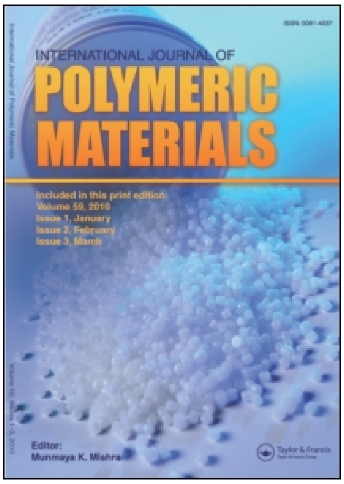

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ON THE FORMATION OF POLY (P-PHENYLENE TEREPHTHALAMIDE) PULPS FROM STIRRED SOLUTIONS

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ON THE FORMATION OF POLY (p-PHENYLENE TEREPHTHALAMIDE) PULPS FROM STIRRED SOLUTIONS

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PPTA (poly (p-phenylene terephthalamide)) may precipitate directly from stirred solution by the use of glycerol or glycerol/water coagulant in fibrous pulp form—short fibers with attached fine fibrils that are called PPTA pulp. Scanning electron micrographs show that the precipitated PPTA pulps have a ribbon-like structure similar to Twaron pulps. The wide-angle X-ray diffraction patters of the resultant pulps exhibit three diffraction peaks at 2θ–20.5, 23.5, and 28.5 corresponding to the {110}, {200}, and {004} crystal faces of PPTA fibers, and the peaks are not as sharp as those of fibers. The process yields PPTA pulps with properties such as specific surface areas and mean length depending on the stirring speed, and the ratio of the viscosity of the PPTA/H_2SO_4 solution to that of the coagulant. The inherent viscosity of the pulps determined by that of the PPTA bulk, which can be easily polycondensated to the desired specification.

Keywords: PPTA (poly (p-phenylene terephthalamide)) pulp, hydrodynamically induced precipitation, morphology

INTRODUCTION

PPTA fibers have many merits, such as superior tensile properties, good chemical and environmental resistance, and excellent thermal properties, including elevated temperature working ability, non-flammability, and high dimensional stability [1], and PPTA pulp is essentially the same polymer, modified in form and size so as to be

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dispersible. The pulp fibers are short (0.5–8 mm) with many fine fibrils attached; the fibrils are complex, curled, branched, and often ribbon-like [2]. By virtue of their extraordinary combination of properties, PPTA pulps have a broad variety of uses, for example, brake pads and linings, friction paper, gasket paper, and compressed gaskets [3].

Traditionally, PPTA pulps have been produced by cutting the PPTA filaments with a special cutting device into short fibers of 20 mm in length. The fibers are then mechanically refined to split the original fiber and to reduce the diameter to about 12 μm, whereas the average length of the fibers is shortened to between 2 and 8 mm [4–6]. The finalized pulps contain an abundance of curling and branching fibrils, which make pulps having higher specific surface area and uniform dispersability in a matrix polymer, whereas a certain length of the pulps provides the matrix with high strength and modulus and PPTA pulps has been proven to be excellent for the reinforcement of elastomers or resins [7]. Unfortunately, in the customary process, the spinning process is very complicated and special cutting device is needed for high strength PPTA filaments, which is economically disadvantageous in industry. PPTA pulps have also been directly made through polycondensation by adding p-phenylene diamine (PPDA) and terephthaloyl chloride (TPC) to a solvent system of N-methyl pyrrolidone (NMP) in the presence of a metal halide salt (such as calcium chloride ($CaCl_2$)) and a tertiary amine (such as pyridine) by H. S. Yoon [8, 9]. Even though this method makes it possible to produce PPTA pulp without difficult and complicated spinning process, the polymerization is rapidly terminated and control of the polycondensation process becomes very difficult because of the additional tertiary amine, which has also caused environment hazard due to nasty odor emitted by the reaction. Recently, Lee reported a new way to prepare the fibrous pulps by a heterogeneous combination of PPTA with poly (vinyl pyrrolidone) (PVP) based on Yoon's method [10]. The PVP should have a viscosity average molecular weight (M_η) greater than 100,000 and its content should be more than 5 wt% so that in the pulp the PVP molecules can surround all of the PPTA domains. The resultant pulps are stalk-free and have a high aspect ratio and also the process has avoided both complicated spinning process and noxious pyridine. However, the high molecular weight PVP has caused a serious processing problem due to its poor solubility and extremely high viscosity. Therefore, it is still a challenge to avoid a complicated spinning process and special cutting device and to obtain stable properties, such as high inherent viscosity, high degree of fibrillation, and a certain mean length in the final product.

A new approach to forming PPTA pulps is introduced in this article. PPTA pulps were directly prepared by adding the PPTA/H_2SO_4 solution to a coagulant under shear flow conditions. That is, a PPTA concentrated sulfuric acid solution was injected into a rapidly stirred coagulant, which was made of glycerol or glycerol/water solution, to form PPTA pulps. The preparation of fibrous PPTA pulps by this precipitation method has not been previously described. The aim of the present work is chiefly concerned with the effect of the processing parameters on the properties of PPTA pulps, and to discuss the mechanism of pulp formation.

EXPERIMENTAL

Materials

PPTA granules were manufactured in the laboratory by polycondensation of p-phenylene diamine (PPDA) with terephthaloyl chloride (TPC) in solvent system of N-methyl pyrrolidone (NMP) with calcium chloride ($CaCl_2$), having inherent viscosity 6.78 g/dl (measured by dissolving PPTA in 96–98% sulfuric acid at 30°C with a capillary viscometer diameter of 0.85–0.90 mm [8–10] and weigh-average degree of polymerization of about 300, according to the Mark-Houwink relationship obtained by Arpin and Strazielle [11]. Concentrated sulfuric acid (99.8%) was created by 96–98% sulfuric acid of A.R. and 50% oleum supplied by the second Zhenxin Chemical Factory, People's Republic of China. Glycerol of A.R. was supplied by the Yi Gali Chemical Agent Company, People's Republic of China. Type 1095 of Twaron pulps was supplied by Akzo Nobel Company of the Netherlands.

Preparation of the PPTA/H_2SO_4 Solutions and Precipitation of the PPTA Pulps

For the dissolution of PPTA granules in concentrated sulfuric acid, they were first dried for several hours at 105°C under vacuum and then dissolved in concentrated H_2SO_4 for 2–3 h under constant stirring at 50°C, forming a yellow viscous transparent solution. The concentration of PPTA solution was set to be 1.0, 1.5, 2.0, 2.5, 3.0 wt%. The PPTA pulp formation experiments were carried out in round bottom flasks with a simple PTFE (polyterafluoroethylene) paddle stirrer driven by a variable speed motor. The method of PPTA pulp formation was coagulation of droplets of PPTA/H_2SO_4 solution in sheared coagulants of glycerin or glycerin/water solution. The PPTA pulps were precipitated in a few minutes, then were filtered and dried under vacuum to constant weight.

Characterization of the PPTA Pulps

Inherent viscosity of PPTA pulp, the degree of fibrillation, and the mean length are three important variables that determine the properties of the pulps [2]. Here, I.V. of the pulp is determined by that of the PPTA granule depending on the polycondensation process. The degree of fibrillation and the mean length can be systematically controlled during the precipitation process.

Observation of the Morphology of the Resultant Pulps

The morphology of pulps was studied by the Camscan Series 4 scanning electron microscope (SEM) from England.

Measurement of Crystallinity of the Resultant pulps

The crystallinity of the resultant pulps was studied by means of wide X-ray diffraction patterns, which were obtained with a Rigaku-D/Max-rb instrument from Japan.

Measurement of the Specific Surface Area of the Resultant Pulps

The photomicrographs show only a two-dimensional image of the three-dimensional fibril structure and it is impossible to characterize the fibril structure with sufficient accuracy by digital image analysis. A reliable and quantified way of measuring the degree of fibrillation of PPTA pulps is to determine the specific surface area with the BET (Brunner-Emmett-Teller) method [12]. The specific surface area, measured in m^2/g, increases as the fiber is fibrillated. The specific surface area of unfibrillated PPTA yarn is less than $1\,m^2/g$, whereas that of typical Twaron pulps has specific surface area of between 5 and $12\,m^2/g$.

Measurement of the Mean Length of the PPTA Pulp

The mean length of the pulps was calculated in the following way: Specimens consisting of a hundred individual pulp entities taken occasionally were dispersed in water, observed by microscopy, the lengths of 20 fibrils were measured and recorded and the mean value calculated.

Observation of Diffusion Process

The process of coagulant diffusing across the boundary between PPTA solution and the coagulant of glycerin was observed with microscopy and recorded by a camera. The color (red ink, supplied by Shanghai Ink Factory of China), which had been added to the coagulant in small amounts, was just sufficient to provide the necessary contrast for the photographic recordings.

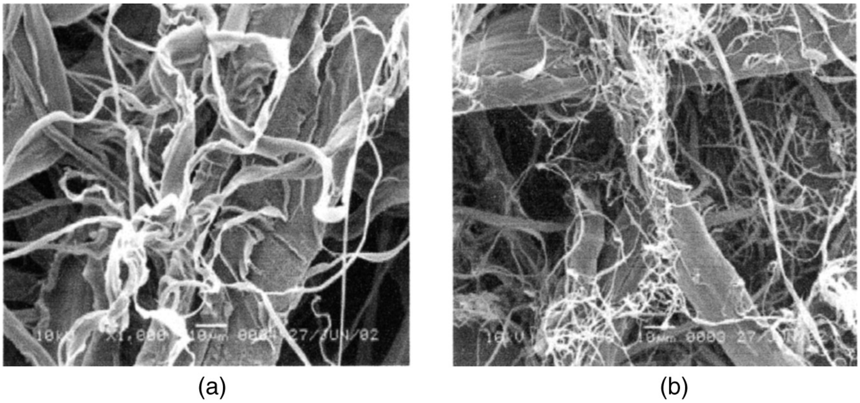
RESULTS AND DISCUSSION

Morphology of the PPTA Pulp

The scanning electron micrographs of typical PPTA pulp produced by this precipitation method and Twaron pulp produced by the traditional spinning-cutting process are shown in Figure 1. The pulp was precipitated by the addition of a 2.5 wt% PPTA solution in concentrated sulfuric acid having intrinsic viscosity 6.87 to 98% glycerin solution that was stirred at 2000 rpm. It can be clearly seen from Figure 1 that the resultant pulp has a ribbon-like structure with many ramifications and different thickness and lengths of the fibrils similar to Twaron pulps, but the size of the fibrils is a little larger. The resultant PPTA pulps were fibrillated only by high shear stirring and were not mechanically refined to reduced diameter like in the production of Twaron pulps.

Crystallinity of the Resultant Pulps

Wide-angle X-ray diffraction patterns for the resultant pulps and Twaron pulps are shown in Figure 2. The X-ray spectra of both the



(a) (b)

FIGURE 1 Comparison of micrographs of the resultant pulps and Twaron pulps; (a) the resultant pulps; (b) the Twaron pulps.

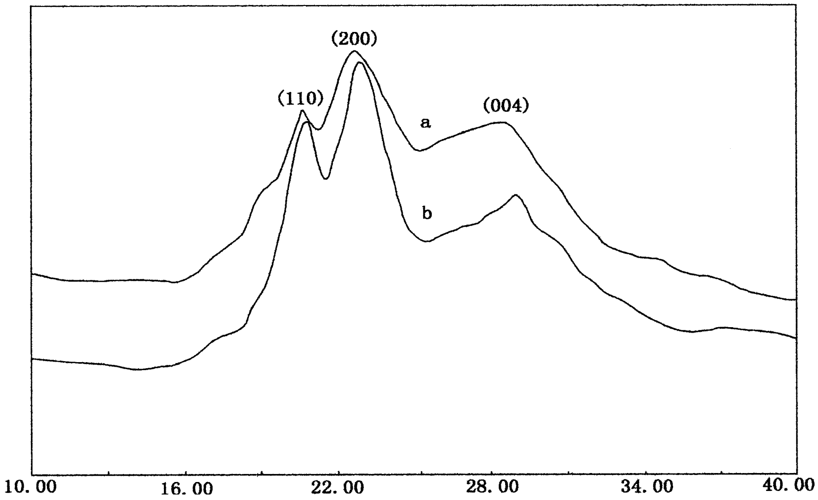


FIGURE 2 Comparison of the crystallinity of the resultant pulps and Twaron pulps; (a) the resultant pulps; (b) Twaron pulps.

PPTA pulps had three diffraction peak at 2θ–20.5°, 23.5°, and 28.5°, corresponding to the {110}, {200}, and {004} crystal faces of PPTA, but the peaks are not as sharp as PPTA fibers [13] and the {200} reflection of PPTA type I crystal is stronger similar to that of the Twaron pulps. The degree of crystallinity of PPTA pulps calculated as 40.5% and 42.5% individually, are much lower than that of PPTA filaments. The crystallinity of resultant precipitated pulps is also a little lower than Twaron pulps for there is no spinning process, but the difference is not obvious.

Influence of Stirring Speed

By keeping constant of all other processing variables during the addition of a 2.5% PPTA solution in concentrated sulfuric acid having intrinsic viscosity 6.87 to 98% glycerin solution, the stirring speed used was varied between 1000 and 3000 rpm. The influence of stirring speed on the specific surface area and mean length of the PPTA pulp was evaluated. The results are shown in Figures 3 and 4. It can be seen from Figure 3 that the specific surface area of the pulp increases rapidly with the increasing stirring speed when it is lower than 2000 rpm and reaches to a nearly constant value at stirring speed greater than 2500 rpm. It is well known that the micro-fibrils are the structural elements of the PPTA fibers and PPTA fibers have a

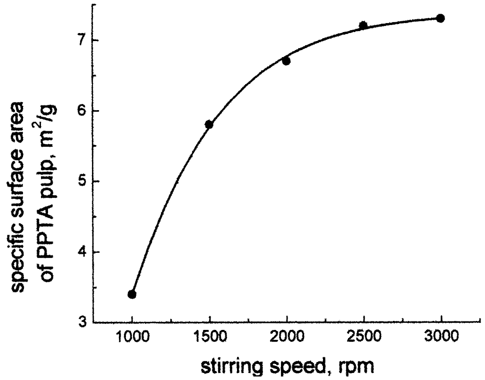


FIGURE 3 The effect of stirring speed on specific surface area of the PPTA pulp.

tendency to be fibrillated under shear strain [14]. In the precipitating process, higher stirring speed leads to higher fibrillation of the obtained PPTA fiber. However the precipitated fiber cannot be more fibrillated by simple shear when the fibrillation reaches certain degree.

Figure 4 shows that the greatest mean length of the pulps is found for about 2000 rpm. According to the mechanism of the formation of the PPTA pulp, which will be discussed subsequently, high stirring speed is necessary for the droplet deformation to form the PPTA fiber. However, the droplet break-up occurs when the shear rate employed is higher than a critical value and PPTA pulp formation will be followed by break-up of the fiber. That is, the influence of the stirring speed on

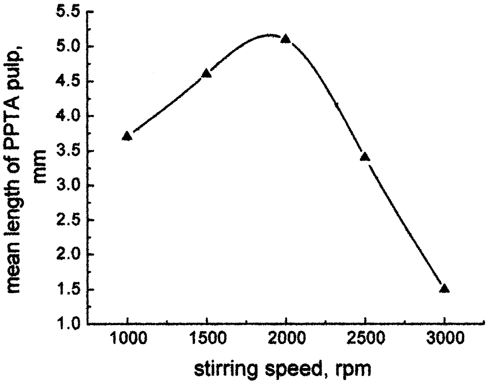


FIGURE 4 The effect of the stirring speed on mean length of the PPTA pulp.

the mean length of the pulp is the result of the balance between PPTA droplet deformation and droplet break-up.

Influence of the Viscosity Ratio of the PPTA Solution to That of the Coagulant

The experiments were carried out by the addition of different concentration PPTA solutions (I.V. = 6.87 dl/g) to 98% glycerin solution that was stirred at 2000 rpm. The viscosity of the PPTA solutions and the viscosity ratios (λ) of the solutions with respect to 98% glycerin solution are shown in Table 1. In these viscosity measurements the shear rate was less than $0.5\,s^{-1}$. At such low shear rates the shear-rate dependence of the viscosity is expected to be negligible.

The effect of the viscosity ratios (λ) of the PPTA solutions with respect to 98% glycerin solution on the specific surface area and the mean length of the precipitated PPTA pulp was studied and the results are shown in Figures 5 and 6.

Figure 5 shows that the viscosity ratio λ seems to have only a slight influence on the specific surface area. Specific surface area is a characteristic of the degree of the fibrillation of the pulp and the fibrillation is the result of splitting the coagulated PPTA fiber lengthwise under high shear. For a given I.V. of the PPTA solution, the splitting is mainly effected by the shearing strain after the formation of PPTA fiber and it is hardly affected by the λ in the precipitating process.

However, it can be seen from Figure 6 that the mean length of the precipitated pulp decreases with increase of the λ. The final length of the pulp may be obtained by considering that the deformation of the drop will cease as soon as strength develops in the precipitated PPTA. Higher viscosity of the drop leads to the higher resistance to deformation and skin formation and results in shorter final length of the pulp.

TABLE 1 Viscosities and Viscosity Ratios of PPTA Solutions to Glycerin Solution Measured at 24°C

Sample	Concentration (wt%)	Viscosity (P)	Viscosity ratios λ
PPTA having I.V. of 6.87 in concentrated sulfuric acid	1.0	15	1.76
	1.5	38	4.47
	2.0	51	6.00
	2.5	64	7.53
	3.0	87	10.24
Glycerin solution	98	8.5	1.00

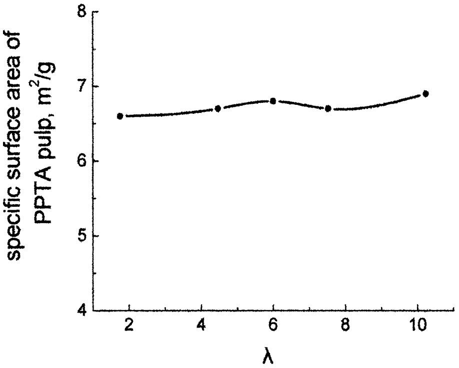


FIGURE 5 The influence of the viscosity ratio of PPTA solution to that of the coagulant on specific surface area of PPTA pulp.

PROPOSED MECHANISM OF THE PRECIPITATION

In discussing the possible mechanism of pulp fiber formation, it is important to note the following observation. When a droplet of viscous PPTA solution is added to a sheared coagulant, it is observed that the drop is elongated and the elongation is greater with the higher stirring speed. A mechanism of the process proposed is that when the viscous PPTA solution is introduced into a rapidly stirred coagulant, it is dispersed into small drops. A simple droplet deformation mechanism is shown in Figure 7, which shows that the originally spherical drop becomes extended to fiber dimensions with increasing time $t_0 < t_1 < t_2$.

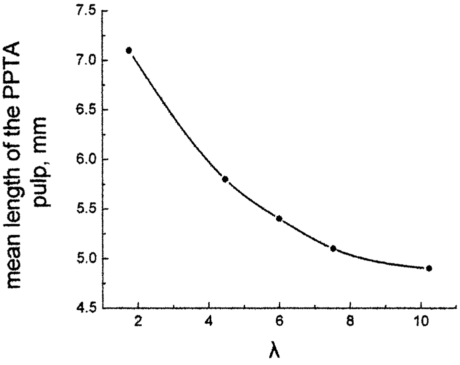


FIGURE 6 The influence of the viscosity ratio of PPTA solution to that of the coagulant on the mean length of PPTA pulp.

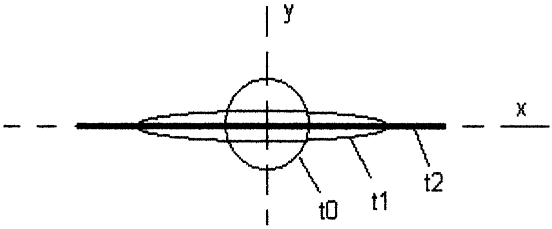
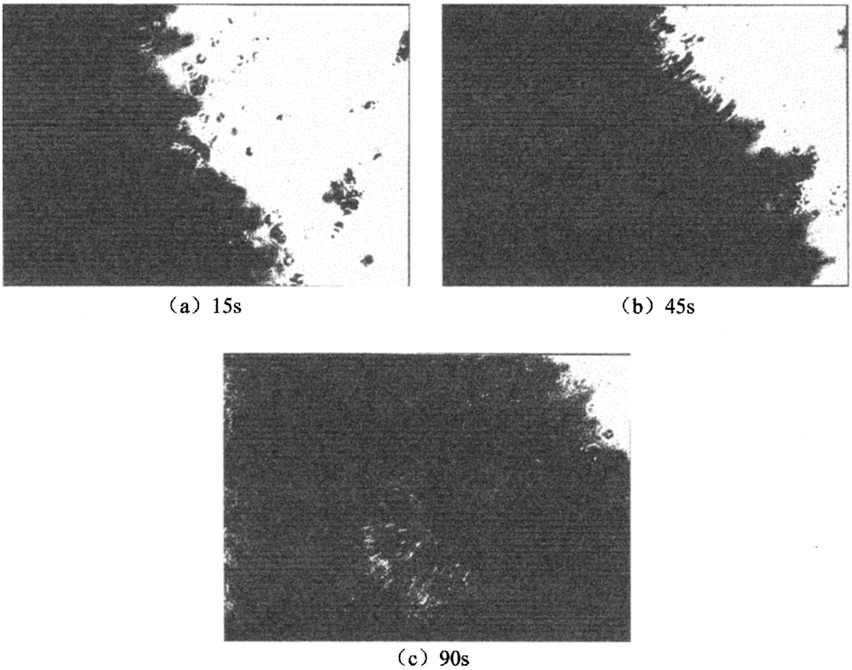


FIGURE 7 Illustration of the proposed mechanism of PPTA pulp formation.

The drops of PPTA solution become increasingly elongated by action of the extensional flow field with increasing time $t_0 < t_1 < t_2$, then coagulated and solidified when sufficient coagulant has diffused across the boundary between PPTA solution and coagulant. The process of the diffusion was recorded by the photographs (a), (b), and (c) of Figure 8, where the dark part is coagulant and light part is PPTA solution. It can be clearly seen that diffusion rate of the coagulant is higher than that of the solvent of the PPTA solution, which was


(a) 15s

(b) 45s

(c) 90s

FIGURE 8 Coagulant diffusing across the boundary between PPTA solution and coagulant.

calculated to be about 10^{-5} m/s. That is, the coagulation step is governed by the diffusion of the coagulant of glycerin into the PPTA solution and the fiber reaches its final length when a critical concentration of coagulant is reached at the core of the elongating drop.

At high stirring speed, the solidified PPTA fibers are fibrillated into fibrils and become PPTA pulps with high specific surface area and mean length.

CONCLUSION

The following conclusions can be drawn based on the information presented:

1. PPTA pulps can be formed by dispersion of the PPTA solution as droplets, deformation of droplets, and subsequent coagulation, and fibrillation of the solidified fiber under high shearing strain. Pulps with different degree of fibrillation and mean length can be obtained by this method to fit various demands.
2. The precipitated pulps are highly ramified with different thickness and lengths of the fibrils; the morphology of the obtained pulps is very similar to that of Twaron pulps.
3. The degree of fibrillation of the pulp increases rapidly with increasing stirring speed when it is lower than 2000 rpm and reaches a nearly constant value at a stirring speed greater than 2500 rpm. The influence of the stirring speed on the mean length of the pulp is a result of the balance between PPTA droplet deformation and droplet break-up. The greatest mean length of the pulps is found for about 2000 rpm.
4. The viscosity ratio λ has only a slight influence on the degree of fibrillation of the PPTA Pulp. However, the mean length of the PPTA pulp decreases with increasing λ.
5. The mechanism of the process is proposed that the viscous PPTA solution is first dispersed as droplets in the precipitant; a droplet deformation process then occurs in regions of the system where flow shear prevails. Subsequently, coagulation occurs when sufficient coagulant has diffused across the boundary between the deformed drop and the coagulant, and then the solidified fiber is fibrillated into fibrils.

In this study, the formation of PPTA pulps by this precipitation method has been first described, and the processing parameters affecting the degree of fibrillation and mean length of the pulps have been investigated. This would provide significant advantage in improving the properties of PPTA pulps. In the future, the deformation and coagulation of droplets of PPTA/H_2SO_4 solution in extensional flow will be further discussed.

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