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Comparison of Some Process Components of Polyester Microfibre Dyeing by Using Mathematical and Experimental Methods

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Abstract: In this paper, a comparison between a mathematical and an experimental method for the evaluation of some process components of polyester microfibre dyeing is presented. In the experimental part, a dyeing procedure was chosen, K/S values of the dyed samples were measured and the coefficients of the mathematical formula presented in the mathematical part were obtained. K/S values of different dyeing procedures were also measured. In the mathematical part, predicted K/S values were calculated by a novel formula. The results of the two methods were then compared. According to the results obtained, the mathematical formula presented in this study can be used for calculating the predicted K/S values at lower dye concentrations.

Keywords: Disperse dye, Dyeing method, K/S values, Polyester dyeing, Polyester microfibre

Introduction

Dyeing can be defined as a process between a textile substrate and a solution or the dispersion of a dye which the textile substrate and the dye are placed in a dyebath so that the substrate absorbs the dye and shows a certain resistance to releasing the dye back to the bath which it has been absorbed [1].

Defining dye/fibre systems by using mathematical equations and experimental methods were given by textile technologists [2,3]. Because of the complexity of the both constituents, expressing the relationship between fibre and dye is a very complex study. Synthetic dyestuffs are produced having the same chemical structure and properties for each batch of the commercial dye for each dyeclass in itself. But textile fibres being natural, regenerated or synthetic, have important differences between each three classes in chemical and physical behavior. Due to the technological processes that the fibres exposure during post-production, properties of fibres may differ from each other although they come from the same origin and belong to the same classification. Under these circumstances, it is very difficult to express the behavior of fibres for dyeing by using plenty of complex equations and also it is very difficult to obtain the results of dyeing prior to the dyeing processes. Dyeing technologists must develop very complex equations which have constants for different types of the technological applications that the fibres meet before dyeing process but it is almost impossible to collect useful data which belongs to the processing background of the fabric to use in a mathematical equation.

Polyester microfibres are a new generation of polyester fibres which are characterized with their low fibre fineness [4]. The fibre fineness of polyester microfibres is below 1.0 denier. Polyester fibres (unmodified) can be dyed to useful depths only by those classes of dye that have low solubility in water. These comprise primarily disperse dyes. Disperse dyes are the most important class of dye used in dyeing of polyester fibres and provide a range of hues with good built-up and with fastness properties adequate for most purposes [5,6]. The rate of dyeing is raised to the level of commercial acceptability, either by raising working temperature to the region of 130 °C, or by dyeing at the boil in the presence of an accelerating agent or "carrier" [5].

The mechanism of disperse dyeing of polyester fibres follows Nernst sorption isotherm [6,7] and the dyeing rate depends on the concentration of dye in solution, the specific surface of the textile substrate, diffusion coefficient of the dye, and the affinity or solubility of the dye in the fibre [8,9]. Shape and slope of isotherms of the disperse dyes are also influenced by the presence of dispersing agents [10].

Computer modeling of dyeing of microfibres with disperse dyes have been studied by other workers in research papers. The extent of dye exhaustion when dyeing polyester microfibres with disperse dyes was expressed in terms of Kubelka-Munk (K/S) values by Uddin *et al.* [11]. In the work of Park and Koncar [12] disperse dyeing process for polyester microfibres were studied considering dye concentration, dyebath temperature, dye liquor flow and fibre count. Diffusion coefficient of disperse dyes on microfibres was computed by Park *et al.* [13] and it was stated that the diffusion coefficient depends on the initial dye concentration, the time and the fibre count for a fixed temperature (130 °C). Surface area of the fibres and diffusional boundary layer influence were also considered in the same work. A mathematical modeling of the diffusion coefficient for disperse dyes was studied by Casetta *et al.* [14] and it was pointed out that the dye uptake is controlled by several experimental parameters such as temperature, initial dye concentration, diffusion coefficients, etc. The dyeing behav-

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iour of disperse dyes were studied as a function of time, initial concentration and the nature of the dyebath in the same work.

A mathematical modeling of disperse dyeing of polyester microfibres is studied according to different molecular sized dyes, differing dyeing methods and dyebath additives in this paper. Experimental and mathematical results are reported and compared.

The nature of disperse dyeing systems allow them to be expressed by mathematical equations which can be derived from dyeing results such as Kubelka-Munk values (K/S). The parameters that express the dye uptake can be used to simulate the dyeing behavior of disperse dyes. The linear part of the Nernst isotherm expresses a partition of the dye molecules between the fibres and the solution. When Nernst isotherm is considered, we observe that at low dye concentrations, a straight line is obtained between the saturation solubility of dye in the bath [C_b (g/L)] and the fiber [C_f (g/kg)] [7]. But it is not always possible to stay in the linear part of the isotherm in commercial dyeing processes. In these processes, the excess amount of dye in the bath forms a solid phase. The disperse dye molecules in dyebath act as a reservoir for the dyeing operation. After the saturation limit of the fibre, this reservoir of dyes remains the same and forms an existing solid phase in the dyebath and the curve of the Nersnt isotherm becomes parallel to the C_b axis. An equation that would predict the dyeing behavior of the disperse dyes must take into account both the partition area (linear part of the Nernst isotherm) and solid phase in the dyebath (Figure 2).

Materials and Method

Materials

The properties of polyester microfibre fabrics used in the experimental part are given in Table 1.

Disperse dyes used in the experimental part are given in Table 2.

Table 1. Properties of the polyester microfibre fabrics

Fabric no.	Description	Weave pattern	Warp yarn (den/fil)	Weft yarn (den/fil)
1	Polyester microfibre	Plain weave	84/96	107/130
2	Polyester microfibre	Plain weave	78/128	78/128

Table 2. Disperse dyes used in the experimental part

Dyestuff no.	Molecular size (according to the manufacturers literature)
I	Big molecular size
II	Big-medium molecular size
III	Small molecular size

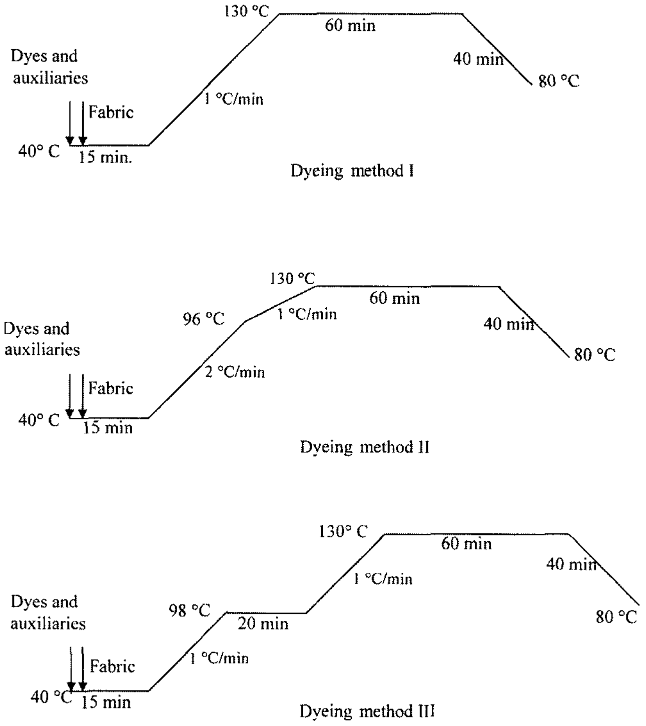

Figure 1. Dyeing methods used in the experimental part.

The dyes do not have any C.I. numbers and the formulae of the dyes could not have been obtained from their manufacturers.

Method

Dyeing methods used in the experimental part are given in Figure 1.

Three anionic levelling agents (Levelling Agents 1, 2 and 3 in Tables 3-14) were used in the dyeing experiments. All the three levelling agents are recommended for polyester microfibre dyeing by their manufacturers.

Formulations of the dyebaths were:

- Disperse dye : x % owf (on weight of fabric)
- Levelling agent : 1 g/*l* (According to the recommendations of the manufacturers)
- Crease inhibitor : 1 g/*l* (It also has a dispersing effect)
- Acetic acid for pH 5 : 1 m*l*/*l*
- Sodium acetate : 1 % (owf)
- Liquor to goods ratio : 1:50
- Sample weight for each dyeing : 3 g

The dyeings were carried out in a laboratory-type dyeing machine (termal HT) under laboratory conditions. All the chemicals used were in commercial purity.

Before the dyeing, the fabrics were desized by using laboratory pretreatment apparatus and were left to dry under laboratory conditions. After the dyeing, the samples were washed with cold water and a reduction clearing was made with sodium dithionite (2 g/*l*) and soda (2 g/*l*) solution at

70 °C for 40 minutes. Later, the samples were rewashed with cold water and were left to dry under laboratory conditions.

The dyeing experiments were carried out in two separate steps. In the first step, three levelling agents and Dyeing Method I were selected as the standard beginning of dyeing process components. The two fabrics were dyed by using these components at five different concentrations of each dyestuff (i.e., 0.2, 0.6, 1, 2, and 3 %). The standard coefficients of the equations that will be presented in the mathematical part were obtained.

In the second step, two different concentrations of each dyestuff (i.e., 1% and 2%) were used with each fabric, levelling agent and dyeing method combination.

Evaluation of the Results of the Dyeing Experiments

The results were obtained according to the colour measurements of the samples with a reflectance spectrophotometer under D65/10 ° illuminant between 400-700 nm.

Colour evaluation of the samples was made according to Kubelka-Munk Equation and K/S values were obtained:

$$\text{Kubelka-Munk Equation, } K/S = (1-R)^2/2R \tag{1}$$

where, K: a constant about the light absorption of the dyed fabric

S: a constant about the light scattering of the dyed fabric

R: reflectance of the dyed fabric, expressed in fractional form

K/S is a colour value dependent on the light absorption of the dyed fabric at maximum absorption wavelength and is associated with the reflectance of the dyed fabric.

Mathematical Part

A series of equations based on dyeings of the selected conditions were obtained in the mathematical part. These equations were solved by using MATLAB Engineering Software in matrices form and predicted K/S values were obtained.

The dye exhaust curves of the dyeings can be expressed by plotting K/S values of dyed fabrics (or logarithm of the K/S values) against the dye concentration [C_b] (% owf or g/*l*) in the dyebath. In Figure 2, an example of the graphs obtained for the first step of the dyeings by using Dye II and one of the levelling agents is presented.

The curves (an example is shown in Figure 2) were obtained after a series of dyeing experiments at different dye concentrations by using three levelling agents and they can be presented by equation (2):

For the selected five different concentrations;

$$(K/S)_i = AX^5 + BX^4 + CX^3 + DX^2 + EX^1 \tag{2}$$

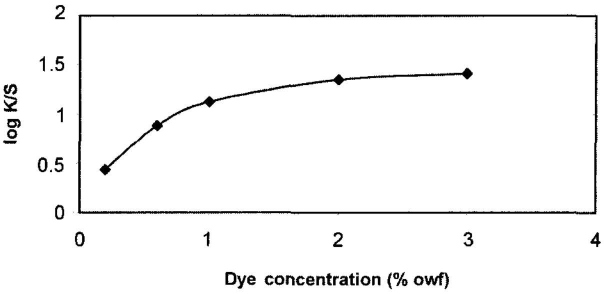

Figure 2. Log K/S versus dye concentration curve.

where, $(K/S)_i$: value obtained for each individual dye concentration (% owf)

X: concentration of dye in percent (%) owf

A,...,E: coefficients of the exhaust curve for the dyeing of the fabric samples

In this study, A,...,E coefficients were obtained by selecting five different dye concentrations (% owf) and computing the related values in MATLAB as discussed above.

For the five different selected dye concentrations, the equations given below can be derived from equation (2):

$$(K/S)_1 = A\,(0.2)^5 + B\,(0.2)^4 + C\,(0.2)^3 + D\,(0.2)^2 + E\,(0.2)^1 \tag{3}$$
$$(K/S)_2 = A\,(0.6)^5 + B\,(0.6)^4 + C\,(0.6)^3 + D\,(0.6)^2 + E\,(0.6)^1 \tag{4}$$
$$(K/S)_3 = A\,(1)^5 + B\,(1)^4 + C\,(1)^3 + D\,(1)^2 + E\,(1)^1 \tag{5}$$
$$(K/S)_4 = A\,(2)^5 + B\,(2)^4 + C\,(2)^3 + D\,(2)^2 + E\,(2)^1 \tag{6}$$
$$(K/S)_5 = A\,(3)^5 + B\,(3)^4 + C\,(3)^3 + D\,(3)^2 + E\,(3)^1 \tag{7}$$

It was observed that the computing became very difficult, results became meaningless and trustable results could not have been obtained when more than 5 different dyestuff concentrations were selected for the derivation of the mathematical equations. The given five concentrations were found as the most suitable ones while searching for the optimum number of different dye concentrations for this research.

A-E coefficients were obtained after expressing the equations (3)-(7) in MATLAB in matrices form. These coefficients are standard coefficients of equation (2) for each fabric and levelling agent combination for the selected standard dyeing method. In this study, Dyeing Method I was selected as the standard dyeing method to obtain the A,...,E coefficients. By using equation (2), the different dyeing methods given in Figure 1 were compared for each levelling agent and each fabric.

When computing the mathematical equations, the results were obtained in Log K/S form and these values were converted to K/S values.

Results and Discussion

Coefficients of equation (2) that were obtained by MATLAB software are given in Tables 3-5.

Table 3. Coefficients of Dye I

Fabric no.	Levelling agent	A	B	C	D	E
1	1	−0.1387	0.9002	−1.8556	1.0258	0.9911
1	2	−0.1056	0.6882	−1.4090	0.6827	1.0465
1	3	−0.0780	0.5041	−0.9957	0.3098	1.1810
2	1	0.1095	−0.7233	1.7006	−2.0511	1.9498
2	2	−0.0234	0.1278	−0.0920	−0.6187	1.5594
2	3	0.0055	−0.0800	0.4379	−1.2034	1.8248

Table 4. Coefficients of Dye II

Fabric no.	Levelling agent	A	B	C	D	E
1	1	0.1477	−1.0413	2.6794	−3.4190	2.7627
1	2	0.0122	−0.1789	0.8881	−2.0343	2.4188
1	3	0.1436	−1.0005	2.5419	−3.2355	2.6777
2	1	0.2309	−1.6321	4.1645	−5.0289	3.4359
2	2	0.1916	−1.3534	3.4738	−4.3104	3.1472
2	3	0.2009	−1.4322	3.7195	−4.6540	3.3382

Table 5. Coefficients of Dye III

Fabric no.	Levelling agent	A	B	C	D	E
1	1	−0.1838	1.2767	−3.0335	2.7668	−0.2355
1	2	−0.2004	1.3752	−3.2130	2.8796	−0.2711
1	3	−0.2088	1.4228	−3.2945	2.9210	−0.2665
2	1	−0.3069	2.0526	−4.6038	3.8615	−0.3366
2	2	−0.2910	1.9577	−4.4351	3.7867	−0.3622
2	3	−0.3344	2.2297	−4.9794	4.1642	−0.4170

Comparison of the mathematical and experimental K/S values are given in Tables 6-11.

Equation (2) was then used to predict K/S values for dye concentrations that were not selected in the experimental part. The validity of the equation was tested for low and high dye concentrations. The predicted values calculated for each dyestuff by using equation (2) for dyeing method I are given in Tables 12-14.

The mathematical and experimental results given in Tables 3-11 show that the results of the mathematical equation are close to the experimental results at 1 % and 2 % owf indicating the validity and reliability of the equation (2) in this concentration range.

The predicted results obtained by using equation (2) given in Tables 12-14 show that at low dye concentrations, the given mathematical method gives acceptable results. This concentration range corresponds to the primary part of the Nernst Isotherm which is linear.

Table 6. Comparison of mathematical and experimental K/S values for Dye I at 1 % owf

Fabric no.	Levelling agent	Dyeing method	Experimental result	Mathematical result
1	1	1	8.3638	
1	1	2	8.1848	8.3714
1	1	3	7.5148	
1	2	1	7.4414	
1	2	2	7.0536	7.9946
1	2	3	7.6608	
1	3	1	8.1556	
1	3	2	8.2735	8.3406
1	3	3	7.5872	
2	1	1	10.0663	
2	1	2	9.3708	9.6716
2	1	3	9.9459	
2	2	1	9.1359	
2	2	2	9.2755	8.9763
2	2	3	9.1038	
2	3	1	9.2494	
2	3	2	9.8165	9.6560
2	3	3	8.9754	

Table 7. Comparison of mathematical and experimental K/S values for Dye I at 2 % owf

Fabric no.	Levelling agent	Dyeing method	Experimental result	Mathematical result
1	1	1	15.9639	
1	1	2	16.2114	16.0472
1	1	3	15.0412	
1	2	1	15.2322	
1	2	2	14.5626	15.2686
1	2	3	15.6678	
1	3	1	16.1967	
1	3	2	16.2410	16.0398
1	3	3	15.6045	
2	1	1	17.6727	
2	1	2	16.7289	17.0294
2	1	3	17.6008	
2	2	1	16.6976	
2	2	2	16.8076	15.9955
2	2	3	16.5889	
2	3	1	16.7289	
2	3	2	17.8457	17.1869
2	3	3	16.8552	

2 and 2.2 % (owf) of dyestuff can be considered as excess dye amounts in the dyebath. It can be said that the solid dyes form an existing solid phase in the dyebath over the

Table 8. Comparison of mathematical and experimental K/S values for Dye II at 1 % owf

Fabric no.	Levelling agent	Dyeing method	Experimental result	Mathematical result
1	1	1	13.6691	
1	1	2	13.6157	13.4741
1	1	3	13.6477	
1	2	1	12.0316	
1	2	2	12.5047	12.7614
1	2	3	12.2377	
1	3	1	13.7554	
1	3	2	13.8098	13.4029
1	3	3	13.1338	
2	1	1	15.0669	
2	1	2	15.2098	14.8013
2	1	3	15.0284	
2	2	1	14.3186	
2	2	2	14.1451	14.0863
2	2	3	14.4245	
2	3	1	14.9519	
2	3	2	14.9266	14.8730
2	3	3	15.0927	

Table 9. Comparison of mathematical and experimental K/S values for Dye II at 2 % owf

Fabric no.	Levelling agent	Dyeing method	Experimental result	Mathematical result
1	1	1	22.8200	
1	1	2	22.7635	22.3975
1	1	3	23.3116	
1	2	1	21.0864	
1	2	2	21.8420	21.5377
1	2	3	21.6611	
1	3	1	22.3752	
1	3	2	23.0200	21.6670
1	3	3	20.9653	
2	1	1	22.4025	
2	1	2	22.6512	22.2535
2	1	3	22.3752	
2	2	1	21.7125	
2	2	2	21.8420	20.8929
2	2	3	21.6868	
2	3	1	22.3479	
2	3	2	22.7072	23.4422
2	3	3	22.4299	

Table 10. Comparison of mathematical and experimental K/S values for Dye III at 1 % owf

Fabric no.	Levelling agent	Dyeing method	Experimental result	Mathematical result
1	1	1	3.7060	
1	1	2	3.8245	3.8967
1	1	3	3.5620	
1	2	1	3.6521	
1	2	2	3.7755	3.7179
1	2	3	3.3840	
1	3	1	3.7017	
1	3	2	3.4851	3.7497
1	3	3	3.6427	
2	1	1	4.2804	
2	1	2	4.5656	4.6430
2	1	3	4.5595	
2	2	1	4.5944	
2	2	2	4.5594	4.5300
2	2	3	4.4604	
2	3	1	4.2309	
2	3	2	4.3466	4.6036
2	3	3	4.2644	

Table 11. Comparison of mathematical and experimental K/S values for Dye III at 2 % owf

Fabric no.	Levelling agent	Dyeing method	Experimental result	Mathematical result
1	1	1	7.3392	
1	1	2	7.6497	7.4782
1	1	3	7.0794	
1	2	1	7.2642	
1	2	2	7.5292	7.2878
1	2	3	7.4455	
1	3	1	7.4720	
1	3	2	7.0504	7.5544
1	3	3	7.4366	
2	1	1	8.5546	
2	1	2	9.2966	9.1875
2	1	3	9.0600	
2	2	1	9.2027	
2	2	2	8.9803	8.9701
2	2	3	9.1309	
2	3	1	8.2607	
2	3	2	8.5455	9.1622
2	3	3	8.5682	

Table 12. Predicted K/S values for Dye I

Fabric no	Levelling agent	0.5 % (owf)	1.5 % (owf)	1.8 % (owf)	2.2 % (owf)
1	1	3.7323	10.8657	13.0263	21.2080
1	2	3.6100	10.7786	12.8063	19.1777
1	3	3.7372	11.6884	13.8231	19.2499
2	1	4.2945	16.5599	18.1191	14.7813
2	2	4.1761	12.7590	14.6292	17.5548
2	3	4.5862	13.9388	15.9799	18.2921

Table 13. Predicted K/S values for Dye II

Fabric no	Levelling agent	0.5 % (owf)	1.5 % (owf)	1.8 % (owf)	2.2 % (owf)
1	1	6.3249	22.0948	24.0603	19.0137
1	2	6.3246	17.1919	19.7066	23.4282
1	3	6.1612	21.9289	23.5381	18.2210
2	1	7.7001	24.2606	25.5992	16.1255
2	2	7.1059	22.3794	23.5193	16.6218
2	3	7.7144	23.1304	24.1770	16.8817

Table 14. Predicted K/S values for Dye III

Fabric no.	Levelling agent	0.5 % (owf)	1.5 % (owf)	1.8 % (owf)	2.2 % (owf)
1	1	1.8570	5.0297	6.0037	10.1763
1	2	1.8298	4.6637	5.6664	10.3711
1	3	1.8517	4.6871	5.7727	10.9815
2	1	2.1892	5.0864	6.3724	15.6591
2	2	2.1108	5.1213	6.3672	14.7594
2	3	2.1828	4.8638	6.1564	16.4055

saturation limit of the fibres. The derived equation may not give true results because of the solid phase. When the initial dyebath concentration is increased and the corresponding predicted K/S values were calculated by using equation (2), a comparison can be made between bigger and smaller molecular sized disperse dyes. Predicted K/S values obtained for high concentrations of big molecular sized dye do not show a trustable relation between the experimental and mathematical parts. Predicted K/S values obtained for high concentrations of small molecular sized dye seem to follow the linear part of the Nernst Isotherm because the predicted values rise gradually. This shows that there is a relation between the linear part of the Nernst Isotherm and the molecular size of the dye in which the subject is out of the scope of this paper. But the observed results may be related to free volume of the fibre fine structures.

Other conclusions due to the fiber fineness of the fabrics can also be achieved. Experimental K/S values of Fabric 2 are slightly higher than the values of Fabric 1 due to the back scattering effect of finer denier fibres of Fabric 2. As coefficients of the mathematical equation were derived from laboratory dyeings, the predicted K/S results also show the same tendency. The derived mathematical formula is affected from all the dyeing components of the dyebath and for that reason it can be taken as an original formulation for each dyebath combination.

Conclusions

In this study, mathematical and experimental results which were obtained with the evaluation of some process components of polyester microfibre dyeing were presented. The comparison of the results for two fabrics, three levelling agents and three dyeing methods were made.

By using the mathematical method given in this paper, predicted K/S values can be obtained for the selected or standard dyeing conditions. The pre-evaluation of the dyestuffs that are used for different purposes can be made and acceptable results can be obtained depending on the nature of the dyestuff and experimental conditions.

The formulation gives results in agreement with the Nernst isotherm. The results obtained by computing are close to the experimental ones when the computing is made under the saturation limit of the polyester fibres where the Nernst isotherm is linear. Also the results are in relation with the molecular sizes of the dyes. It is concluded that the molecular size of the disperse dyes and the free volume of the fine structures of fibres are closely related in dyeing. We can assume that the free volume for the penetration of disperse dyes is filled with the dye molecules. As the dye molecules in the dyebath and the ones on the fibre are related to each other by the linear part of the Nernst isotherm, the occupation of the free volumes in the fibres must be related with the molecular size. The validity of the derived equation seems to be related to the molecules' filling capacity of the free volumes.

It is pointed out by Stevens [6], Casetta *et al.* [14], Becerir [8], Becerir and Iskender [9] and Zollinger [10] that the dyeing rate and amount of the dyes taken by the fibres are related to various dyebath components. The mathematical approach given in this research takes account these components in a single formulation and expresses the dyeing behavior well in K/S terms under the fibre saturation limits.

The given mathematical approach can be used to predict the K/S values for different dyeing components when the dyeings are made under dye saturation limits of polyester fibres.

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