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SELECTION AND RESEARCH OF NEW MODIFICATIONS OF STATIONARY PROMOTED NICKEL-COPPER-ALUMINUM CATALYSTS

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ABSTRACT

The paper presents the results of research and development of a continuous technology for the pre-contact hydrogenation of cottonseed oil on stationary and powdered nickel-copper catalysts. It was found that the recommended technology allows to significantly increase the productivity of hydrogenation plants and reduces the content of trans-isomerized fatty acids in solid fat. This ensures an increase in the physiological and nutritional value of margarine products based on food solid fat.

KEYWORDS: *Fisher Criterion, The Response Function, Trans-Isolation, Import-Substitution, Catalysis, Vanadium + Rhodium Or Palladium.*

INTRODUCTION

Food fats are an essential food item. According to physiological norms, the recommended fat content in the human diet is 30-33% - the total energy value of food. In the world, more and more attention is paid to research work on the catalytic modification of vegetable oils and fats to improve the quality and ensure the food safety of target fats. The creation of new generation catalysts for the production of food-grade fats is an urgent problem. In this direction, scientific research work on improving the properties of food-grade fats for targeted purposes, optimizing their composition and technological processes is receiving significant development.

Solving the problems of the quality and safety of edible fats and products of their processing is one of the priority directions in the implementation of the concept of state policy in the field of healthy nutrition of the population of the Republic. Despite the intensive development of the theory of heterogeneous catalysis, including hydrogenation catalysis, the selection and synthesis of catalysts are mostly empirical. In this case, the reference points are theoretical studies and experimental work related to the study of the catalytic properties of individual metals, oxides, their combinations, etc. [1].

Scientists and specialists have proposed improved technologies for the catalytic hydrogenation of vegetable oils and fats using powdered and stationary catalysts. Optimal technological modes of production of edible fats based on sunflower, cottonseed, soybean and palm oils have been developed. Recommendations are given on the use of edible, hydrogenated fats for the production of a wide range of margarine products.

At the same time, little attention was paid to the development of the technology for the hydrogenation of oils and fats, in particular, cottonseed oil using catalysts of a new generation to improve the quality and ensure food safety of the resulting products.

There is no scientifically substantiated technology for the hydrogenation of cottonseed oil for the production of high-hard edible fats with a minimum content of trans-isomerized fatty acids. The influence of technological modes and the nature of catalysts on the formation of the quality and physicochemical characteristics of high-hard edible fats has not been studied; the role of the nature of the hydrogenated raw materials and the component composition of the catalysts used on the nutritional value and safety of the products obtained has not been established and justified [2, 3].

Modification of alloyed nickel-aluminium catalysts is achieved by introducing metals that change the fine structure of the alloy and its properties after more or less deep leaching. The choice of promoters and their combinations is determined by the results that have been accumulated by science in the study of the catalytic and other properties of these promoting additives [4].

The relevance of the work. The action strategy (2017-2021) for the further development of the Republic of Uzbekistan specifies the tasks "... for the development of industries, modernization and diversification of industry, the use of resource and energy-saving methods, ensuring food safety of products, the production of competitive and export products for import substitution ..." [5].

In this regard, scientific research aimed at the production of high-quality food-grade fats for targeted purposes using vegetable oils, in particular, soybean, sunflower, safflower, and sesame oils for the preparation of a wide range of food products is of particular importance.

Therefore, the search for possibilities for the production of hydrogenated fats based on vegetable oils using new generation catalysts, the establishment and substantiation of the scientific and practical foundations of catalytic processes is of great scientific and practical interest [5-6].

Uzbekistan has a sufficient raw material base and opportunities for organizing and mastering new technologies for the production of hydrogenated fats and catalysts for these purposes. In this regard, carrying out scientific and experimental research in the direction of developing the technology of hydrogenation of oils and fats on catalysts of a new generation using the technology of stepwise hydrogenation, improving the quality and ensuring food safety of the obtained edible fats for target purposes is relevant [7, 8].

METHODS

Vegetable oils, stage-by-stage hydrogenation technology, new catalytic systems, technology for the production of food-grade fats, improving the quality and ensuring food safety of fats, technological modes and processes. Stage-by-stage hydrogenation of vegetable oils on catalysts of a new generation, production of food-grade fats and their use.

The aim of the work. Research and improvement of continuous technology for the hydrogenation of fats on stationary catalysts using them as a forecontact, reducing the content of trans isomerized acids in salomas (solid fat), improving their quality, nutritional value, and increasing the productivity of technological equipment.

RESULTS AND DISCUSSION

In our experimental work, the nickel-copper-aluminium alloy is promoted with rhodium, palladium and vanadium. It should be noted that a comprehensive study of the promoting effect of vanadium, especially in conjunction with rhodium and palladium, has not yet been carried out.

It is known that vanadium reduces the catalyst's ability to isomerize and transesterify fatty acid glycerides. Considering these properties of vanadium, it was introduced into the composition of a nickel-copper-aluminium catalyst promoted with rhodium (0.5 %) or palladium (0.05 %).

The activity and selectivity of the catalyst were studied depending on the vanadium content (0.5–2.5 %).

Changes in the activity of nickel-copper-aluminium catalysts depending on the vanadium concentration at constant rhodium and palladium contents are shown in Figs. 1 and 2. As follows from these data, vanadium increases the activity of the catalyst. However, the activity of catalysts increases disproportionately to the mass fraction of vanadium.

The study of the hydrogenating properties of new modifications of stationary nickel-copper-aluminium catalysts was carried out at 200 °C, a pressure of 300 kPa, and a hydrogen supply rate of 60 h^{-1}. In all cases, cottonseed oil (iodine value 112 mg of iodine) was hydrogenated at a constant rate (1.0 h^{-1}). The results of the study of stationary catalysts are shown in the table. 1 and 2.

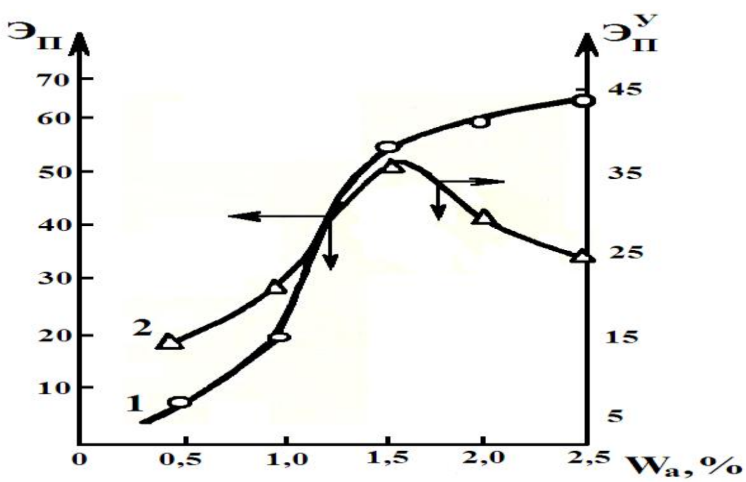

Figure 1. Promoter (1) and specific promoter (2) vanadium effects in nickel-copper-rhodium-aluminum catalyst (rhodium 0.5%)

TABLE 1. INFLUENCE OF VANADIUM ON THE PROPERTIES OF NICKEL-COPPER-PALLADIUM-ALUMINIUM CATALYST (PALLADIUM 0.05%)

Mass. proportion of vanadium in the alloy,%	Activity, iodine number.	Relative activity,%	Selectivity,%	Content of trans isomers,%
0,0	51,3	100	92	45
0,5	52,9	103	88	39
1,0	53,8	104	84	30
1,5	56,4	109	80	26
2,0	57,0	111	79	24
2,5	67,5	112	76	22

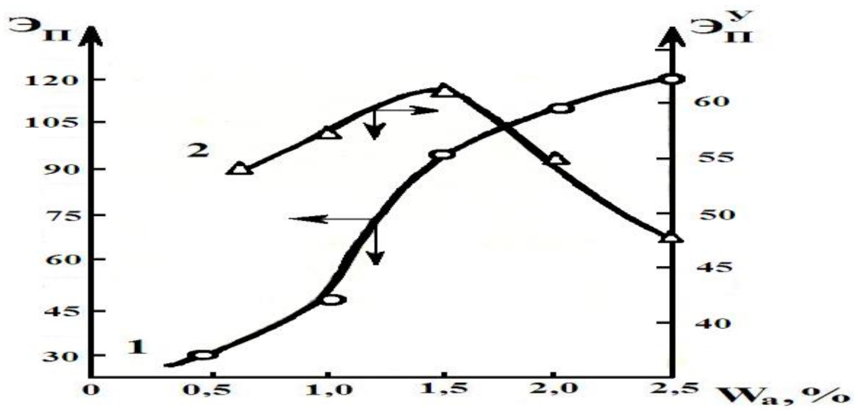

Figure 2. Promoter (1) and specific promoter (2) vanadium effects in nickel-copper-palladium-aluminium catalyst (palladium 0.05%)

To determine the degree of influence of the amount of the promoter (vanadium) on the hydrogenating properties (activity, selectivity, and isomerizing ability) of the stationary catalyst, the experimental design method was used.

TABLE 2. INFLUENCES OF VANADIUM ON THE PROPERTIES OF A NICKEL-COPPER-RHODIUM-ALUMINIUM CATALYST (RHODIUM 0.5%)

Mass. proportion of vanadium in the alloy,%	Activity, iodine number.	Relative activity,%	Selectivity,%	Content of trans isomers,%
0,0	52,0	100	82	42
0,5	52,5	101	80	38
1,0	53,1	102	78	32
1,5	54,9	106	76	24
2,0	55,0	106	75	24
2,5	55,3	106	75	23

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The response function - activity ($У_1$), selectivity ($У_2$) and isomerizing ability ($У_3$) of the catalyst depended on the concentration of the following metals in the alloy,% nickel (X_1), aluminium (X_2), vanadium (or another promoter) (X_3) and copper (X_4). The obtained results of planning the experiment made it possible to find the corresponding regression equations.

Checking the adequacy of the obtained regression equations by Fisher's criterion showed that the greatest influence on the hydrogenating and other of the above properties of the nickel-copper-aluminium catalyst is exerted by vanadium as a promoter when its content in the alloy is 1.5%.

Indeed, summarizing the data obtained, we can conclude that the introduction of paired combined additives (vanadium + rhodium or palladium) in an amount of 0.05–2.5% by weight of the alloy increases the activity, selectivity of hydrogenation and reduces the accumulation of trans-isomerized acids in salomas. The greatest promotion effect is observed when the following amounts of promoters are added to the catalyst: 0.5% rhodium + 1.5% vanadium and 0.05% palladium + 1.5% vanadium. However, even with an optimal concentration of a promoter (or a system of promoters) in the alloy, the activity of the resulting catalysts is, of course, the same. Thus, based on the results of studies of several stationary catalysts, highly efficient stationary alloyed promoted nickel-copper-aluminium catalysts were found with the aim of recommending them for pilot-industrial testing and implementation in the technology of continuous hydrogenation of cottonseed oil to obtain edible fat and confectionery fat. Technological modes of the process of obtaining food fatty masses were tested in a hydrogenation unit (capacity 15-20 t/day) of a column type, as well as in existing industrial autoclaves. Research and testing were carried out by varying the technological parameters of hydrogenation to control the fatty acid composition and the content of trans-isomerized acids in the salomas. The results are presented in Tables 3, 4, 5, and 6 and Fig. 3 and 4.

TABLE 3. SEQUENTIAL HYDROGENATION OF COTTONSEED OIL ON A STATIONARY CATALYST PROMOTED WITH PALLADIUM AND VANADIUM

$П^{60}_{Д}$	Fatty acid composition of hydrogenates, %			Selectivity, %	Increase in the content of trans isomers, %	$T_{ПЛ}$, °C	Salomas hardness, g/cm	К.ч., mg KOH/g
	$C^0_{14\text{-}18}$	$C^{1=}_{18}$	$C^{2=}_{18}$					
Ex. oil 1,4580	26,3	19,6	54,1	–	–	–	–	–
1,4575	27,6	25,2	47,2	94,7	7	25,0	–	–
1,4573	27,8	25,8	46,4	95,0	8	26,5	–	–
1,4562	30,8	29,0	40,2	97,0	9	26,9	–	–
1,4559	33,4	31,4	35,2	97,4	10	27,3	–	–

TABLE 4. SEQUENTIAL HYDROGENATION OF COTTONSEED OIL ON A DISPERSED NICKEL-COPPER CATALYST

$П^{60}_{Д}$	Fatty acid composition of hydrogenates, %			Selectivity, %	Increase in the content of trans isomers, %	$T_{ПЛ}$, °C	Salomas hardness, g/cm	К.ч., mg KOH/g
	$C^0_{14\text{-}18}$	$C^{1=}_{18}$	$C^{2=}_{18}$					
1,4530	29,5	61,6	8,9	83	24	34,6	360	0,76

1,4523	30,5	60,7	8,8	88	21	34,5	390	0,48
1,4523	29,7	58,8	11,5	85	16	37,1	470	1,16
1,4521	33,5	59,2	7,3	93	17	36,5	520	0,83

As can be seen from Tables 3 and 4, the partial hydrogenation of cottonseed oil to a residual linoleic acid content of 35-47% on a stationary catalyst promoted by palladium and vanadium makes it possible to obtain liquid or liquid salomas with a melting point of no more than 30 °C.

The subsequent hydrogenation of this solid fat on a powdered catalyst makes it possible to obtain standard-quality salomas for margarine products and confectionery fat with a melting point of 34-36 °C and a hardness of 360-500 g/cm with a trans-isomer content of 23-34%. This is less than the content of trans-isomers in salomas obtained by the conventional method. The same result was obtained by hydrogenation on a stationary nickel-copper-rhodium-vanadium-aluminium catalyst followed by post-hydrogenation on a powdered nickel-copper catalyst (Tables 5 and 6).

As shown in these tables, the hydrogenated oil was obtained on a stationary catalyst at a volumetric oil supply rate from, 5 to 3.2 h^{-1}. Under these conditions (temperature 165-170 °C, hydrogen pressure 250 350 kPa), industrial batches of partially hydrogenated cottonseed oil with an iodine number of 96.3–03.5 were obtained.

TABLE 5. SEQUENTIAL HYDROGENATION OF COTTONSEED OIL ON A STATIONARY CATALYST PROMOTED WITH RHODIUM AND VANADIUM IN PILOT INDUSTRIAL CONDITIONS

Sample, no.		1	2	3	4	5
Volumetric oil feed rate, h^{-1}		1,5	1,8	2,4	2,8	3,2
Speed of oil supply to the autoclave, t/h		-	-	-	-	-
Iodine number, % J_2		96,3	98,9	99,8	101,8	103,5
K.n, mg KOH/g		0,5	0,4	0,4	0,3	0,3
Fatty acid composition of hydrogenates, %	$C^0_{16\text{-}18}$	30,2	29,5	28,3	28,0	27,4
	$C^{1=}_{18}$	27,8	26,5	25,7	25,6	24,6
	$C^{2=}_{18}$	$C^{2=}_{18}$	44,0	45,0	46,4	47,8
Selectivity, %		68	68	73	78	83
Increase in the content of trans-isomers, %		17,2	13,0	10,2	6,0	6,0
$T_{ПЛ}$, °C		30,2	26,5	24,0	21,0	-
Salomas hardness, g/cm		--	-	-	-	-

TABLE 6. SEQUENTIAL HYDROGENATION OF COTTONSEED OIL ON A DISPERSED CATALYST UNDER EXPERIMENTAL AND INDUSTRIAL CONDITIONS

Sample, no.	1	2	3	4
Volumetric oil feed rate, h^{-1}	-	-	-	-
Speed of oil supply to the autoclave, t/h	6,0	6,5	8,0	8,2
Iodine number, % J_2	71,3	74,4	80,0	80,4

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K.n, mg KOH/g		0,81	0,9	0,75	0,67
Fatty acid composition of hydrogenates, %	C^{0}_{16-18}	31,0	29,8	27,7	27,0
	$C^{1=}_{18}$	55,1	53,9	51,6	52,5
	$C^{2=}_{18}$	13,9	16,3	16,3	20,5
Selectivity, %		86,8	89,4	92,0	94,4
Increase in the content of trans-isomers, %		18,6	16,4	14,9	14,2
$T_{ПЛ}$, °C		36,1	35,8	34,4	34,1
Salomas hardness, g/cm		500	420	340	260

It should be noted that hydrogenation on a stationary catalyst, as expected, proceeded according to the total kinetics of the zero-order. Indeed, the relationship between the volumetric flow rates of oil and iodine number section of hydrogenated feed had been distinct linear (Fig.3). Also confirmed that the selectivity of the stationary catalyst decreases sharply with increasing depth of hydrogenation (Fig.4). Given the zero-order of the reaction, a linear relationship could be expected between the iodine number of the hydrogenate produced on the stationary catalyst and the trans-isomer content. This conclusion is also confirmed during pilot tests (Fig. 5).

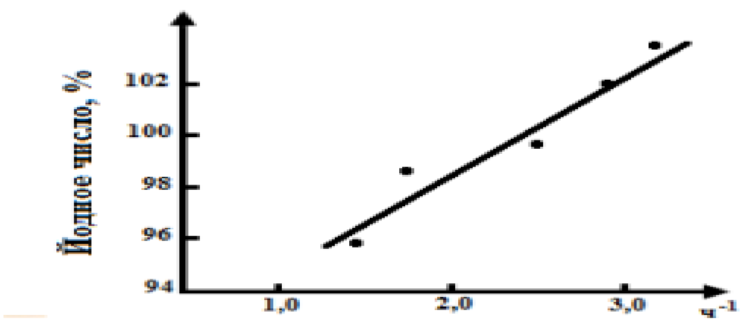

Figure 3. Zero-order of the cottonseed oil hydrogenation reaction on a stationary catalyst

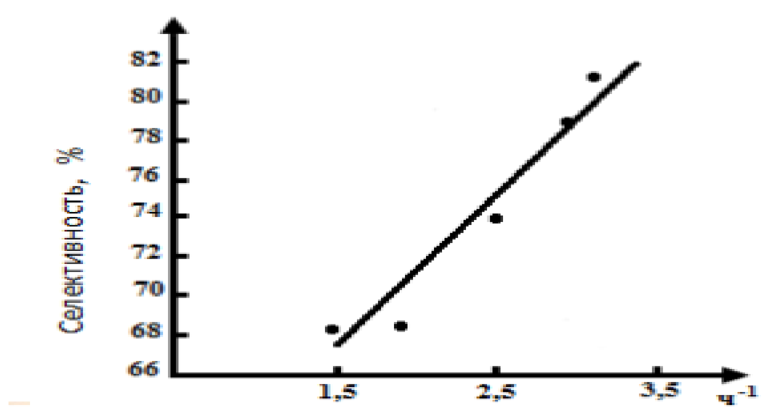

Figure 4. Effect of the volumetric oil feed rate on the selectivity of hydrogenation on a stationary catalyst

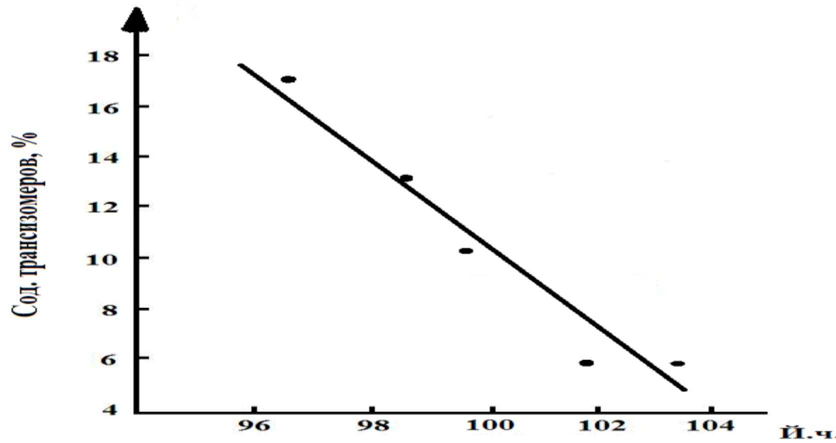

Figure 5. A linear relationship between the content of trans-isomers and the depth of oil hydrogenation on a stationary catalyst

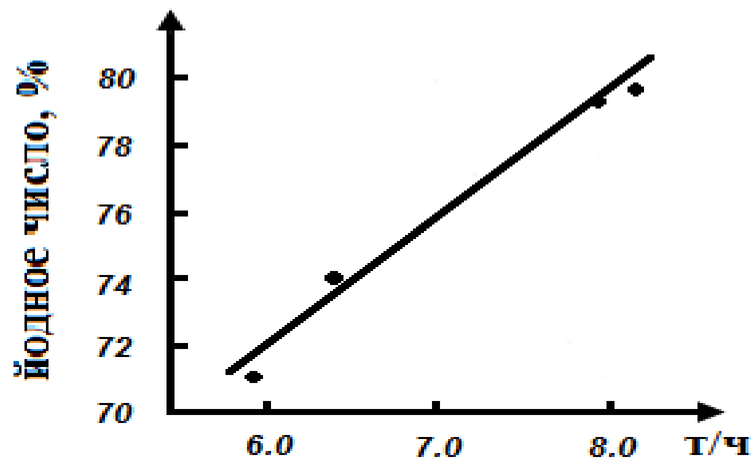

Figure 6. Zero-order of reaction in continuous hydrogenation of cottonseed oil on a powdered catalyst

Further, these hydrogenate were subjected to deeper hydrogenation to the iodine number 71-80 on a powdered catalyst. As can be seen from Fig. 6, a linear relationship was also observed between the hourly performance of the process on a powdered catalyst and the salomas iodine number. This means that the final stage of the process is also described by a total kinetic equation of zero order. And in this case, salomas with a melting point of 34-36 °C were obtained, having a hardness in the range of 260-500 g/cm and containing trans-isomers in an amount of 27 to 30 %, that is, less than in ordinary salomas. Tests at the pilot plant of the Tashkent (OFC) also showed that the new hydrogenation scheme allows the use of a low-activity nickel catalyst and thereby significantly reduce its consumption while increasing the plant's productivity.

Thus, it is confirmed that for the production of plastic food hydrogenated fats, it is advisable to use the technology of pre-contact hydrogenation of cottonseed oil with the use of a stationary, vanadium–promoted (1.5%), alloy nickel-copper–rhodium-aluminium catalyst at the initial stage and subsequent hydrogenation of partially hydrogenated oil on a powdered nickel-copper catalyst.

CONCLUSION

New modifications of stationary nickel-copper-aluminium alloy catalysts with the addition of vanadium (0.5-2.5%), rhodium (0.5%) and palladium (0.05%) in the process of pre-contact hydrogenation of cottonseed oil were investigated and developed. It is shown that the lowest content of trans-isomerized acids in salomas is achieved at a content of 1.5% vanadium in a stationary promoted catalyst. A continuous technology of pre-contact hydrogenation of cottonseed oil on stationary and powdered nickel-copper catalysts has been investigated and developed for the first time. It is established that the recommended technology allows to significantly increase the productivity of hydrogenation plants and reduces the content of trans-isomerized fatty acids in salomas. This ensures an increase in the physiological and nutritional value of margarine products based on food salomas. The influence of technological modes (temperature, pressure, oil and hydrogen feed rate) of cottonseed oil hydrogenation on new modifications of stationary nickel-copper-aluminium promoted catalysts is studied. Based on the obtained results, the technological parameters for the production of food and confectionery salomas by a combination of stationary and suspended catalysts are established. The mechanism and kinetics of the process of nonselective hydrogenation of unsaturated fatty acids on a stationary catalyst at the beginning of the process have been established by studying the regularities of the continuous technology of pre-contact hydrogenation of cottonseed oil. Further, by hydrogenating the partially hydrogenated oil on a powdered catalyst, the selectivity of the process is increased.

By the method of precontact hydrogenation of cottonseed oil, edible fatty oils (the content of trans-isomerized acids 7-10%) with the specified physicochemical properties corresponding to the quality requirements of the standards were obtained. Based on the obtained salomas, confectionery products with high-quality indicators are made. Comparative estimates of the viscosity of salomas obtained on powdered and stationary nickel-copper catalysts are carried out. It is shown that as the iodine number of the hydrogenate decreases, its viscosity increases. An increase in the melting and solidification temperature of salomas also leads to a change in its viscosity. Under constant conditions of continuous hydrogenation and with the stable activity of the catalyst, with an increase in the content of trans-acids in the hydrogenated, its viscosity increases.

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