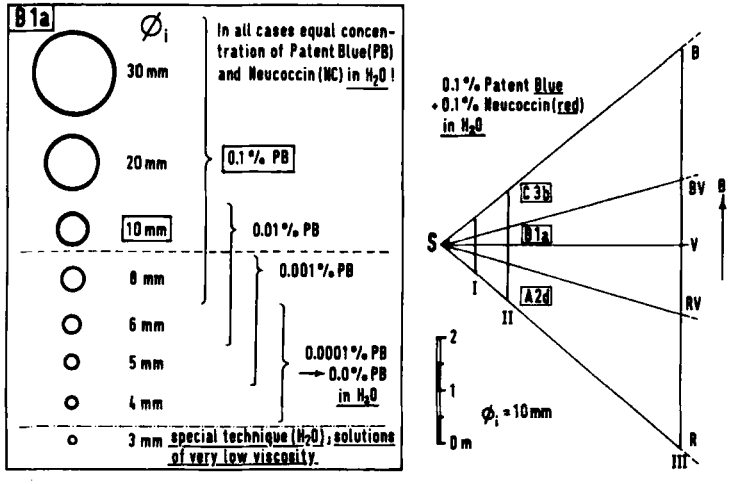

FIG. 6. Favorable tube diameters for laminae column foaming of aqueous solutions of Patent Blue and Neucoccin. Relation between column length and separation efficiency in the same system; R = red, RV = reddish-violet, V = violet, BV = bluish-violet, B = blue.

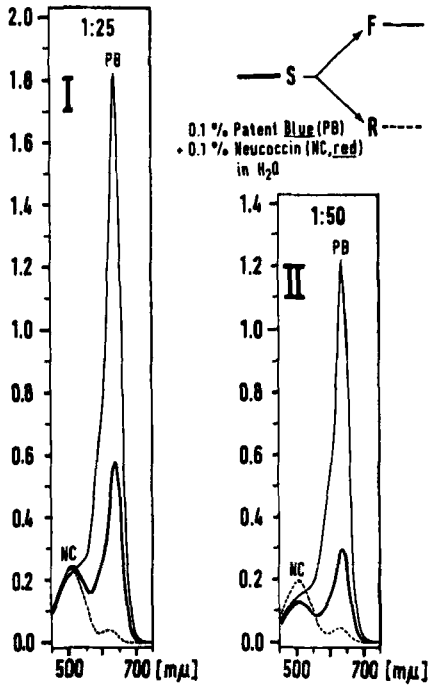

FIG. 7. Laminae column foaming of a solution of Patent Blue (0.1%) and Neucoccin (0.1%) in water; $\ell = 7.5$ m, i.d. $= 10$ mm, $p = 80$ mm Hg (valve); $t_I = 1$ h, $t_{II} = 4$ h; dilution I $= 1:25$, dilution II $= 1:50$.

In the 2-m column with 10 mm i.d. at, for instance, a laminae interval of 5 mm and a throughput rate of 0.5 m/sec, 100 laminae are produced per second, corresponding to about 75 cm²/sec of laminae faces. The whole column with its reflux-wetted wall surface of about 600 cm² contains an average of 150 cm² of laminae faces = 300 cm² of free laminar surface. From 10 cm³ of starting liquid in 150 cm³ column volume during the 10 min required for steady state about 9 m² of free laminar surface are formed.

Laminae column foaming, combined with gas circulation, is useful particularly for fundamental studies in foam separation, because liquid and gas can be readily varied. The surface produced is clearly determinable from the number of laminae, and the enrichment and washing can be studied particularly effectively with dyestuff solutions by the simple units of laminae and wetted wall. In the literature, to date it seems that only McBain et al., studying the Gibbs adsorption

theorem, added a short length of tube containing slowly moving *planar laminae* behind a bubble-separation column (*10*). However, they did not work out an effective method of separation by means of controlled production and destruction of laminae.

Acknowledgment

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