Research of phase changes in process of storage of fine dispersed aqueous suspensions of inorganic substances

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Abstract. In the work were proposed to use the method of digital holographic interferometry on the example of suspensions of fine dispersed silica, developed by different ways, for studying fine dispersed suspensions of inorganic substances in combination with the process of their sedimentation. A comparison of experimental results obtained by this method and by method of dynamic light scattering is presented. The high sensitivity of the interferometric method, particularly during assessing of changes of suspensions with nanosized particles is shown.

1. Introduction
At present time the use of substances in dispersed state is widely used to create new composite materials, to improve the physico-mechanical properties of industrial structural materials, in biomedical technologies [1-3]. The development of nanotechnologies with application of nanodispersed ingredients requires corresponding development of diagnostics of parameters of such small-scale objects.

There is a number of methods of characterization of parameters of fine dispersed inorganic suspensions, such as scanning electron and probe microscopy, dynamic light scattering, x-ray diffractometry. Each of these methods has its methodological peculiarities and during studying of specific objects has both certain advantages and certain disadvantages and conflicts of interest [4-6]. In addition these methods are usually expensive and time-consuming. The development of new methodologies for the study of substances in fine dispersed state, including nanodispersed state, it is highly relevant, because each new method improves the accuracy of measurement results obtained by other methods.

In this work the possibility of characterizing parameters of fine dispersed inorganic suspensions during using the method of digital holographic interferometry for observing the process of sedimentation of suspensions with particles of substance, which size is less than one micron, is considered.

2. Object and methods

2.1. Object of research
The objects of study in this work are aqueous suspensions of fine dispersed quartz, particles of which are obtained by different methods and used for different purposes. The particles of suspension 1 are obtained by method of condensation of silicon dioxide from the gas phase, such particles are used in...
biomedical technologies and during creation of polymeric composite materials for various purposes with improved physico-mechanical properties. Particles of suspension 2 are obtained from the solid phase by method of grinding in a planetary-centrifugal mills and they are used as industrial additives, which improve the operational properties of building materials.

Initial state of SiO₂ for production of suspension 1 – dry powder; for production of suspension 2 – pasty mixture with water in a weight ratio of 1.3:1.0. Work preparations were 0.1%-0.5% aqueous suspensions of the researched substances.

2.2. Experimental methods
For studying changes of optical characteristics of the sample in the process of radiation exposure and during postexposure period was used experimental stand designed for studying phase transformations of transparent objects by method of digital holographic interferometry (DHI) [7], a block-scheme of which is shown on figure 1a. At this stand the unit of the object (2) placed outside of the main scheme of interferometer (1).

The object of study is a preparation of suspension in transparent cuvette with the size of 10x10x40 mm (figure 1b). The cuvette is rigidly mounted in a special cassette and installed in the object beam in accordance with the optical scheme of interferometric experiment. The object beam of interferometer (532 nm) tests the working area of the object with the size at least 25x25 mm and passes through the sample as shown on figure 1c. The stand has a computer terminal to control a registration of sequence of digital holograms and their further processing.

The digital interferogram of the current state of the object represents the spatial distribution of the phase difference of the testing radiation in the plane of the observation of object, corresponding to the change of the sample at time tᵢ compared to initial (at time t₀) – \( \varphi(x,z) = \varphi(x,z) - \varphi(x,z) \). A typical view of the interferogram of the sample state in a certain period of process of sedimentation is shown on figure 1d. Interference pattern in this case takes the form of horizontal interference fringes which characterize the change of optical thickness of the sample, \( \Delta(nL) \), by height of the cuvette, z, by changing the concentration and size of particles during their sedimentation.

Interferometric measurements were accompanied by the measurement of the same sample parameters using method of dynamic light scattering. Both samples represented an identical cuvettes filled with the preparation just after its production. The sample area that is tested by laser beam (655 nm) during using method of dynamic scattering is shown on figure 1b. In stable condition of the sample, fixed in the unit Horiba LB-550, were carried out measurements of the distribution of particles of preparation of each suspension by sizes in the initial state (t₀) and at specific moments of time of process of sedimentation (tᵢ).
3. Experimental results
On figures 2, 3 and in table the results of the research of suspensions 1 and 2 by two methods are shown. The distribution of particles by size (figure 2a and figure 3a) was characterized by the value of the characteristic diameter of the particle, \(D_{\text{char}}\), determined at \(q_{\text{max}}\), and by half-width of the distribution of \(\Delta D\). By method of DHI was determined the dependence of \(\Delta n(z)\) in each experiment. \(\Delta n\) characterized the change of the refractive index towards the upper level of the suspension (\(z = 0\)).

**Table 1.** Estimation of the parameters of suspensions 1 and 2 in the process of sedimentation.

| \(N_e\) | Method of dynamic light scattering | Method of digital holographic interferometry |
|---------|----------------------------------|---------------------------------------------|
|         | \(D_x\), nm \(\Delta D\), nm | \(t_i\) \(D_x\), nm \(\Delta D\), nm | \(t_i\) | \(\Delta n, 10^{-5}\) (\(z = 20\) mm) |
| 1       | 220 210                          | 20 days 220 210                           | 72 hours | 0.8 |
| 2       | 670 850                          | 20 hours 580 1100                        | 24 hours | 16,1 |

**Figure 2.** Research of the suspension 1: – distribution of particles by sizes (1 – initial, 2 – after 20 hours, 3 – after 20 days), b – interferogram of the suspension during sedimentation during 72 hours, c - the change of the refractive index of the suspension by height of the liquid column.

**Figure 3.** Research of the suspension 2: – distribution of particles by sizes (1 – initial, 2 – after 2 hours, 3 – after 20 hours), b – interferogram of the suspension during sedimentation during 24 hours, c - the change of the refractive index of the suspension by height of the liquid column.

4. Conclusions
The experiments showed that the parameters of the suspension 1 with the SiO\(_2\) particles from 14 nm to 600 nm (\(D_x=220\) nm) determined by the method of dynamic scattering, practically don’t change during 20 days of storage. At the same time the method of DHI allows to detect the change \(\Delta n(z=20) = 0.8\cdot10^{-5}\) after 72 hours of storage of the suspension (remind that \(\Delta n=0\) at \(t=0\)). The parameters of the suspension 2 (\(D_x=670\) nm) demonstrate well diagnosed changes of the parameters by both methods in the first day of storage. Thus, during estimation of changes of suspensions parameters with inorganic nanoparticles with the size of less than 500-600 nm (in the case of substances with density close to
SiO$_2$) method of DHI allows us to carry out such diagnostics with greater accuracy than the method of dynamic light scattering.

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