Appendix 12b

REPORT

of dissertation for the acquisition of:

educational and scientific degree " **doctor** "	X
scientific degree **"Doctor of Science"**	
	the true is indicated by the sign "X"

Author of the dissertation:

		Venetsia	Nikolaeva	Garova	
academic position	scientific degree	name	middle name	last name	workplace

Topic of the dissertation:

ANODIC BEHAVIOR OF ZINC

Scientific area:

4	Natural Sciences, Mathematics and Informatics
code	name

Professional area:

4.1	Physical Sciences
code	name

Scientific specialty:

Structure, Mechanical and Thermal Properties of Condensed Matter

The report was written by:

Assoc. Professor	Dr	Svetoslav	Mihailov	Kolev	
academic position	scientific degree	name	middle name	last name	workplace

1. Meeting the minimum requirements under the Regulations:

A) The candidate meets the minimum requirements	20 points	X
B) The candidate doesn't meet the minimum requirements	0 points	
		one of the answers given is marked with the sign "X"

It is mandatory to fill in if answer B is marked. The publication activity of the candidate is analyzed. The response of the results achieved (quoted) is analyzed.
The doctoral student Venetsia Garova has published the results of her dissertation in three scientific papers – two in a journal with impact factor and one in a chapter of a monograph. Concerning the two papers with

impact factor, six independent citations have been found. Also, her dissertation results have been presented at five conferences – three international and two national ones. The doctoral student's performance satisfies the requirements set by the relevant Regulations. The papers presented correspond to 55 points as per Appendix 5a.

2. The relevance of the topic of the dissertation:

A) The topic is relevant and new (there are no known results on the topic by other authors)	8 points	
B) The topic is relevant and results from other authors are known	6 points	X
C) The topic is not relevant, but results from other authors are known	2 points	
D) The topic is not relevant and no results from other authors are known	1 point	
E) The topic does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The evaluation of the relevance of the dissertation must be substantiated
Studying the anodic Zn behavior is important in view of the massive interest in applying Zn as an anode in batteries, for galvanic deposition of anticorrosion coatings, for fabrication of nanoparticles of controlled size and shape, for the development of photocatalysts, supercapacitors, gas sensors, etc. The dissertation presented is focused on studying the anodic polarization of Zn in galvanostatic regime. Research in this field is practically lacking, which has stimulated this detailed investigation of the process. The dissertation work has emphasized the study of the deposited coating characteristics and conductance – a porous layer with p-conductance. The research results are of importance in what concerns the understanding and explaining the processes taking place in the film formation as dependent on the electrolyte's concentration, content, pH and temperature, and on the current density.

3. Type of research:

A) Theoretical	4 points	
B) Applied	4 points	
C) Theoretical with application elements	4 points	X
D) It does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The level of research must be substantiated if answer D is marked.

4. Objectives of the research:

A) Realistic and of scientific and / or applied interest	8 points	X
B) Realistic, but not of scientific and / or applied interest	3 points	
C) Unattainable (unrealistic)	0 points	

		one of the answers given is marked with the sign "X"

Objectives must be specified. The type of the set objectives must be justified.
The main objective of the dissertation is studying the anodic behavior of Zn in water-borates electrolytes and sodium-based water solutions, as well as characterizing the coatings thus obtained. To reach the objective thus defined, the work was directed to solving the following main tasks: 1. Studying the dependence of Zn anodic behavior kinetics in in water-borates electrolytes and sodium-based water solutions as dependent on the forming electrolyte's concentration, content, pH and temperature, and on the current density during the formation process; 2. Characterizing the films obtained by means of X-ray diffraction, reflection infrared spectroscopy, micro-Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and atomic-force microscopy. 3. Studying the dissolution process by means of optical emission spectroscopy with inductively coupled plasma. The goals set are realistic and are of scientific and applied interest.

5. Contributions of the dissertation:

A) With lasting scientific and / or applied response, they form the basis for new research and applications	20 points	X
B) They are of significant scientific and / or applied interest, complete and / or summarize previous research	16 points	
C) They are of scientific and / or applied interest	12 points	
D) Lack of significant contributions	8 points	
E) Lack of contributions	0 points	
		one of the answers given is marked with the sign "X"

Contributions must be specified. The type of results achieved must be justified.
1. The Zn anodic behavior was studied in water-borates electrolytes and sodium-based water solutions. The anodic polarization was studied in a galvanostatic regime. The experimental conditions (electrolyte content and concentration, current density, pH and temperature) were varied in the widest possible limits. 2. The effect was studied of the base used on the reaction kinetics. The water-borates solutions were prepared using water solutions of H_3BO_3 with concentration from 0.1 to 3 weight percent. Their pH value was adjusted by adding NaOH or NH_4OH to 5.8, 7 or 8.2. At the beginning, the kinetic curves exhibited well expressed induction periods within the entire range of current densities, concentrations, pH values and temperatures. It was found that these periods' duration depended on all of the above parameters. The induction periods were reduced by increasing the current density, but did not reach zero. The periods were the shortest at neutral pH, most probably due to the low degree of dissolution. It was further found that the type of base used (NaOH *или* NH_4OH) did not affect significantly the kinetics. 3. The relation was established between the Zn anodic behavior kinetics in sodium-based water solutions and the forming electrolyte concentration. At concentrations exceeding 0.08M to 1M, the induction periods appeared prior to the voltage increase; while at concentrations higher than 1M, the forming potential practically did not rise. A bending point arose at concentrations between 0.001M and 0.08M, where the process rate began to slow down. The kinetic curve slope before the bending point increased, while decreasing after that point. Both slopes decreased as the forming electrolyte concentration was raised. Also, raising the concentration led to a decrease of the voltage at which the kinetic curve slope changed (U_{bend}). At the same time, the electricity quantity passing before the kinetics change (Q_{bend}) increased.

4. The scanning electron microscopy and the atomic force microscopy studies demonstrated that during the early stages of anodic polarization, prior to the bending point, a film was formed which filled the electrode surface roughness, so that it became smoother than following the electro-polishing. Around the bending point, the surface was covered by plate-like formations of hexagonal shape. Long after the kinetic rate change, the roughness decreased again, probably due to crystallites size increase.

6. Conclusion

A) The evaluation of the dissertation is **POSITIVE**	This evaluation is assigned to a total number of at least 40 points	X
B) The evaluation of the dissertation is **NEGATIVE**	This evaluation is assigned to a total number below 40 points	
		one of the answers given is marked with the sign "X"

To be filled in at the request of the member of the scientific jury
Bearing the above ion mind, I hereby convincingly give my positive evaluation of the presented dissertation and recommend that the esteemed Scientific Jury award the Eng. Venetsia Nikolaeva Garova the educational and scientific degree " **doctor** ".

28.03.2025	The report was written by:	
date		signature