

# Needleless Electrospinning

## Relaxation time of the aqueous solutions of poly (vinyl alcohol)

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*Relaxation time reflects dynamic phenomena in the early stages of electrospinning after an abrupt application of an external electric field. Experimental counterpart of relaxation times, i.e., characteristic hydrodynamic times, have been measured using a laboratory device designed especially for this kind of experiments. The experiments supporting the hypothesis are carried out with aqueous solutions of poly (vinyl alcohol) of various concentrations. Experimental data are compared with theoretical predictions of relaxation times aiming to a deeper analysis of dynamic phenomena during the earliest stages of electrospinning. Qualitative and quantitative comparison of theoretical and experimental relaxation times determined that characteristic hydrodynamic times are encouraging. Moreover, the experimental apparatus for characteristic hydrodynamic time investigation revealed regular discharges in a spinning zone of the electro-spinner that imminently precede electrospinning jet appearance. Results of the work contribute to a deeper understanding of a spinability of polymeric solutions using electrospinning and are an inspiration for new electrospinning variants.*

**Keywords:** nanofibers, needleless electrospinning on the rod, polyvinyl alcohol aqueous solutions, rod, relaxation time

Up to now, two methods using high voltage are known for obtaining nanofibers, namely needle electrospinning and needleless electrospinning. Both methods seem to be different, however they are based on the same electrospinning mechanism. Needle electrospinning has been especially used by researchers in laboratories [1, 2]. Using needle electrospinning, spinable polymeric solutions are easily spun and controlled to achieve desired products, there is only one jet per needle and the spinning area is very small (0.5-1.0mm<sup>2</sup>). In order to commercialize the products resulted from electrospinning technology, emphasis has been given to the increasing of production capacity and the quality of nanofibers, promoting the needleless electrospinning technology, a procedure in which a relatively large number of polymeric jets (usually 3.000-4500 jets per one square meter of the surface of spinning electrode) are created spontaneously from a free surface of the liquid. That is why needleless electrospinning

becomes a very popular method, a commercial technique to produce nanofibers membranes, which has a few advantages: there is no risk of obstruction of the needle; it can be obtained a variety of polymeric nanofibers; there can be used different materials substrates; controlled diameters of nanofibers; the nanofibers may have a certain uniformity, the desired quantity; there is the possibility to incorporate nanoparticles, having also a broad portfolio of applications [3-7].

Needleless electrospinning mechanism with rod (Technical University of Liberec, Nonwoven Department) is equipped with an electrode rod with a diameter of 8 mm and a length of 170 mm (fig. 1a). The electrode (fig. 1b) is mounted on a plastic holder. As a collector, was used a metallic device on which were collected nanofibers obtained from polymeric jet.

The collector is supported by a mobile metallic rod, which can be adjusted to the electrode as needed. As the

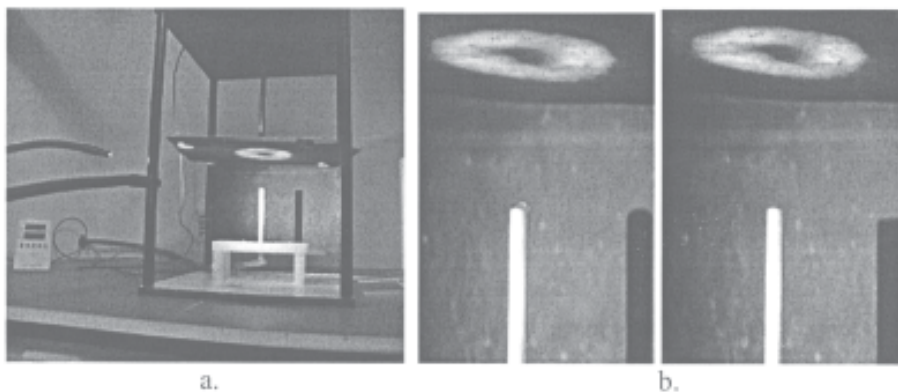


Fig. 1. Needleless electrospinning device with rod: a. General view of needleless electrospinning device with rod; b. The electrode rod with and without the polymeric droplet and the metallic collector for deposit the nanofibers [8]

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PVA weight concentration (%)	Surface tension $\gamma$ (mN/m)	Dynamic viscosity $\eta$ (Pa s)	Mass density $\rho$ (kg/m <sup>3</sup> )	Kinematic viscosity $\nu$ (m <sup>2</sup> /s)
5%	43.5 ± 0.1	0.01436 ± 0.00003	994.7 ± 0.6	0.000014455
6%	43.5 ± 0.1	0.0174 ± 0.0001	1000.7 ± 0.4	0.000017521
7%	43.5 ± 0.1	0.01897 ± 0.00002	1002.3 ± 0.4	0.000018962
8%	43.5 ± 0.1	0.0381 ± 0.0001	1003.2 ± 0.3	0.000038114
9%	43.5 ± 0.1	0.0532 ± 0.0001	1004.1 ± 0.2	0.000053147
10%	43.6 ± 0.1	0.1073 ± 0.0002	1005.4 ± 0.4	0.00010686
11%	43.7 ± 0.1	0.1220 ± 0.0001	1005.8 ± 0.5	0.00012139
12%	43.7 ± 0.1	0.2008 ± 0.0001	1006.9 ± 0.4	0.00019944
13%	43.7 ± 0.1	0.311 ± 0.002	1007.6 ± 0.4	0.00031045
14%	43.8 ± 0.1	0.4994 ± 0.0004	1008.5 ± 0.5	0.00049548
15%	44.3 ± 0.1	0.5054 ± 0.0004	1009.1 ± 0.1	0.00050109

**Table 1**  
SURFACE TENSION  $\gamma$ , DYNAMIC VISCOSITY  $\eta$ , MASS DENSITY  $\rho$  AND KINEMATIC VISCOSITY  $\nu$  VALUES OF INVESTIGATED AQUEOUS PVA SOLUTIONS HAVING CONCENTRATIONS FROM 5%wt UP TO 15%wt

collecting substrates, were used black paper, aluminum foil or nonwoven. The electrode is connected to the positive terminal (pole) of the high voltage source while the collector is grounded. High voltage is applied to the polymeric solution so that the electric charge is inserted into the fluid. When the charge inside the fluid reaches a critical moment, the repulsive electrostatic force overcomes the surface tension and the polymeric jet erupts inside the droplet, resulting in the formation of a Taylor cone. Once a critical voltage is exceeded, a charged jet ejects from the apex of the cone and is deposited on the collector's surface [8].

Needleless electrospinning method or liquid free surface method takes to formulate a hypothesis about the evolution of electrohydrodynamic jets of a free liquid surface under the action of an external electrostatic field. Electrohydrodynamic theory of electrospinning of free fluid surfaces seems to complement existing analysis regarding the electrospinning technology introduced by Taylor. While Taylor is primarily concerned with the geometry of the liquid cone (Taylor cone) and the critical voltage, in the context of electrical and capillary pressures acting on balance, this theory adds a generalized approach to the study of the dynamics of wave's surface. Physics of the jets is an extremely attractive and active domain. Attention of researchers in this area is mainly focused on the behaviour of the jet and its physical mechanisms [9, 10].

The present study is based on the recently efforts to bring electrospinning technology at an industrial level, by causing simultaneous multiple polymeric jets from a free liquid surface. In particular, the study faces with electrospinning from free liquid surfaces and validates the hypothesis which explains the self-organization phenomenon of jets on free liquids surfaces in terms of electrohydrodynamics instability of surface waves, called Tonks-Frenkel instability. Hypothesis, based on a deep analysis of dispersion law, explains that above a certain value of critical intensity of electrical field applied, the system begins to self-organize due to a mechanism of "rapid forming of instability". The mechanism plays a key role in the selection of a particular wave, with a wave length of which amplitude grows faster than the others. The rapid growth of the stationary wave, in agreement with the hypothesis, marks the beginning liquid surface whose jets are originary from the wave crests [10-13].

It is also of interest to investigate and measure the hydrodynamic time of polymer solutions. The relaxation time reflects dynamical phenomenon in the early stages of electrospinning after a sudden application of an external electric field. Relaxation times were measured using a

laboratory device particularly designed for this type of experiment.

## Experimental part

### Materials

Experiments were carried out with aqueous solutions of poly (vinyl alcohol) Sloviol<sup>R</sup>, purchased from Novacke Chemicke Zavody, Slovakia, with a molecular weight 130000g/mol and a viscosity of 10.4mPa. Distilled water was utilized as a solvent for obtaining PVA solutions with different concentrations, ranging from 5% wt up to 15% wt. Homogeneity of the PVA solutions was ensured by keeping them on a magnetic stirrer Heidolph Vibramax 100 for three hours before each measurement. The values of surface tension, measured using digital Tensiometer Krüss K9, were recorded for each concentration and the viscosity data of polymeric solutions were obtained using Haake Roto Visco 1 Thermoscientific. To determine the polymeric solution density, 10mL of the polymeric solution was weighed in a Pentometer. All these measurements were repeated 5 times to obtain standard deviation values. The dynamic viscosity is determined for shear rates  $\dot{\gamma} \in (50..600)s^{-1}$ . All values are measured at temperature of 20°C. All the aforementioned data of PVA solutions are introduced in table 1.

### The scheme and the measurement principle of relaxation time of the PVA polymeric solutions

Experiments regarding electrospinning of PVA solution in water were carried out with a needleless electrospinning device with a rod, different from that used to determine the relaxation time of the polymer, but which operates on the same principle. In the case of application, the device serves for electrostatic spinning of polymeric solution droplet placed on the top of a metallic rod, which represents here the positive electrode.

All experiments were carried out with droplets having a volume of 1.5mL, dose sufficient to cover the diameter of the rod and the height of the droplet (h) has values between 10mm and 13mm. The shape of the polymeric solution droplet was carefully controlled by the amount of polymer. For a better view of electrospinning process, it was used a lighting device with two terminals which can be directed on the rod and the collector too. There is not a special room to control temperature and humidity. Digital thermometer displays the temperature and atmospheric humidity, respectively. The ambient temperature was between 19°C – 23°C and atmospheric humidity ranged within 35% and 51%. It is important that the device gives the possibility of repeated measurements and in particular,

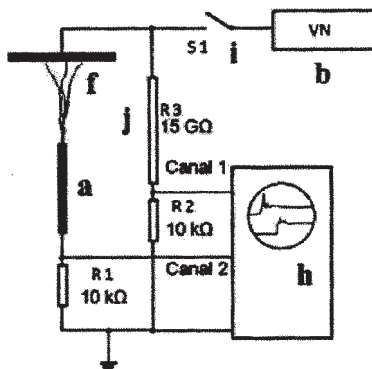
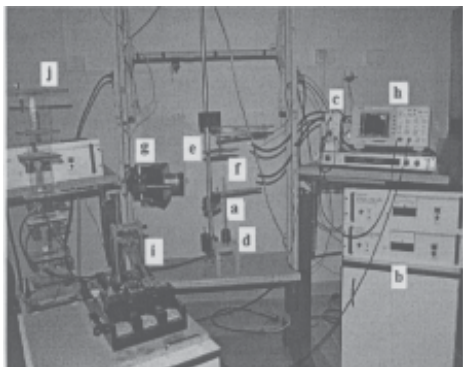


Fig. 2. Components and tools scheme of device for measure relaxation time of the polymer [12] and electrical scheme of electrospinning device with a rod: a - electrode rod, b - high voltage source, c - resistor, d - insulating stand using a chuck, e - circular collector, f - polymeric jet, g - stereopticon Meopta, h - oscilloscope, i - quick-acting switcher, j - tension divider

compliance of the same initial conditions at the beginning of electro-spinning. Each individual measurement is carried out from a new droplet. Photographic snapshots and also video records of electrospun polymeric droplets were taken using Nikon Coolpix 4500 camera.

The electrical scheme of electrospinning device with a rod is schematized in figure 2 as well as all the equipment necessary to measure the relaxation time of the polymer.

Measurements were performed on a mobile structure described above, built and assembled by Engineer Pokorny from Technical University of Liberec, Nonwovens Department. Components and auxiliary equipments were attached to the structure for the measurement and electrostatic spinning:

- *Central rod* (fig. 2a) and *the collector* (fig. 2e) are especially placed for electrostatic spinning. The rod electrode has an 8mm diameter  $r$  and a length  $l$  of 218mm and it was mounted on an insulating stand using a three jaw chuck. As a collector, was used a flat circular metallic plate of 150mm diameter. The distance between the top of the rod spinning electrode and the disk collector was 100mm and can be modified as needed. The collector, grounded, with negative polarity, is placed above the metallic rod, at a controllable distance and the rod was connected at the positive pole of high voltage source. The collector is connected to the resistance of the resistor circuit. The polymeric solution feed the top of the metallic rod electrode using a micropipette. If the distance rod-collector is smaller, the electric field intensity must be increased. But first uses lower values of voltage needed to start electrospinning;

- *High voltage power supply* (fig. 2b), model AU-60PO.5-L (300 W), manufactured by Matsusada Precision Inc., provides high voltage to the collector, being one of the basic requirements necessary for electrostatic spinning. It was used a positive high voltage source, the output voltage of 0-50kV and 6mA current output;

- *VISTION resistor* (fig. 2.c) - connected to the oscilloscope on channel 1;

- *Meopta magnification device* (fig. 2g), attached to the iron support of the device, was used for projection and expansion of the polymeric droplet dosed with a micropipette. Visualizations were directed on a screen, a millimeter paper mounted on a wall;

- *The oscilloscope* RIGOL DS1102C (fig. 2h) - records time delay of Taylor cones forming;

- *The switcher* (fig. 2i) - The electric current switch on is supplied in stages. The circuit is wired to provide a quicker start-up signal and thereby, to ensure a more accurate reading of the time formation of the Taylor cone, required to determine the relaxation time of the polymer;

- *The voltage divider* (fig. 2j), the signal from the oscilloscope is divided into two resistors, R1 and R2. The voltage divider is connected once through R1 to the channel CH2 of the oscilloscope, and also through R2 to the

electrode rod and switcher by grounding wire cable. Despite voltage divider, remains current on the rod electrode. It is therefore necessary, before each measurement, to discharge residual current from the circuit, to remove the old polymeric solution from the rod electrode and to inject the same amount of polymeric droplet.

## Results and discussions

On the oscilloscope screen, the effective start of the electrospinning process appears under the form of peaks which started to grow from smoothly liquid surfaces after a sudden interruption of the field and develop a system of conical peaks called Taylor cones. Taylor cone formation is the beginning of electrospinning. The time required for the formation of Taylor cone is called further "hydrodynamic time" (which studies the laws of fluids motion). Characteristic of the hydrodynamic time has the same order as the reciprocal value of the growth rate of the wave, denoted here as relaxation time. These times are of dynamic nature and are therefore dependent on the viscosity [10-19]. A sequence of PVA droplets movement and correlations of these movements with oscilloscope record (the growth stages of a Taylor cone) is introduced in figure 3. Thus, figure 3a describes signal from the channel 2 which records the voltage modifications from the electrical circuit and figure 3b collects snapshots obtained using high-speed Olympus Speed 3 camera, whose frequency is  $5000s^{-1}$  for Taylor cone.

The snapshots are denoted using capital letters A-L, which appear also in the oscilloscope record in Figure 8.a, where they localize the observed events on the time axes and correlate them with the voltage signal. It is obvious from figure 8.a and 8.b. that the first sharp peak on the oscilloscope record, denoted as letter B, precedes the jet appearance, since a jet firstly appears at the snapshot I. Subsequent peaks, probably caused by discharges in the form of small droplets are associated to instantaneous images C-H. The average time delay between these neighboring peaks is 0.24ms. The appearance of a jet, snapshots I-L is accompanied by a monotonic voltage increase without next peaks.

The experimental apparatus designed by us for characteristic hydrodynamic time measurements revealed a new phenomenon coming imminently before the appearance of a jet. This phenomenon regularly discharges in the spinning zone that exhibit as regular voltage peaks. The switch on point appears as a peak at time  $t_1$ . The first sharp peak (caused most probably due to individual's ions and free electrons moving between electrodes), as has been mentioned previously, was used to determine the time moment  $t_2$  of the delayed signal in channel 2. The time difference  $\Delta t = t_2 - t_1$  is the characteristic hydrodynamic experimental time [12, 16]. Oscilloscope records provide us informations on the characteristic



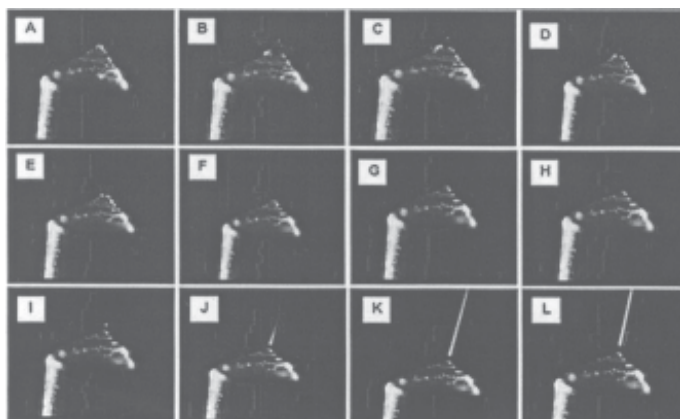
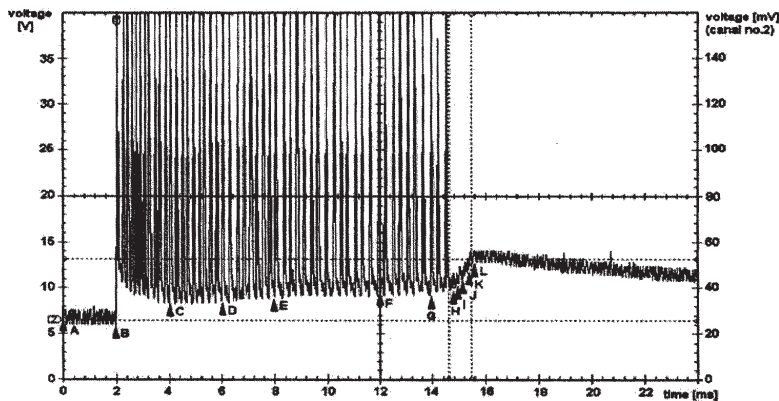


Fig. 3. Signal from the channel 2 which records the voltage modifications from the electrical circuit and Taylor cone snapshots obtained using high-speed Olympus Speed 3 camera: a. Voltage-time relationship from channel 2 (CH2) of the oscilloscope obtained for 12 % wt PVA, b - Taylor cones snapshots (the events recorded by camera, denoted by capital letters, are assigned to particular time instants in the oscilloscope record)

hydrodynamic time which are compared with theoretical predictions of relaxation times, in order to offer a deep analysis of dynamic phenomenon.

A series of PVA solutions with concentrations ranging from 5 to 15wt% were prepared for measuring relaxation time. These solutions were characterized as reported in table 2.

Theoretical source of relaxation time for viscous conductive liquids is introduced and compared with experimental measurements of the hydrodynamic time, aimed at a deep analysis of dynamic phenomena during the early stages of electrospinning.

The microphotographs of nanofibrous mass obtained during the experiments, using electronic scanning microscope PHENOM G2 pro, are shown in figure 4.

The final study of this research considered the importance of relaxation time in electrospinning, who depends directly or indirectly on polymer concentration, surface tension, viscosity, electric field, ambient

conditions. From results, we found out that relaxation time and electric charges are essential parameters for beads formation in electrospinning solution.

When the relaxation time is smaller, the orientation of the molecule is easy, so jet will be stronger and fibers with small diameter are obtained. Fluid elasticity is also one of the essential properties which can control the morphology of the fibers obtained by electrospinning. For fluids with low viscosity or low relaxation time, the formation of “beads-on-string” appears. A viscous liquid will also produce thicker nanofibers in electrospinning. The diameter of a fiber is also directly proportional to the concentration of the polymer solution. As thinner nanofibers are preferred for industrial applications, it is therefore important to understand how relaxation time impacts electrospinning and therefore the diameter of nanofibers. Through a series of mathematical equations, the study tested fluids with low concentration and high relaxation time to confirm how high relaxation time could help improve the stability of low

PVA concentration (%)	Surface tension $\gamma$ (mN/m)	Dynamic viscosity $\eta$ (Pa s)	Theoretical relaxation time (s)	Experimental relaxation time T (-)	Electrical critical intensity E (V/m)	Electrospinning number $\Gamma$ (-)	Fiber morphology
5%	43.5 $\pm$ 0.1	0.01436 $\pm$ 0.00003	0,0544	0,378088176	3061174,481	2,014568157	beads-on-string
6%	43.5 $\pm$ 0.1	0.0174 $\pm$ 0.0001	0,0632	0,439910391	3370184,022	2,434485187	beads-on-string
7%	43.5 $\pm$ 0.1	0.01897 $\pm$ 0.00002	0,0752	0,523646783	3495483,668	2,616782007	beads-on-string
8%	43.5 $\pm$ 0.1	0.0381 $\pm$ 0.0001	0,0608	0,423469004	3420809,059	2,505046323	beads-on-string
9%	43.5 $\pm$ 0.1	0.0532 $\pm$ 0.0001	0,076	0,529454935	3549246,78	2,695477835	beads-on-string
10%	43.6 $\pm$ 0.1	0.1073 $\pm$ 0.0002	0,074	0,515392742	376071,756	2,434485187	fiber, few beads
11%	43.7 $\pm$ 0.1	0.1220 $\pm$ 0.0001	0,0804	0,559702283	3378341,85	2,434485187	fiber, few beads
12%	43.7 $\pm$ 0.1	0.2008 $\pm$ 0.0001	0,223	1,55283235	3308863,8	2,334104937	fiber, few beads
13%	43.7 $\pm$ 0.1	0.311 $\pm$ 0.002	0,1114	0,775854623	3332581,662	2,366863904	fiber, few beads
14%	43.8 $\pm$ 0.1	0.4994 $\pm$ 0.0004	0,2592	1,804591578	3289227,706	2,302021403	uniform fiber
15%	44.3 $\pm$ 0.1	0.5054 $\pm$ 0.0004	0,2048	1,422021142	3679726,747	2,863905326	uniform fiber

**Table 2**  
SURFACE TENSION  $\gamma$ , DYNAMIC VISCOSITY  $\eta$ , MASS DENSITY  $\rho$ , RELAXATION TIME  $s$  AND FIBER MORPHOLOGY OF INVESTIGATED AQUEOUS PVA SOLUTIONS WITH CONCENTRATIONS RANGING FROM 5%wt TO 15%wt

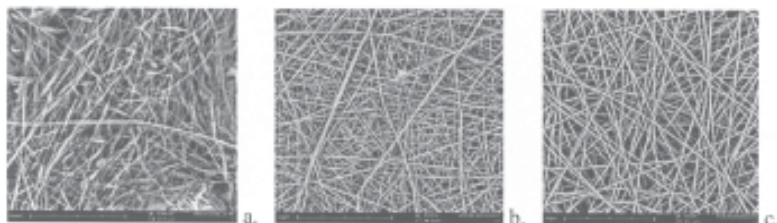


Fig. 4. Nanofibrous layers obtained from the rod-like needleless electrospinner from: a.5%wt, b.10%wt, c.15%wt aqueous solutions of PVA

concentrated polymers when producing nanofibers. As a result this can be used in future studies to improve the properties of nanofibers produced through electrospinning.

## Conclusions

Description of electrospinning process is a very complex matters. It is a physical process, chemical and mechanical phenomena that are influenced by weather conditions, field interactions with the environment and other unexplained laws.

This article has taken the task to measure relaxation times, one of the parameter used to explore the construction of the Taylor cone. Theories are included in the Journal of Applied Physics [6], which deals with electrostatic spinning of the free liquid surface.

To compare the predicted course of the dependence of the dimensionless relaxation number ( $T$ ) with electrospinning number  $\Gamma$ , it was necessary to obtain experimental data, using a complex statistical calculations. The experiment was performed on 5% to 15% aqueous PVA polymer concentrations. Individual measurements of each polymer contained numerous repeated measurements for various electric fields. During the measurements, it was found a critical voltage for obtaining intensity values of  $E_c$ , which determines the moment when the stationary wave on the surface of the liquid becomes unstable and will create the Taylor cone. Substituting the values of the experiment, were obtained curves that are in good agreement with the theoretically predicted course of the dependence of the dimensionless relaxation time. Confirmation of the theory, based on the experiments, is possible for a better understanding of the dynamic dependencies at the beginning of the electrospinning.

It would be useful to confirm this theory also to another type of polymer. Hopefully, the results achieved in this work, would attract more attention for applying the electrohydrodynamic theory for engineering purposes of electrospinning technology.

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