

## Synthesis of Powder Materials with Particles Encapsulated into Carbon Containing Nanostructural Films

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### Abstract

Particles of a complex structure: a quartz nucleus encapsulated into metalpolymer carbon containing nanosize film of the type “cluspol” have been obtained as a result of mechanochemical treatment of quartz with carbon containing organic compounds. Electronmicroscopic investigations show the diversity of morphological forms and nanostructural carbon formations on the surface of modified quartz particles. Depending on the regimes of mechanochemical treatment, the obtained materials are characterized by considerable changes in electromagnetic properties. The choice of carbon containing modifiers provided a highly active physico-chemical state of quartz of a prolonged action.

### Introduction

Progress in technology requires that novel materials with a designed complex of properties and necessary quality should be created. Conventional technologies have been realized practically completely, and the development of novel functional materials can only give principally new results under the conditions of a complex use of the achievements obtained in several scientific fields: physical chemistry of organic and inorganic materials as well as high molecular compounds, physics and chemistry of surface, physics of ultradisperse particles, nanochemistry, etc. Of the great variety of up-to-date materials, composition systems are the most preferable as the combination of organic and inorganic compounds, metals and ceramics, amorphous and crystalline substances, the presence of phases of different degrees of dispersity in one substance allows obtaining products with quite various properties. At present, nanostructural materials the properties of which significantly differ from those of coarse-grained analogues hold

a special place. When obtaining powder nanosystems, the material may not only be a homogeneous ultradisperse powder but also nanolayer formations on the particles of a micron size. Creation of such microcomposition formations with nanosized morphology of their constituents is one of the perspective directions in the development and production of materials with a designed complex of properties.

When obtaining such composition nanomaterials, carbon- and silicon containing systems are paid special attention due to the specific character of their properties and a wide spectrum of application and because of the fact that both carbon and silicon are basic elements for creation of different polymer systems. Surface nanostructures play a significant role in such objects as highly disperse adsorbents, catalysts, fillers of composition materials as well as in the materials for electron industry.

A mechanochemical synthesis has great advantages compared to other methods when obtaining highly disperse nanostructural powders. In the process of intensive dispersion of particles in dynamic mills, there takes place a chemical interaction between the substances being ground and a gaseous medium. Particles with a layer change in the phase composition, structure and

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properties are synthesized with the corresponding choice of the regime of mechanical action on the powder mixture. Under the conditions of mechanical grinding of inorganic substances in the presence of organic compounds (both monomers and polymers), there takes place the formation of chemical bonds between the fresh surfaces stripped in the process of destruction and organic radicals. It is stated [1-3] that inorganic substances being ground initiate polymerization of monomers, and the polymer formed is able to get grafted to the freshly stripped active surface in the process of grinding. As a result, the particle is encapsulated into a polymer "shirt".

The process of encapsulation of an inorganic matrix into a polymer film is conditioned by the occurrence of free active radicals and free ions and, hence, is related to the shift of electrons in the mass of inorganic substance under the impulse of mechanical energy [3]. An important role in initiation of mechanochemical polymerization and grafting of polymer fragments to the surface of inorganic polycrystalline substance is played by electron emission under the conditions of mechanodestruction, the manifestation of which was experimentally stated and investigated in detail [4]. Finally, the compounds which should be referred to the class of polymetalorganosiloxanes are formed on the surface [5]. The properties of these compounds are determined by the number of carbon and hydrocarbon radicals and their distribution in the silicate matrix in the simultaneous presence of metal atoms. The "carbonization" degree of the surface of quartz particles in the course of formation of different silicon-organic polymer compounds of a cross-linked structure depends on the organic substance being used resulting in modification of the surface of the particles being dispersed and the conditions of mechanical action. The specificity of formation of polymer structures on the quartz surface is also conditioned by the fact that quartz is a good piezoelectric. Dielectric polarization of the particles under mechanical action must contribute to polymerization of the surface. On the other hand, the development of a dense elastic film on the surface of the deformed quartz particle will allow to fix the deformed state, i.e. to resist the process of relaxation, restructurization and annihilation of the defective structure. A film with different variations of electromagnetic properties may be obtained by grafting sufficiently complex metal-organic complexes with transition metals to the surface.

Combination of the ferromagnetic surface layer which is strongly bound with the piezoelectric nucleus of the particle of a microcomposition structure makes it possible to form new controlled properties of the material being dispersed.

In the papers published earlier [6-9] we showed the possibility of obtaining highly disperse materials on the basis of quartz by mechanochemical synthesis, the obtained materials possessing simultaneously magnetic, dielectric and electric properties. The properties of the material being produced depend on the regimes of mechanochemical action and the kind of organic materials (additives-modifiers): different carbon containing compounds providing the formation of nanostructured layers of the thickness 10-50nm on the surface and encapsulating the quartz particle into films of different structure and density.

The aim of the present investigations is to analyze such systems to elucidate the peculiarities of the morphology of synthesized surface layers on the quartz particle in relation to the specific character of the properties of investigation objects.

## Experimental

For mechanochemical synthesis, we used quartz of 99.8% grade and carbon containing compounds (alcohols, acids, polymers) as modifiers. Dispersion of quartz was carried out in a mill of a centrifugal-planetary type (a mechanical reactor) at the rate of the platform rotation 700 revolutions/minute. The rate of the grinding vessels was 1200 revolutions/minute. The value of acceleration during the treatment in the centrifugal mill amounted to 20 g. The time of action varied from 5 to 90 min (with every 5 min stop). The ratio of the mass of the powder and the milling balls ( $M_p/M_b$ ) was 1/2 and 1/4.

The obtained material was studied by the methods of X-ray phase, X-ray structural and electron-microscopic analysis and EPR-spectroscopy. Measurements of the density, specific surface, specific volume of pores and the amount of carbon in the modified sample were carried out by standardized techniques. The sequence of the structural rearrangement of surface carbon containing layers of quartz particles depending on the modifier and conditions of mechanochemical treatment was analyzed.

*X-ray structural and X-ray phase analyses* were carried out on diffractometer "DRON-4M" using cobalt ( $Co - K_{\alpha}$ ) radiation. The width of the main

line of compounds ( $\text{SiO}_2$ ) was evaluated after the mechanical activation. To determine the widening of the quartz line which is related to the sizes of the substance crystallites and deformation of the crystalline lattice, additional X-ray patterns were taken at a low rate 1-2 grad/min in the range from 40 to 80 ° $\theta$ .

Electron-microscopic analysis was carried out using an electron translucent microscope Jem – 100CX; U-100kv. The samples were prepared by the method of suspension in distilled water followed by ultrasound dispersion. In the process of investigation it was stated that water interacts with alcohol residues, after grinding quartz, with the formation of silicon acid which not only dissolves the surface layer but also penetrates into the inside part of quartz particles. Therefore, further preparation of the samples for investigation was carried out by the method of dry preparation. Particles of rock crystal prepared by grinding in an agate mortar without a dispersing medium were studied as reference nonmodified quartz.

EPR-spectroscopy was carried out on the apparatus EPR – 10min with the sensitivity  $5 \cdot 10^{10}$  spin/Gauss. The range of magnetic field scanning is 300-5000 Gauss. The time of photographing a spectrum is from 10 to 60 minutes. The frequency of modulation 100 kHz is from 0 to 10 Gauss. The power of microwave frequencies is up to 5 mV.

## Results and discussion

Taking into account the fact that intensive dispersion in the mill-activator resulted in saturation of the particle with defects which determine the different levels of power state of the material and, hence, its chemical activity in regard to the reagents introduced into the mechanical reactor, we, first of all, investigated the changes in the structural characteristics of the material under study-quartz depending on the time of grinding (and activation). The presence of defects in quartz after mechanical treatment was evaluated by X-ray structural analysis (XSA) according to widening of X-ray lines at the semi height of the peak. The sizes of crystallites were estimated with the accuracy of quartz lines widening for intraplane distance 1.98 Å where there is no effect of dominating direction. The results of measurements showed (Figure 1) that both the width of lines and the size of quartz crystallites change non-linearly with the time of treatment in a mechanical reactor. Definite

periodicity in the increase and decrease of these characteristics, i.e. in the presence of defects in the structure of particles, is observed.

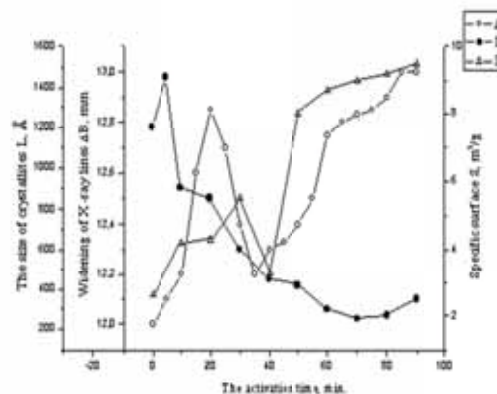


Fig.1. The change in widening of X-ray lines ( $\Delta B$ ), the size of crystallites ( $L$ ) and specific surface ( $S$ ) of the particles of quartz powder with the time of treatment in a mechanical reactor.

The observed dependency indicates the process of accumulation, redistribution, coagulation and regeneration of defects in the volume and on the surface of the particles being ground. The width of X-ray lines at the semi height of the reference quartz sample is 8.5 mm. Grinding of quartz during different periods of time results in widening of quartz lines from 12.1 to 13.0 mm. The measurement error is within  $\pm 0.1$  mm. Widening of lines is a general indication of the increase in dispersity, accumulation of defects both inside the particle resulting in the decrease of the sizes of crystallites which compose it and on the surface resulting in its amorphization. The obtained regularities allow revealing a number of extremely points indicating the peculiarities of structural changes in quartz.

So, at the time of treatment 15-20 min there takes place an abrupt increase in widening of X-ray lines and retardation in the change of crystallite sizes due to, probably, the increase in the dispersity of particles, accumulation of surface defects and, on the contrary, to regeneration of volume defects. The time interval of treatment 30-40 minutes, judging by the intensity of the decrease in both the width of X-ray line and the size of crystallites, is characterized by the most significant volume changes in the structure of the material being dispersed. Recombination of surface defects and coagulation of particles are possible indicating the decrease of the specific surface of powder particles

after 40 minutes of treatment. Judging by the presented results of measurements of all three characteristics ( $\Delta B$ ,  $L$ ,  $S$ ), a longer treatment of quartz (50 min and more) is related to both the decrease in the size of crystallites and the change in the structure and state of the surface layers of particles.

The most effective period of time, when treating quartz with different organic additives modifying the surface of particles, is 15-20 minutes. A combined treatment of quartz with alcohols, acrylic acid and polystyrene also results in the extremely widening of X-ray lines after 15-20 minutes of treatment, but within 12.0 mm, with simultaneous decrease in the size of crystallites (up to  $370\text{\AA}$ ), i.e. at a more significant volume change in the structure of particles. Thus, deeper structural changes in both the volume of the particle and on its surface take place in the presence of organic modifiers. The latter is shown in the results of measurements of the specific surface and specific porosity of particles (Table 1). The increase of specific surface with simultaneous decrease of dispersity, i.e. agglomeration of particles, as it was shown earlier [6, 7], is caused by effect of a complex transformation of the structure of surface layers of quartz particles being dispersed in the presence of modifiers.

**Table 1**

The change of specific surface ( $S_{sp}$ ) and specific volume of pores ( $V_{sp}$ ) under the conditions of mechanochemical treatment of quartz with different modifiers.

Material	$\tau_{act}$ , min	$S_{sp}$ , $\frac{m^2}{g}$	$V_{sp}$ , $cm^3/g$
Quartz (initial)	0	2.64	0.01
Quartz (act.)	10	4.56	0.04
Quartz (act.)	20	4.64	0.11
Quartz+ 5% ethanol	20	5.14	0.32
Quartz+5% butanol	20	6.50	0.18
Quartz+5% glycerin	20	10.5	0.64
Quartz+ 5%acrylic acid	20	77.6	0.62
Quartz+5% polystyrene	20	21.0	0,30

Electron-microscopic investigation of quartz particles showed the peculiarities of the structure of surface layers and its transformation depending on the kind of the modifier and conditions of mechanochemical treatment. It follows from our

earlier published works [10, 11] that when grinding quartz in a mill without modifying organic additives, there takes place partial amorphization of the surface layer of the particle and introduction of ultradisperse iron from the walls of the grinding vessel and balls into it. That considerably changes the electrophysical properties of the powder like material. The main part of the volume of such particles remains crystalline according to the results of electron microdiffraction [10]. When introducing an organic additive into the quartz being dispersed, the structure of particles undergoes significant changes. The surface layer may be a multilayer formation with the structure of different density (Figure 2b). Electron microdiffraction of quartz particles modified in the presence of butanol (Figure 2c) shows the formation of carbonaceous structures on the quartz particle surface.

The more complex is the carbon containing modifier in its structure (in the sequence-monatomic and multiatomic alcohol, acids and polymers), the more diverse is the morphology of the modified surface layer of the quartz particle under the conditions of mechanochemical treatment.

These changes, first of all, are related to the participation of carbon of the modifying additive. So, when using multiatomic alcohol, e.g. glycerin, the peculiarity of the structural composition is the formation of spherical particles and their dendrite-like aggregates (Figure 3) with high specific surface.

Modification of quartz particles by acrylic acid in the process of mechanical treatment results in the formation of a dense, quite homogeneous organic film on the surface and the presence of highly disperse crystallites in the surface polymer layer. Also, the formation of a homopolymer which is not bound with the surface of quartz is observed. The microdiffraction picture shows the formation of quartz-organic composites in such cases (Fig. 4). When introducing, in addition to acrylic acid which is used as a modifier, chlorides and oxides of metals, in particular, sodium chloride and zinc oxide, the particles of quartz acquire a more rounded "spherical" shape and the modified layer of a quartz particle is characterized by different density and a heterogeneous microcomposition. Electron-microscopic pictures vividly illustrate the fact that a quartz particle modified by mechanochemical treatment is a multilayer formation of different structures and forms with elementorganic compounds on the surface. The

microdiffraction picture in Figure 4a shows a three-dimensionally ordered (prior graphite structural

packing [13]) carbonaceous substance on the particle surface.

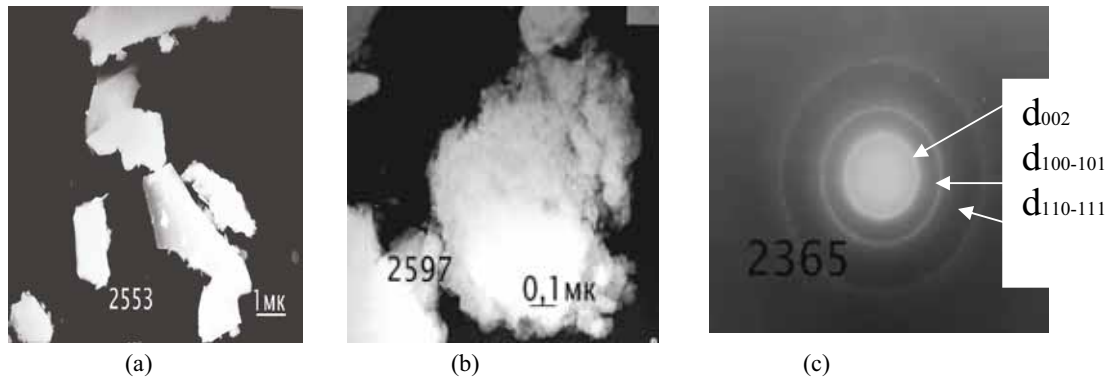


Fig. 2. Electron-microscopic pictures (a,b) and electron microdiffraction (c) of quartz particles in the initial(a) and modified (b,c) states.

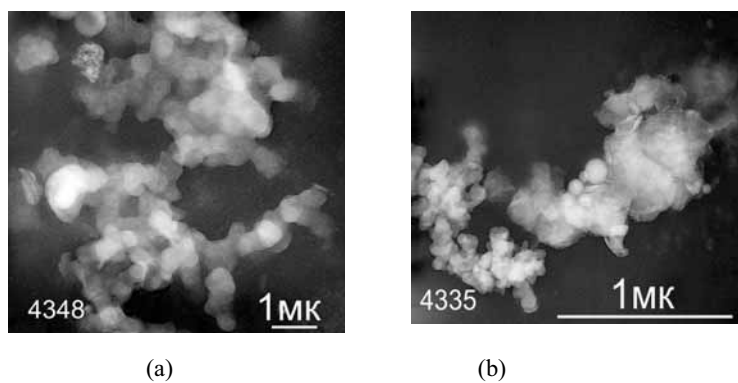


Fig. 3. Electron-microscopic pictures of quartz particles modified in the presence of glycerin.

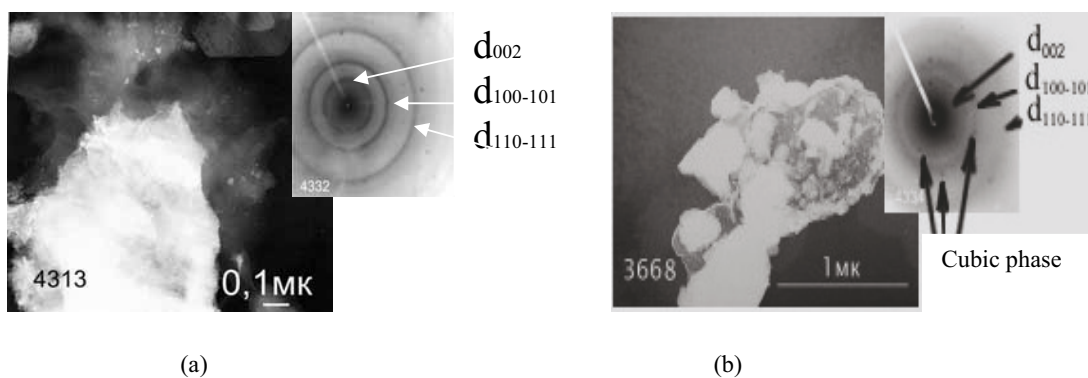


Fig. 4. Electron-microscopic pictures and electron microdiffraction of quartz particles modified in the presence of acrylic acid (a) and acrylic acid with sodium chloride (b).

The electron diffraction pattern of Figure 4b shows the presence of a metal-silicon-carbon compound (point reflexes) and a weakly crystallized silicon-carbon substance (reflexes are shown by arrows).

The diversity of structural forms of the modified surface of quartz is most vividly observed when using polystyrene as a modifier. Under the combined with polystyrene treatment of quartz there simultaneously takes place the destruction of a quartz particle and the destruction of polystyrene molecules into polyene and aromatic constituents. In this case, "carbonization" of the active surface of

quartz proceeds with participation of polycyclic aromatic molecules with simultaneous participation of polyene compounds. That corresponds to the known notions on soot formation depending on the raw materials being used [13]. Depending on the amount of the modifier being used (from 3 to 10%), the time of mechanical action and variation of mechanical conditions of action, there are being formed structurized or tracery films which are cross-linked with the surface of the particle or rolled in the form of tubes of different configurations with the size of 50-70 nm (Figure 5).

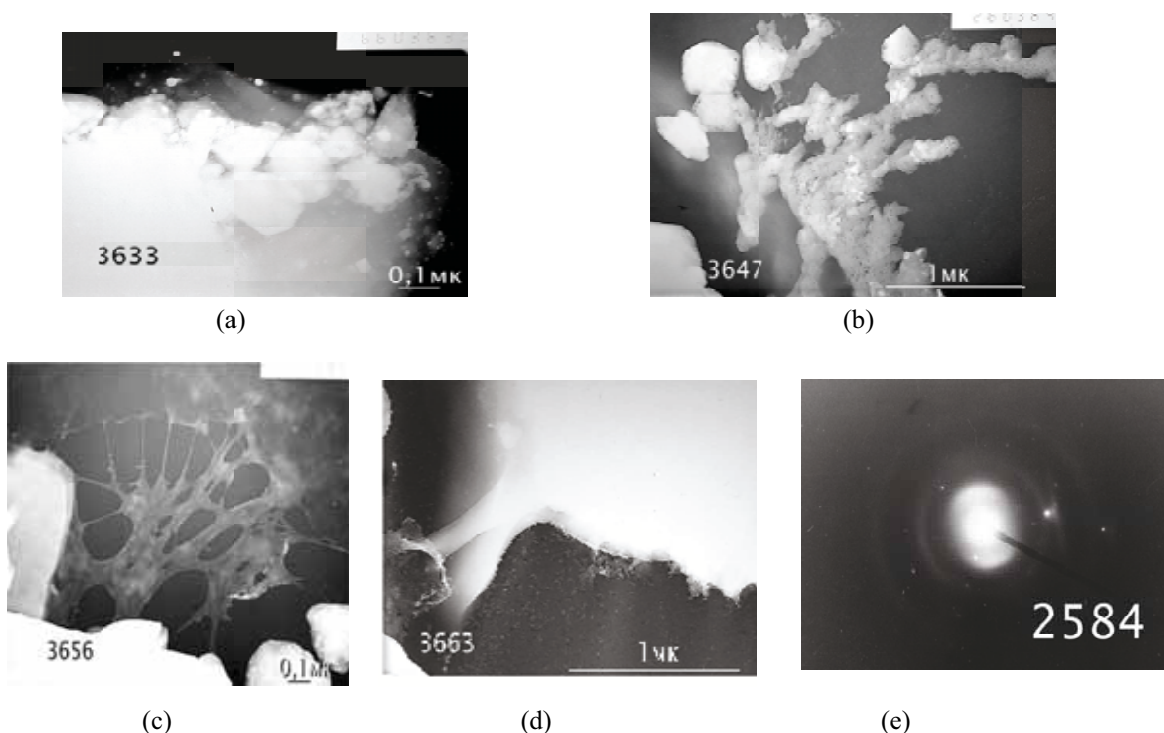


Fig 5. Electron-microscopic pictures (a-d) and electron microdiffraction (e) of quartz particles modified by combined with polystyrene mechanical treatment during 10(a), 20 (b) and 30 (c,d) minutes at the ratio  $M_p/M_b=1/2$ (a-c) and  $1/4$  (d).

The increase in the time of treatment finally results in coagulation of dispersed particles with the modified surface layer and in the formation of dendrite-like formations the growth of which proceeds according to the principle of similarity of fractional structures. Flat and rolled in tubes films of carbon formations are formed on the surface of such particles. As the results of electron microdiffraction showed, the characteristic peculiarity of carbon formations on the surface of

quartz mechanochemically treated in the presence of polystyrene is their texturization, that is the dominating orientation of carbonaceous particles of film formations (Figure 5e).

Thus, in the process of mechanochemical treatment of quartz with organic compounds, there takes place a complex multi-stage process of formation of novel carbon containing structures on the surface of the particle as a result of grafting to radical centres ( $\equiv \text{Si}^*$  and  $\equiv \text{SiO}^*$ ) emerging on the

surface of the crack of groups of destructurized organic compounds. The degree and form of "carbonization" of the quartz surface are conditioned by the kind of the modifier being used. The amount of bound carbon in modified quartz was determined by the adsorption-gravimetric method. The results of the carried out

measurements are present in Table 2. At the same mass amount of the modifier being used and the same time of treatment maximum amount of bound carbon (2.6 %) was detected in the samples with polystyrene, which showed the greatest variety of structural forms on the surface of the modified particle.

**Table 2**

The content of carbon and iron in the modified surface layer of a quartz particle after mechanochemical treatment

Material	$\tau_{act.}$ , min.	C,%	Fe,%
Quartz (initial)		0.08	0.05
Quartz (act.)	10	0.08	2.32
Quartz (act.)	20	0.08	3.34
Quartz + 5% ethanol	20	1.06	11.62
Quartz + 5% butanol	20	1.76	14.86
Quartz + 5% ethylene glycol	20	1.45	6.78
Quartz + 5% glycerin	20	1.53	4.94
Quartz + 5% acrylic acid	20	2,03	5,62
Quartz + 5% polystyrene	20	2,60	7,08

According to the results of the investigations carried out earlier [6-9, 10, 11], when grinding quartz in steel vessels and by steel balls, ultra disperse particles of iron got introduced into the modified surface of quartz particles. Due to the formation of the ordered structure with defects and the presence of iron containing clusters in the surface layer of particles, the modified powder of quartz displays the phenomenon of ferromagnetism [8, 9]. X-ray phase and X-ray spectral analyses as well as EPR-spectroscopy showed the presence of both the bound and free iron in quartz. The content of iron in quartz varies (Table 3) depending on the conditions of mechanochemical treatment (time, the number of balls, kind and amount of modifiers). In the initial quartz, iron admixtures make up 0.05 weight %, after grinding during 10 - 30 min the content of iron increases from 2.32 to 3.75 weight %, respectively (at the ratio  $Mp/Mb = 1/2$ ) and up to 5.36 weight % at the ratio  $Mp/Mb = 1/4$ , after grinding quartz in the presence of alcohols, especially monatomic ones, the content of iron in quartz increases several times. When modifying quartz by acrylic acid and polystyrene, the content of iron in it is considerably lower (Table 2) in comparison with the material treated by monatomic alcohols, but in the latter case ferromagnetism of the material increases to a much more extent.

The presence of iron on the surface of quartz after mechanochemical treatment is a significant but not a sufficient factor for developing magnetic properties in the dispersed material. A magneto ordered state of the deformed particles is also determined by the formation of a collective spin of the defective structure of the "carbonized" surface layer of the particle. Maximum indexes of magnetization of the material are obtained when using polystyrene as a modifier [14]. It is the ultradisperse particles of iron in quartz modified by polystyrene that are centers of growth of nanostructured carbonaceous formations on the surface of particles.

The observed surface formations may be referred to "cluspols" [15, 16], i. e. the surface appears to be metalcomplexes in a polymer matrix. Such formations may display both magnetic and conducting properties. Measurements of electrical resistance of the ground quartz were carried out on the screened fraction of the powder less than 60  $\mu\text{m}$  which was pressed in ampoules with the density  $(3.7 - 4.0) \cdot 10^{-3} \text{ g/mm}^3$ . The results of measurements showed the decrease of specific resistance of quartz after grinding by more than an order of magnitude. The longer the period of grinding, the lower is the resistance of quartz powder. When adding different modifiers into quartz during the period of grinding,

both the increase and the decrease of specific resistance of the material are observed. When treating quartz by alcohols, the increase of electrical resistance is observed, and when using acrylic acid and polystyrene, on the contrary, its decrease is observed (Table 3). In the first case, the observed changes in electrophysical properties may be related to the formation of a polymer dielectric film on the surface of the particle. In the latter case, as it was shown above according to the results of electron diffraction, the process of carbonization

proceeds most actively up to the formation of particles of reduced carbon on the surface of quartz.

Both electric and magnetic characteristics of mechanochemically treated quartz change with time, i.e. the material "ages" (Table 3). However, when using carbon saturated modifiers, such as polystyrene and acrylic acid, this process is slow. And the presence of reduced carbon built up in structure of the surface layer of modified quartz stabilizes both the conducting and magnetic properties of the material.

**Table 3**

The change of specific resistance and magnetic permeability of quartz powder depending on the time of ageing after grinding during 5 minutes with different modifiers.

Material	specific resistance, p. $10^6, \Omega \cdot m$		magnetic permeability, $\mu$ .	
	the time of ageing, $\tau_{st}$ , days		the time of ageing, $\tau_{st}$ , days	
	0	30	0	30
Quartz	1.1	6	2.0	2.0
Quartz + butanol (5 %)	6.0	15.0	4.0	3.2
Quartz + polystyrene (5%)	2.5	3.5	29.0	27.0
Quartz + acrylic acid (5%)	1.2	2.5	17.0	15.0

The greatest effect of mechanochemical modification of quartz by carbon containing compounds was obtained in the change of sorption properties of the material in the course of purification of water against contamination with organic compounds (phenol), sulphur and heavy metal (lead) ions. Table 4 shows the results on purification by modified quartz from different kinds of contamination. Synthesized material with carbonized surface provides purification of water from phenol up to 89%, from lead ions – 92%, from sulphur ions -80%. In each case, the greatest effective sorption ability is determined by a concrete modifier. The greatest effect was obtained on the material, when, during modification, apart from organic compounds, carbon was introduced additionally in the amount not more than 2-3%. Sorption ability of such material increased by 25-30% due to the formation of nanosites with excess concentration of carbon (carbon clusters) in the surface modified layer. Thus, heterogeneity of the surface of the modified quartz particle was enhanced. Taking into account the fact that in the surface layer of the particle there are ultradisperse

(of the size of about 10 – 15nm) particles of iron, galvanocouples (cathode - anode) are practically formed on the sites saturated with iron and cluster aggregates of carbon. The presence of numerous nanosized galvanocentres on the surface of a quartz particle may intensify the process of purification of water from different elements dissolved in it.

Thus, high sorption ability of the synthesized material may be presented as a result of formation of a heterogeneous structure of a nanosize scale in the surface layer of particles of a micron size. The obtained results on the structural investigations of modified quartz particles are in a good agreement with the experimental data reported in the work [17]. In different systems, including silicon containing ones, apart from point defects, there are always structural microdefects in the form of clusters – small aggregates of Si atoms and SiO<sub>2</sub> molecules and other adsorbed molecules, chemical groupings with local concentrations significantly exceeding average values on all the area. The mentioned nanosize heterogeneities markedly influence the electrophysical, chemical and other characteristics of thin-film structures.



**Table 4**  
The degree of purification of water from different kinds of contamination by quartz powder modified by different organic compounds.

Material	The degree of purification								
	Phenol			lead ions			sulphur ions		
	The time of mechanochemical treatment, min.								
	10	20	30	10	20	30	10	20	30
Quartz + AA*	67.0	66.0	47.0	89.0	85.0	91.5	77.0	45.7	65.0
Quartz + AA* +C	78.0	70.0	66.0	95.0	89.0	90.0	65.0	57.5	52.0
Quartz + PS*	72.0	86.0	88.0	94.0	70.8	74.4	52.0	49.9	70.0
Quartz + PS*+C	89.0	85.0	81.3	93.0	90.0	95.0	48.0	78.0	69.4

AA\* - acrylic acid, PS\* - polystyrene

## Conclusions

Thus, on the basis of the results of the carried out investigations it was stated that quartz undergoes significant changes after mechanochemical treatment in a centrifugal-planetary mill in the presence of different organic additives. The obtained powder material displays conducting and magnetic properties and sorption activity to different compounds. The observed transformation of properties was caused by the formations of new compounds in the surface layer of the particle. The results of electron-microscopic investigations of quartz particles modified by carbon containing compounds show the peculiarities of nanostructural changes in the surface depending on the kind of organic modifiers. In the surface layer we detected the presence of nanoparticles of metallic iron in the organic film capsulating the particle as well as the formation and growth of carbon tracery films and other nanosized carbon structures. The formation and growth of carbon films and tubes on the surface of quartz particle indicate the sequence of processes of structural transformation of modified quartz when being mechanochemically treated. The heterogeneous distribution of reduced carbon on the surface of the modified quartz particle, i.e. the formation of carbon complexes and simultaneous presence of iron particles, is the basis for presenting the modified surface as a set of galvanocouples determining the sorption activity of the synthesized material.

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