

# Development of aggregationally and sedimentationally resistant nanosuspension for efficient polymer modified bitumen

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**Abstract.** It is shown by researches, made in Russia and abroad, that carbonic primary nanomaterials increase indexes of physic-mechanical properties of oil bitumen and building materials on its basis. Considerable technological problem, which restrains both theoretical knowledge development and practical realization of volumetrical materials nanomodification technology, is the absence of efficient way of carbonic primary nanomaterials distribution in the volume of oil bitumen. The results of realization of the way of combining mentioned nanomaterials with bitumen melt through inclusion of precursor compatible with all the components (oil bitumen and nanomaterials) are discussed in the work. Distribution of carbon primary nanomaterials in the carrier-medium is conducted with ultrasonic dispersion. In this research, studying of primary nanomaterials distribution was conducted with application of laser diffractometry, colorimetry, and calculation of disperse system range was conducted with application of Smolukhovskiy's theory. Kinetic parameters of disperse composition change are found out in process of precursor preparation the same as in process of its storing in normal conditions. According to the mentioned dependences optimal dispersion regimes were defined, which provide high aggregational and sedimentational resistance of precursor of carbonic primary nanomaterials.

## 1. Introduction

With the range of researches, it is shown that nanotechnology is a universal material sciences' instrument of managing of structure building of materials substance, the efficiency of which depends on quality of materials substance formed with application of microtechnologies, i. e. level of exhausting their receipt-technological resources [1]. This principle got the name "principal of receipt-technological dualism" [2]. Analysis of the efficiency of primary phase of nanotechnology application – managing of structure building of materials substance through primary nanomaterials inclusion (nanosized particles) – shows that for homogeneous materials on microsized scale level (metals, glass, polymers) the effect of nanosized particles inclusion is considerably higher than by inclusion of primary nanomaterials into micrononhomogeneous materials (which in fact have composite structure; artificial stones on mineral cements). So, for example, by inclusion of carbonic nanotubes into aluminum the size of the effect is 1400-2800 Mpa/%, into polymer – 500-1800 Mpa/%, and into



cement composites – 100-450 Mpa/% [3...5].

According to this, oil bitumen is an interesting object for research, it is used as a sticking component (cement) for making many materials for building: lutes, isolating and roofing materials, asphalt concretes and others [6...9]. Bitumen is a high molecular organic disperse system physical and structural properties of which are restraining factor in full usage of practical results from nanomodification and do not allow to estimate reliably the uniformity of nanomaterials distribution in the material volume.

Progressive driver of research development in this direction is development of nanoparticles inclusion methods, methods allowing to conduct the estimation of efficiency of nanoparticles disperse processes and their distribution in material volume reliably, and also modeling and forecasting of stability of received systems within the time.

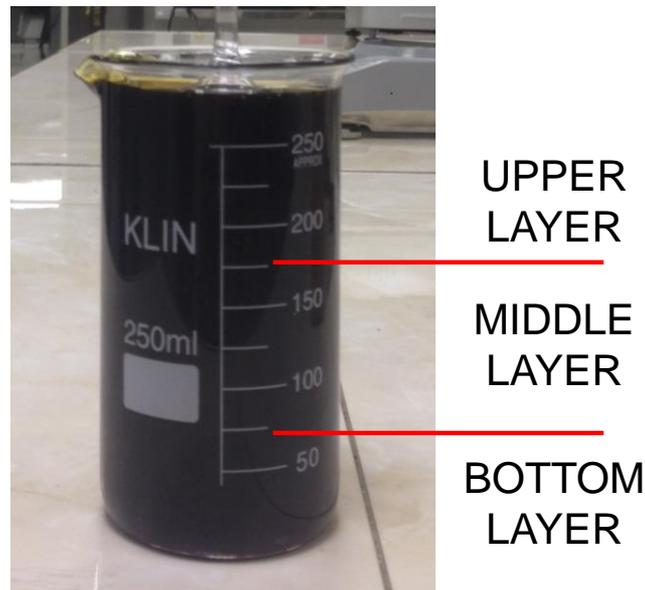
## 2. Experimental methods

According to modern views [10...12], plasticizing agents inclusion into bitumen increases solubilizing ability of disperse medium, which inhibits the reduction of solvate shell thickness in pyrobitumen complexes and increases technological effectiveness of product making and its properties, which is not always observed by polymer inclusion into bitumen and absence of plasticizer. In this connection, as a technological solution for providing of practical realization of nanotechnologies principles it is offered to use the method of primary carbonic nanomaterials inclusion into bitumen through carrier-medium which is plasticizing medium (industrial oil) – light, low-friction liquid, complex mixture of carbons of paraffin, naphthenic and aromatic series.

The efficiency estimation of the chosen technological solution was conducted using various carbonic nanomaterial (CNM): single-shell carbonic nanotubes (SCNT), synthesized at Russian Academy of Sciences (RAS) in the town of Chernogolovka; multi-shell carbonic nanotubes “Taunit” (MCNT) - one-dimensional nanoscale filiform formations of polycrystalline graphite produced at PLC “NanoTechCentre”, Tambov; technical carbon P803 (TC) or soot – high-disperse amorphous carbonic product, particles of which are globules, consisting of degraded graphite structures produced at PJC “Tuimazytekhuglerod”, Tuimazy.

For providing aggregational and sedimentational resistance of the system on the first phase, it is necessary to reach even distribution of carbonic nanomaterial in plasticizing medium. Establishing of rational parameters of homogeneous carbonic nanosuspensions preparation was conducted using complex approach, based on defining optical density and refractive index (table 1, 2), with Photometer KFK-3 and Refractometer IRF-22 respectively, taking into account variation of CNM concentrations and time of ultrasonic dispersion (USD). Relying on analysis of domestic and foreign science literature [13...16], and recommendations of carbonic nanomaterials producers the range of nanoobjects variation in the interval 0.00005...0.01 % from bitumen mass was taken.

Preparation of nanosuspensions in laboratory conditions was conducted with ultrasonic disperser Vibra-Cell VCX 750, with frequency of ultrasonic waves 22 kHz and power 750 W. For defining optical density ( $\lambda = 400$  nm) with the help of calibrated long-run funnel selection of not less than three probes from different layers (upper, medium, bottom) of liquid column was conducted.



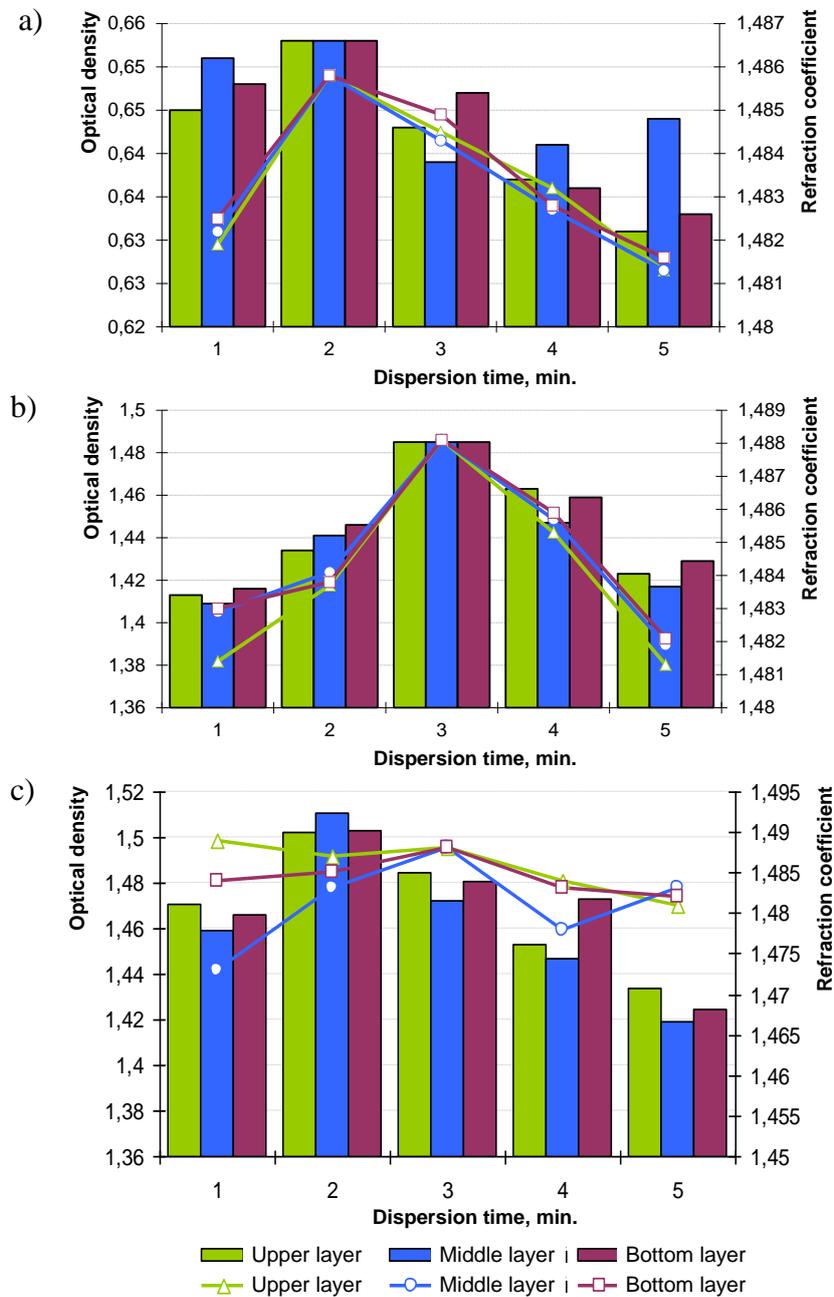
**Figure 1.** Scheme of probes selection from the volume of nanomodified plasticizing medium

It is necessary to note that difference in optical density and refractive index indications was not fixed in probes selected from the same layer. For estimation of ultrasonic impact on plasticizing medium, it was exposed to “idle” (without nanomodifier) processing. Changes in optical density and refraction index before and after impact were not fixed.

### 3. Results and Discussion

During the experiment, it was defined that CNM concentration in researched range does not influence on technological parameters providing reaching homogeneity of nanomodified plasticizing mediums. In all range of concentrations, similar dynamics of changes in optical density and refractive index indications is observed. Received differences of change of researched indications are represented on the example of their composition 0.00005% for SCNT (Figure 2a), 0.0005% for MCNT (Figure 2b), 0.1% for TC (Figure 2c).

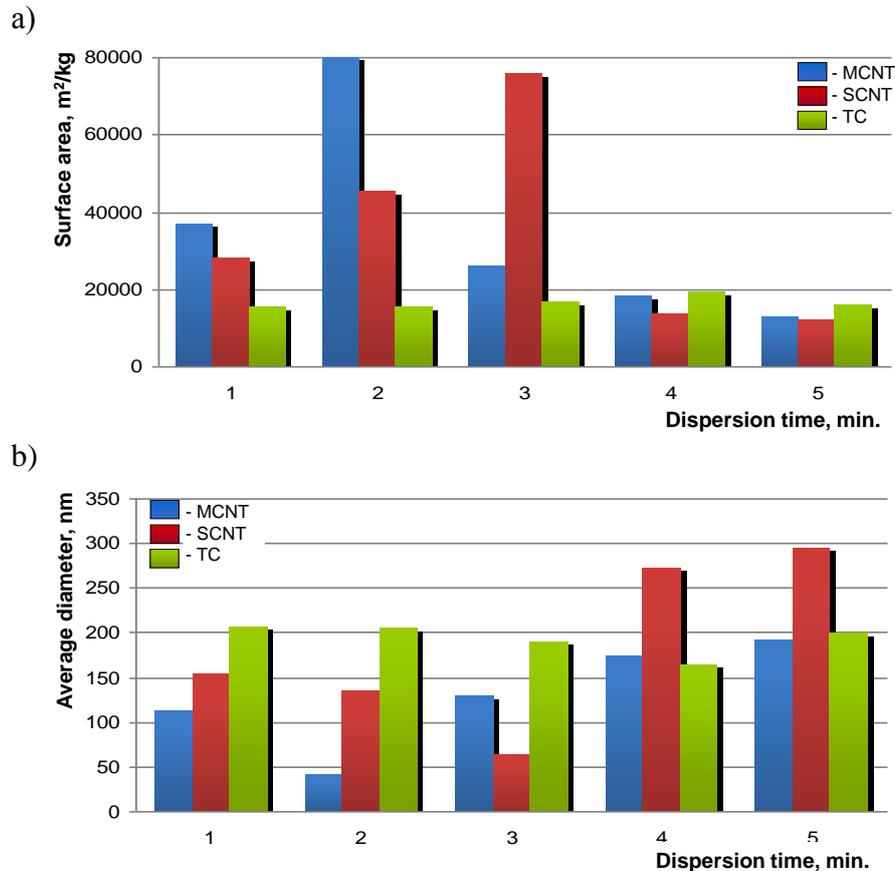
The analysis of received results showed that stability in optical density and refractive index indications on probe volume is reached at the time of dispersion of SCNT – 2 minutes, MCNT – 3 minutes. In addition, it was defined that this time corresponds maximal values on researched indications (Figure 2). The following increase of processing leads to reduction of non-transparency measure of material layer – optical density, which is obviously connected with aggregating of nanoobjects and their segregation and sedimentation. During studying the system “TC – plasticizing medium” it was not managed to fix stability in optical density indications in probe volume.



**Figure 2.** Dynamics of change of optical density and refractive index in volume of plasticizing medium from USD time: a) SCNT; b) MCNT; c) TC

Based on received results we can suggest that the given USD time will be optimal both for homogeneous distribution, and effective dispersion of nanoobjects in volume of plasticizing medium. Estimation of disperse composition of primary carbonic nanomaterials in plasticizing medium was conducted with analyzer of particles size Zetatrax by the method of laser diffractometry.

For studying the level of CNM dispersion the probe was selected experimentally taking into account receptiveness for providing the necessary reproducibility not less than 95%. Results of specific surface and average current diameter dependence on the time of CNM ultrasonic dispersion are shown in Figure 3.



**Figure 3.** Dynamics of change of: a) specific surface area; b) size of average current diameter of CNM from dispersion time in plasticizing medium

According to processing and analysis of received data it was defined that for SCNT the time for sufficient dispersion is 2 minutes, for MCNT – 3 minutes. In mentioned time intervals we observe maximal specific surface 80000 m<sup>2</sup>/kg (SCNT) and 75860 m<sup>2</sup>/kg (MCNT), and minimal average diameter – 41 nm and 62 nm, respectively, which correlates with results on optical density refractive index. Received results characterize the given disperse systems as colloidal ones. By dispersion of TC in medium in researched interval of ultrasonic impact duration, we did not manage to reach colloidal state of the system.

For corroboration and scientific substantiation of received results about evenness of primary carbonic nanomaterials distribution in carrier-medium the modelling of researched processes in disperse system was conducted using Laplas's hypsometrical distribution indication, which describes potential spontaneous distribution of particles in liquid column height, taking place as a result of gravity impact and diffusion of disperse phase in suspension and is calculated according to formula [20]:

$$\frac{n_1}{n_2} = \exp\left(g \frac{(\rho_f - \rho_c) \pi}{kT} d^3 \Delta h\right), \quad (1)$$

where  $n_1$  and  $n_2$  – number of particles on column height of nanosuspension sample, respectively  $h_1$  and  $h_2$ ;  $\Delta h = h_2 - h_1$ ;  $\rho_f$  – particle's material density (CNM), kg/m<sup>3</sup>;  $\rho_c$  – carrier-medium density (plasticizing medium), kg/m<sup>3</sup>;  $d$  – particle's diameter, (nm);  $g$  – gravitational acceleration, m/s<sup>2</sup>;  $T$  – temperature, °C;  $k$  – Boltzmann constant ( $1.386 \cdot 10^{-23}$  joule · K<sup>-1</sup>).

From the formula follows logically that even CNM distribution in volume of plasticizing medium is reached in case when  $n_1/n_2 \rightarrow 1$ .

**Table 1.** Evenness of CNM distribution in volume of plasticizing medium

Type of CNM	Ratio $n_1/n_2$ at USD, minutes				
	1	2	3	4	5
SCNT	12.30	<b>1.08</b>	29.27	109.12	213.12
MCNT	213.12	39.60	<b>1.30</b>	87.15	260.91
TC	88954.64	64135.14	6717.50	289.22	24959.90

Analysis of calculation results  $n_1/n_2$  for samples of nanosuspensions with different ultrasonic dispersion time showed that evenness of SCNT distribution is reached at 2 minutes, MCNT – at 3 minutes. Ultrasonic dispersion of technical carbon during 1...5 minutes does not provide even distribution, which correlates with the results received experimentally (Figure 2), so it was not considered in the following researches.

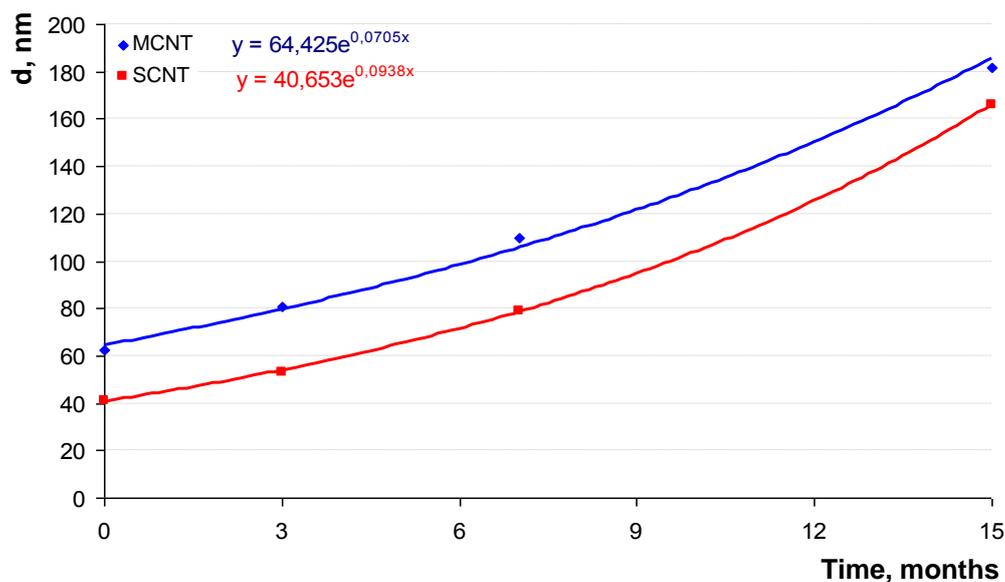
As a measure of agregational resistance we can consider the speed of its coagulation, which is a change of partial concentration of disperse particles in unit of volume per unit of time. There is quick one, when all collisions of particles lead to their adhesion, and slow, when not all collisions of particles are effective.

Defining of the type of coursing coagulation in systems with SCNT and MCNT is possible through comparison of numerical indications of coagulation speed constant, calculated according to experimental data, with theoretical. If experimental constant is lower than theoretical one, then there is a slow coagulation.

In the first case the constant of quick coagulation speed is defined from Smolukhovskiy's kinetic equation (formula 2) on the basis of data of numerical particle concentration change of disperse phase at time, calculated on experimental data of kinetics of the average diameter of CNM particles (Figure 4).

$$\frac{1}{v_t} - \frac{1}{v_0} = kt, \quad (2)$$

where  $v_t$  – particle concentration (SCNT, MCNT) in nanosuspension at time moment  $t$ ;  $v_0$  – particles concentration (SCNT, MCNT) in nanosuspension at the initial time;  $k$  – constant of coagulation speed;  $t$  – time moment.



**Figure 4.** Kinetics of change of CNM particles average diameter

Defining of constant is conducted graphically (Figure 5). For this, it is necessary to build dependence  $\frac{1}{V_t} = f(t)$  - inversely oriented unit to CNM concentration in the medium volume as a function on time and define slope ratio of the straight line towards axis x, numerical indication of which will correspond to the constant of coagulation speed.

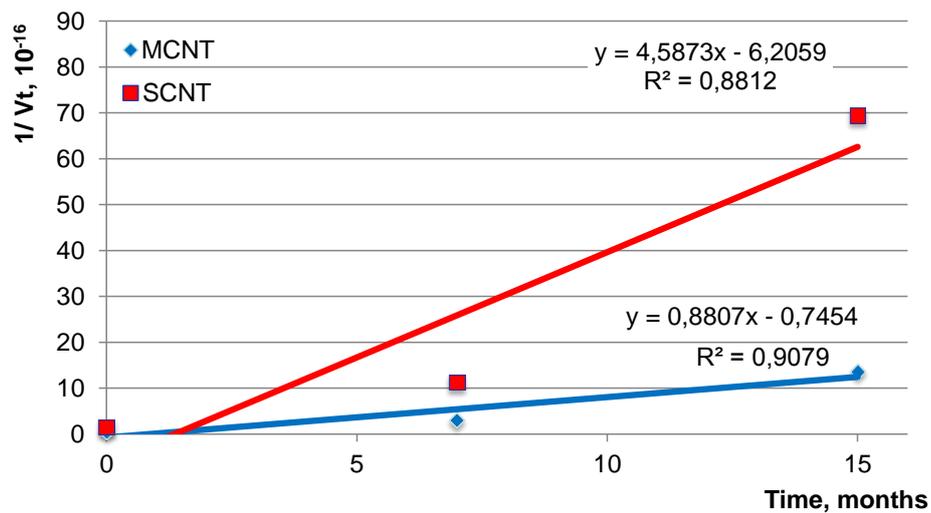


Figure 5. Dependence 1/Vt on time

The analysis of Figure 5 allowed to define that the slope ratio of time kinetic dependence of inversely oriented unit to SCNT concentration in researched nanosuspension equals  $4.58 \cdot 10^{-16}$ , MCNT –  $0.88 \cdot 10^{-16}$ .

In the second case, the constant of coagulation speed is calculated on the basis of dependence established by Smolukhovskiy:

$$k = 8\pi Dd/2, \tag{3}$$

where  $d$  – particles diameter, m;  $D$  – diffusion index, calculated with formula:

$$D = \frac{RT}{N_A 6\pi\eta r}, \tag{4}$$

where  $R$  – absolute gas constant ( $8,314 \text{ joule}/(\text{mole}\cdot\text{K})$ );  $N_A$  – Avogadro constant ( $6.022 \cdot 10^{23} \text{ mole}^{-1}$ ),  $T$  – absolute temperature, K;  $\eta$  – viscosity, Pa·c;  $r$  – particles radius, m.

Table 2. Calculated values of diffusion index and constant of coagulation speed

Type of CNM	Indication	
	Diffusion index	Constant of coagulation speed
SCNT	$5.42 \cdot 10^{-13}$	$2.79 \cdot 10^{-19}$
MCNT	$6.53 \cdot 10^{-13}$	$5.12 \cdot 10^{-19}$

Comparative analysis of coagulation speed indication values, received by calculation and experiment, showed prevalence of the last one, which indicates about quick coagulation processes, coursing in the researched systems, for describing of which the theory of M. Smolukhovskiy is fair. The basic point of the theory is that particles of disperse phase approach as a result of Brownian motion, cohere, making an aggregate which makes following Brownian motion as a comprehensive whole. That is why about ability of researched systems (with SCNT and MCNT) to keep at time their primary parameters it was estimated through the speed of coagulation coursing. The speed of particles coagulation in system is characterized by the change of their number in volume unit per time unit.

According to the theory of quick coagulation for calculation of the number of aggregates  $n$  of

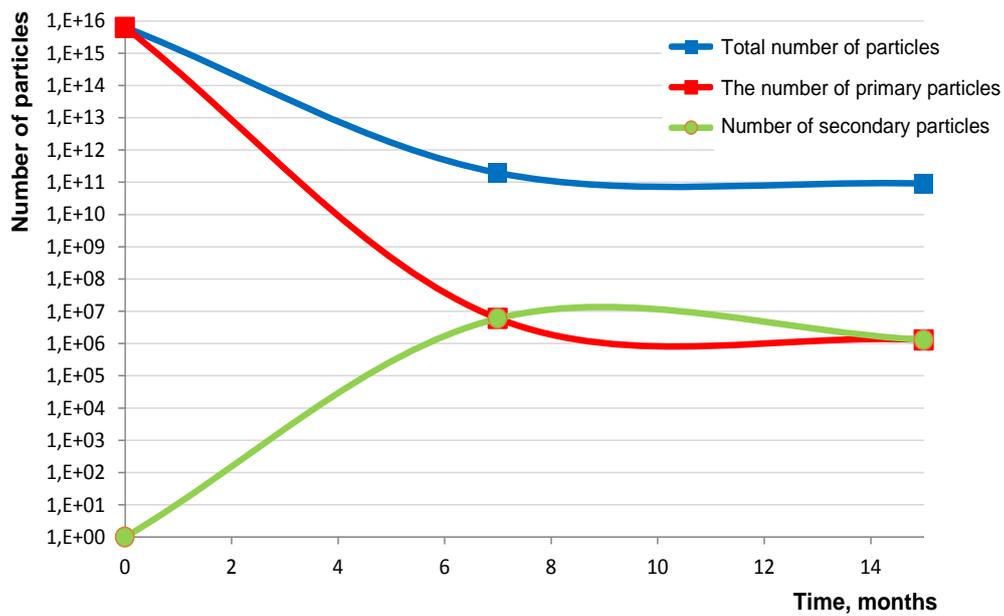
different range  $m$  at the time moment  $t$  the following formula is applied:

$$n = n_0 \frac{(t/\theta)^{m-1}}{(1+t/\theta)^{m+1}} \tag{5}$$

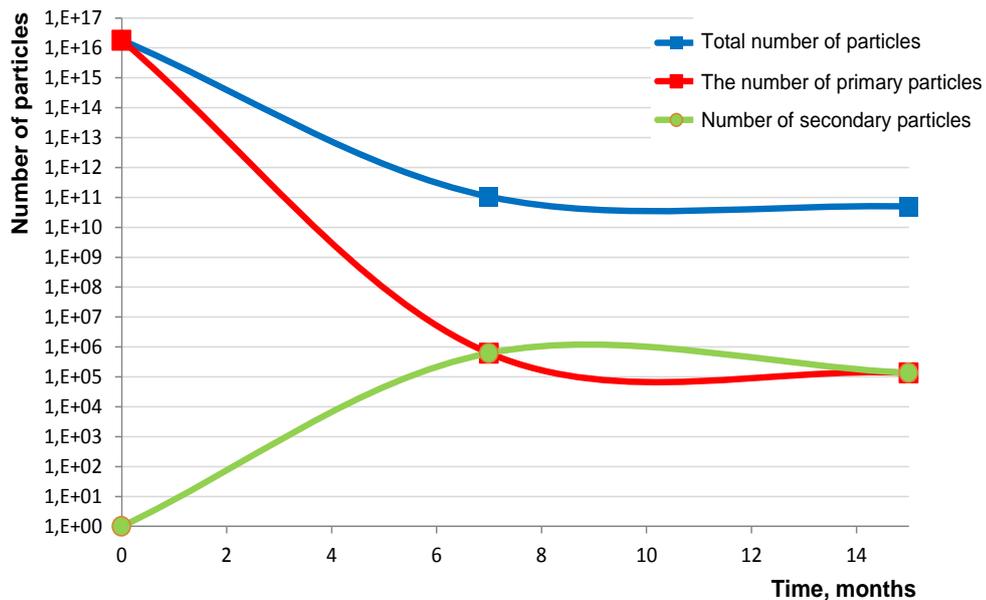
where  $n_0$  – primary number of particles (before coagulation);  $\theta$  – time of half coagulation, calculated on formula:

$$\theta = \frac{t}{\frac{n_0}{n} - 1} \tag{6}$$

The results of calculation on the number of carbonic nanomaterials aggregates in researched systems are shown in Figures 6 and 7.



**Figure 6.** Change of number of SCNT aggregates in nanosuspension



**Figure 7.** Change of number of MCNT aggregates in nanosuspension

Observed character of common number of particles change and number of first range particles at time for SCNT and MCNT (Figures 6 and 7) corresponds to monotone decrease, which reflects the process of aggregates building – particles of the following range. It is necessary to mention that intensity of the first range particles decrease is higher than the common number of particles has, as double, triple etc. aggregates start occurring. This is indicated by the character of change of the second range particles number, where the curve goes through the maximum, the height of which decreases as the size of the particles grows. During the first 7 months the coagulation process is observed, which is characterized by increasing of the second range particles number on 850000 and 88000 per month for SCNT and MCNT respectively. Therefore, the speed of coagulation in the system containing particles of dispersed multi-shell carbonic nanotubes is 10 times less than speed of nanosuspensions coagulation containing single-shell carbonic nanotubes.

#### 4. Conclusions

We offer in this work the method of CNM inclusion into organic cement by precursor, which is a complex mixture of hydrocarbons, prepared with ultrasonic dispersion. The methodology is offered, which allows making the estimation of efficiency of nanoparticles dispersion processes and their distribution in material volume and is based on complex approach, based on defining of optical density and refractive index.

On the basis of the results of defining average diameters of dispersed CNM with laser diffractometry it is fixed that optimal time of ultrasonic dispersion (USD) of carbonic nanomaterials is: SCNT - 2 minutes; MCNT - 3 minutes, when maximal diameter is reached: 41 and 62 nm respectively. Disperse system “TC - plasticizing medium” does not have sedimentational resistance.

Kinetic modeling of even distribution of primary carbonic nanomaterials in precursor medium was conducted with Laplas’s hypsometric distribution, this allowed to define that the received disperse system with MCNT will be stable, with evenly distributed in volume nanophase, for not less than 2 months, then the beginning of aggregation process is observed, in disperse system with SCNT – for not less than 7 months. During received time intervals, nanodisperse systems will be in stable state and they will be characterized by constancy of properties indications.

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#### References

- [1] Korolev E V 2017 Nanotechnologies in building materials science. *Vestnik MGSU*. **12** Issue 7 (106). pp. 711-717.
- [2] Korolev E V 2013 The principle of realization of nanotechnology in building materials science. *Building materials*. **6** pp. 60-64.
- [3] Ognev A Yu, Bazarkina V V, Batayev I A, Batayev V A 2011 Aluminum composite material with nanodispersed reinforcing phase formed by accumulated rolling. *Metal processing (technology, equipment, tools)*. **3** (52). pp. 40-42.
- [4] Gunyayev G M, Kablov Ye N, Aleksashin V M 2010 Modification of structural carbon plastics by carbon nanoparticles. *Russian Chemical Journal*. **1** Pp. 4-18.
- [5] Usov B A, Okol'nikova G E 2015 Investigation of the effect of CNTs on the strength, structure, and phase composition of a cement stone. *System Technologies*. **16** pp. 81-95.
- [6] Pokonova Yu V 2008 Oil bitumen. *St. Petersburg: Polygraph. pr-e "Ricon"*. p.153.
- [7] Cabrera J G 2003 Performance and Durability of Bituminous Materials. *CRC Press*. p.348.
- [8] Francken L 2004 Bituminous Binders and Mixes. *CRC Press*. p.352.
- [9] Read J, Whiteoak D, Telford T 2003 *The Shell Bitumen Handbook*. p.460.
- [10] Abdullin I.A. 2006. Composite materials with a polymer matrix. *Textbook. Kazan: Publishing house KSTU*. p.144.
- [11] Ayupov D A, Muraf A V, Hakkimulin Yu N, Khozin V G 2009 Modified bituminous binders for construction purposes. *Building materials*. **8** pp. 50-51.

- [12] Becker Y, Mendez M P, Rodriguez Y 2001 Polymer modified asphalt. *Vision Technological*. **9**(1) pp. 39-50.
- [13] Rudenskaya I M, Rudenskiy A V 2010 Organic binders for road construction. *Moscow: INFRA-M*. p.256
- [14] Polacco G, Stastna J, Biondi D, Zanzotto L 2006 Relation between polymer architecture and nonlinear viscoelastic behavior of modified asphalts. *Curr Opin Colloid Interface Sci*. **11**(4):230. p 45.
- [15] Bogomolov A I 1995 Chemistry of oil and gas. *3rd edition, supplemented and amended*. Ed. Proskuryakova V.A. *St. Petersburg: Chemistry*. p.446.
- [16] Loos M 2014 Carbon Nanotube Reinforced Composites: CNT Polymer Science and Technology. *William Andrew*. p.304.
- [17] Jenny H, Eric A, Grulke Z, George Z, Fran L 2003 Dispersion of carbon nanotubes in liquids. *Journal of dispersion science and technology*. **24** Issue 1. pp. 1-41.
- [18] Kim S W 2012 Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. *Carbon*. **50** Issue 1. pp. 3-33.
- [19] Zhang P 2015 Dispersion of multi-walled carbon nanotubes modified by rosemary acid into poly (vinyl alcohol) and preparation of their composite fibers. *RSC Advances*. **5** Issue 68. Pp. 55492-55498.
- [20] Gelfman M I, Kovalevich O V, Yustratov V P 2010 Colloid chemistry. *5 th ed., Sr.-St. Petersburg: Lan Publishing House*. p.336.
- [21] Shchukin Ye D, Pertsov A V Amelina Ye A 1982 Colloid chemistry. *Moscow: Moscow State University*. p.348.
- [22] Korolev E V, Inozemtsev A S 2012 Efficiency of physical effects for the dispersion of nanosized modifiers. *Building Materials*. **4** pp. 76-79.