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Highly Porous Polyacrylonitrile Fibres with Antibacterial and Antifungal Properties

Abstract

Highly porous polyacrylonitrile fibres with antibacterial and antifungal properties were obtained. These fibres are characterised by a radial differentiation of their structure which is consistent with the assumed model. The influence of fibre spinning conditions on the porous structure and the moisture absorption and strength properties of fibres was examined. Under conditions selected to ensure advantageous fibre properties, PAN fibres were spun from spinning solutions containing bioactive agents. The tests of antibacterial and antifungal effects performed on the fibres obtained show that the addition of even low quantities of bioactive agents brings about the inhibition of bacteria and fungi growth.

Key words: *polyacrylonitrile fibre, porous fibres, fibre structure, antibacterial properties, antifungal properties*

Introduction

Improved comfort of use is one of the basic requirements imposed on textile fabrics, especially sports clothes, socks, tights and internal textile elements of footwear. In order to provide clothing with properties which would support the functioning of the user's organism and ensure an appropriate physiological state, the fibres used for its manufacture must have a suitable porous structure. A developed system of pores in the fibre structure should allow fast moisture transport to the environment, to eliminate wetness which reduces the comfort of the clothes used. Fibres that meet such requirements are known under the trade names *Dunova* [1] and *Aqualon*. They are mostly produced from polymers with added expanding agents.

The possibility of preparing highly porous polyacrylonitrile fibres by changing the mechanism of solidification from diffusion to a drop-wise process has been presented in paper [2], which describes a general principle of fibre spinning that allows the production of fibres with a high total volume of pores and internal surface whose structure is of the sheath-core type, including a porous core and a system of capillaries in the external layer (sheath). The fibre structure and the absorption & strength properties of the resultant fibres depend on the conditions of fibre spinning [3,4].

An additional factor which extends the range of applications of this type of fibres is their antibacterial and antifungal properties. It is assumed that a spongy structure with a large internal surface, practically free from the skin layer, should be more advantageous for fibres with such properties, as this facilitates moisture absorption as a result of direct contact between the open pore system and the moist medium. At the same time, it would be easier for antibacterial and antifungal agents to migrate from the inside of the modified fibres.

Without a well-oriented external skin layer, proper fibre strength properties should be provided by a compact and better-oriented internal layer. As fibres with biological activity have become more and more important in various fields, especially in the textile and footwear industries [5], more attention has been paid to hydrophilic than hydrophobic fibres [6]. It is moisture absorption capability which ensures good performance of bioactive fibres, supporting their biological activity and the transport of active substances. The fibres' biological activity is usually controlled by the hydrophilicity of the fibre-forming polymer, the amount of the active compound added and the way it is combined with the fibre material.

A review of fibres with antibacterial and antifungal properties currently manufactured from various polymers and the mechanism of action of additives is presented in [7]. In the case of hydrophobic fibres such as polyacrylonitrile fibres, the factor which decides moisture absorption and biological activity (besides general porosity) is the character of the porous structure formed during spinning. The present study aimed at preparing highly porous polyacrylonitrile fibres with a structure consistent with the assumed structural model and which showed antibacterial and antifungal properties.

Experimental

Characteristics of the spinning solution

Spinning solutions were prepared using a terpolymer made in Hungary, the raw material for Mavilon fibres,

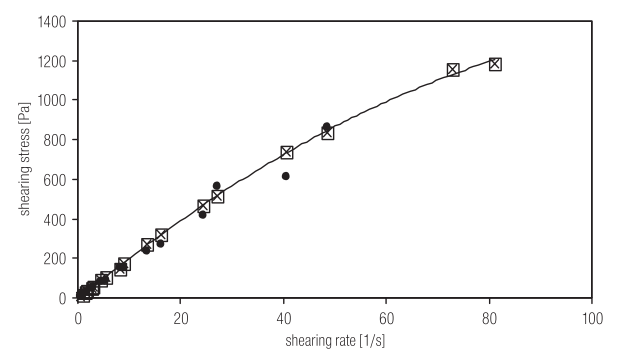

Figure 1. Dependence of shearing stress on shearing rate for the initial solution with a concentration of 22%, and for the same solution stored for 6 days. (× - measuring points for the initial 22% solution; • - measuring points for the same solution stored for 6 days).

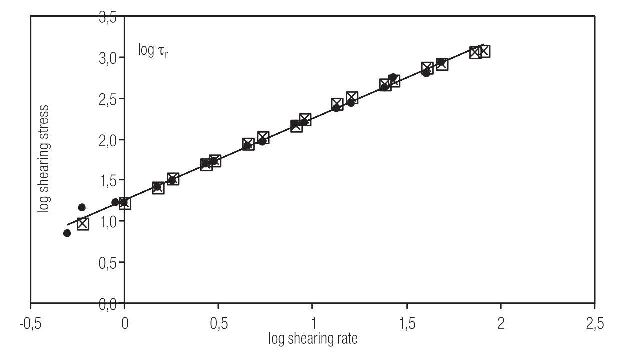

Figure 2. Dependence of shearing stress on shearing rate presented in logarithm coordinates for the initial solution with a concentration of 22%, and for the same solution stored for 6 days. (× - measuring points for the initial 22% solution • - measuring points for the same solution stored for 6 days).

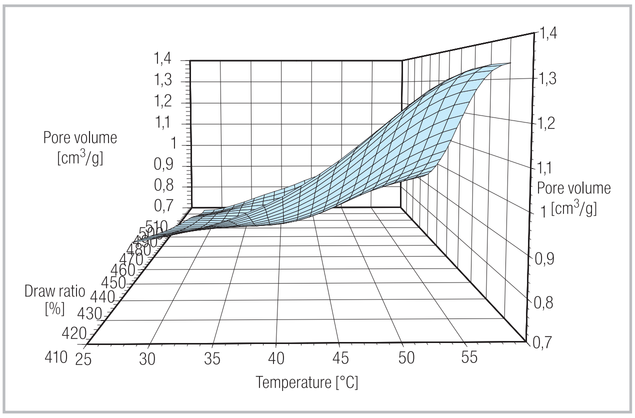

Figure 3. Dependence of total pore volume on coagulation bath temperature and total draw ratio.

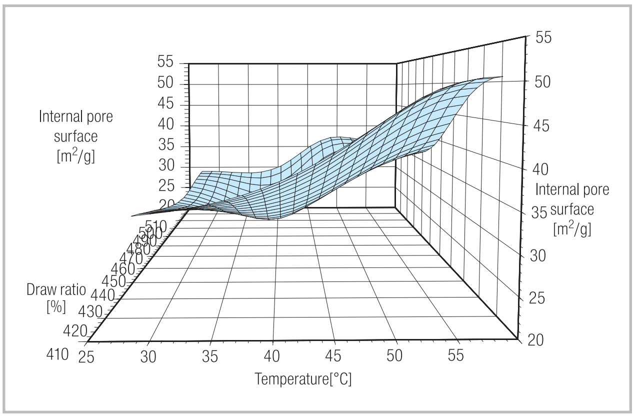

Figure 4. Dependence of total internal pore surface on coagulation bath temperature and total draw ratio.

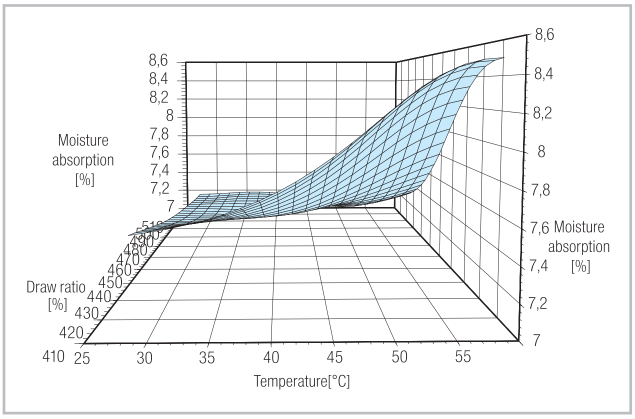

Figure 5. Dependence of moisture absorption at 100% RH on coagulation bath temperature and total draw ratio.

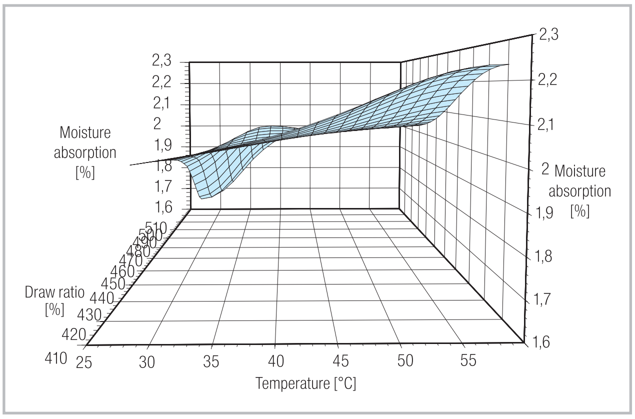

Figure 6. Dependence of moisture absorption at 65 % RH on coagulation bath temperature and total draw ratio.

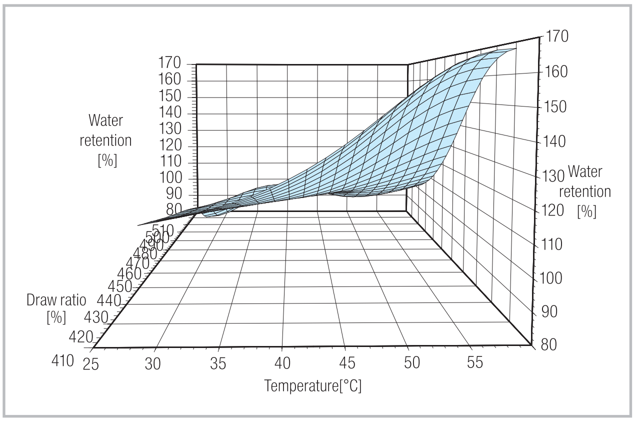

Figure 7. Dependence of water retention on coagulation bath temperature and total draw ratio.

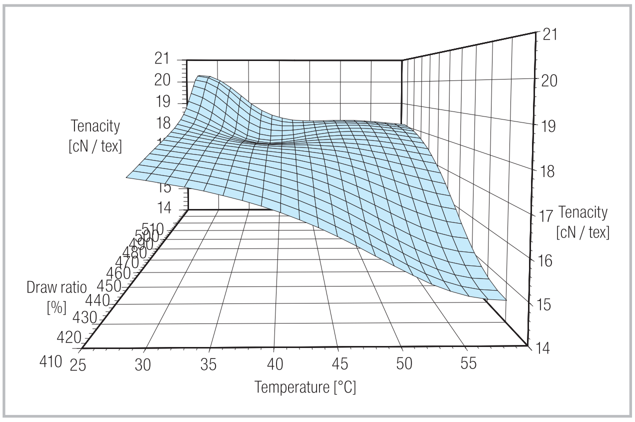

Figure 8. Dependence of fibre tenacity on coagulation bath temperature and total draw ratio.

which contains 93-94 % by wt. of acrylonitrile units, 5-6% by wt. of methyl methacrylate units, 1% by wt. of sodium allylsulphonate. The limiting viscosity number of the terpolymer determined in dimethylformamide (DMF) at a temperature of 20°C was 1.29 dl/g.

A spinning solution of the terpolymer in DMF, containing 22% of the fibre-forming material and with a dynamic viscosity of about 29.7 Pa·s, as selected in preliminary experiments, was used for rheological measurements to determine the stability of rheological parameters for 6 days. The measurements were carried out with the use of a Rheostat RV rotary rheometer at 20°C using an H cylinder. The shear rate range was 0.16 - 1.46·10^2 sec^{-1}.

Based on the flow curves shown in Figure 1, we may state that the solution under investigation is a non-Newtonian fluid thinned by shearing without a flow limit, showing good stability of the rheological parameters for a long period of time. The flow curve of the initial solution and of the one stored for 6 days at 20°C are practically the same. The rheological parameters n and K of the Ostwald-de Wales equation

$$\eta = K \cdot \dot{\gamma}^{n-1}$$

for both solutions determined from the flow curves presented in the loga-

Table 1. Percentage content of capillary sets with various radii in polyacrylonitrile fibres spun at various temperatures of the solidification bath.

Set of capillaries		Temperature of the solidification bath [°C]							
		27.5		39		50		60	
		Pore content	Total of pore content	Pore content	Total of pore content	Pore content	Total of pore content	Pore content	Total of pore content
nm		%	%	%	%	%	%	%	%
Very large	7500	8.47	30.2	7.21	27.49	6.12	21.73	4.55	14.29
	3750	12.81		13.65		10.34		6.33	
	1875	8.92		6.63		5.27		3.41	
Large	750	7.78	25.17	9.75	38.99	8.23	30.18	6.01	40.91
	375	10.07		16.76		12.03		18.83	
	150	7.32		12.48		9.92		16.07	
Medium	75	7.09	25.85	8.97	22.42	9.28	32.28	13.15	33.77
	41.5	5.95		5.46		7.59		8.93	
	26.8	9.61		6.82		12.03		8.77	
	15	3.2		1.17		3.38		2.92	
Small	12.3	2.97	18.76	2.14	11.1	2.74	15.82	2.11	11.05
	10.3	3.66		4.48		3.59		2.76	
	8	3.89		2.34		2.95		2.44	
	6	7.32		0.78		4.64		2.44	
	4	0.92		1.36		1.9		1.30	

rithmic coordinates (Figure 2) are similar, and amount to:
-n=0.996, K=1.259 for the initial solution;
-n=0.992, K=1.253 for the solution after 6 days of storage at 20°C.

Fibre formation

Polyacrylonitrile fibres were spun from solution in DMF by the wet process, using a laboratory spinning machine whose construction made it possible to change the technological parameters within a wide range and to stabilise them at required levels, including continuous control. A 500-orifice spinneret with an orifice diameter of 80 µm was used. The value of the as-spun draw ratio selected in preliminary experiments ranged from 74 to 75%.

Based on general rules of highly porous fibre spinning and preliminary experiments, the solidification process was carried out in a mild bath with a selected DMF content of 55%. The bath temperature ranged from 27.5°C to 60°C. The fibre drawing process was performed in a single stage in superheated steam at a temperature of 135°C. Once the solvent was washed out, the fibres were dried under isometric conditions at a temperature of 120°C.

The porous structure, absorption and strength properties of the resultant fibres were determined in accordance with the procedures stated in (4). The changes in the structure of fibre cross-sections were measured under an optical microscope conjugated with a computer-aided analyser of microscope images. Antibacterial properties were obtained by adding 1.3% of Triclosan to the spinning solution, and determined according to standard SN 195920; antifungal fibres were produced by adding Miconazol and tested according to standard SN 195921 [8].

Results and Discussion

To increase the coagulation ability of the bath, its temperature was raised to such a level that would ensure the preparation of highly porous fibres with improved absorption properties as well as the mechanical properties required in the textile processing. A series of experiments was carried out at variable temperatures of the solidification bath within the range of 27.5°C to 60°C.

The drawing operation was performed in two variants:
- with variable deformations approaching the maximum value,
- with a constant draw ratio value of 334-354%.

Considering the effect of the solidification bath temperature on the fibre structure and properties, we can see that with the increase in temperature up to 60°C there is a considerable increase in the total pore volume from 0.7 to 1.3 cm^3/g (Figure 3), and in the total internal surface from 22.8 to 50.6 m^2/g (Figure 4). The increase in general porosity is accompanied by the improvement of fibre absorption properties (Figures 5 and 6), and a double increase of water retention from 80 to 168% (Figure 7). However, the raised temperature of the coagulation bath results in a decrease in fibre tenacity from 20 cN/tex to 12 cN/tex for fibres solidified at 60°C (Figure 8), with the fibre elongation at break being simultaneously increased within the range of 9-10%.

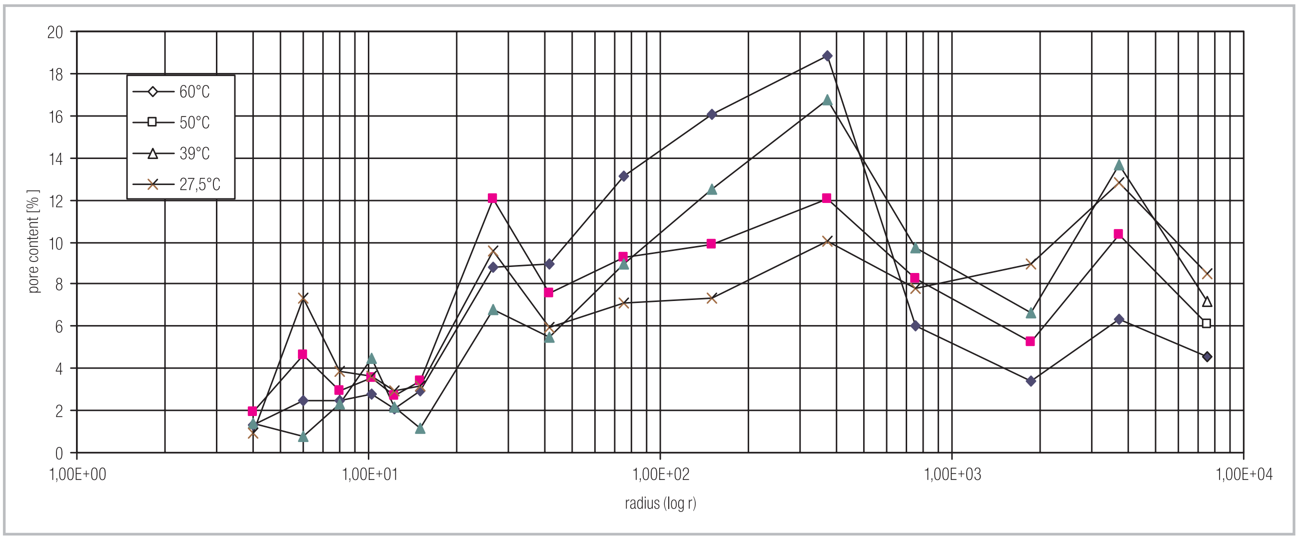

Figure 9. Dependence of percentage contents of pores on the radii for the fibres spun with a variable coagulation bath temperature.

Table 2. Properties and radial differentiation of PAN fibres formed with decreased deformation during drawing (the fibres were formed with a constant draw ratio of about 350%).

Temperature of coagulation bath	Moisture absorption at 100% RH	Moisture absorption at 65% RH	Water retention	Tenacity	Elongation	Radial differentiation of fibre structure
°C	%	%	%	cN/tex	%	
60.0	9.01	1.86	176.07	12.14	8.92	sheath-core
50.0	7.97	1.86	107.17	16.17	9.96	sheath-core
39.0	7.63	1.89	110.44	15.59	9.80	porous external layer-core
27.5	7.27	1.85	86.79	18.68	10.00	porous external layer-core

The character and level of changes in absorption properties of fibres and their water retention are associated with the total pore volume and internal surface, as well as with the type of the porous structure being formed. The fibres spun within the temperature range from 27.5 to 60°C show different contents of capillary sets, described as small pores, medium pores, large pores and very large pores; their radii are given in Table 1.

The curves of pore distribution versus their radii (Figure 9) are characterised by a wide maximum, including the final range of medium and large pores. The maximum within the range of small pores is low, and indicates that the formed structure cannot be considered as fine-porous. The total content of small and medium pores does not exceed 50%, while the presence of a considerable maximum in the area of very large pores is disadvantageous. Although the value of water retention is associated with their content, the latter cannot be too high as it may determine the character of porosity and bring about structural defects.

The decreased content of this type of pores is demonstrated by the fibres prepared when the solidification process is carried out at a temperature of 60°C, but when this temperature is 27.5°C the obtained fibres have a structure which is characterised by similar contents of four capillary sets, with the content of small pores being the highest of the series, amounting to 19%.

Considering the relationship between the character of the porous structure formed and the absorption properties of the fibre obtained at variable temperature of the solidification bath, we may state that the water retention values are associated with the high content of pores large enough to be capable of filling themselves with water yet small enough to hold water during its mechanical removal. In this case, high retention values are connected with the appearance of a wide maximum (Figure 9) comprising the final range of medium pores and the range of large pores. The value of this maximum increases considerably with the increasing temperature of the solidification bath. The highest values of retention (at a level of 168%) are shown by the fibres solidified in the coagulation bath at 60°C which, in addition to a high total pore volume, show high pore contents of the above-mentioned range.

Moisture absorption is connected with the presence of pores with dimensions allowing moisture absorption on the capillary condensation basis. The limited content of small pores in the formed structure, together with the lack of high maximum in the pore distribution curve associated with the fine-porous character of the structure, create conditions for moisture absorption (at 100% RH) at a lower level than that assumed of 7-9%. The moisture absorption at 65% RH ranges from 1.7 to 2%. The height of the weak maximum within the range of medium pores, whose content also decides about the fine-porous structure, increases with the increases in the coagulation bath temperature.

The highest values of moisture absorption at 100% RH at a level of 9-8.5%, obtained for the fibres solidified at a temperature of 60°C, are linked with the highest content of medium pores (with the small pore content being quite low), and the highest values of total pore volume and internal surface amount to 1.4 cm^3/g and 50.6 m^2/g respectively.

Generally, the character of the structure formed within the wide range of coagulation bath temperature may be described as a structure with a quantitative predominance of medium and large pores. From the comparison of the moisture absorption and strength properties of the fibres obtained with the use of two drawing variants (deformations close to maximum and constant values of draw ratio, see Table 2), it follows that, with the same relationship character of the parameter examined versus the coagulation bath temperature, the use of lower deformations results in higher values of moisture absorption and lower values of strength properties as compared with the fibres drawn with higher deformations close to maximum values.

To obtain both fibre tenacity of about 20 cN/tex and good moisture absorption properties at the same time, it would be recommended to carry out the drawing process at deformation values increased up to 510%. The solidification process should be performed in mild baths, where the coagulation conditions are intensified only slightly by increasing the bath temperature to a level of 27.5°C. The highly porous fibres obtained under such conditions are characterised by the modified cross-section according to the assumed structural model. From the analysis of fibre cross-sections, it follows that too high an intensification of the fibre solidification conditions (up to 50-60°C) brings about the development of a differentiated structure of the sheath-core type, with a porous core and better oriented external layer-sheath. With the decrease in the coagulation bath temperature and moderation in the solidification conditions, the fibre structure is gradually transformed into the structure characterised by a porous external layer and a more compact-oriented core with a higher light transmittance, which is clearly visible in the form of a bright interior in the fibre microphotograms.

The fibres' strength properties depend on both the structural element orientation and the core content in the cross-section area [2]. Under selected conditions fibres were spun from a spinning solutions containing *Triclosan* or *Miconazol* of 1.3% by wt. in relation to the fibre material. Depending on the drawing variant used (deformations close to the maximum, amounting to 511-515%, and deformations decreased to 350.7%), the moisture absorption of the resultant fibres ranges from 1.78% to 1.98% at 65% RH and from 7.2 to 7.6% at 100% RH. The water retention value amounts to 78.9-89.5%, while the fibre tenacity ranges from 18.7 to 21.2 cN/tex with the elongation at break of about 10%.

The addition of *Triclosan* to the spinning solution, even in low quantities, allows the preparation of fibres with good antibacterial properties against *Escherichia coli*, with the bacteriostasis zone amounting to 2.5 mm. However, the effectiveness of *Triclosan* as a antifungal agent added in the same quantity to the spinning solution is insufficient, while good antifungal effects against *Penicillium funiculosum* are demonstrated by the fibres containing *Miconazol* in which no fungi growth is observed. The addition of higher quantities of antibacterial and antifungal agents is believed to further improve the protective action of these modified fibres.

Conclusions

- Highly porous polyacrylonitrile fibres have been obtained which are characterised by antibacterial and antifungal properties, as well as by a radial differentiation of structure with a compact oriented core and a porous external layer containing a system of open capillaries.
- Such a structure can be formed by the use of a mildly increased content of solvent coagulation bath, where the solidification conditions are intensified by increasing its temperature to the level which allows high moisture absorption values and a fibre tenacity of about 20 cN/tex to be obtained.
- The increase in the coagulation bath which results in the increased rate of diffusion processes brings about increased fibre porosity and moisture absorption values, with the fibre tenacity being decreased at the same time.
- The moisture absorption properties of fibres depend on the total pore volume and internal surface, as well as on the character of the formed porous structure. The very high water retention values are associated with the dominating quantities of medium pores (from their end range) and large pores. The lack of a clearly fine-porous character of the fibre structure results in slightly lower than assumed values of moisture absorption at 100% RH.
- The addition of *Triclosan* and *Miconazol* to the spinning solution makes it possible to prepare PAN fibres with antibacterial and antifungal properties.

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Acknowledgement

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