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**Author: KUDRYAVTSEV Pavel Gennadievich**, D.Sc., Professor of HIT (Israel), Academician of International Academy of Sciences for Ecology and Human Safety and Russian Academy of Natural Sciences, author of more than 150 publications including «Nanomaterials based on soluble silicates» (in cooperation with O. Figovsky) and 30 inventions; 52 Golomb Street, POB 305 Holon 5810201, Israel, 23100, e-mail: pgkudr89@gmail.com;

**Author: FIGOVSKY Oleg Lvovich**, Full Member of European Academy of Sciences, Foreign Member of REA and RAASN, Editor-in-Chief of Journals SITA (Israel), OCJ and ICMS (USA), Director R&D of INRC Polymate (Israel) and Nanotech Industries, Inc. (USA); Chairman of the UNESCO chair «Green Chemistry»; President of Israel Association of Inventors; Laureate of the Golden Angel Prize, Polymate INRC; P.O.Box 73, Migdal Ha'Emeq, Israel, 10550, e-mail: figovsky@gmail.com

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## NANOCOMPOSITE ORGANOMINERAL HYBRID MATERIALS. PART II

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### EXTENDED ABSTRACT:

The paper addresses the issues of alkoxide method of sol-gel synthesis and non-hydrolytic method of sol-gel synthesis and colloidal method of sol-gel synthesis. The authors also consider an alternative approach based on the use of soluble silicates as precursors in the sol-gel technology, of nanocomposites. It was shown that nanocomposites can be produced through aerogels. The paper also analyzes the mixing technologies of nanocomposites preparation. It has been demonstrated the possibility to change the types of nano-phase which is used for obtaining nanocomposites in different approaches. Various models of packaging spherical, fibrous and layered nanoparticles, introduced into the structure of the nanocomposite, in the preparation thereof were examined.

**Key words:** Nanocomposites, sol-gel synthesis, soluble silicates, metal alkoxide, sols, gels, aerogels, packing of spherical nanoparticles, packing of fibrous nanoparticles.

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**2. Mixing technologies of nanocomposites**

A method for producing polymer nanocomposites in the melt, so-called extrusion method, consists in mixing the molten polymer with nanosized material particles, surface modified with organic compounds. During the intercalation, the polymer chains substantially change their shape and lose conformational entropy. As the driving force of this process is likely when mixed, the most significant contribution is made, the enthalpy of interaction in the system, the polymer – nanoscale filler. It should be added, for example, that the polymer nanocomposites based on clay materials is successfully produced by means of extrusion [104, 107]. The advantage of an extrusion method is the absence of any solvents, which eliminates the presence of hazardous effluents, the process rate considerably higher and technological design of manufacture considerably easier. That is, for the preparation of polymer nanocomposites in industrial-scale extrusion method is the most preferred, less costly raw material and maintenance of the technological scheme.

The polymer-silicate nanocomposite silicate modified with organic substances, in obtaining, swells in a solvent such as toluene or N-dimethylformamide. Then, it is added to the polymer solution which penetrates into the interlayer space of the silicate. Then, solvent removal is carried out by vacuum evaporation. The main advantage of this method consists in that the «polymer-layered silicate» can be obtained based on a polymer of low polarity or non-polar material. Nevertheless, this method is not widely used in industry due to the high solvent consumption [105].



By using mixing technologies, an important factor is the viscosity and fluidity of the reaction mixture. This is especially important for highly filled compositions, where low binder content, that is in the liquid phase. In industrial practice, a relatively long known way to increase mobility and moldability of the composition, based on the use of hydrophilizing, or hydrophobizing, surface-active agents (surfactants). They can significantly reduce the amount of solvent or liquid binder phase in the compositions while maintaining or even improving their rheological properties. Thus, in organic solvents such as ionic and nonionic surfactants (alkyl sulfonates, alkylbenzenesulfonates and the fatty acid content greater than  $C_9$ ) allow obtaining compositions based on liquid glass with a high fluidity. These substances have lubricity and reduce frictional forces between the particles of the composite material. Thus the use of surfactants to the compositions based on liquid glass, allowing to further reduction of the binder content in the composition and bring it up to  $5 \pm 0.5\%$ . Such mixture has good mobility, adequate for the manufacture of complex shape products by free casting.

A method for producing polymer nanocomposites in the melt consists in mixing the molten polymer with the particles modified with organic substances, nanosized dispersed material. Preparation of polymer nanocomposites such as clay filler in the synthesis of the polymer is the intercalation of the monomer in the clay layers. Monomer migrates through the galleries organo-clay material and polymerization takes place within the layers. The polymerization reaction may be initiated by heating, irradiation or appropriate initiator [106].

The nature of the rheological properties of the compositions is influenced by various factors: the size of the starting particle agglomerates; microstructures formed by them; forces acting between the particles and contribute to the formation of agglomerates; processes that take place in a structured composition on flowing. After having been applied shear forces, macroscopic agglomerates of filler destroyed in the first place, this is reflected in the results of rheological measurements. Transitional period, corresponding to the period of time from the beginning of the destruction of macroscopic agglomerates until the equilibrium, is characterized by a gradual change in the intensity of the scattered light. In the systems studied, the destruction of the agglomerates, to form separate particles, and their stable compounds, and to achieve their uniform distribution in vol-



ume of binder was confirmed by microscopic observation of samples dispersion compositions [162].

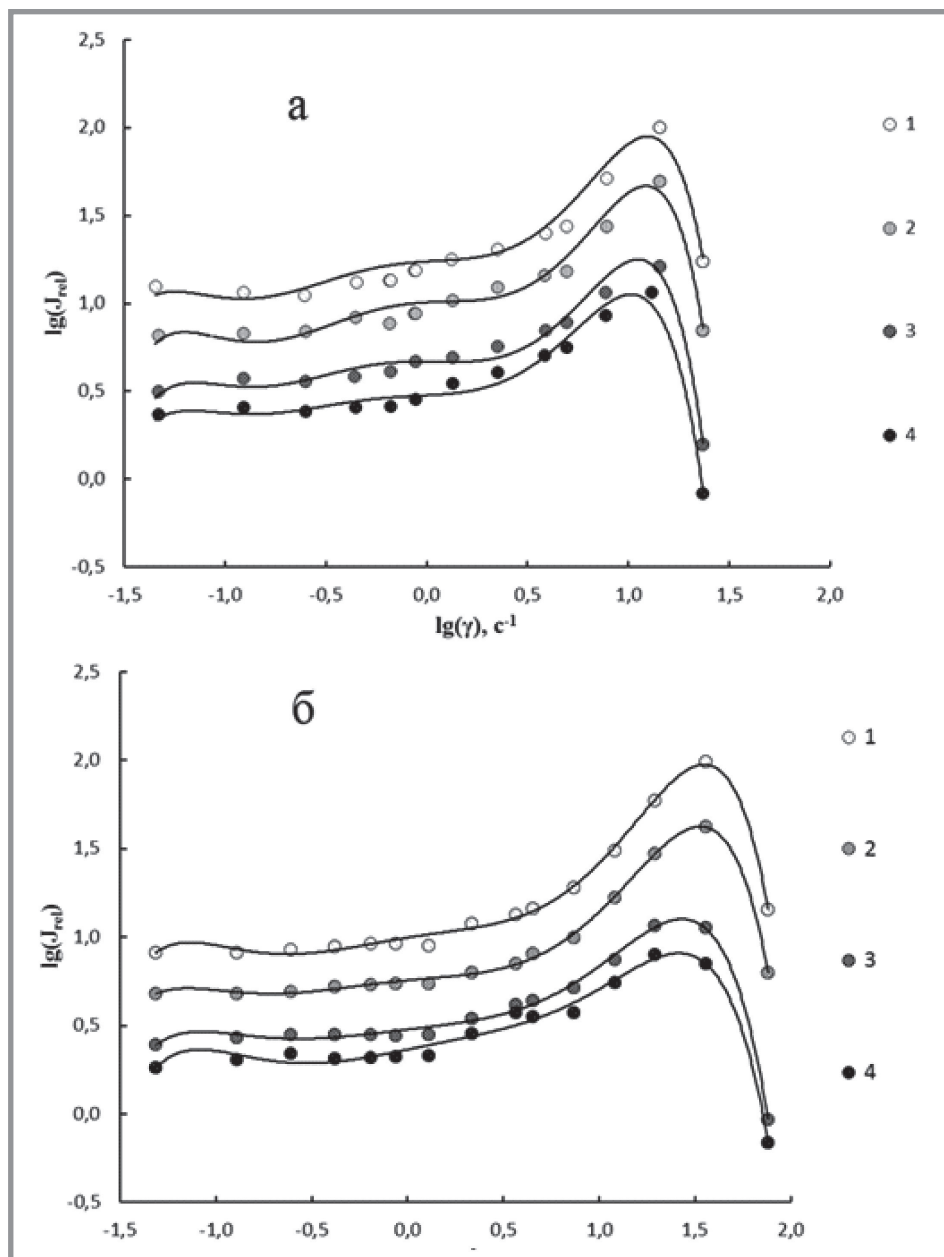
Particles of fine filler are also capable of forming a continuous structure, penetrating the entire volume of the system and lead to changes in the macroscopic properties of the oligomeric composition. Primarily it is an increase energy dissipation during flow, and hence the change of rheological properties, namely to increase the viscosity of the composition. In case of use, electrically conductive filler such as carbon black, when creating continuous spatial structures will happen significantly change of the properties of the composition, the material becomes electrically conductive. Obviously, the length of the continuous chains must be commensurate with the distance between the electrodes. Consequently, the conductivity of filled compositions is more sensitive parameter creation process continuous spatial structures of particles than the viscosity of the composition. The sharp increase in viscosity appears to occur during the formation of the local structures of the filler particles. The dimensions of such structural formations not commensurate with the size of the space between the electrodes, hence, the composite retains dielectric properties.

Thus, to obtain conductive compositions on the basis of highly dispersed; components necessary to construct chains of particle sizes which are many orders exceed the sizes of the particles themselves, and the number of particles in the chain of thousands or tens of thousands. It is obvious that such complex associates easily susceptible to damage. Possible to assume that these large particles, in turn, could become centers of structure formation carbon black particles. Dimensions of continuous chains of carbon black particles required to produce an electrically conductive system, in this case would be dramatically reduced.

Fig. 11-a, shows the relative change of the composition flowing through the electric current showing how with all equal conditions, the electrical conductivity of the composition with graphite and carbon black is more than the electrical conductivity of the composition, with only carbon black.

These studies showed that introduction in oligomer 22 wt.% graphite does not produce electrical conductivity of the test composition, but an oligomer containing 3 wt.% carbon black has conductive properties (see Fig. 11 a). However, the introduction of graphite into the composition containing 3 wt. % carbon black, leads to a sharp increase in the electrical conductivity of the whole system. The increase of the shear rate leads to





**Fig. 11. Dependence of the relative electrical conductivity of a composition (comprising 3 wt. % carbon black) on shear rate at 60 (a) and 80°C (b). Graphite content (wt.%): 1 – 20, 2 – 10, 3 – 5, 4 – 2.5.**

the destruction of the internal structure of the composition and reduction of its electrical conductivity. Fig. 11-b, shows similar curves for elevated temperature. As follows from the data presented the effect of graphite increases with increasing shear rate. The maximum effect of graphite at a temperature of 60°C corresponds to a shear rate of  $10 s^{-1}$ . Increasing the

temperature to 80°C, leads to an increase in this value to a shear rate, approximately,  $20 \text{ s}^{-1}$  [163].

### 3. Different types of nanophases

#### 3.1. Nano-sized filler

Long time to obtain the nanoparticles were a core part of nanotechnology. To the same subject, belonged basic postulates of nanotechnology, those were laid down at the beginning of the last century, in the ideas of R. Zsigmondy and T. Svedberg. However, the essence of nanotechnology and nanomaterials formulated R. Feynman, who offered two diametrically opposed approaches to the creation of nanomaterials «*bottom-up*» and «*top-down*». The first of these methods is linked to the implementation of processes in atomic and molecular self-assembly or assembly technology of the final products. The second is related to the processes of mechanical disintegration, severe plastic deformation, decomposition of solid solutions, etc. [138, 143, 181, 182]. Actually other technological approaches do not exist.

«*Top-down*» is based on reducing the size of the physical bodies, by mechanical or other treatment, up to objects with ultra-microscopic, nanometric parameters. This variant obtaining nanomaterials has fundamental physical limitations. For example when using photolithography techniques is the dimensional limitations associated with the wavelength of incident radiation. By mechanical action on the material requires the application of sufficiently high energy to create a new surface when the particles break down to the submicron level. In addition, any mechanical impact has a bilateral in nature by virtue of Newton's third law. When destroying some material, the particles of the destroying tool can get to it. Thus, you bring to the product obtained as a result of this impact, the particles of the instrument itself. On the nanometric scale, these contamination even in an amount of about several ppm, prove fatal.

The idea of technology «*bottom-up*» is that the assembly of produced «construction», is carried out directly from the lower-level elements (atoms, molecules, etc.), which are stacked to the desired order.

An important aspect of this approach is that it has been included in the essence of the nature of the chemicals. For centuries, chemists were engaged in obtaining new, more complex chemicals, by assembling them out



of individual atoms or groups of atoms, complicated molecules from more simple molecules. Giant crystals obtained by laying in the correct order of individual atoms or molecules. The main problem is only how, to control this process to stop it at the desired level, which corresponds to the desired level of nanometer dimensions.

Of course, the first path is not closed today. There are a lot of technological methods, and new methods of crushing of materials without contamination of their by foreign impurities are constantly being created. There are methods involving the use of explosive technology, and high-energy flows, plasma, radiation, laser, acoustic and other methods.

But nevertheless assembly «*bottom-up*», the most natural process in which there are no fundamental limitations and physical prohibitions on the possibility of obtaining structures in the range from the atomic to the macroscopic level.

In connection with this, we consider the chemical methods for the preparation of nanoparticles which may be the fillers in nanocomposites.

There are many chemical methods that can be used to obtain nanoparticles of various materials. Naturally, different classes of chemical substances and compounds obtained by various methods appropriate to the chemical properties of substances from which are obtained nanoparticles.

For example, to obtain the metal nanoparticles can be applied several types of reducing agents, e.g. complex hydrides, alkyl hydrides, etc. Thus, molybdenum nanoparticles can be prepared by reduction of a molybdenum salt using sodium *tri*-ethylhydroborate  $\text{NaB}(\text{C}_2\text{H}_5)_3\text{H}$ , dissolved in toluene. This reaction gives a good yield of molybdenum nanoparticles with dimensions of  $1\div 5\text{ nm}$ . Reaction equation is as follows:



Nanoparticles of alumina can be obtained by decomposition of adduct, tri-ethylamine and aluminum hydride  $(\text{C}_2\text{H}_5)_3\text{N}:\text{AlH}_3$ , dissolved in toluene, followed by heating to  $105^\circ\text{C}$  for two hours. As a catalyst for this reaction titanium *iso*-propoxide is used. The choice of catalyst, determines the size of the nanoparticles formed by this reaction. When using titanium *iso*-propoxide it is possible to obtain particles with a diameter of  $80\text{ nm}$ . To prevent agglomeration of nanoparticles to solution surfactants such as oleic acid [143] may be also added.



Obtaining metal nanoparticles in the conditions of highly energy impacts on the chemical system are associated with the appearance of strong reducing agents with high activity, such as hydrated electrons, radicals and excited particles.

Photochemical (photolysis) and radiation-chemical (radiolysis) recovery differ by energy. For photolysis, are typical of energy less than 60 eV, and for radiolysis – more than 100 eV. The main features of chemical processes under the influence of high energy radiation include: non-equilibrium in the distribution of particles by energy, the overlap of the characteristic times of physical and chemical processes. Decisive role for the chemical transformations of the active particles has a multichannel, and non-stationary processes occurring in reacting systems.

Photo- and radiation-chemical reduction, when compared with the chemical method has certain advantages. These processes are different higher purity nanoparticles produced by such recovery, as there are no impurities are obtained using conventional chemical reducing agents. Moreover, using techniques photo- and radiation-chemical reduction is possible synthesis of nanoparticles in solids at low temperatures.

Photochemical reduction in solution is the most often used for the synthesis of noble metal particles. Upon receipt of such particles from the corresponding salts, as the medium use their solutions in water, alcohol and organic solvents. In these media by exposure to light are formed active species. However, as a result of photoreduction is not only a process of preparation of nanoparticles of a certain size, but there is a formation of larger aggregates.

As an example of photochemical production of films of metals, nanometer thickness, discloses a method for applying a metallic coating to a substrate. The substrate is placed in a reactor with a pressure of about 10 Pa. Next, the substrate is heated to a temperature of 50–70°C, is fed into a reaction zone a mixture of hydrogen and precursor vapor, and the substrate was subjected to UV radiation in the wavelength range 126–172 nm. Here the flux of hydrogen was fed at a rate 0.3–4.0 liter/h, and vapors of the precursor at a temperature of 25–50°C was fed at a rate of 2÷4 l/h, with the help of the carrier gas, argon. As a result, chemical reaction of reducing the corresponding metal from the precursor to the metallic state takes place. In this case, on the surface of the substrate, a film is formed, consisting of grains of metal, the sizes of 100÷150 nm. Decomposition of the pre-





cursor is achieved through the photo dissociation of hydrogen and oxygen with the formation of highly reactive particles such as the H, O, O<sub>3</sub>, which sharply reduce its decomposition temperature. In the metallic coatings can be prepared from Pd, Pt, Ni and Cu. As the substrate, use copper, polymers, ceramics, silicon. As precursors using volatile organometallic compounds such as fluorinated β-diketonates (hexa-fluoro-β-diketonate – HFA) palladium (Pd(HFA)<sub>2</sub>), platinum (Pt(HFA)<sub>2</sub>), nickel and copper, as well as volatile, trimethyl derivatives Pt (IV) ((CH<sub>3</sub>)<sub>3</sub>Pt (HFA)Py) [195].

Radiation-chemical reduction for the synthesis of metal nanoparticles, due to their availability and reproducibility, is becoming more widespread. In the synthesis of metal nanoparticles in a liquid phase, issues related to the spatial distribution of the primary and intermediate products are of great importance. When radiolysis unlike photolysis for the intermediate active particles or radicals observed uniform distribution by volume, it promotes the synthesis of nanosized particles with a narrow size distribution.

Currently, for the formation of metal nanoparticles are widely used porous inorganic materials such as zeolites. Solid zeolites having pores and channels are strictly certain size, are convenient matrices for stabilizing the nanoparticles with desired properties. Typically one uses two basic methods for preparation of nanoparticles in the pores of the zeolite. One of them is related to the direct adsorption of metal vapor in the pores, thoroughly dehydrated zeolites. Another more widely used method is based on chemical transformations of precursors introduced into the pores in the form of metal salts, metal carboxylates, metal complexes and organometallic compounds. In a similar way, for example in the channels of the molecular sieves were obtained nano-wire with a diameter of 3 nm and a length of hundreds of times larger. High thermal and chemical stability of zeolites with introduced inside the nanoparticles can be considered as the most promising catalysts.

To chemical methods for the synthesis of oxides and sulfides nanoparticles, relate different versions of the sol-gel synthesis. When implementing the process of the sol-gel synthesis various precursors, such as salts, alkoxides, chelate compounds, etc are also used. The process is catalyzed by a change in pH, of the initial solution. In acidic media are formed linear chains in alkaline media – having branched chains. Replacing metal alkoxides the corresponding compound of thioalcohols M(SR)<sub>n</sub>, and reacted with hydrogen sulfide can be obtained nanoparticles of metal sulfides.



A separate group of methods for the synthesis of nanoparticles are reactions in micelles, emulsions, suspensions, and dendrimers (nanoreactors). Micelles – particles in colloidal systems consisting of insoluble in this medium of the nucleus, which is very small in size, surrounded by a stabilizing shell of the adsorbed ions and solvent molecules. They are associates of the characteristic structure, the shell of which is constructed of a plurality of amphiphilic molecules consisting of long-chain radicals lyophobic and lyophilic polar groups.

For the preparation of nanoparticles of metals and their compounds micelles, emulsions, and dendrimers are used, that can be regarded as a kind of nanoreactors which can synthesize particles of a certain size.

Issues related to obtaining solutions of colloidal particles  $\text{SiO}_2$  – silica sols, were discussed in detail in [56, 119, 123, 167, 183]. However, for various fillers for nanocomposites, is important to obtain a wide range of particle sizes, from a few nanometers to hundreds of nanometers. Therefore, to obtain concentrated and stable silica sols are necessary enlargement of particles and ensure a monodisperse of system.

Uncontrolled growth of particles ultimately is carried out due to the change of amount or the disappearance of the other portion of the particles. To increase the rate of particle growth it is necessary to increase the solubility of silica; it can be achieved by increasing temperature and increase in pH to 9÷10.

The most versatile is the so-called method with a feeder. This method is intended to produce monodisperse silica sols with particle sizes up to 150 nm. It was proposed by Bechtold and Snyder and developed by Shabanova N.A. [183]. One of the important conditions for the success of the implementation of this method is: the quality of the feeder, feeding rate, reducing the polydispersity of the sol.

Effective implementation of the growth process is achieved by strict regulation of feed rate of the feeder – active polysilicic acid. It has been established that taking the feeder feed rate proportional to the area of grown particles possible not only achieve lowering the polydispersity of sols, but also significantly accelerate the process. At high speed of, filing a feeder will be a significant super saturation in silicon oxide. This leads to the formation of new fine particles of silica. On these particles subsequently would be delayed active silica which enters the system with a feeder, thus, increasing of the particle size will be not substantial. Supplying a flow of



the feeder into a reaction vessel it is necessary be carried out so that the supersaturation, created in the system, was not significant, and the whole, polysilicic acid, spent on growing of primary particles.

Hindrance to the normal course of the process:

- Irregularity of filing of the feeder (increased polydispersity of the sol);
- The duration of the synthesis (polydispersity increases, the average size does not increase significantly);
- Lack of vigorous stirring, perhaps the local formation of a new phase, the particle growth is slowing due to weak convection, as during the process, the number of particles remains constant, while the volume of the system increases to 20 to 25 times.

The average particle size of these papers is determined by the method developed by Sears [121] as well as by ultracentrifugation by which is determined the distribution function of particle size.

All experiments were performed on samples of sols with baseline pH 7.5÷10.0. The choice of this pH range is due to the fact that in this range the polymerization of silicic acid leads to the formation of spherical colloidal particles of SiO<sub>2</sub>. Increasing the particle size of SiO<sub>2</sub> of more than 10 nm, is accomplished by carrying the process of heterogeneous polycondensation of active, polysilicic acids on pre-formed particles.

The following processes are possible when adding, polysilicic acid in the sol:

1. Condensation on the particles;
2. The formation of new particles;
3. Losses on the walls of a chemical reactor.

Given the heterogeneous nature of the polycondensation, and a material balance obtained the relation [183], that connects critical feed rate, of the silicon acid in the solution ( $W_{kr}$ ) with a concentration of SiO<sub>2</sub> in the system. It was obtained for conditions precluding the formation of new particles:

$$W_{kr} = KS_{o\text{ud}}(C_o V_o)^{1/3}(C_t V_t)^{2/3}C_f^{-1}, \quad (8)$$

where  $S_o$ ,  $V_o$ ,  $S_{o\text{ud}}$  – concentration, volume and surface area of the germinal sol;

$C_t$ ,  $V_t$  – total concentration and volume of the system;

$C_f$  – concentration in the feed solution SiO<sub>2</sub> («feeder»).



Value of the constant  $K$  is approximately equal to  $5 \cdot 10^{-3} \text{ gSiO}_2/(\text{m}^2 \cdot \text{h})$ .

As can be seen from the equation, as the increase in the total concentration ( $C$ ) of the system or volume ( $V_f$ ), the feed rate of the silica can be increased.

Before carrying out process, the initial solution is to be prepared in the following way: a certain volume just prepared nucleated sol having a concentration of 3,0÷4,0%, stabilized by the addition of alkali to a pH of 7.5÷8.0 and boiled for about 1 hour. In this case there is an acceleration formation of primary particles, which then act as the nuclei of condensation. Their diameter increases during this period up to 4÷6 nm. The obtained sol feed off at boiling with fresh sol. Friable particles of fresh sol, getting in the heat-treated sol dissolve faster and stand out silicic acid, is deposited on the previously formed sol particles.

It is expedient to carry out the process of growth of particles at a certain increase of volume, i.e. with partial evaporation. This technology is particularly preferred for production of concentrated silica sol having a particle size of 15 nm and above. The influence of the following factors on the efficiency of particle growth: feeding speed of the feeder, the ratio of the volume of the feeder to the original sol volume.

In the first experiments investigated the effect of feeding speed of the feeder, on the growth of the colloidal particles. The parameters such as concentration of the starting sol, the concentration of feeder, the feeder volume and pH, were constant. The feed rate of the feeder changed in the range from 2 to 25 ml/min, the value the specific surface of sols increased from 256 to 412 m<sup>2</sup>/g (see Fig. 12). The minimum specific surface correspond feed rate of feeder 3÷5 ml/min, was selected as the optimal rate of 5 ml/min.

In further experiments constant speed of 5 ml/min was set, the ratio of the feeder to the volume of the original sol was changed. This ratio was varied in the range 5÷30, with all other things being equal. Data from these experiments are presented in Table 1 and Fig. 13. In this range,  $V_f/V_0$  particles increased by 3 times. To further increase the particle size requires considerable lengthening the time of their growth, which can be measured by several days and more, depending on the desired nanoparticle size. Thus, for a given system conditions for growing colloidal nanoparticles with sizes > 10 nm are experimentally determined.



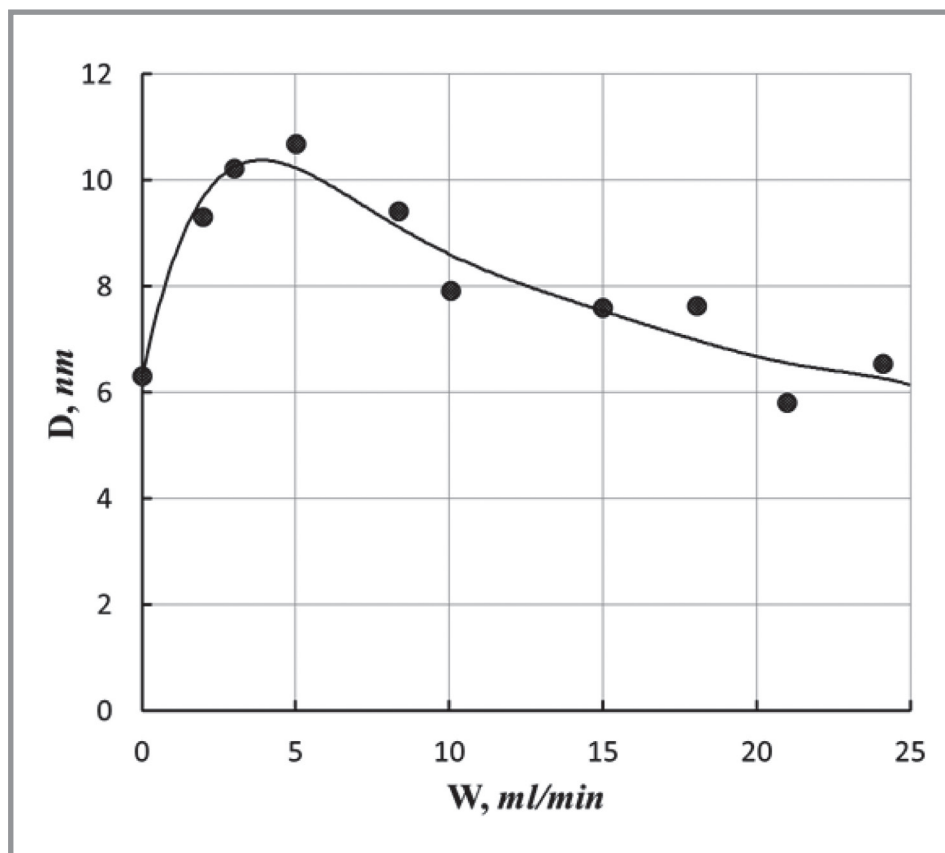


Fig. 12. The dependence of the silica sol nanoparticle size, on the feed rate of the feeder.  
The ratio  $V_f/V_o = 10$ .

Table 1.

### Growing of particles with partial evaporation

№	$V_o, ml$	$C_o, g\text{-eq/l}$	$S_{o\text{ud}}, m^2/g$	$W, ml/min$	$C_f, g\text{-eq/l}$	$V_f, ml$	$S_{t\text{ud}}, m^2/g$	$D_f, nm$	$V_p, ml$
1	200	0,5	500	5	1.6	350	256.0	10.7	1000
2	200	1,6	256	5	3.1	350	199.0	13.6	2000
3	250	3,1	199.0	5	3.1	500	179.0	15.2	3000
4	200	3,1	179.2	5	2.1	860	170.2	16.0	4500
5	200	2,1	170.2	5	–	–	173.4	15.7	5700



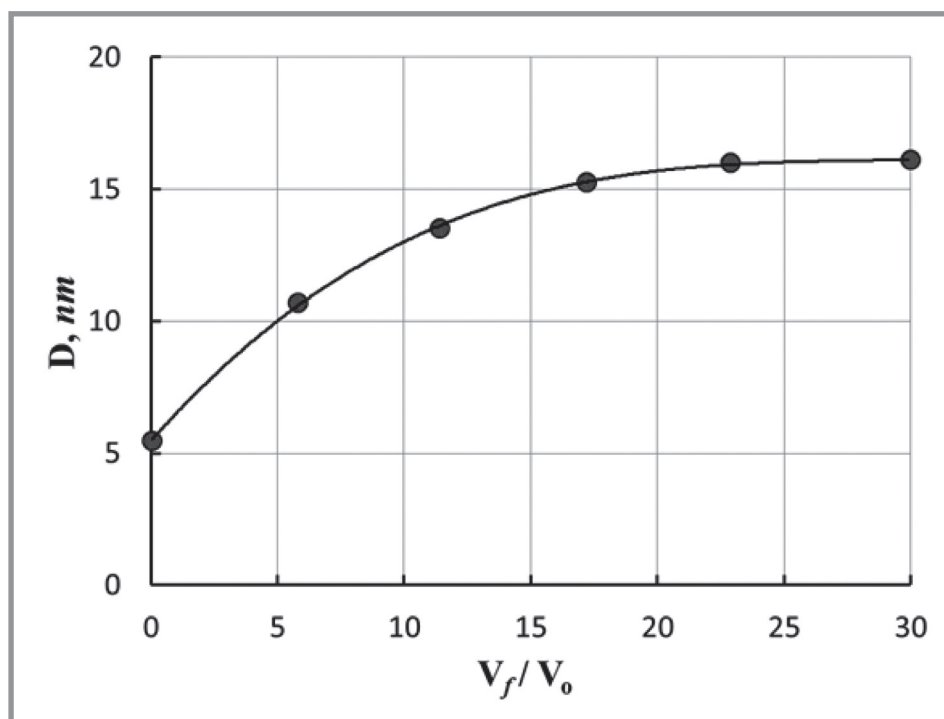


Fig. 13. The dependence of the nanoparticle size silica sol on the ratio  $V_f/V_o$ .

Thus obtained, the nanoparticles of silica or other nanosized materials can interact both among themselves as well as with monomer and polymer components in the medium around them. An important aspect of this issue is their interaction with the polymer matrix, at their introduction in the composition with a polymeric binder. Interactions of the polymer chains with nanoparticles are very diverse. They differ in nature and intensity, and often occur simultaneously. Polymer chains with chemisorption can form a covalent, ionic or coordination chemical bonds with surface atoms of the metal layer or of the corresponding compound. In recent years, namely, covalent bonds cause the greatest interest in the design of nanomaterials from molecular building blocks [155–158]. For this purpose, the particles further functionalized for subsequent covalent binding of them with other components.

### 3.2. Nano-sized binder

Quaternary ammonium silicates (QAS) are organo-mineral surfactants with the general formula  $([R^1R^2R^3R^4]N)_2(SiO_2)_{n-1}SiO_3$  where  $R^1, R^2, R^3, R^4$  are various organic radicals. In comparison with sodium/potassium sili-



cates, stable aqueous solutions of QAS may easily have  $n$  (modulus) 5–10 and more. Variations of modulus and radicals allow changes in properties of QAS in a very large spectrum [70]. QAS are compatible with many of mineral and organic compounds with pH enough high to avoid precipitation of silica [196]. QAS have good adhesion to hydrophilic and hydrophobic surfaces and have the following applications.

1) As quaternary ammonium compounds:

- As biocides; as catalysts;
- In textiles (if two long chains) – as textile softeners for home use;
- As the final rinse in the washing machine; as a rinse after shampooing, emulsifiers;
- In metal working – as additives to acid used in the cleaning and pickling of steel to prevent hydrogen corrosion;
- In road building, bentonite treatment, oilfields;
- As antistatic in polymers – e.g., in PVC belting;
- For the preparation of excellent quality toner;
- As components in special systems of water purification [125];
- As components in self-setting aqueous mixtures for the manufacture of chemically resisting materials as additives in concrete and coatings [126];
- In structure-directing agents, e.g., for the synthesis of molecular sieves with high-modulus silica [127];
- As raw material for preparation of organosiloxanes [128];
- With aggregated titanium dioxides pigment products containing QAS – for pigment preparation [129];

2) As silicates:

- For blends of hydrophilic medical use [127];
- As binders for concrete;
- For reinforcement of concrete, other building destinations;
- For coatings, linings and claddings.

QAS-based compositions provide coatings characterized by excellent adhesion, thermal stability, fire- and corrosion resistance. Depending on additives, they may be insulators or electric conductors.

However, elaboration of QAS-based materials is very complicated because of difficulties in modeling of QAS system. Silica and solid QAS have branched cross-linked structure not available for traditional methods of simulation.



Existing methods of study of such processes comprise two principal approaches: modeling by Monte-Carlo random simulation, and the thermodynamic description.

The Monte-Carlo approach considers the solid-phase process of microporous cluster formation as a random process, in which the initially empty space is divided into cells every of which can be eventually filled with a solid particle (silica). The probability of such event is assumed independent of the pre-history of the process. The main drawback of this approach consists in the ignorance of the determination of this process. Therefore, such approximation is applicable only to solid structures with very low density, in which the probability of neighborhood of two or more empty cells is negligible [130–132]. The applicability of Monte-Carlo approach is limited by three principal factors: finite size of the studied system (for various capacities of computers, from some thousand to some million cells), negligibility of surface tension, and absolute randomness of micropore formation processes. Therefore, the validity of Monte-Carlo approach for major part of real systems is very doubtful.

Available alternative approach, may relate to the thermodynamic definition of the considered process, which does not take into account the possibility of deposition of silica [133, 134]. Thermodynamic approach uses macroscopic description based mostly on such or such distribution of structural elements in energy. This approach is well applicable to a system consisting of a very large number of cells and allows obtainment of very important information about microporous system and dependence of its properties on preparation conditions. However, since energy distribution is not directly related to internal surface area, this one cannot be found from equations of thermodynamic model [71, 135].

The problem of silica aggregation from quaternary ammonium solution in limited volume has been considered. The system has been described by a model combining Monte-Carlo approach with thermodynamic limitations. Thermodynamic characteristics have been estimated by statistical polymer method (equilibrium version). The model has been employed for estimation of such properties as monomer concentration and tortuosity. The results of computer simulation have been used for forecasting of properties of coatings and practical preparation of samples coated with quaternary ammonium silicate-based composition [139].





In recent years begun to develop application silicate polymer composite materials, which are water soluble silicates with additives of active substances furan series. They operate under acidic and neutral media and under the influence of elevated temperatures. The materials are cheap and easy to manufacture non-toxic, non-flammable. Cost of polymer silicate materials commensurate with the cost of cement concrete and several times lower than the cost of polymer concrete. Silicate Polymer materials as concrete, mortar, putties used for making constructions of various purpose, monolithic and tile lining. There is a certain perspective, in composite materials based on liquid glass binder modified with furfuryl alcohol.

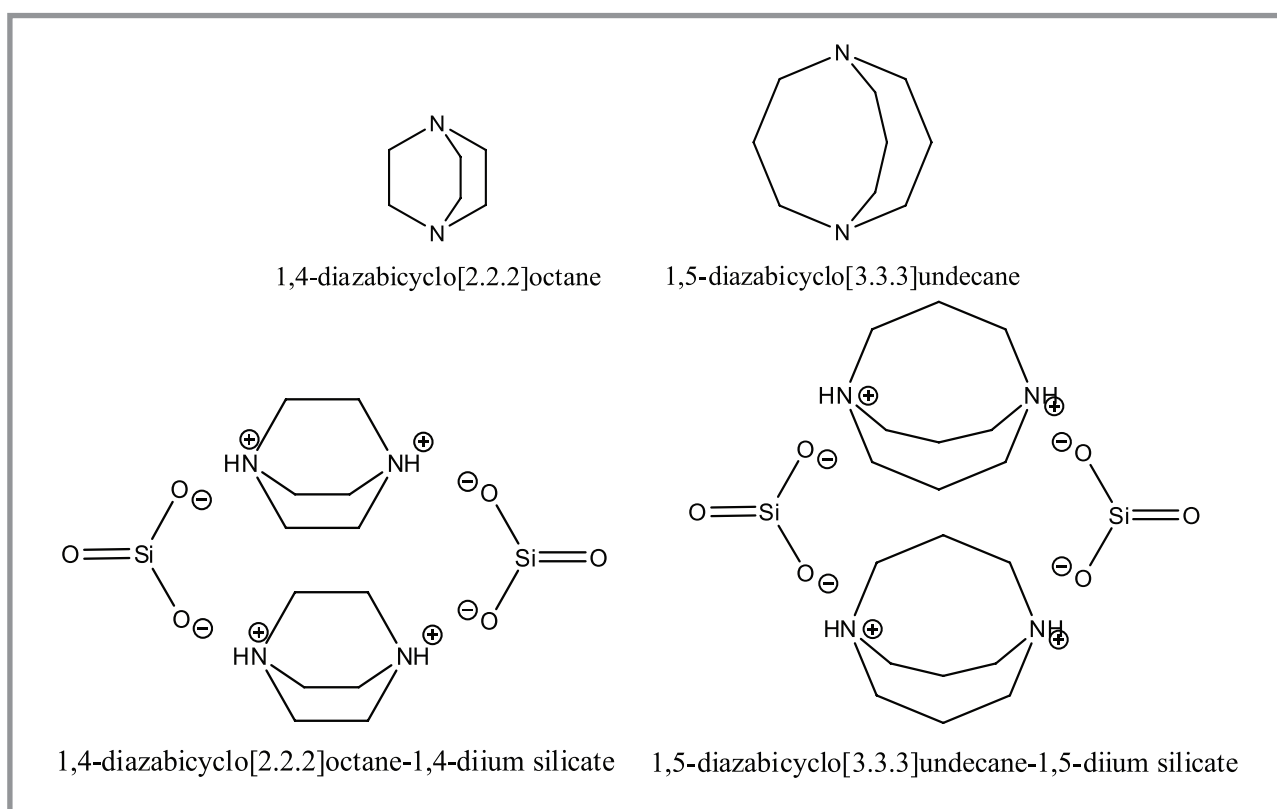
A significant increase in strength, thermal and fire resistance, of silicate matrix is achieved by introducing into the composition of esters of orthosilicic acid and furfuryl alcohol (*tetra*-furfuryloxysilanes – TPS). Effect is achieved by strengthening of contacts between the globules of silica gel and modification of the alkaline component, due to the «inoculation» of the furan radical. Introduction to the binder, additives TFS leads to the formation of nanoparticles of  $\text{SiO}_2$ , and furfuryl alcohol, which fills the matrix, and forms the crosslinked polymer. These particles act as centers of nucleation and crystallization. Adding TPS increases the mechanical and chemical resistance of the binder, and this approach began to be widely used for the preparation of acid-resistant concrete and coatings [140, 141].

This effect can be explained by the following considerations. On the thermal stability of oxo-compounds can be judged by the relative strength of the interatomic bonds M–O and C–O, in their crystal-structure. The length of the M–O and C–O, within the coordination polyhedron, can vary significantly, indicating that their energy non-equivalence. During the dehydration and with thermal influence may change denticity, of a certain part of the ligands. In the forming structure, they can begin simultaneously to perform the function as a ligand, and a solvate that is absent in the system. Increasing denticity of ligands leads to distortion of the oxygen environment of the matrix element, or filler, with a corresponding change in the distance M–O and C–O in the structure, and hence to changes in their strength.

For increasing the strength, the acid resistance, heat resistance and flame resistance of construction materials and structures of them *tetra*-furfuryloxysilane (TPS) are input to the binder composition. They are synthesized by *trans*-esterification of *tetra*-ethoxysilane, and furfuryl alcohol.



Composition of the resulting binder comprises: a liquid glass – 80÷95 wt.% *tetra*-furfuryloxysilane (TFS) – 2÷7 wt.%, hardener, sodium hexafluorosilicate – 13 wt.%. Thus as part of the liquid glass used organic alkali liquid glass, wherein the organic cation is taken 1,4-diazabicyclo[2.2.2]octane-1,4-dium or 1,5-diazabicyclo[3.3.3]undecane-1,5-dium silicates – 2÷4 wt.%. (See Fig. 14).



**Fig. 14. The structural formulas of 1,4-diazabicyclo[2.2.2]octane-1,4-dium and 1,5-diazabicyclo[3.3.3]undecane-1,5-dium and their silicates.**

Water-soluble silicate containing an organic alkali cation was prepared by reaction the salt of an organic quaternary ammonium derivative with amorphous silica. Soluble organic alkali silicates, such as *tetra*-butylammonium silicate (TBAS) was used as a binder component for self-extinguishing.

Developed nanostructuring binder prepared laminar mixing liquid glass containing cations of alkali metals such as sodium; furfuryl-tetra-silicate (TFS) and a water-soluble silicate, a water-soluble silicate contain-

ing an alkali organic cation such as diazabicyclo[2.2.2]octane-1,4-dium or 1,5-diazabicyclo[3.3.3]undecane-1,5-dium [142].

After mixing all components of the binder, it is necessary to use for 2÷3 hours. Adding of hardener is carried out together with fine ground mineral filler.

Introduction of *tetra*-furfurylsilane, which is nanostructuring component in the binder, that leads to the formation of nanoparticles of SiO<sub>2</sub>, and furfuryl alcohol. SiO<sub>2</sub> nanoparticles act as centers of nucleation and crystallization. Furfuryl alcohol fills the silica matrix is destroyed, and thus is polymerized. Adding TFS increases the mechanical and chemical resistance of the binder and is widely used for the preparation of acid-resistant concrete and fillers. Liquid glass with an additive of 1,4-diazabicyclo[2.2.2]octane-1,4-dium silicate is compatible with an aqueous dispersion of chloroprene rubber and polyurethanes, as well as most synthetic latexes based rubbers.

Composite materials of interpenetrating inorganic and organic polymer networks are disclosed in [122, 197].

### 3.3. Synthesis of nanophase in the matrix of the composite structure

It is of interest, the introduction of the carbon material in a sol-gel process for obtaining nanocomposites as additives for modifying the functional properties of the nanocomposite, as well as the kind of pore-forming component (see. Fig. 4). Pore-forming components are substances that disappear at various stages of forming and processing of materials to form pores. Carbon materials in the process of annealing in an oxygen atmosphere, converted into gaseous products. Ability to control the nanosizes of the objects consisting of carbon materials during their introduction to the structure of the nanocomposite, determines the feasibility of their use to obtain the structures with specified pore sizes [143].

For these technological methods, uses the term «template synthesis» and input particles is called a template. New materials with a narrow pore size distribution are necessary to create semiconductor gas sensor devices a new generation composite membranes, sorbents for chromatography and others.

Highlight the role of porous materials obtained by the sol-gel method, in the development of technological operations applying dielectric coatings



with low values of relative dielectric permittivity, in micro and nanoelectronics [144].

At the present stage of development of silicon nanoelectronics carried out intensive works to decrease the values of resistance of materials by replacing aluminum in conventional conductive materials on the copper conductors (or copper in a shell from  $\text{TiO}_2$ ). To reduce the capacitance values are intensively developing research on materials with low values of the effective relative dielectric permittivity [145]. One of the main technological methods to reduce the average value of the dielectric permittivity is the formation of an insulating layer with nanopores of sol-gel method.

Another promising area of technology is the formation of the catalytically active nanoparticles on the pore structure. The use of such substrates gives the material in the form of «nano grass» from the silicon, or heterostructure nano-wires [146, 147]. On the basis of obtained in this manner nano-wire manufactured devices, for nano-electronics and nano-opto-electronics [148], for sensor techniques [149] and for photonics [150]. To date, developed the technology of heterostructure nanowires (nanofilaments) with a change in the composition of both along the growth axis (axial nanowire heterostructures), and in the radial direction (radial nanowire heterostructures). In the review [148] summarizes the data on such structures on semiconductor compounds  $\text{A}_3\text{B}_5$ ,  $\text{A}_2\text{B}_6$  and solid solutions based on them. As the catalyst, usually used nanoparticles Au, and nanofilaments growth occurs by a mechanism «vapor-liquid-crystal».

Interest to metal-polymer nanocomposites obtained by the method of synthesizing nano-phase in the structure of the composite matrix, is caused by a combination of unique properties of nanoparticles of metals, their oxides and chalcogenides. Furthermore, these materials also possess unique mechanical, film forming, and other properties and possibilities of their use as magnetic materials for recording and storage of information, as sorbents, catalysts and sensors. Monomeric and polymeric metal carboxylates are classic examples of such starting materials [184]. Carboxylate compounds such as monomeric or polymeric structure may be used as molecular precursors of nanocomposite materials. In addition, the carboxylate groups belonging to macroligands are effective stabilizers of nanoscale particles. Sometimes, these properties are manifested in the form of a polyfunctionality of one system. The amphiphilic nature of carboxylated polymers and copolymers, allows encapsulating the metal



nanoparticles and combining them with the polymer and inorganic matrices, as well as with biological objects. It also allows you to attach to the nanoparticles properties such as solubility in different environments, the ability to self-organization, etc. [185].

Processes of steric stabilization, flocculation, phase separation, electrostatic and van der Waals interactions determine the aggregative stability of the particles in the polymer matrix. In the work [186] it was shown that the van der Waals attractive force acts between the two surfaces of the nanoparticles that are not coated with a polymer, up to 200 nm, causing their aggregation. At the same time, the presence of an adsorbed layer of polyacrylate or polymethacrylate of ammonium on the surface of nanoparticles leads to the appearance repulsive forces between the two surfaces at a distance of 35 nm. Moreover, ammonium polymethacrylate provides stronger repulsion than ammonium polyacrylate. This effect is apparently connected with an additional steric barrier due CH<sub>3</sub>-group. Conformational effects of polymer chain are particularly sensitive to reaction conditions such as pH of the medium.

Accordingly, the thermal conversion processes of unsaturated carboxylate metal complexes allow combining the synthesis of nanoparticles with their simultaneous stabilization in a polymer matrix formed by the decarboxylation. It is possible to assume that almost complete homogeneity of thermal conversion processes of monomeric carboxylates is the cause of a fairly narrow character size distribution of metal nanoparticles, and also their morphological features associated with the spherical shape. In this case there is only a partial heterogeneity in the macroscopic defects area [187].

Other monomeric carboxylates, most frequently used as starting products in the preparation of nanostructured metals are metal octanoates and oleates. Thermolysis of their complexes in combination with surfactants and other reagents usually carried out in a solution of high-boiling solvents (octadecane, octadecene, docosane, octyl esters, etc.). The undoubted advantage of the process of thermal decomposition of the carboxylate compounds in an inert solvent is the possibility to control synthesis of monodisperse nanocrystals, with a high yield, a narrow size distribution and high degree of crystallinity [188–191].

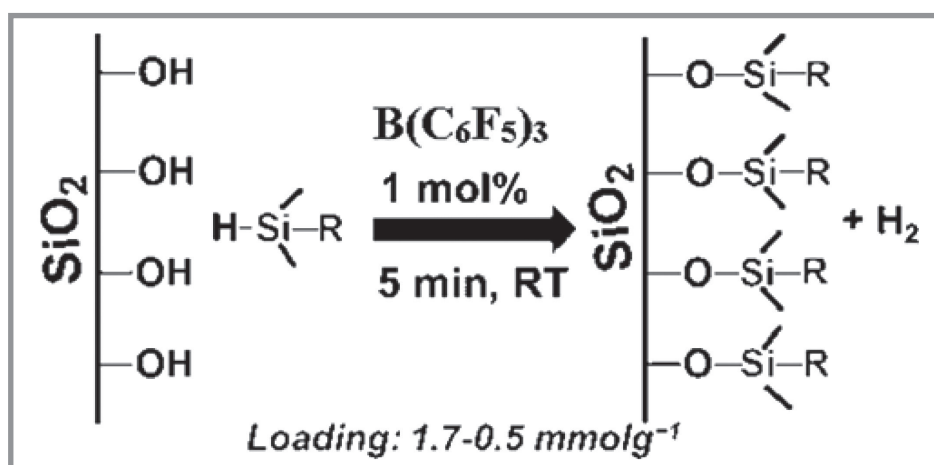
A promising direction is to conduct these processes, in the pores of silica gel matrix, which will allow obtaining materials with unique optical and



sensory properties. There is the possibility of combining these processes with processes of the sol-gel synthesis.

Thus, methacrylate substituted metaloclusters  $\text{Hf}_4\text{O}_2(\text{OCC}(\text{CH}_3)=\text{CH}_2)_{12}$  and methacrylo-yl-propyl-*tri*-methoxysilane  $\text{CH}_2=\text{C}(\text{CH}_3)(\text{COO})-(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ , used for hybrid thin films based on silica gel with embedded oxo-clusters hafnium [191–193]. Chemical bonding of the components was carried out with the use of photochemical polymerization of methacrylate groups. Alkoxy silane undergoes hydrolysis and condensation with the formation of oxide grid  $\text{SiO}_2$ . Heat treatment at  $\geq 800^\circ\text{C}$ , of the hybrid nanocomposite is accompanied by pyrolysis of the organic part, and sealing of the oxide network. This leads to the formation of nanostructured oxide material. Thus it is possible to obtain a monolithic gels and thin films. Carboxylate ligands in organo-mineral composites offer a high degree of cross-linking, through coordination bonds between the polymer and the mineral component.

In [194] the author has proposed a new synthesis method of organo-mineral nanocomposites on the silicon oxide matrix, using borane compounds as homogeneous catalysts that promote Si–H bond activation. He also describes an innovative method for modifying the surface of silica, using a hydrosilanes, as modifier precursors, and *tris*-(*penta*-fluorophenyl)-borane ( $\text{B}(\text{C}_6\text{F}_5)_3$ ) as catalyst.



**Fig. 15. Schematic diagram of the silica gel surface modification, using dehydrogenative reaction between the silanol groups and hydrosilanes [194].**

Since the surface modification reaction, between surface silanol groups and hydrosilanes, is the dehydrogenative, passing and stopping of the reaction can be easily confirmed with the naked eye. This new process, without participation of the metal compounds can be carried out at ambient temperature and requires less than 5 minutes to complete. Hydrosilanes carrying different functional groups including alcohols and carboxylic acids were immobilized by this method. Ideal preservation of sensitive functional groups which are easily destroyed when using other methods of synthesis, making this technique attractive for the diverse applications.

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**Contact information****Figovsky Oleg Lvovich**  
**[figovsky@gmail.com](mailto:figovsky@gmail.com)**

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**Автор:** КУДРЯВЦЕВ Павел Геннадьевич, профессор, D.Sc. Холонский технологический институт (Израиль), академик МАНЭБ и РАЕН, автор 150 научных работ, в том числе «Наноматериалы на основе растворимых силикатов» (в соавторстве с О.Л. Фиговским), имеет более 30 изобретений; 52 Golomb Street, POB 305 Holon 5810201, Израиль, 23100, e-mail: pgkudr89@gmail.com;

**Автор:** ФИГОВСКИЙ Олег Львович, действительный член Европейской академии наук, иностранный член РИА и РААСН, главный редактор журналов SITA, OCJ и RPCS, директор компании «Nanotech Industries, Inc.», Калифорния, США, директор Международного нанотехнологического исследовательского центра «Polymate» (Израиль), зав. кафедрой ЮНЕСКО «Зелёная химия», президент Израильской Ассоциации Изобретателей, лауреат Golden Angel Prize, Polymate INRC; P.O.Box 73, Migdal Ha'Emeq, Израиль, 23100, e-mail: figovsky@gmail.com

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## НАНОКОМПОЗИТНЫЕ ОРГАНОМИНЕРАЛЬНЫЕ ГИБРИДНЫЕ МАТЕРИАЛЫ. ЧАСТЬ II

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### АННОТАЦИЯ К СТАТЬЕ (АВТОРСКОЕ РЕЗЮМЕ, РЕФЕРАТ):

В работе рассматриваются вопросы, связанные с алкоголятным и негидролитическим методами золь-гель синтеза, а также коллоидным методом золь-гель синтеза. Также для нанокompозитов обсуждается альтернативный подход, основывающийся на использовании растворимых силикатов в качестве продукта предшествующей стадии в золь-гель технологии. Показана возможность получения нанокompозитов из аэрогелей. Был выполнен анализ использования смешанных технологий при приготовлении нанокompозитов. Авторы описывают возможность изменения различных подходов в типах нанофаз, используемых для производства нанокompозитов. Исследованы различные модели упаковки сферических, волокнистых и слоистых наночастиц, введенных в структуру нанокompозита.

**Ключевые слова:** нанокompозиты, золь-гель синтез, растворимые силикаты, алкоголяты металлов, золь, гели, аэрогели, упаковка сферических наночастиц, упаковка волокнистых наночастиц.

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**Контактная  
информация:**

**Фиговский Олег Львович  
figovsky@gmail.com**

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