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R E V I E W

on the competition for the occupation of the academic position "Professor" in the field of higher education **4.** Natural sciences, mathematics and informatics, professional direction 4.2. Chemical sciences, scientific specialty "Electrochemistry", at the Institute of Physical Chemistry "Acad. Rostislav Kaishev" - BAS, announced in State Gazette no. 99/13.12.2022

Candidate: Assoc. Prof. Dr. Maria Hristova Petrova-Nikolova
Reviewer: Prof. Dr. Eng. Plamen Kostadinov PETKOV, Department of "PHYSICS", University of Chemical Technology and Metallurgy

1. Application data.

The documents submitted by the candidate during the competition meet the requirements of the National Rule and the Regulations for the terms and conditions for acquiring scientific degrees and occupying academic positions in IPC - BAS. The candidate has submitted a complete list of her scientific publications - 70 items: - articles in refereed publications - 56 items; author's abstract of a doctoral dissertation; three patents and 87. participation with poster and oral reports at scientific forums. For the participation in the competition, Assoc.Prof. Petrova submitted a list of a total of 27 titles of publications in refereed Bulgarian and foreign scientific journals, 12 reports in full text from international conferences and 58 participations in scientific forums; six other documents (in the form of official notes and certificates from an employer, project manager, funding organization or project contractor and other relevant evidence) supporting the applicant's achievements are also presented. Thus, the attached documents enable a comprehensive objective assessment of the candidate's scientific, teaching and administrative activities.

2. Applicant data.

Ms. Maria Petrova was born in 1963 in Sofia. In 1981, she graduated with honors from her secondary education at 91 SES "Prof. Konstantin Galabov" and entered the University of Chemical Technology and Metallurgy, specialty "Electrochemistry". She graduated from higher education in 1986 with a Master's degree in electrochemistry. The next year, after successfully passing the competition, she became a full-time doctoral student at the IPC – BAS. In 1991, she brilliantly defended her dissertation on the topic "Mechanism of electroextraction of zinc from sulfate solutions in the presence of inorganic impurities and organic additives" and received the scientific and educational degree "Doctor of Chemistry". Since 1993, she has been appointed to an position – research assistant III degree in the "Electrochemical Coatings" section. In the next four years, she successfully climbed the professional ladder to become a research associate of the 1st degree. As a research scientist, Dr. Petrova specializes in the field of applied electrochemistry in various world scientific centers: University of Karlsruhe, University of Dortmund, Institute of Microtechnology – Mainz, Germany, TU Vienna, Institute of Electrochemistry, Austria. In 2004, Dr. Petrova qualified as an associate professor in the "Electrochemistry and Corrosion" section at IPC-BAS. As a consequence of the research activity and scientific contributions, four years later the candidate is the Scientific Secretary of the Institute (2008-2012). At present, Assoc. Prof. Petrova is a member of the Scientific Council of the IPC – BAS and several responsible committees within the institute.

3. General characteristics of the scientific works and achievements of the candidate.

The candidate's scientific interests are in the field of applied electrochemistry, and Assoc.Prof. Petrova focuses her research on cutting-edge materials and technologies for optoelectronics and sensors, based on electrochemically obtained metal, alloy and modified polymer coatings. The materials for the competition, full of electrochemically obtained metal, alloy and modified polymer coatings, meet the minimum national requirements, which the candidate exceeds more than 2 times (in group "B" - 100 items, in group "D" - 453 items, in group "D" - 874 items and in group "E" - 640 items). The total number of independent citations of these articles is more than 437, with the Hirsch index (h-index) being 10. The distribution of the scientific articles by quartiles is also very good and fully meets the requirements of IPC – BAS: - Q1 – 1 item; - Q2 – 17 pcs.; - Q3 – 3 pcs. Q4 – 4 pcs.; SJR – 2 pcs.; national patents – 3 pcs. The experimental results of the habilitation student are due in no small measure to the participation in national and international scientific research projects financed mainly by the Ministry of Education and Science (BSF), in which she is a participant in 6 of them, and the leader of 4 projects. During the implementation of the projects, Assoc.Prof. Petrova shows herself as a talented experimenter and undoubtedly a leading specialist in the field, and this opinion is the result of the author's position in the reviewed articles. The scientific works submitted by the candidate do not repeat those from previous procedures, both for the acquisition of the AP "Associate Professor" and for the acquisition of the PhD degree. Having read the scientific publications submitted for the competition, I declare with conviction that there is no evidence, signal or suggestion of plagiarism in accordance with the law. In conclusion, the scientific production not only meets, but also significantly exceeds the minimum national requirements (according to Article 2b, paragraphs 2 and 3 of the N R) and, accordingly, the additional requirements of the IPC - BAS for occupying AP "Professor" in the scientific field and professionally direction of the competition.

4. Characteristics and assessment of the candidate's teaching activity

The habilitation candidate definitely has teaching talent and sufficient teaching experience. Regardless of the specifics of the activity at BAS, Assoc. Prof. Petrova develops a basic course "Anorganische Chemie" for the needs of the Faculty of German Engineering Education and Industrial Management at TU - Sofia. Since 1995, she has been a part-time teacher of German, and in 2011 she co-authored and published a teaching aid on applied chemistry - "Chemie - Handbuch für Laborübungen". For these nearly 30 years, the habilitation has been directly involved in the training of more than 500 engineers with double degrees practically on a German educational program This fact gives me reasons to evaluate the pedagogical activity of the candidate as fully relevant to the conditions in the IPC - BAS.

5. Analysis of the candidate's scientific and scientific-applied achievements.

Research results have a scientific-applied nature and can be classified as obtaining new data and proving existing hypotheses with new means. The candidate's scientific activity is definitely focused on creating cutting-edge materials and technologies based on electrochemically obtained metal, alloy and modified polymer coatings with protective, decorative and electrocatalytic properties. The main scientific contributions can be systematized in two areas:

- Investigation of the electroextraction process of zinc from sulfate electrolytes;
- Chemical deposition of metal coatings on various types of substrates.

The object of analysis, however, will be only the second area, since only it falls within the limits of the competition. Chronologically I would note here:

1. Chemical deposition of nickel/phosphorus and copper dispersion coatings on solid (non-metallic and metallic) substrates.

1.1. Pretreatment of non-metallic substrates.

The influence of pretreatment of non-metallic substrates (mainly acrylonitrile butadiene styrene - ABS) on the qualities of the layers has been clarified. Based on a large number of experiments, a technological sequence has been proposed - degreasing, pickling, chemical deposition. The criteria for the effectiveness of the pretreatment are the properties of the subsequent nickel-phosphorus coatings applied by a chemical nickel plating process. It was established that degreasing in a solution of the surfactant (sodium lauryl sulfate - NaLS) provides a more uniform subsequent pickling of the dielectric surface. On the other hand, the addition of NaLS and Pd(II) in the pickling solution leads to an increase in the degree of roughness of ABS compared to samples treated in a solution without these additives, to a better adhesion between the deposited metal coating and the substrate, as well as increasing the thickness of the Ni-P coating. For additional roughening of the surface before staining, "surface swelling" is applied, and the technological parameters for achieving optimal quality of the layers - composition, temperature and treatment time - have been clarified. Chemically deposited copper and nickel-phosphorus coatings were obtained, uniform over the entire surface of the polymer samples without cracks and with maximum adhesion.

1.2. Chemical deposition of dispersed coatings with various micro- and nanoparticles.

1.2.1. Chemical deposition of nickel/phosphorus dispersion coatings.

ABS backing

Dispersive coatings based on two types of dispersoids were obtained: - microparticles - SiC and diamond; - nanoparticles - SiO_2 and TiO_2. The morphology (SEM), the content of dispersed particles included in the coating (EDS) and specific electrical resistance were examined on the obtained dispersion coatings. For the first time, NiP-disperse coatings on ABS-polymer with SiC dispersoid were deposited electroless from alkaline electrolytes. To obtain thinner layers, it is necessary to replace the microparticles with nanoparticles. The influence of TiO_2 and SiO_2 nanodispersoids with sizes between 30nm and 60nm on the changes in the thickness of NiP-dispersed coatings, on the titanium content, resp. silicon in these coatings and on their specific electrical resistance. It was found that the duration of deposition of the dispersed coating has no effect on both the silicon content in it and the specific electrical resistance. The kinetics of chemical deposition of NiP-dispersed coatings on ABS is invariant to the nature of the solid nanoparticles embedded in the coating as long as they are of similar size and charge. Metal backing NiP- and dispersed NiP-coating with nanodispersoids of Al_2O_3, SiO_2, TiO_2 on different metal substrates (Al, Fe, Ti, Ni, Cu) were obtained. A comparison was made of the results obtained from electroless and galvanically deposited dispersed nanocoatings. It has been found that a quality dispersion coating can be obtained without special pre-activation with a palladium salt, which is only necessary for copper substrates. The optimal conditions of preliminary preparation of the various metal substrates (Al, Fe, Ti, Ni) have been determined. The kinetics of the process is limited by the addition of nanoparticles in the electrolyte at the expense of the type of substrate. The reasons for concentration dispersion of nanoparticles in the coating are clarified and a new generation of activating solution based on palladium sulfate and a complexing agent is proposed. The developed technology is applied in the production of printed circuit boards and in particular in the deposition of the final two-layer Ni/Au coating on the exposed copper surfaces. NiP dispersion coatings (from an acidic electrolyte) with diamond particles on a steel substrate were obtained. It was found that the highest percentage of inclusion of particles is found in the small sizes (4÷8μm and 10÷20μm), and these coatings show better wear resistance compared to dispersed coatings with larger particle sizes. the microhardness of the deposited nickel coating has a maximum value that is approximately twice that of the nickel matrix without dispersoid.

1.2.2. Chemical deposition of copper dispersion coatings on an ABS substrate.

The optimal composition of the copper electrolyte was established in relation to the concentration of NaOH, Trilon B, of two stabilizers: stabilizer 1 - from the group of organic nitrogen-containing compounds and stabilizer 2 - from the group of sulfur-containing compounds. A patented copper electrolyte composition provides a constant deposition rate over time and allows a significantly faster increase in deposition rate with increasing HCHO and $CuSO_4.5H_2O$ concentration. The chemically deposited copper coatings were found to have a very fine crystalline structure, with coherent scattering regions that were orders of magnitude smaller than matte copper coatings electrochemically deposited from a simple (uncomplexed) sulfuric acid electrolyte. For the first time, copper microdisperse (with SiC and polyamide) and nanodisperse coatings (with SiO_2) from alkaline electrolytes on ABS substrates were chemically obtained. The resulting dispersion coatings are characterized by a four to five times higher wear coefficient and on this basis technologies have been developed with their application in micromechanics. When replacing SiC with nanosized SiO_2 (30nm ÷ 60nm), the same dependence of coating thickness/SiO_2 concentration is observed, namely, as the concentration of SiO_2 in the electrolyte increases, the thickness of the Cu-SiO_2-dispersed coating decreases. The deposited Cu-SiO_2-dispersed coatings have a significantly greater thickness compared to the Cu-SiC-coatings under the same conditions of their preparation. It was found that the nature and size of the dispersoid particles did not significantly influence the kinetics of the autocatalytic reduction of copper (II) ions on the support surface.

1.3. Chemical deposition of environmentally friendly copper electrolyte coatings.

Non-toxic electrolytes excluding hydrogen-containing compounds such as (HCHO, N_2H_4, etc.) have been proposed. In this case, the role of the reducer is performed by Sn^{2+} ions, which are previously adsorbed on the surface of the dielectric in the activation process. A direct method is proposed - treatment in a solution containing: relevant metal ions (Cu^{2+}), complexing agents, pH-correctors, buffering substances, etc. The optimal concentrations of the solutions for: degreasing, staining, reduction, pre-activation, activation in a colloidal solution have been determined - a composition protected by a patent. The qualities of the layers are relevant to those obtained with a classic electrolyte with a formaldehyde reducer. For the first time, quality copper coatings were obtained on a nanoporous anodic alumina (AAO) matrix on an aluminum substrate. The contact-deposited copper layer at the Al/AAO interface is used to catalyze the chemical deposition of a copper coating. The optimal compositions and modes of operation of the copper electrolyte have been established and it has been established that at a pH greater than 5 chemical copper is found mainly in the form of Cu_2O. Conducted systematic research on the properties and performance of combined Al-O-Ag coatings obtained on technically pure AA1050 aluminum. A comprehensive model describing the kinetics of formation of complex Al-O-Ag coatings and the interrelationship between the applied growth conditions and the obtained characteristics, properties and morphology of the coatings is proposed.

2. Chemical deposition of nickel/phosphorus and copper dispersion coatings on flexible substrates.

The inclusion of dispersed particles in the metal matrix on flexible substrates leads to the production of a new generation of dispersed materials characterized by certain chemical and physical properties. In essence, it is again about non-metallic pads, but with completely different characteristics than ABS. Optimum results are on a substrate made of polyethylene terephthalate (flexible pressed textile - PET. A technology for pre-treatment of the substrate before the deposition of the metal coatings has been developed, and also the compositions and conditions for the chemical deposition of copper and nickel metal coatings have been established. New data have been obtained for composite coatings with included different types and sizes of dispersoids: diamond, ZrO_2, SiO_2, Al_2O_3, TiO_2, αBN and cBN.

2.1. Chemical deposition of nickel/phosphorus dispersion coatings.

NiP dispersion coatings were obtained on a flexible PET substrate with electrolytes optimized in terms of composition and mode of operation with different types of dispersoids: diamond, SiC, ZrO_2, BN (alpha and cubic). The stability of the solution for chemical nickel plating with the use of various stabilizers, as well as the influence of certain surface-active substances, was established. A laboratory technology has been developed and experimented for both chemical and electrochemical deposition of dispersion coatings based on a nickel matrix with dispersoid diamond particles (with sizes from 3/7μm to 225/300μm). Complex studies were conducted and regarding the behavior of the remaining dispersoids, leading to the conclusion - the dispersion coatings are promising in terms of the possibility of their use as abrasive tools for surface treatment of hard materials.

2.2. Chemical deposition of copper dispersion coatings.

Dispersed copper coatings, despite being little used, find practical application due to their high thermal conductivity, high resistance to electromigration and low specific resistance. With the aim of their application in various fields, dispersed coatings deposited on flexible substrates with different types of dispersoids have been obtained and studied: - nanosized - SiO_2, Al_2O_3 and TiO_2 - microsized - graphite, SiC, diamond, hBN and cBN. For the first time, chemical composite Cu/D, Cu/BN and Cu/SiC coatings with a wide range of dispersoid sizes (from 3/7μm to 100/125μm) were obtained from trilonate electrolyte on a flexible polyethylene terephthalate substrate. The most suitable hydrodynamic regime and processing of the dispersed particles with a suitable surfactant (NaLS) allowing inclusion in a copper matrix of dispersed particles with sizes up to 20/28μm have been determined. Studies have been conducted confirming the possibility to incorporate unmetallized and pre-metallized cBN grains into a copper matrix deposited on PET. Dispersoid SiC coatings (from 10/7μm to 75/63μm) have been proposed as material for abrasive grinding tool. Copper coatings on woven and non-woven flexible materials have also been developed incorporating nanoparticles (SiO_2, Al_2O_3 and TiO_2) which are uniform in thickness, semi-glossy, impart a beautiful appearance to fabrics and can be used as radio shields against electromagnetic interference , as well as find applications in industry, agriculture and household.

6. Critical notes and recommendations.

I have no critical remarks.

7. Personal impressions of the candidate.

I have known Associate Professor Petrova for a long time, as a colleague from the neighboring Institute of the BAS. Of course, we have met at conferences and scientific juries. I have not had the opportunity to work in a general research project, but in my capacity as a member of the BSF Board of Directors, I have had the opportunity to observe projects that she leads or participates in. I have been left with the best impressions of her performance.

CONCLUSION

Having read the materials and scientific works presented in the competition and based on the analysis of their significance and the scientific and applied contributions contained in them, I confirm that the scientific achievements meet the requirements of National Rule, the

Regulations for its application and the relevant Rules of the IPC - BAS" for occupying the academic position "Professor" in the scientific field and professional direction of the competition. In particular, the candidate exceeds the minimum national requirements in the professional direction, as no plagiarism was found in the scientific works submitted for the competition. Based on the above, I recommend the scientific jury to propose to the competent scientific council of the Institute of Physical Chemistry "Acad. Rostislav Kaishev" at the Bulgarian Academy of Sciences, to elect **Associate Professor Dr. Eng. Maria Hristova Petrova-Nikolova** to occupy the academic position "Professor" in professional field 4.2. "Chemical Sciences" (Electrochemistry).

Sofia, 21.03.2023.   Prepared the review: