International Science Journal of Engineering & Agriculture
2024; 3(4): 51-59
https://isg-journal.com/isjea
doi: 10.46299/j.isjea.20240304.05
ISSN: 2720-6319

Evaluation of the forces acting on nanoparticles when creating a coating from suspension

Oleksandr Kuzma
Head of Department MPDE/ Faculty of Physics and Mathematics, Sikorsky KPI, Kyiv, Ukraine
ORCID 0000-0001-5670-8794

To cite this article:
Kuzma Oleksandr. Evaluation of the forces acting on nanoparticles when creating a coating from suspension. International Science Journal of Engineering & Agriculture. Vol. 3, No. 4, 2024, pp.51-59. doi: 10.46299/j.isjea.20240304.05.
Received: 07 02, 2024; **Accepted**: 07 31, 2024; **Published**: 08 01, 2024

Abstract: The analysis of data on the flow parameters of barium titanate nanoparticle suspensions at different concentrations and dynamic actions in the aspect of studying the destruction of particle aggregates was carried out in previous works [1-5]. Dynamic processes in macrosuspensions under the influence of vibration or ultrasound were described earlier [6-9]. Another form of sharp change in interacting connections between inclusions takes place during the formation of layers of particles on charged surfaces - electrophoretic coating under the action of an electric field [10-13]. Changes in the resulting forces of particles interaction in micro aggregates in both cases lead to a change in the macro-characteristics of the suspension flow, some rheological models of which were proposed and studied yet in [14-15]. In this paper, we propose and evaluate preliminary approaches for dynamic force formulas for that principal parts for electrophoretic coating for single particle from such suspensions and suggest next steps for further construction of the process equations in further work and verification of agreement with experimental data. It can be further noted that these studies are necessary for the next stage of creating new layered nanomaterials and developing small but powerful capacitors, acoustic sensors, etc.

Keywords: Average, aggregates of nanoparticle, $BaTiO_3$, charged surfaces, coating, dielectric, dynamical, gravitation, energy, electrophoresis, equation, forces and coordinates generalized; ferroelectrics, electric field, interaction, ,layer, particles, suspension.

1. Introduction

Data for analysis on the rheological characteristics of $BaTiO_3$ barium titanate suspensions were obtained at the I. Frantsevich Institute of the NAS of Ukraine using a rotary viscometer and in other laboratories. Some of them are described and analysed together with the author. These works also discuss some aspects of the dynamical growth–destruction of nanoparticle aggregates or self-organization of barium titanate suspensions, and additional data are provided and analyzed.

Now we will consider the applicability of some techniques from previous works, devoted to dynamic effects and interphase interaction, to the problem of electrophoretic coating from such suspensions.

2. Object, subject and target of research

Our first step towards modeling the conditions of dynamic destruction of the structure of nanosuspensions was made in the paper. [1, 2]. For this, a comparison of interaction forces and generalizing dynamic (rotational) forces, which can similarly be obtained from the Lagrange equations of motion [6-9] for vibration or acoustic actions for microsuspensions in low-viscosity liquids, was carried out. The following attempt was also made to analyze the characteristics of the suspension of barium titanate particles, especially the effective viscosity, and to consider the changes in the suspensions during the dynamic destruction of the aggregates. The data used are described and analyzed together with the author in [1, 2], as well as in [12-13] and others. In addition, some aspects of dynamic growth–destruction of nanoparticle aggregates or self-organization of barium titanate suspensions are discussed, new data are given and analyzed.

These studies were continued in works [3, 5, 11], where the factor of the average distance between particles was also taken into account. In this article, we considered the processes of obtaining homogeneous electrophoretic coatings for some data [10-13] and proposed some suspensions of barium titanate nanopowders, formed by changing the conditions of formation and deposition.

To continue the research, we will use the previously made assumptions. The particle sizes of suspensions of ferromagnets (barium titanate) are considered close to the experimental 100-200 nm, the shape is spherical, the basis of the suspension is a liquid with a relatively low characteristic viscosity and compressibility. Volumetric concentrations are small and medium, up to 0.2.

Now we will consider the applicability of some techniques from previous works, devoted to dynamic effects and interphase interaction, to the formulation and study of the problem of electrophoretic coating from such suspensions.

Such processes can be used in the production of small-sized capacitors, devices for generating and receiving ultrasonic waves with ferroelectric parts, etc.

3. Literature analysis

The initial data were obtained for a low-concentration nanosuspension of barium titanate (volume concentration c=1-10%) on a rotary viscometer (rotational viscometer) of the Ivan Frantsevich Institute of Materials Science of the National Academy of Sciences of Ukraine (IPMN of the National Academy of Sciences of Ukraine) and described in [1-2]. Further, additional results were obtained for suspensions of medium concentration (c=10-20%), and for the effective viscosity, they are given for an extended range of concentrations in [2-5].

In these works, discussions and studies were conducted based on the methods [6-8], which considered the problem of oscillations of small spherical bubbles, solid particles or a swarm of bubbles in a cylindrical vessel during vertical oscillations. The velocity potential of an incompressible [6,7] or compressible [8] inviscid fluid is constructed under the condition of axial symmetry.

Controlled self-assembly of nanoparticles can lead to new materials, and bottom-up approaches are a very promising and important strategy for materials synthesis. In some suspensions, particle movements occurred under the influence of an electric or magnetic field [10-13], acoustic waves [6, 8, 9] or vibrations. Some aspects of ultrasound medicine for the dynamics of nanosuspensions are described in [9]. Particles form fibrillar structures that can significantly change the rheological properties of suspensions. In these works, attention is focused on data and research for such a suspension as the first stage of the process of obtaining appropriate thin films and aggregates with titanium barium nanoinclusions according to the dynamic failure criterion. It can be obtained by comparing the interaction forces and the generalizing dynamic (rotational, vibrational) forces that can be obtained from the Lagrangian equations of motion similar to Ref. [6-8]. In works [10-13], the consolidation of a suspension of titanium barium nanopowder under the action of an electric field is considered and some data are given. Some problems of invasive ultrasound medicine related to the dynamics of suspensions are described in [9]. In works [2, 3, 5], we made the next attempt to analyze the characteristics of the current suspension of barium titanate particles, especially the effective viscosity, and consider its changes during the destruction of aggregates. Since there is no exact model for suspensions, we propose a rheological approach to the dynamics of dispersed systems using the Rebinder, Krieger Dougherty, and Casson models [14-15]. New data were also included and details of relevant ones were considered.

Since in this case the forces of repulsion and attraction of particles also act, the dynamic movement of such suspensions somewhat resembles an electrophoretic process. When the forces of the opposite direction are equalized, the process of increasing the aggregates must end, and they collapse. Both processes are somewhat similar, and we are now discussing a method to construct such a force, similar to [3, 6-9], to study the electrophoresis process, which was also studied in [10-13], etc.

4. Research methods

The main force in processes of electro coating from suspensions is the Coulomb's one, which depends on electrostatic field strength E and the charge and characteristics of the suspension particle (or aggregate of particles of barium titanate) q_p is

$$F_{Coul} = q_p(a_p, n, q_0, r)E, \quad (1)$$

were q_p - the radii of spherical particles, n - the average number of particles in the aggregate, q_0 – average charge (or it's density) for a separate inclusion, r - radius-vector (coordinates) of it's center (analog to L in [3]). The electrostatic field strength E in the suspension varied in [10] within 10–20 V/cm, but it is believed that it depends on the ferroelectric properties of the $BaTiO_3$ coating layer when approaching the surface. In this work, the coating was formed by powder with a roughness (radius ap) in the range of 90–150 nm.

This force F Coul should attract particles from the aggregates to the coating layer on the surface in contact with the electrode. The thickness of the layer is limited because there is another force, repulsion, F rep, which must increase with the thickness h of the layer. When the forces of repulsion and attraction of particles equalize, the electrophoresis process must end. Some aspects of this are considered in [10, 11]. Here it is proposed to use some similar results from works [2, 3], where the criterion of dynamic destruction obtained by comparing the formulas for generalizing dynamical (centrifugal) forces Fcf and dissipation ones Fdis with the interaction force Fin is estimated. Since in this case the forces of repulsion and attraction of particles also take place, the dynamic movement of such suspensions somewhat resembles an electrophoretic process. When the forces of the opposite direction are equalized, the process of increasing the aggregates must end, and they collapse. The both processes are somewhat similar and now we discuss the method for construction of such force analogical to [3, 6-8] for aim of study process of the electrophoresis.

For a pair of spherical particles with equal radii at the average distance Lav (for the electrophoresis this parameter changes to the distance to the surface of the coating layer), these papers described a formula for the interaction energy U. This interaction force Fin equals to the sum of the derivatives of the molecular U1 and the electrostatic potential energy U2 .

$$F_{in}^{(1)} + F_{in}^{(2)} = d(U_1 + U_2)/dL|_{L=Lav}, \quad (2)$$

where form of potential energy of intermolecular attraction U1 depends on the range of distances L

$$U_1 = a_p\,[-A/12L],\ L >> 10^{-8}\mathrm{m} = 10\ nm,\ A \approx 10^{-18} j. \quad (3)$$

At the contact distance L (near 180-300 nano m, nm) force value $F_{in}^{(1)}$ will been approached to magnitude 10^{-14}-10^{-13} Newtons. Energy of electrostatic repulsion

$$U_2 = a_p 64\,\pi(NT)\,[th(q\psi/(4T)]^2 e^{-k_1 L}/L \quad (4)$$

$$k_1 = [8\,\pi\varepsilon NT]^{1/2}, \quad (5)$$

where ψ – electrostatic potential on the surface of Nano particle, q – electrostatic charge of ion electrolyte, ε – dielectric constant, which depends to ferroelectric properties, T-temperature in energy units (J, eV). For ferroelectric material, such as barium titanat, dielectric constant isn't really constant value. Under normal conditions without strong electric fields ε is variating near 1360.

For energetic electrostatic potential $u = q\psi/(4T) >> 1$ formulas (4), (5) are simplified to such:

$$U_2 = \varepsilon(\pi T)^2 |ln(k_1 L)| . \qquad (6)$$

It is necessary to take into account other factors that reduce the attraction of particles to the surface, for example, a drop in the intensity of the external electrostatic field, when part of its effect is absorbed due to a change in the dielectric constant and thickness of the layer and due to the polarization of this volume of ferroelectric material.

When the repulsion becomes greater than the attraction, the growth of the aggregates [2, 3] or the layer coating mass [10-13] must stop. It is necessary to take into account other factors that reduce the attraction of particles to the surface, for example, a drop in the intensity of the external electrostatic field, when part of its effect is absorbed due to a change in the dielectric constant and thickness of the layer and due to the polarization of this volume of ferroelectric material. Both of these factors increase the effect on reducing the force of attraction of particles from the suspension when the thickness of the coating layer increases. Therefore, the condition of equality of oppositely directed forces and the end of the process is achieved with thinner coatings.

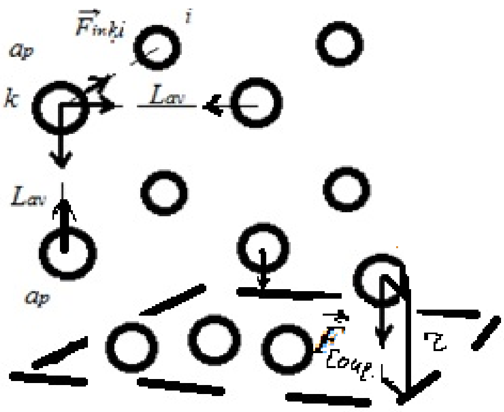

Figure 1. Scheme for packing into an aggregate in comparing with gathering on a charged surface.

Fig. 1 shows cube scheme from [3, 4] to describe approaches to the packing of nanoparticles in the processes of growth or destruction of agglomerates by dynamic forces. This scheme may be primary used for modelling of coating layers. Processes of sedimentation under gravitation is more slow than electro coating [3], analogue dynamical destruction of aggregates because corresponding forces are usually greater then gravitation's one.

Some of the interaction forces (F_{in}), not likely centrifugal, dissipative resistance ones, are the analog to the Coulomb's one (1), which are considered in [3].

The cube packing (figure 1) is one of the simplest and convenient scheme for beginning of study for corresponding of average distance L_{av} from concentration c:

$$c = v_p / v_{cube} = (4/3\pi\, a_p^{\ 3})/ L_{av}^3, \qquad (7)$$

where v_p is volume of particle or the correspondent displaced fluid volume of liquid phase, v_{cube} - volume of the cube with side L_{av}. From this is followed:

$$L_{av} = (4\pi/(3c))^{1/3} a_p. \qquad (8)$$

This scheme is no longer correct for closely packing, but may be considered for low and medium concentration (for example, c=0.2 is equivalent Lav =2.7144 ap but spherical particles have contact even at c=0.5236 and Lav is about 2ap)

The mass m_l of the displaced fluid volume of liquid phase (ethanol, ethyl alcohol) and mass m_p of each equal barium titanate sphere particle, and corresponding densities for the volumes v_p , v_{cube} are the same [2].

Additionally to force Fcf k that refers to the particle k caused by the rotation of the volume of suspension, on each inclusion would act interaction Finki between particle k and i (Fig. 1) and dissipative resistance Fdis force. For the Newtonian character of the flow Fdis are nearly equal for each equal particle. The Stokes' forces depend on the velocity and the effective viscosity. The value depends on movement and concentration of particles in suspension, their interaction, hydrodynamic effects, etc. Such a complex problem can be solved only by dividing it into separate, simpler parts, as for modeling a rheological problem based on experimental data and estimating forces for paired inclusions or one near a charged surface instead of theoretically unsolved multibody problems.

The nonlinear forces themselves must be constructed to obtain and study the Lagrange's equations of motion (of the second kind). They will be similar to those constructed for micro- or nanoparticles or inclusions [3, 4, 6, 7] in a liquid under vibration or under acoustic influence. That system of nonlinear differential equations even for single inclusion will contain terms associated with generalized forces, which are the corresponding derivatives of energy, as well as generalized coordinates of motion, their derivatives, and dissipation forces. As a result, these equations will have a very complex nonlinear character, which will be additionally complicate due to the effects of the interaction of the electric field with the polarized surface of the ferroelectric, the influence of temperature, viscosity and the concentration of the suspension, which makes it even more difficult to compile and study such equations in comparison with the considered early ones. In addition, the difference will be that the goal of the research is not to obtain conditions for the dynamic destruction of aggregates of particles [3, 4, 10, 11], but to find conditions for the completion of the formation of the coating layer (when the balance of attractive and repulsive forces is achieved). And here, as in work [11] we can indicate that some aspects of the dynamic destruction of suspensions are also somewhat similar to the action of the electric force around a layer on a charged surface. This happens because the coating layer will reach such a large number of particles that the repulsive forces (like as rupture force for dynamic destruction of aggregates [3]) will already exceed the weakened attractive forces.

5. Research results and prospects for further research development

As result, we attempted to compare basic macro characteristics processes the dynamical destruction of the suspension structure and changing its structure during electrophoretic coating up to the cessation of the growth of the coating thickness [10].

Effective viscosity is a macro-characteristic of the suspension, which indirectly indicates how many particles interact with each other during movement. If more particles interact, the viscosity is higher (Fig. 2). The characteristics of the thickness (or mass) of the layer of particles on the charged plate are somewhat similar (Fig. 3 from [10]). Since the more particles interact with the surface, the thicker their layer will be large in the coating (as weight in those curves).

Another analogy is that both processes have their saturation, after which the growth of both parameters decreases and stops.

Since we do not yet have defined models for the analysis of dependencies for the layer, we will analyze in more detail Fig. 2.

There, for further steps we have interpolated the data for $\eta_{ef}(c)$ for diapason of concentration $0 \le c \le 0.2$.

Interpolation curves were calculated and built from data for c=0,01;0,05;0,1;0,15;0,2. In fig. 2 curves 1, 2, 3, correspond to the experimental data with shear rates D = 50, 100, 1000 s-1. It shows that in the range c=10-20% vol. change in the nature of flow, especially at smaller D, becomes visible. That is due to increased interaction between particles.

To assess the scope of theoretical relations for term effects in experimental viscosity data applied formula Krieger-Dougherty (9) [14], and G. S. Hodokov's formulas are next (10) [3, 14-15]:

$$\eta_{ef} = \eta_0 [1-c/c_{max}]^{-\eta_0 c_{max}}, \quad (9)$$

$$\eta_{ef} = \eta_0 / [1-(1.5(1-c)^{1,5}+1)c],\ c<0.15;$$
$$\eta_{ef} = k\eta_0 / [1-(1.5(1-c)^{1,5}+1+\Delta)c],\ 0.15\le c\le 0.25. \quad (10)$$

Curve *4* on Fig. 2 was built on the formula (10) and correspondence with curve 3 for concentration less 5% and D=1000 s^{-1} is well, and influence of interaction of particle is small, range of aggregation is too small.

Curves 5 and 6 on Fig. 2 build the first and second parts of formula (10) respectively. It should be noted that from empirical values micro suspension k = 4-5, Δ=0,1-3 proposed in [3] were selected k = 5, Δ=2 for sizes of particles near 20-30 μm, and some corresponding between carve 1 (D=50 s^{-1}) and carve 6 took place. It can be proposed that sizes aggregates of nano particles are in the rough nearly 20-30 μm, on 2-3 order larger then individual nanoparticles, because hydrodynamic forces of objects with similar dimension can have similar influence on parameter of flow [2, 3].

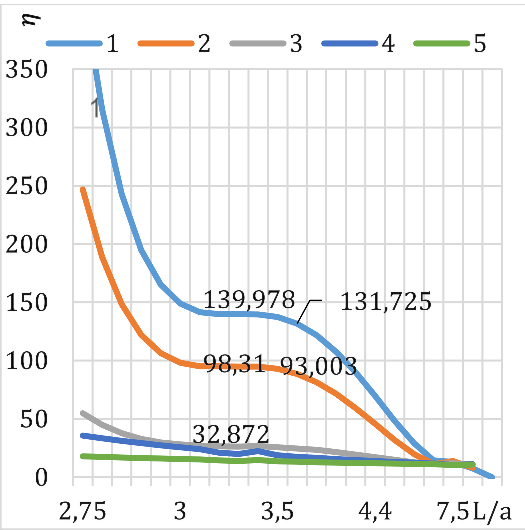

Figure 2. Effective viscosity η_{ef} (L_{av})

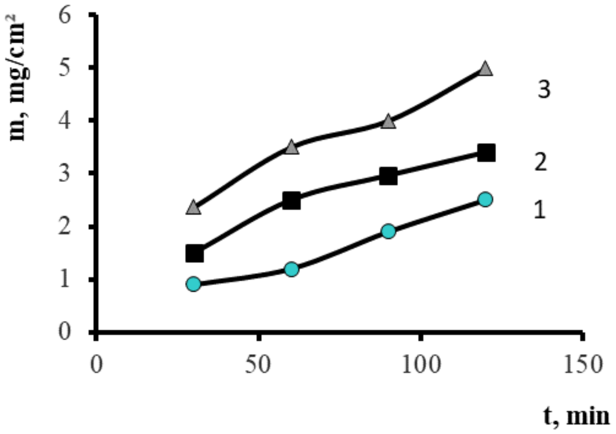

Figure 3. Electrophoretic coatings [9] from BaTiO3- weight dependence of time deposition and tension electric field, V/cm: 1-20; 2-50; 3-100.

The rheological model, which better takes into account the presence of aggregates of particles and the structuredness of suspensions, is a generalized model of Casson [15], that also was described in [2]. There was concluded, that suspension of the barium titanate for $c>0.2$ has non-Newtonian character of flow corresponding to the generalized Casson model. For the study decreasing and increasing of aggregates' or beginning of self-organizing we attempt to estimate the orders of forces and useful for this purpose.

Firstly, for c<0,2 on basis of (7), (8) can be built the dependence between η_{ef} and L_{av} /a_p (Fig. 2).

Since we have not yet defined models for analyzing dependencies for the layer, we will analyze Fig. 2 in more detail.

There are curves with same numbers corresponding to ones from [3]. Some calculated values of ηef for start and end of the flat parts of experimental curves 1 – 3 are shown on the curves for the next analysis (for curves 3 only flat finish point is shown due to curve's flatly character near it). Comparing the nature of the dependences in Figures 2 and 3, it can be shown that the growth of the effective viscosity depends on the concentration in the suspension with the strengthening of interaction forces and the growth of the weight of aggregates, which is analogous to the process of weight growth of electrophoretic coatings from aggregates, and accordingly both processes can be investigated by similar approaches for forces and equations. The average distance in the first case must be taken between the particles, in the other - between the particle and the surface of the layer.

And here, as in work [11], we can indicate that some aspects of the dynamic destruction of suspensions are also somewhat similar to the action of the electric force around a layer on a charged surface. This happens because the coating layer will reach such a large number of particles that the repulsive forces (like as rupture force for dynamic destruction of aggregates [3]) will already exceed the weakened attractive forces.

6. Conclusion

We discussed the applicability of approaches to obtaining forces and equations of motion based on [3, 6-8] for a somewhat similar coating process. But the formulas will have a very complex nonlinear character due to the effects of the interaction of the electric field with the polarized surface of the ferroelectric, the influence of temperature, viscosity and concentration of the suspension, that for single particle their formulation and research are even more difficult compared to the considered early ones. In addition, the difference of both processes will be that the goal of the study is not to obtain conditions for the dynamic destruction of particle aggregates [3], but to find conditions for the completion of the formation of the coating layer (when the balance of attraction and repulsion forces is achieved). Recall here it is indicated that the difference between centrifugal and external forces for neighboring inclusions is smaller than for different sides of a large aggregate, and this aspect is also somewhat similar to the action of the electric force around a layer on a charged surface (which is consistent with the results of comparing the nature of the dependences on Fig. 2 and 3). This happens because the coating layer will reach such a large number of particles that the repulsive forces (or rupture forces, centrifugal forces for dynamic destruction of aggregates) will already exceed the weakened attractive forces and polarisation in greater volume will begin play its role too. Accordingly, electron microscopic studies [10] of the surface of the coating showed that in ethanol the structure of the coating is heterogeneous, the size of aggregates of particles and pores is from 0.5 to 2 μm.

We tried here to compare two main macro characteristics of the processes: the effective viscosity of the suspension and the weight of the electrophoretic coating from it on the charged surfaces.

It is clear that they are connected due to the concentration of the suspension, and despite all the differences, they have something similar. Some comparative analysis of data was carried out regarding the dynamic destruction of the suspension structure, viscosity reduction, and some results during electrophoretic coating from the same suspension up to the cessation of thickness (mass) growth.

Also, on the basis of previous works, an approach to the construction of forces for a single particle near the charged surface and to the estimation of the maximum thickness of the coating is proposed.

The results are discussed and it is predicted that they can be used for further research on the process and in the future in the development of the technology of forming small multilayer capacitors, as well as in the development of devices for the generation and reception of ultrasonic waves with ferroelectric parts. etc.

7. Acknowledgements

This study was carried out according to the initiative scientific topic of O. V. Kuzma, registered in 2024 at I. Sikorsky NTUU KPI "Investigation of equations of motion and effective characteristics of suspensions with micro- or nano-inclusions under various types of disturbances."

References:

1) M. Zagorny, A.Zhygotsky, A.Ivanchuk, O. Kuzma, A. Pozniy, A.Ragulya, “Barium Titanate Nanoparticles Self-organization from PVB-ethanol Suspensions”, J. Chem. Eng. Chem. Res., vol. 2, 4, pp. 547-555, 2015.

2) O.V. Kuzma, ‘The dynamic destruction aggregates in nano suspensions into rotary viscometer’, 2017 IEEE 7th International Conference Nanomaterials: Application & Properties (NAP), 4 p.

3) Oleksandr Kuzma, ‘The Influence of an Average Distance Between Particles into the Dynamic Destruction of Nano Suspensions’, 2020 IEEE 10th International Conference Nanomaterials: (NAP), 4 p.

4) M. Zagorny, N. Tyscenko, A.Ragulya, O. Lavrynenko. A. Kasumov, F. Melnyk, O. Kuzma, A. Ievtushenko, “Optical and Photocatalytic Activity of Polyaniline/TiO2 Composites with Anatase and P25 Nanoparticles”, J. of Nano- and Electrpnic Physics (JNEP), vol. 13, 5, pp. 05034 (6 pp.), 2021.

5) Oleksandr Kuzma On the analysis of Effective Viscosity for the Nanosuspension into a Rotary Viscometer, Almonac Nauky, Kyiv, 5 (38), 2020, pp. 43-45.

6) V. D. Kubenko, V. M. Kuz'ma, G. N. Puchka,. Dynamics of Spherical Bodies in Fluid under Vibration. 1989. (written in conjunction with A. V. Kuz'ma - P. 122-128).

7) V. D. Kubenko, A. V. Kuz'ma, “Influence of the boundary of a column of incompressible liquid in investigating axisymmetric oscillations of a solid sphere in a cavity”, Intern. Appl. Mech., vol. 35, iss. 12, pp 1199–1206, December 1999.

8) O.V. Kuzma. The behavior of particles into column of a compressible liquid, disturbed by source of oscillations on the axis of symmetries, Res. Bul. of NTUU “KPI” (Naukovi visti) 4 (2006) 66-72.

9) O. Kuzma. Vibration effects on inclusions inside invasive waveguide/ Proc. of the XXVI Int. Scient. and Practical Conf., Helsinki, Finland, July 05 – 08, 2022, p. 289 -292.

10) Anna Barshchevskaya, Oksana Korniienko, Maksym Zahornyi, Alexander Zhygotsky, Anna Ivanchuk, Saide Umerova, The Consolidation of Titanium Barium Nanopowder Suspension by Electric Field Action, J. of Chem. and Technol., 2019, 27(2), 101-110.

11) Oleksandr Kuzma . On Aspect of the Formation of Electrophoreting Coating from Nano Suspension under Electric Field Action. Proceed. of the 10th Int. Scien. and pract. conf. Cognum Publishing House. London, UK. 2023. Pp. 300-303. https://sci-conf.com.ua/x-mizhnarodna-naukovo-praktichna-konferentsiya-science-and-innovation-of-modern-world-15-17-06-2023-london-velikobritaniya-arhiv/

12) Zagorny M. N. Fabrication of titanate barium films by electrophoretic deposition technique / M.N. Zagorny, X. Pidsosonnyi, A. Ivanchuk, A. Zhygotsky, A. Ragulya // J. Chem. Chem. Eng.– 2014. – Vol. 8. – P. 254 – 259.

13) Kuscer D. Patterning of lead-zirconate-titanate thick-film structures by electrophoretic

deposition from ethanol- based dispersions / D. Kuscer, S. M. Bernardo, M. S. Zarnik, B. & Malič // J. Europ. Ceram. Soc. – 2016. – Vol. 36. – P. 291–297.

14) M. Krieger, Irvin, Rheology of monodisperse latices, Adv. in Coll. and Interf. Sci. 3 (1972) 111-136.

15) Casson N. A, Rheol. of disperse systems, ed. C.C.Mill. L, 1959, P. 84.