

stabilizing action of a high-molecular compound is sufficient activity of the surface of nanoscale metal particles with respect to the polymer forming a highly strengthened adsorption-solvated structured film on the surface of the dispersed phase. Protective polymers form sufficiently strong structural grids in the volume of the dispersion medium on the surface of the particles of the dispersed phase. The degree of stabilization can be different - these are continuous transitions from the formation of structures only with adsorption layers to the structuring of the entire volume of the dispersion medium. Especially stable are colloidal adsorption layers, which are formed at significant concentrations of high molecular substances [24].

Sometimes a structural grid appears in the solution, where the metal particles are arranged in groups, forming chains of various shapes and lengths. In it, colloidal particles bind units of different or identical macromolecules. It should be taken into account that the processes of particle coarsening and adsorption of macromolecules on the surface of the initial and emerging particles simultaneously (and influence each other) take place in the system. In this case, the aggregate stability depends on the ratio of the rate constants of coagulation and adsorption [25]. When two nano-sized metal particles covered by a layer of adsorbed soluble polymer chains approach each other to distances less than the total thickness of the adsorption layers, an interaction appears between the layers, which leads, in most cases, to the formation of repulsive forces between the colloidal particles.

The quantitative contribution of the polymer component to the interaction energy of the particles depends both on the parameters of the adsorption layer of the polymer on the surface (the proportions of the elementary links of the macro-molecule contacting the surface, the degree of coverage of the latter polymer, the thickness of the polymer layer, etc.) and the parameters of the macro-molecules in solution. The adsorbed polymer layers on the surface of nanoscale particles can be considered as a kind of medium - polymer solution, which determines the interaction forces between the particles of the dispersed phase. It is obvious that at very high packing density of adsorbed molecules on the surface, when macromolecules almost lie on it, the interaction between the particles is negligible. When the particles approach and overlap the adsorbed layers of the polymer, an interaction arises due to the "meshing" of the loops. It is the area of such overlap that can be considered as a medium (polymer solution). With mutual penetration of two adsorption layers, it is possible to exhibit effects due to a decrease in the number of possible conformations of the macro-molecular chain and a change in the concentration of segments in the overlap zone, accompanied by a change in polymer-solvent interaction and the appearance of local osmotic pressure [25].

Despite the fact that the main theoretical provisions concerning the formation and stabilization of colloidal dispersions are mainly related to polymer emulsions, they, apparently, can be fully applied to nanoscale particles. The differences can be of a quantitative rather than qualitative nature. In particular, as already noted, the attractive forces between particles of dispersions of organic polymers are much less than between particles of metals, their oxides and salts. Many aspects of the effect of additions of high molecular compounds on the stability of nanoscale particles have been studied, but the mechanism of the stabilizing action of polymers has not been completely clarified, and the theoretical basis for their scientific selection for these purposes is in the initial stage of development. This is due to the great complexity of polymer dispersed systems and the variety of factors responsible for the stability of metal-containing nanoscale particles. Experimental data suggest that the most promising stabilizers among non-ionic polymers will be those that form a sufficiently thick or dense adsorption layer on the surface of the particle. For charged macromolecules, the use of similarly charged polymers with a high charge density is more promising.

In general, the stabilizing effect of a high-molecular compound is determined by a number of additional factors, in particular, the degree of polymerization, the type and number of functional groups, the nature of their distribution along the chain, and so on. The strength and rigidity of the protective layers, their spatial extent, as well as the way of polymer attachment to the particles, are the most important characteristics of the stabilizing action. In the theory of systems under consideration, two groups of problems can be distinguished with a certain degree of conventionality [26]. One of them is the subject of study of classical colloid chemistry and physical chemistry of surface phenomena. This includes, for example, a description of the electro-surface phenomena in colloidal systems. Another group of problems is associated with the traditional sections of the physicochemistry of polymers. One is usually distracted from the details of the interaction between colloidal particles themselves and focus on the pure polymer contribution depends on the

concentrations of dissolved macro-molecules, the nature of their interaction with particles, thermodynamic properties of the solvent and the like. In a real situation you need a combination of these approaches to stabilization of nanoparticles.

A distinctive feature of carbon nanotubes is that they have a large surface energy, and, therefore, show an increased tendency to aggregate. Currently, the process of their agglomeration is one of the most serious obstacles to their wide application. To solve this problem, many researchers suggest a surface modification of carbon nanotubes. In earlier studies, a scientific team of specialists from the Russian Chemical Technical University named after D.I. Mendeleev demonstrated the possibility of adsorption modification of carbon nanotubes by various surface-active substances [27-30]. However, the process of processing solids in disperse systems, including carbon nanotubes, is affected not only by the ratio of the selected components, but also by various technological parameters. Having investigated the influence of various technological parameters on the processing and modification processes, it is possible not only to correct the system, but also to obtain the initial data for scaling the process to an experimental installation.

3. METHODS

The processing of carbon nanotubes was carried out on a laboratory dispersing unit LDU-3MPR (Production by LLC Labotex Russia). Control over the process was carried out by changing the hiding power of the paste. The formulation for the modification was created on the basis of studies previously conducted by the scientific team, and includes carbon nanotubes, surfactants (cationic acrylic block copolymer and non-ionic polyethylene glycol monooleate).

4. DATA, ANALYSIS, AND RESULTS

The most important technological parameters in the processing of such systems are, - the angular velocity of rotation of the mixing device, the temperature and the number of dispersing bodies. Thus, for example, the shear stresses and the shock pressure created by the agitator depend directly on its angular velocity. To investigate the effect of the angular velocity of the mixing device on the process of modifying carbon nanotubes, a multi-plate mixer was chosen, as is most often used for similar purposes. The modification was carried out with a solvent - ethyl cellosolve.

It should be noted that when a multi-plate mixer is used, the energy transfer in the container is due to the adhesion forces of the processed mixture to the disks and cohesion forces of the system itself. Under the action of the stirrer, vortex flows and the radial flow of dispersing bodies are formed in the container, as a result of which the process of processing takes place (also called "dispersion"). In view of the large circumferential velocities, large velocity gradients appear around the disks, which results in high shear stresses. Figure 1 shows a typical graph of the change in hiding power as a function of the processing time of carbon nanotubes (modification).

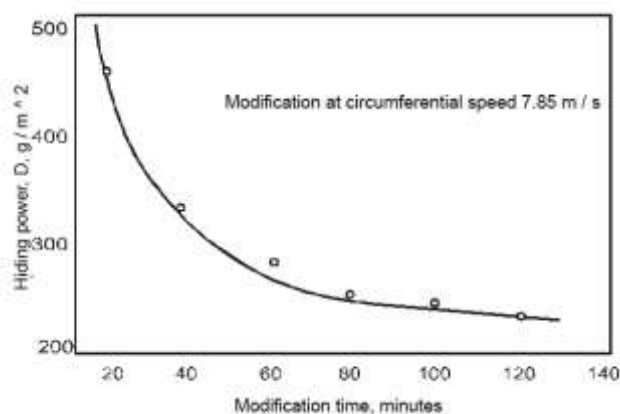


Figure 1: A typical graph of change in hiding power as a function of time when modifying carbon nanotubes.

This graph is typical for dispersing pastes of medium and low viscosity, first a sharp decrease in the spreading rate, caused by the destruction of large aggregates, then, after a certain limit, the curve goes smoothly, which is due to the destruction of strong aggregates of small size, and finally the exit to the plateau in the self-similar region, where the processes of disaggregation are balanced by secondary coagulation and flocculation. When plotting the dependence of the hiding power on the angular velocity

shown in Figure 2, after reaching the self-similar region (about 120 minutes from the beginning of the modification), it turned out that the curve is complex.

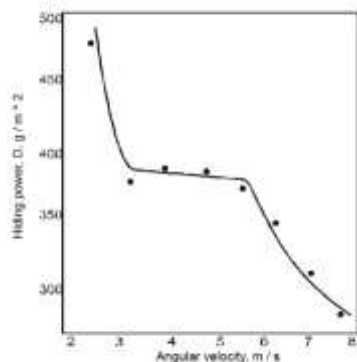


Figure 2: Effect of angular velocity on the spreading rate, after 120 min from the beginning of the modification.

At the beginning, when the circumferential velocity is increased from 2.35 to 3.14 m / s, the hiding power decreases, since shear stresses increase, the turbulence increases and the flow profile becomes similar to undulating. In the speed range from 3.14 to 5.49 m / s, the curve emerges on a plateau with a slight slope, in our opinion, this may be due to the fact that large aggregates are effectively destroyed in the wave-like pasta flow, but the process of destruction of small aggregates does not occur in due measure. Only at angular velocities above 6.0 m / s there is a sharp drop in hiding power, which, in our opinion, is due to the fact that the process begins, in which smaller aggregates are also destroyed: bodies and paste, under the action of centrifugal force, are discarded wall of the dispersing glass, strike against it, and, upon returning to the centre of the disk, their friction between themselves and the disk occurs, which causes large shear stresses.

Thus, the modification of carbon nanotubes is advisable to conduct at angular velocities above 6.0 m / s. Another technological parameter that has a significant impact on the progress of the processing of polymer composites containing carbon nanotubes (including the process of their modification) is temperature. It is known that in most cases the temperature increase leads to an intensification of the processing process, mainly due to an increase in the concentrations corresponding to the beginning of the structuring of the film former solution, the growth of the surface activity of special additives, and a decrease in the effective viscosity of the system. Traditionally, the process of dispersing medium viscosity and low viscosity pastes is carried out at temperatures not exceeding 50°C. Since at higher temperatures the saturated vapour pressure increases and mass evaporation of the solvent occurs, which leads to a disruption in the formulation ratio of the paste components and the increase in the viscosity of the system.

Therefore, as the upper temperature limit, we chose the temperature 50°C, and the lower temperature limit of the paste was chosen 18°C, since this is the minimum temperature to which you can cool the paste with water in the warmer months. Figure 3 shows the variation of hiding power versus the time of modification of carbon nanotubes at different temperatures.

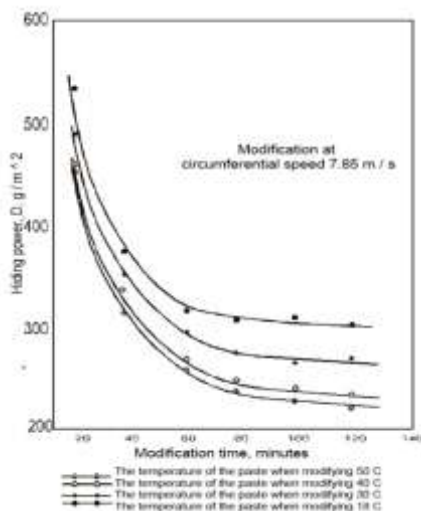


Figure 3: A change in the spreading power of pastes when modifying

carbon nanotubes, at different temperatures.

As can be seen from Figure 3, all the dependencies of the hiding power variation on the modification time at different temperatures are identical, however, with the temperature increase the process intensifies, as indicated by the data on the dependence of the hiding power on the temperature after 120 min. from the beginning of the process (self-similar region), presented in Figure 4.

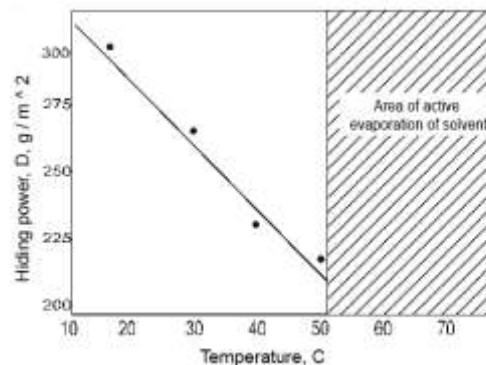


Figure 4: The effect of temperature on spreading rate, after 120 minutes from the beginning of the modification

It is obvious that at high temperatures, mass-exchange processes that intensify the process of destruction of the film-forming associates are accelerated, the desorption of water and air vapour from the surface of carbon nanotubes is facilitated, and the adsorption of surface-active substances on them is accelerated, accompanied by the Rebinder effect. Thus, the process of modifying carbon nanotubes is expedient to conduct at elevated temperatures, up to 50°C inclusive.

Many authors distinguish three regimes characterizing the behaviour of solid-state particles in a liquid medium during the dispersing process. With a small content of the solid phase, the effect of particle collisions is small and the behaviour of the particles is determined by the viscosity of the medium. At some intermediate content of particles the number of collisions between them increases and the inertial forces become more noticeable in comparison with the viscosity of the medium. At a high content of particles of the solid phase, their displacement is so slowed down that the inter-particle contact predominates in the dynamic behaviour of the medium. If a small number of dispersing bodies are introduced into the paste in a spherical shape, then as a result of structural breakdown, the effective viscosity of the system, the Toms effect, decreases somewhat, with an increase in the number of these bodies, they become constituents of new structural formations. The relative displacement of the milling bodies destroys these formations and the effective viscosity decreases with simultaneous destruction of the pigment aggregates.

The change in the size of dispersing bodies affects not only the effective viscosity of the system, but also the hydrodynamics of its flow. As an object of study, we chose a glass bead with a diameter of 1.4 to 3.5 mm, while the volume of the beads loaded did not change. As a result of the studies, it turned out that when the size of the beads was reduced from 3.5 to 1.4 mm, the dependence of the change in the spreading rate over time was typical for the processing of filled composites, at first a sharp decrease in the hiding power, then a smooth decline before reaching the self-similar regime. To identify the results obtained, it was suggested to calculate the volumetric productivity of the disperser when using a particular type of bead [8]. A typical schedule for the calculation is shown in Figure 5.

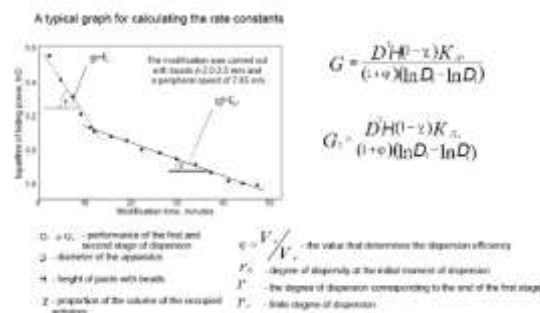


Figure 5: An example of calculation of volumetric productivity during the process of modification of carbon nanotubes.

As a result, it turned out that the maximum value of volumetric productivity, both in the first and in the second stage, is observed when using beads $d = 2.0\text{-}2.5$ mm (Figure 6.).

Due to the increasing bead diameter the shear stresses decrease, therefore it is natural that the productivity of both stages, when using beads $d = 3.0\text{-}4.0$ mm, is less than in the case of using beads with $d = 2.0\text{-}2.5$ mm. When using beads with $d = 1.4\text{-}1.8$ mm, the performance of both stages is also noticeably less, in comparison with the case of using beads with $d = 2.0\text{-}2.5$ mm. In our opinion, this may be due to the fact that, in addition to the process of disaggregation under the influence of shear stresses, secondary coagulation and flocculation occur. These side processes are probably due to the fact that the process of stabilizing disaggregated particles of the dispersed phase lags behind the process of disaggregation. It follows that for carrying out the process of modifying carbon nanotubes, it is advisable to use beads with a diameter $d = 2.0\text{-}2.5$ mm.

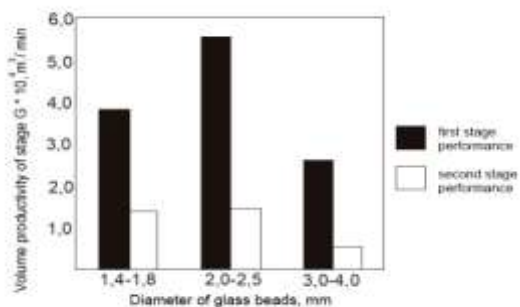


Figure 6: The dependence of volume productivity on the diameter of dispersing bodies - glass beads.

5. DISCUSSION

Despite the fact that the process of modification of carbon nanotubes and their introduction to polymer matrix is regarded by many researchers, analyzing the results of this work, it can be stated that the use of the above methodology enables the processing of carbon nanotubes at the production equipment, which is widely used in the paint industry, dissolvers and agitator bead mills. The use of such highly efficient equipment as a bead mill in the first place makes it possible to reduce the unit cost of a product. This is achieved by the fact that the use of a bead mill makes it possible to achieve a productivity of up to 150kg / h, while the ultrasonic bath mentioned by various authors, which is often mentioned by various authors, allows producing no more than 1kg / h. In addition, for energy consumption bead mills are more economical, since they are equipped with motors up to 10 kW, while the use of ultrasonic baths, with commensurate overall dimensions, requires a supply of at least 30 Kw [31,32]. I would also like to note that the use of ultrasound should necessarily be followed by subsequent centrifugation and evacuation, which is also quite energy-consuming.

In addition, bead mills are completely hermetic, which eliminates the release of organic solvents into the environment, in comparison with planetary mills [33]. It should be noted that in addition to reducing the cost of production of nanostructured paints of barrier type and improving its environmental friendliness, the proposed methodology will make it possible to obtain an aggregate-resistant system in time, which is not always possible with ultrasound applications. In the organization of production, one of the most significant technological standards is the step-by-step control over the conduct of production processes. At the same time, the control methodology should be accessible, operational and informative. These requirements are fully met by the evaluation proposed in this paper for the process of processing of nanostructured paint-and-lacquer compositions of barrier type, according to the spreading rate. The technological parameters evaluated in this work will allow organizing the mass-scale for real industrial volumes.

6. CONCLUSION

As a result of the conducted studies, the influence of various technological parameters on the process of processing (modification) of carbon nanotubes was shown. It is established that the process must be carried out with an angular velocity of rotation of the stirring device of at least 6 m / s. It was noted that a slight increase in temperature, up to 50°C, has a favorable effect on the process of modification. The influence of dispersing

bodies, glass beads, on the process of modifying carbon nanotubes was also studied and recommendations on the use of such dispersing bodies were given. The data obtained show that for the process of modifying carbon nanotubes in a medium of oligomer solutions, it is possible to use the scientific approaches underlying the physico-chemical processes for obtaining filled paint systems. Using the principles of stabilization, providing the aggregative and sedimentation stability, using the control technique proposed by the authors, in terms of the spreading capacity of the material, it is possible to obtain a composite material with high performance properties that do not change over time (when storing the material).

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REFERENCES

- [1] Homenick, CM., Lawson, G., Adronov, A. 2007. Polymer grafting of carbon nanotubes using living free radical polymerization. *Polymer Reviews*, 47, 265–90.
- [2] Aleksashina, E.V., Mischenko, S.V., Sotskaya, N.V., Tkachyov, A.G., Vigdorovich, V.I., Dolgihh, O.V. 2009. Activation of carbon nanotubes by acid. «Kondensirovannyye sredy i mezhfaznyye granitsy» (Condensed Matter and Interphases), 11 (2), 101–105.
- [3] Simmons, T.J., Bult, J., Hashim, D.P., Linhardt, R.J., Ajayan, P.M. 2009. Noncovalent Functionalization as an Alternative to Oxidative Acid Treatment of Single Wall Carbon Nanotubes with Applications for Polymer Composites. *ACS Nano*, 3, 865–870.
- [4] Jeynes, J.C.G., Mendoza, E., Chow, D.C.S., Watts, P.C.R., McFadden, J., Silva, S.R.P. 2006. Generation of Chemically Unmodified Pure Single-Walled Carbon Nanotubes by Solubilizing with RNA and Treatment with Ribonuclease A. *Advanced Materials*, 18, 1598–1602.
- [5] Spitalsky, Z., Tasis, D., Papagelis, K., Galiotis, C. 2010. Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. *Progress in Polymer Science*, 35, 357–401.
- [6] Yu, A., Ognev, Teplih, A.M., Bataev, V.A., Bataev, A.A. 2009. Obtaining a nanocomposite based on a polymer matrix and multilayered carbon nanotubes. Conference proceedings of Intern. Nanotechnology Forum «Rusnanotech 09», Moscow.
- [7] Abazova, O.A., Kushkhov, K.H.B., Khashirova, S.U.Y., Mikitaev, A.K. 2012. Development of polymer nanocomposites based on polypropylene and the mother carbonate concentrate of carbon nanotubes. New polymer composite materials VIII International Scientific and Practical Conference, Nalchik, 3-5.
- [8] Gilman, A.B., Yablokov, M.Y., Kuznetsov, A.A. 2012. Composite materials based on carbon nanotubes modified in low-temperature plasma. Materials of the International Scientific and Technical Conference INTERMATIC, Moscow, 2, 95-98.
- [9] Chou, W.J., Wang, C.C., Chen, C.Y. 2008. Characteristics of polyimide-based nanocomposites containing plasma-modified multi-walled carbon nanotubes. *Composites Science and Technology*, 68 (10-11), 2208-2213.
- [10] Ramos-deValle, L.F., Neira-Velazquez, M.G., Hernandez-Hernandez, E. 2008. Surface modification of CNFs via plasma polymerization of styrene monomer and its effect on the properties of PS/CNF Nano composites. *Journal of Applied Polymer Science*, 107 (3), 1892-1899.
- [11] Xu, L., Fang, Z., Song, P., Peng, M. 2010. Functionalization of Carbon Nanotubes by Corona Discharge Induced Graft Polymerization for the Reinforcement of Epoxy Nanocomposites. *Plasma Processes and Polymers*, 7 (9-10), 785-793.
- [12] Pomogailo, A.D., Rosenberg, A.S., Uflyand, I.E. 2000. Nanoparticles of metals in polymers. M.: Chemistry, 672.
- [13] Pomogailo, A.D. 1997. Polymer-immobilized nanoscale and cluster metal particles. *Russian Chemical Reviews*, 66 (8), 679-716.
- [14] Simmons, T.J., Bult, J., Hashim, D.P., Linhardt, R.J., Ajayan, P.M. 2009. Noncovalent Functionalization as an Alternative to Oxidative Acid

Treatment of Single Wall Carbon Nanotubes with Applications for Polymer Composites. *ACS Nano*, 3, 865-870.

[15] Jeynes, J.C.G., Mendoza, E., Chow, D.C.S., Watts, P.C.R., McFadden, J., Silva, S.R.C. 2006. Generation of Chemically Unmodified Pure Single-Walled Carbon Nanotubes by Solubilizing with RNA and Treatment with Ribonuclease A. *Advanced Materials*, 18, 1598-1602.

[16] Carbon Nanotubes. 2006. Properties and Applications. Edited by Michael J. O'Connell. CRC Press and Taylor & Francis Group: Boca Raton, FL.

[17] Sgobba, V., Rahman, G.M.A., Ehli, C., Guldi, D.M. 2006. Covalent and noncovalent approaches towards multifunctional carbon nanotube materials. In: Langa F, Nierengarten JF, editors. Fullerenes, principles and applications. Cambridge, UK: RSC Nanoscience and Nanotechnology Series, 329-79.

[18] Tasis, D., Tagmatarchis, N., Bianco, A., Prato, M. 2006. Chemistry of carbon nanotubes. *Chemical Reviews*, 106, 1105-36.

[19] Brzhezinskaya, M.M., Vinogradov, N.A., Vinogradov, A.S., Muradyan, V.E., Shul'ga, Y.M., Polyakova, N.V. 2008. Characterization of fluorinated multiwalled carbon nanotubes by x-ray absorption spectroscopy. *Physics of the Solid State*, 50 (3), 587-594.

[20] PRF. 2013. Patent of the Russian Federation No. 2474534 Beeva DA et al. A method for processing carbon nanofillers.

[21] Aleksashina, E.V., Mischenko, S.V., Sotskaya, N.V., Tkachyov, A.G., Vigdorovich, V.I., Dolgihh, O.V. 2009. Activation of carbon nanotubes by acid. «Kondensirovannyye sredy i mezhfaznye granitsy» (Condensed matter and interphases), 11 (2), 101-105.

[22] Zakharychev, E.A., Ryabov, S.A., Semchikov, Y.D., Razov, E.N., Moskvichev, A.A. 2013. An investigation into the influence of functionalization degree on some properties of multi-walled carbon nanotubes. *Vestnik of Lobachevsky University of Nizhni Novgorod*, 1 (1), 100-104.

[23] Wang, Z., Shirley, M.D., Meikle, S.T. 2009. The surface acidity of acid oxidized multi-walled carbon nanotubes and the influence of in-situ generated fulvic acids on their stability in aqueous dispersions. *Carbon*, 47, 73-79.

[24] Brian, P. 2011. Grady Carbon Nanotube-Polymer Composites: Manufacture, Properties, and Applications. John Wiley & Sons, 352.

[25] Heister, E., Lamprecht, C., Neves, V. 2010. Higher Dispersion Efficacy of Functionalized Carbon Nanotubes in Chemical and Biological Environments. *ACS Nano*, 4 (5), 2615-2626.

[26] Tchoul, M.N., Ford, W.T., Lolli, G. 2007. Effect of Mild Nitric Acid Oxidation on Dispersability, Size, and Structure of Single-Walled Carbon Nanotubes. *Chemistry of Materials*, 19, 5765-5772.

[27] Panferov, I.I., Apanovich, N.A., Demicheva, O.V., Zaitseva, O.E. 2012. Investigation of the effect of surfactants on the process of carbon nanotube dispersion in solutions of epoxy oligomers. Successes in chemistry and chemical technology. Proceedings Volume XXVI, of the Russian Chemical Technical University named after D.I. Mendeleeva, Moscow, Russia, 3 (132), 66.

[28] Fetisova, O.E., Apanovich, N.A., Tseitlin, G.M. 2007. Investigation of the effect of adsorption modification of carbon nanotubes on the properties of nanostructured paint and varnish compositions. All-Russian Conference "Young Scientists and Innovative Technologies". Theses of reports, Moscow, Russia, 147.

[29] Fetisova, O.E., Apanovich, N.A., Tseitlin, G.M. 2007. Investigation of the effect of adsorption modification of carbon nanotubes on the spreading power of nanostructured paint and varnish compositions. Successes in chemistry and chemical technology. Scientific works of the Russian Chemical Technical University. DI. Mendeleev, XXI (6), 14-17.

[30] Fetisova, O.E., Apanovich, N.A., Tseitlin, G.M., Sinitsin, S.A., Kozyreva, N.A. 2006. Investigation of the effect of surfactants on the properties of nanostructured paint and varnish compositions. *The chemical industry today*, 11, 19-25.

[31] Indeykin, E.A., Leibzon, L.N., Tolmechev, I.A. 1986. Pigmenting of paint and varnish materials. L.: Chemistry, 160.

[32] Marakhovsky, P.S., Kondrashov, S.V., Akatenkov, R.V., Aleksashin, V.M., Anoshkin, I.V., Mansurova, I.A. 2015. On the modification of heat-resistant epoxy binders with nanotubes. *Bulletin of the Moscow State Technical University. Bauman. Series: Mechanical engineering*, 2 (101), 118-127.

[33] Patent. RU 2494961

