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Spectrum of Electrochemical Noise and Its Relationship with Passivation Processes of Stainless Steels AISI 304 and AISI 316

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Abstract

The present work describes the researches regarding the passivation processes of stainless steels AISI 304 and AISI 316, performed using the method of electrochemical noise. Researches were carried out using the circuit designed with three identical electrodes in three various corrosion environments: 10% $FeCl_3$, 0.1M $NaHCO_3$ + 0.1M Na_2CO_3, 20% NaCl. Results of measurement have been processed mathematically using the MathCAD system. From the received data, the "noise" polarization resistance on electrodes in the investigated environments was counted. The calculated "noise" polarization resistance has been compared to polarization resistance received by the method of linear polarization. It has been found experimentally that steel AISI 316 is less inclined to formation of pittings in comparison with AISI 304.

Key words: *electrochemical noise, stainless steels, pitting corrosion, "noise" polarization resistance*

Introduction

Lately, for research of various corrosion processes with traditional methods of the polarization resistance, impedance, voltammeter methods, etc., a method of measurement and an estimation of electrochemical noise gained wide application [1]. Origination of electrochemical noise (current and/or potential fluctuation) largely caused by heterogeneity of investigated metals surface, which depends on local and general passivation of a surface of metal. Current and potential fluctuations with small amplitude, as a rule, are characteristic for metals, which are in a passive condition. Current and potential fluctuations of considerable amplitude can arise as far as a metal surface is activating at the expense of a breakdown of its passive film. Herewith, the value of amplitude characterizes the degree of passivation and dynamics of depassivation process of metal surface [2].

Application of a method of measurement of electrochemical noise for research of processes of passivation of stainless steels AISI 304 and AISI 316 in various corrosion environments, and also working out of programs of mathematical machining of the gained data for their comparison with given gained by a classical method of the polarization resistance (a linear polarization method) [3] were a research aims. Sampling above the specified steels is caused by their industrial extending, except that, stainless steel AISI 316 contains molybdenum in the composition (Tab. 1), which does its more resistant to pitting corrosion unlike stainless steel AISI 304 [4].

Experimental Setup

In this research, the technique of measurement of electrochemical noise with three identical electrodes (fig. 1) was used. For measurement of fluctuations of potential on investigated electrodes used digital oscilloscope-recorder PCS-500. Management of the oscilloscope has carried out by means of program PC LAB 2000 in which installed following parameters: time scale - 100 s/div.; the scale of amplitude potential - 15 mV/ div.; sensitivity on potential - 100 μV. For measurement of fluctuations of a current arising on electrodes, the digital ampermeter-recorder M3500A connected to the personal computer used. Management and current record was carried out through the software of the device integrated in the MS Excel. At current measurement on the device following parameters were installed: measurement period - 1 s; a current range - 10 mA; sensitivity on a current - 0,01 μA. In Table 1, chemical compositions of investigated stainless steels AISI 304 and AISI 316 are shown.

Table 1. Chemical composition of stainless steels AISI 304 and AISI 316

Material	Chemical composition, %								
	C	Si	Mn	P	S	N	Cr	Mo	Ni
AISI 304	0,06	0,9	1,7	≤0,04	≤0,01	≤0,01	18,5	-	10,0
AISI 316	0,06	0,85	1,8	≤0,04	≤0,01	≤0,01	17,5	2,0	12,0

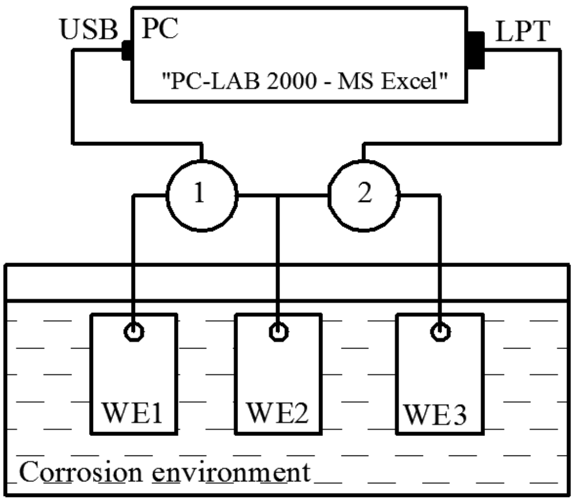

Fig. 1. The schema for the measurement of electrochemical noise:
1 – ampermeter-recorder M3500A; 2 – oscillograph-recorder PCS-500;
USB and LPT – ports connection; WE1…WE3 – working electrodes

As a corrosion environments for measurements of current and potential fluctuations on investigated samples of stainless steels, the following solutions were used: 10 % $FeCl_3$, 0.1M $NaHCO_3$ + 0.1M Na_2CO_3 (pH 10) and 20 % NaCl.

Researches were carried out in glass thermostatic to an electrochemical cell in which three identical electrodes with sizes 20×30×1 mm were placed. Before immersion in a solution, samples were carefully ground to graininess P1200, washed out and degreased. Shunts for weigh samples in a solution were made of a wire of the same steel quality, as the samples. Before measurement of current and potential fluctuations, a sample stood in an investigated solution throughout an hour then was subjected to measurements. The time of measurement of electrochemical noise for each experiment made was 1000 s.

Diagram of a current and potential spectrum for each solution by results of research were plotted. The obtained data were subjected to mathematical processing with the Mathcad system which included: polynomial approximation for all range of measurement of a current and potential with polynomial extent “3”; finding of a root-mean-square deviation of current and potential; calculation of “noise” polarization resistance, as the relation of a root-mean-square deviation of potential to a root-mean-square deviation of a current. Calculated data on “noise” polarization resistance compared to the data of the polarization resistance gained by a classical method under the circuit design with two identical electrodes by means of the device developed in Institute of electric welding by Paton (system of corrosion monitoring of pipelines [5]) in the same corrosion environments.

Results and Discussions

The results of research obtained investigating corrosion solutions are shown in Figures 2-7. In Figures 2, 3 the results of measurement for spectra of electrochemical noise in 10 % $FeCl_3$ on stainless steels AISI 316 and AISI 304 are shown:

– On stainless steel AISI 304 over a period 1000 s current fluctuations of various amplitude from 0.5×10^{-4} A (min) to 1.7×10^{-4} A (max) have been observed that is connected with formation and development pittings on a electrodes surface. On the diagram of current fluctuations an initial raise of current with 1.2×10^{-4} A to 1.3×10^{-4} A during 9 s, is caused by breakdown of a passive film and formation pittings, further during 11 s falling of current to value 1.0×10^{-4} A (partial reduction of a passive film - partial passivation), and the subsequent raise of a current over a period 24 s to value 1.28×10^{-4} A (breakdown of a passive film and local dissolution of active centers) have been observed. Through 92 s after the beginning of measurement has been observed falling of a current to value 0.7×10^{-4} A (partial passivation of surface) then raise of current to value 1.7×10^{-4} A throughout 192 s, caused by activation of the local centers of a surface and growth pittings in metal depth. After achievement of the current maximum value its prompt falling over a period 148 s to value 0.5×10^{-4} A (passivation of the formed surface local centers) has been observed. Raise during 66 s a current to value 1.54×10^{-4} A - breakdown of a passive film, a growth pittings and transition in a passive condition at the expense of sharp falling of a current over a period 107 s to value 1.54×10^{-4} A. Further, the analogous situation with transitions from an active condition in passive, but only with much smaller amplitude observed.

– On stainless steel AISI 316 value of current in an initial time of measurement made 7.7×10^{-5} A, over a period 504 s falling of a current to value 0.1×10^{-5} has been observed, that is caused with almost full passivation of samples metal surface. Further prompt growth of a current over a period 89 s to value 9.97×10^{-5} A (local breakdown of a passive film), current falling over a period 138 s to value 3.5×10^{-5} A (partial passivation), current raise over a period 20 s to value 8.2×10^{-5} A, and its falling during 236 s to value 0.1×10^{-5} A (full passivation) have been observed.

– Values of potential fluctuations on stainless steel AISI 304 for all period of measurement fluctuated over the range from +0.03 V to -0.03 V with amplitude of separate peaks from 0.011 V to 0.053 V. Potential fluctuations on electrodes are caused by a leakage of the non-stationary processes connected with a various condition of a passive film of electrodes surface of, and with processes of a charge/discharge of double electric layer capacity also.

– Values of potential fluctuations on stainless steel AISI 316 for all period of measurement changed over the range from +0.006 V to -0.013 V with amplitude of separate peaks from 0.013 V to 0.082 V. On the diagram, more considerable potential fluctuations, in comparison with AISI 304, with transitions through a zero that are connected with slow enough process of transition samples metal surface from passive condition in active, and on the contrary are observed. Also is observed presence of separate peaks with amplitude from +0.006 V to -0.058 V, that, as well as in the previous case, is connected with a leakage of non-stationary processes, etc.

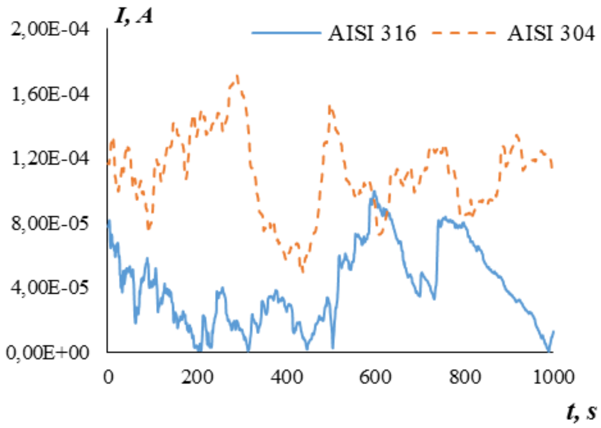

Fig. 2. Results of measurement of current fluctuations in 10 % $FeCl_3$

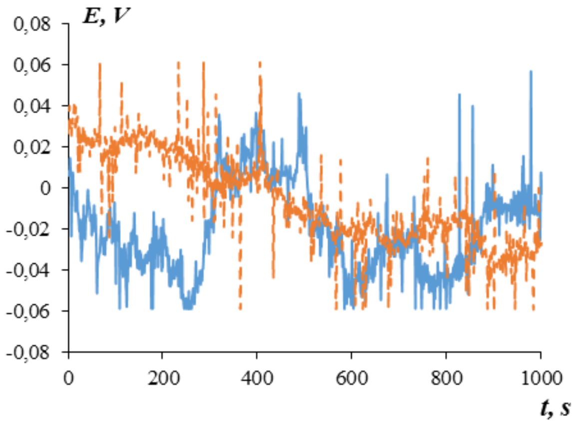

Fig. 3. Results of measurement of potential fluctuations in 10 % $FeCl_3$

In Figures 4-7 measurement results of electrochemical noise spectra in 0.1M $NaHCO_3$+0.1M Na_2CO_3 and 20 % NaCl on stainless steels AISI 316 and AISI 304 are presented:

- Surfaces of stainless steels AISI 316 and AISI 304 in solution 0.1M $NaHCO_3$+0.1M Na_2CO_3, and for stainless steel AISI 316 and in 20 % NaCl, are in passive condition to what testifies level of current fluctuations, nearby 2×10^{-7} A. Fluctuations of values of potential on the given steels in the specified solutions as it was mentioned above, is connected with a leakage of non- stationary processes, a various condition of a surface of electrodes, and also with processes of a charge/discharge of a double electric layer.
- On a surface of stainless steel AISI 304 in 20 % NaCl there was insignificant activation of electrodes surface to what indicative raise of level of values of current fluctuation to 1×10^{-6} A. Breakdown of passive film on an electrodes surface in 20 % NaCl also there was at fluctuations of values of potentials which changes over the range from -0,03 V to +0,017 V.

Figures 8-10 present the spectra of “noise” polarization resistance calculated in Mathcad system on stainless steels AISI 316 and AISI 304 for 10 % FeCl3, 0.1M NaHCO3+0.1M Na2CO3 and 20 % NaCl solutions: in 10 % $FeCl_3$ on both steels surfaces the spectrum of calculated “noise” polarization resistance does not exceed 2×10^3 Ohm, except separate peaks amplitude to 4×10^5 Ohm, which are connected with passivation of local sections of samples surface; in 0,1M $NaHCO_3$+0,1M Na_2CO_3 on both steels the fluctuation of calculated “noise” polarization resistance are over the range from 2×10^5 to 6×10^5 Ohm, with presence of separate peaks by amplitude over the range from 4×10^6 to 8×10^6 Ohm, which are caused by passivation of separate sections of samples surface; in 20 % NaCl the fluctuation of calculated “noise” resistance for both steels are over the range from 2×10^5 to 5×10^5 Ohm, with amplitude of separate peaks over the range from 7×10^5 to 3×10^6 Ohm, which are connected with passivation of local sections of samples surface. Table 2 shown the average values of calculated “noise” polarization resistance for both steels in all investigated corrosion environments. For comparison results of measurement of the polarization resistance in solutions specified above gained by classical method of linear polarization of samples stainless steels AISI 316 and AISI 304 on device “System of corrosion monitoring of pipelines” (SCMP) are shown in Table 2 also.

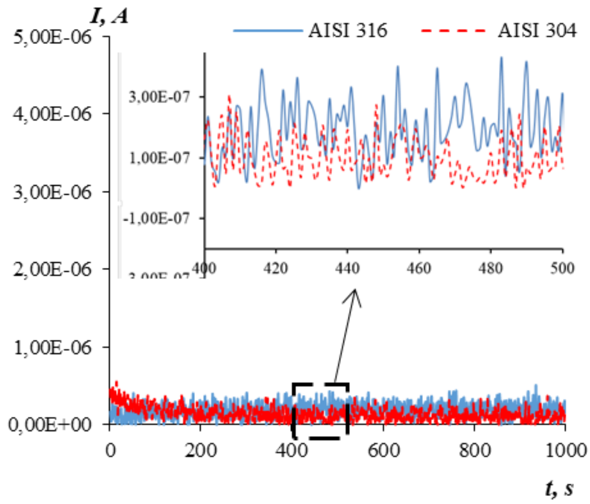

Fig. 4. Results of measurement of current fluctuations in 0.1M $NaHCO_3$ + 0.1M Na_2CO_3

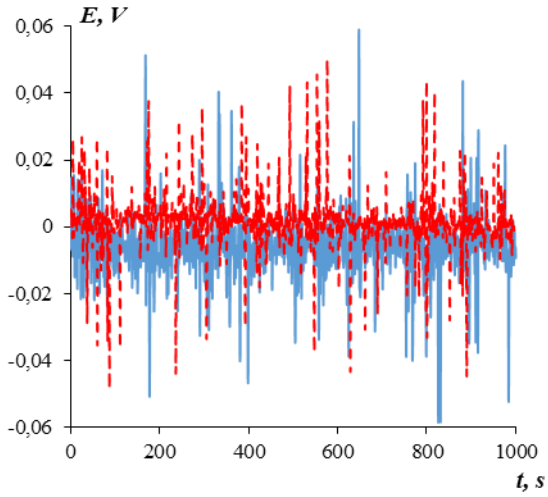

Fig. 5. Results of measurement of potential fluctuations in 0.1M $NaHCO_3$ + 0.1M Na_2CO_3

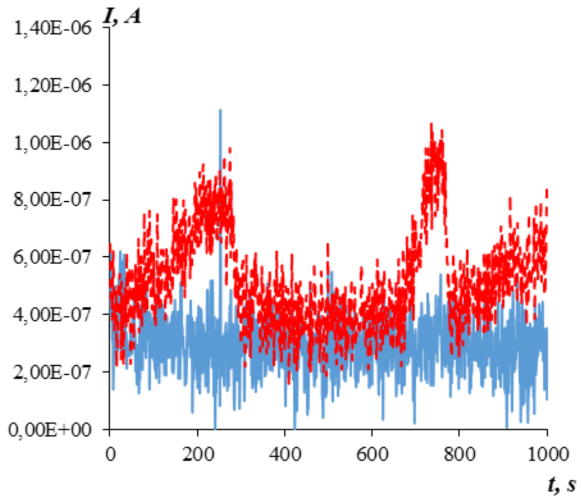

Fig. 6. Results of measurement of current fluctuations in 20% NaCl

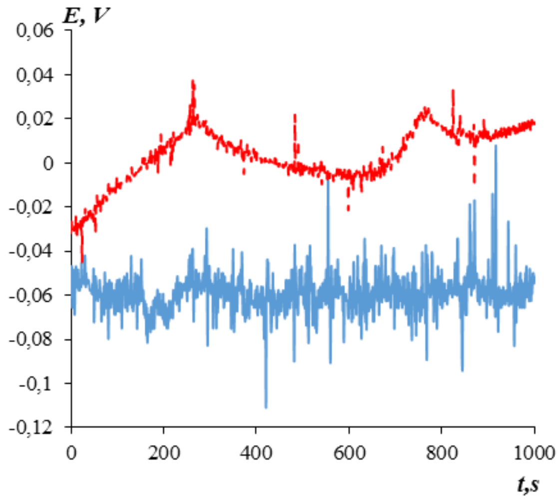

Fig. 7. Results of measurement of potential fluctuations in 20% NaCl

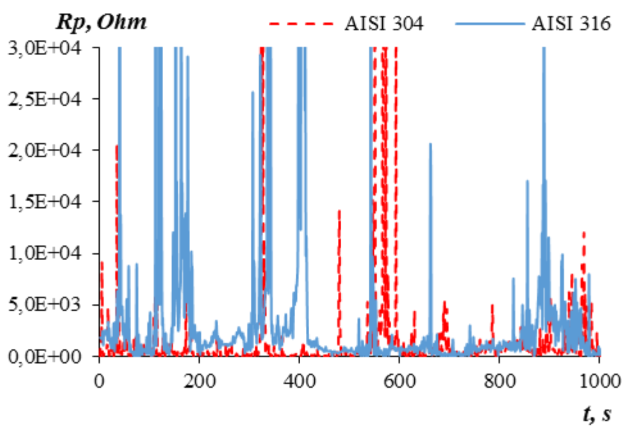

Fig. 8. The calculated "noise" polarization resistance for 10% $FeCl_3$

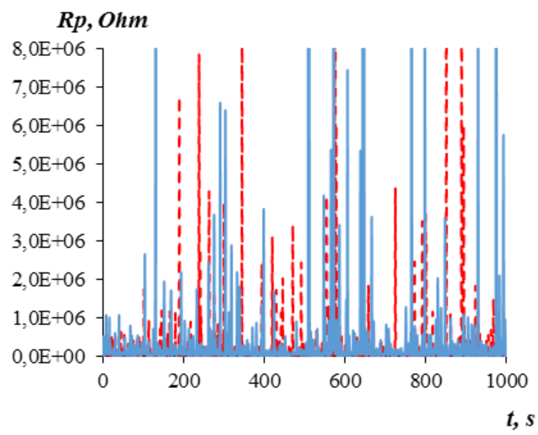

Fig. 9. The calculated "noise" polarization resistance for 0.1M $NaHCO_3$ + 0.1M Na_2CO_3

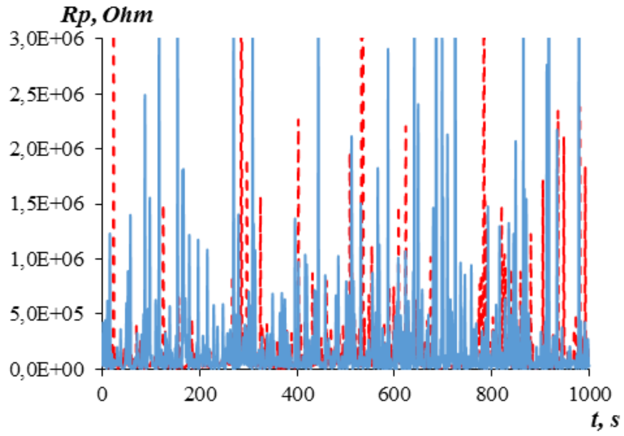

Fig. 10. The calculated "noise" polarization resistance for 20% NaCl

Table 2. Average values of the calculated "noise" polarization resistance and polarization resistance calculated by LP method

Environment / Material	0,1M $NaHCO_3$ + 0,1M Na_2CO_3	20% NaCl	$FeCl_3$
"Noise" polarization resistance, Ohm			
AISI 304	$37{,}6\times10^3$	$47{,}1\times10^3$	$0{,}436\times10^3$
AISI 316	$74{,}04\times10^3$	$79{,}3\times10^3$	$0{,}967\times10^3$
Polarization resistance by LP method, Ohm (SKMP)			
AISI 304	$30{,}5\times10^3$	$20{,}7\times10^3$	$0{,}147\times10^3$
AISI 316	$27{,}2\times10^3$	$19{,}4\times10^3$	$0{,}386\times10^3$

From the experimental data shown to Tab. 2 follows:

- On the stainless steel samples AISI 316 the calculated "noise" polarization resistance twice above than on the stainless steel samples AISI 304 for all investigated corrosion environments that testifies about more propensities of stainless steel AISI 316 to passivation in investigated environments.
- Values of the polarization resistance for stainless steels samples AISI 304 and AISI 316 in investigated environments gained by linear polarization method on SKMP have satisfactory coincidence to mean of the counted "noise" polarization resistance. The difference in resistance values due to two key aspects of: at measurement by linear polarization method on working electrodes the difference of potentials ($\Delta E = 10\,mV$) moves, that results in certain excitation of perturbation superficial passive film and double electric layer, while the method of measurement spectra electrochemical noise fixes the truth value of current and potential in certain moment of time.

Conclusions

1. The interconnection between spectra of electrochemical noise and passivation processes on stainless steels samples surface AISI 304 and AISI 316 in investigated corrosion solutions is established: 10 % $FeCl_3$, 0.1M $NaHCO_3$+0.1M Na_2CO_3 and 20 % NaCl. It has been experimentally set and shown that on spectra of current fluctuations it is possible to observe a process forming of passive film formation on surface accompanied by sharp falling of current, and the breakdown of passive film characterized by discontinuous change of current. Moreover, the transition of passivation in depassivation due to the development of pitting corrosion.

2. The “noise” polarization resistance on stainless steels AISI 304 and AISI 316 in investigated solutions have been calculated having satisfactory convergence with the polarization resistance values gained by linear polarization method on SKMP. By results of mean of the calculated “noise” polarization resistance, it is established that stainless steel AISI 316, in comparison with stainless steel AISI 304, is less inclined to local (pitting) corrosion.

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References

1. Chviruk, V.P., Polyakov, S.G., Gerasymenko, Y.S. – *Electrochemical monitoring anthropogenic environments*, monography, Kiev, 2007.
2. Kottis, R.A. – Sources of electrochemical noise in corroding systems. *J. of Electrochemistry*, Vol.42, No. 5, 2006, pp. 557-566.
3. Epelboin, J., Gabrielli, C., Keddam, V., Raillon, L. – *J. Electroanal. Chem,* Vol. 105, No. 3, 1979, pp. 389-394.
4. Polyakov, S.G., Nyrkova, L.I., Melnychuk, S.L. – Control of local corrosion of pipelines from chrome-nickel steels. *J. of Physical-chemical mechanics of materials*, No. 6, 2007.
5. Klymenko, A.V., Kovalenko, S.Y., Polyakov, S.G. – *System of corrosion monitoring of pipelines*, Patent of Ukraine No. 96346, IPC (2011.01) F17D 5/06, G01N 17/02, G01R 29/24, H04Q 9/00, G06F 15/00, G06N 7/00. Applicant and patentee: Electric Welding Institute by Paton NAS of Ukraine, no. a201000932; app. 29.01.2010; printed 25.10.2011, journal No. 20.

Spectrul zgomotului electrochimic și relația acestuia cu procesele de pasivare a oțelurilor inoxidabile AISI 304 și AISI 316

Rezumat

În prezenta lucrare, sunt descrise cercetările efectuate privind procesele de pasivare a oțelurilor inoxidabile AISI 304 și AISI 316, utilizând metoda zgomotului electrochimic. Cercetările au fost efectuate utilizând un circuit cu trei electrozi identici în trei medii corozive diferite: 10% $FeCl_3$, 0.1M $NaHCO_3$ + 0.1M Na_2CO_3, 20% NaCl. Rezultatele măsurătorilor au fost procesate cu ajutorul sistemului MathCAD. Din datele recepționate, s-a contorizat rezistența la polarizare a “zgomotului” în mediul investigat. Rezistența la polarizare a “zgomotului” calculată a fost comparată cu rezistența la polarizare recepționată prin metoda polarizării liniare. S-a constatat experimental că oțelul AISI 316 este mai puțin susceptibil la apariția pitting-ului în comparație cu oțelul AISI 304.

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