



Geo-nanomaterials

UDC 544.72: 538.9

ON THE PRIORITY OF SAINT-PETERSBURG MINING UNIVERSITY IN THE FIELD OF NANOTECHNOLOGY SCIENCE AND NANOMATERIALS

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Data are analyzed from dozens of scientific studies by professor P.P.Weimarn in 1910-1915 and reasoning by a whole number of well-known Russian experts which testify that the principal stipulations of the nanotechnological approach were conceptually formulated more than a hundred years back by the said Professor of the Mining Institute in Saint-Petersburg. It is for the first time that the interrelation is reviewed of the studies by P.P.Weimarn who stood at the cradle of nanotechnology with contemporary studies at the Saint-Petersburg Mining University. An upgraded temporal sequence is proposed (1910-2010) of forming nanotechnological knowledge that is associated with the names of scientists who made the most significant input into the process.

Reasons are discussed for the long years of oblivion suffered by the first publications on “dispersoidology”, composed in Russia at the Mining Institute, which are pioneering in nanotechnology and nanomaterials science. Information is provided on the priority designs of the last few years on synthesizing surface nanostructured dispersed metals performed at the Mining University.

Key words: scientific priority, nanotechnology, nanomaterials, P.P.Weimarn, dispersoidology, matter surface and dispersion, ultradispersed state

How to cite this article: Syrkov A.G. On the priority of Saint-Petersburg Mining University in the field of nanotechnology science and nanomaterials. *Zapiski Gornogo instituta*. 2016. Vol.221, p.730-736. DOI 10.18454/PMI.2016.5.730

Introduction. The issue of priority in nanotechnology science is currently quite discussable and does not have an unequivocal answer. Meanwhile the answer to that question is topical not only from the aspect of history of science and is interesting not only for scientists since it touches on the priority of specific scholars, universities and countries in building such a promising interdisciplinary field as “nanotechnology and nanomaterials”.

Quite a wide-spread opinion holds R.Feinman, a Physics Nobel Prize winner to be the Godfather of nanotechnology. Other outlooks of historical roots of nanotechnology are also known. For example, V.Yu.Kireev starts the genealogy of nanotechnology from Michael Faraday who had produced stable colloidal red color solutions of gold back in 1857 [11].

A number of authoritative domestic experts in nanotechnologies (V.A.Zhabrev, V.T.Kalinnikov, A.I.Nikolaev, V.I.Margolin, et al.) have come to the conclusion that “Pyotr Petrovich Weimarn (1879-1935), our compatriot should be considered the founding father of nanotechnology” [2, 13, 14, 23]. P.P.Weimarn had graduated from the Empress Catherine II Saint-Petersburg Mining Institute (1908) and had become a Professor at that Institute later.

The fact of priority in the range of nanotechnology per se by a scientist from the Mining Institute (no the Saint-Petersburg State Mining University) is interesting for at least two reasons. First of all, many, especially in the West, believe that the first cornerstones into the building of a new science – nanotechnology – were put by R.F.Feinman, the American physicist when he delivered his famous speech at Christmas dinner of the American Physical Society on the eve of 1960 [22]. Second, it is unusual that the priority of P.P.Weimarn who had worked 45-50 years earlier, was discovered by scientists whose activities are not related to the Mining University in any way. These scientists are working in other universities or academic institutes which are professionally dealing with and specialize in nanotechnologies. These facts are important from the point of view of objectivity of conclusion on the priority of Prof. Weimarn. However a counter question arises: why is it that the Mining University itself failed to insist on its own priority prior to publication by Zhabrev, Margolin, Kalinnikov et al. and did not employ that extra powerful information resource e.g. to found its own scientific school in nanotechnology or gain respective grants?

The task of this publication – consists in providing extra arguments in favor of P.P. Weimarn as one of the founders of the science of nanotechnologies analyzing (including a comparative chronology) his studies and their interlinks with contemporary studies conducted at the Mining University.

Study techniques: the analytical, historical, textual and comparative approaches.



Analysis results and their interpretation. From the point of view of theoretical physical concepts, the nano world was discovered about 90 years ago when our compatriot G.A.Gamov (1904-1968) derived a solution of the Schrodinger equation describing the tunnel effect. That solution explained many experimental data and served as a foundation for nuclear science and technology and the basis for building a scanning tunnel microscope (STM). However, results predicted by Gamov were only implemented in tunnel diodes (Yu.S.Tikhodeev) 30-50 years later, and the STM appeared in 50-60 years (Binnig and Rohrer) [2].

So what makes it possible to insist that it was Professor P.P.Weimarn who stood at the spring of nanotechnological science? The authors proving the priority of Weimarn on the basis of analysis of some of his works start from the statement that it was particularly him who had put together the fundamental elements of nanotechnology and turned it into a science [2, 13, 14, 23]. Then all the competition who managed to obtain samples of substances containing nanoparticles, as it was found quite later, or developed techniques enabling one to assess the size of such particles fall off automatically. It makes sense, because



Pyotr Petrovich Weimarn
(1879-1935)

we would have hit a dead end accounting for such competition. The point is that mankind has been using nanoparticles for a very long time at the level of craftsmanship (oftentimes intuitively). Recall the Egyptian blue ink (ink containing colloidal particles of calcium silicate), the Lycurgus Cup (nanoparticles of gold and silver in a glass matrix), the secret of Bulat steel, etc. [23].

So what did Weimarn do? He postulated on the basis of his own experiments and theoretical ideas that between the world of molecules and the world of microscopically visible particles there lies a specific form of substance with a complex of physical and chemical properties specific to it: the ultra-dispersed or colloidal state formed when that dispersity is within 10 mcm – 1 nm size, films still having certain thickness and particles ranging from 1 to 100 nm crosssection [3, 7-10]. Weimarn believed it necessary too to abandon the term “colloid” and substitute it with the concept of “dispersoid”, renaming colloid chemistry dispersoidology, a “science of surface properties and processes taking place on them” [3-5, 7, 9].

Note that he wrote about these and many other issues that retain their topicality even now in his studies dated between 1910 and 1915. He was already a professor of the Mining Institute then heading the laboratory of physical chemistry. Insisting that certain special conditions may be produced for any substance to bring it into a highly dispersed quite stable state, Weimarn refers to experiments with a couple of hundred various systems [3].

We find from studies by Weimarn that he cooperated with well-known scientists from German universities, edited books translated into Russian, such as a monograph by Wolfgang Ostwald [15]. Beside that he referred quite actively on the then fresh studies by well-known scientists: W.Nernst, W.Biltz, H.Steigmuller and others. Weimarn was never afraid to start discussions with generally recognized authorities [3-5]. Indeed, in his study on counteractive and expansive energy he criticized the opinions of N.S.Kournakov on separating chemical compounds into Bertollides and Daltonides [5].

The scope of issues touched upon by Weimarn is really impressive. Not only did he divine the appearance of new fields of natural science (the science of nanotechnology being one of them), but also pointed to relationships between his own results and the theory of atoms and molecules and the periodic law by Mendeleev [4]. It is no wonder that W.Ostwald, a Nobel Prize winner in chemistry called Professor P.P.Weimarn a genius scientist, while the Austrian mineralogist Felix Corn a called one of the first colloid minerals discovered “Weimarnite” [23]. Studies by Weimarn had a global recognition when he was 36.

In the opinion of V.I.Margolin, V.A.Zhabrev and their co-authors, Pyotr Petrovich Weimarn formulated conceptually all the principal modern stipulations of the nanotechnological approach [2, 23], having done that many decades ahead of his Western colleagues. In one looks up the text of Feiman lecture “There is plenty of room at the bottom: an invitation to enter a new field of physics” [22], one would hardly find any basics of some conceptual approach there. Feiman only suggested to pay more attention to the poorly studied area of physics related to controlling the structure of matter within the range of very small dimensions. He suggested producing super-miniature devices that would be the ana-



logs of the then available micro-mechanisms, of the type of “tiny robots”, and then build as small tools as possible, etc. That may hardly be called a prediction of the advance of new science and a new scientific paradigm [23]. To pay him due tribute, studies [2, 23] also analyze strong aspects of the speech and workable predictions by Feinman. What is undisputable, in the opinion of the authors of those studies, is the priority of the very term “nanotechnology” which was introduced into scientific practice by Norio Taniguchi, a Japanese scientist in 1974.

Accounting for all these facts and opinions [23] the author of the current paper suggests and updated chronology of the greatest achievements in nanotechnological science, relating it to the names of scientists that have worked within the last hundred of years:

***P.Weimarn → G.Gamov → I.lengmur → V.Aleskovskiy → R.Feinman →
K.Dreksler, T.Syntola → Zh.Alferov → G.Binnig, G.Rorer →
A.Geim, K.Novoselov → ...***

Such a scheme (with a dotted space instead of the name Gamov) was first presented by the current author in his report to the Plenary Session of the International Symposium “Nanophysics and Nanomaterials” (N&N-2015) on November, 24, 2015, where it was welcomed by the Symposium participants, including Professor V.I.Margolin.

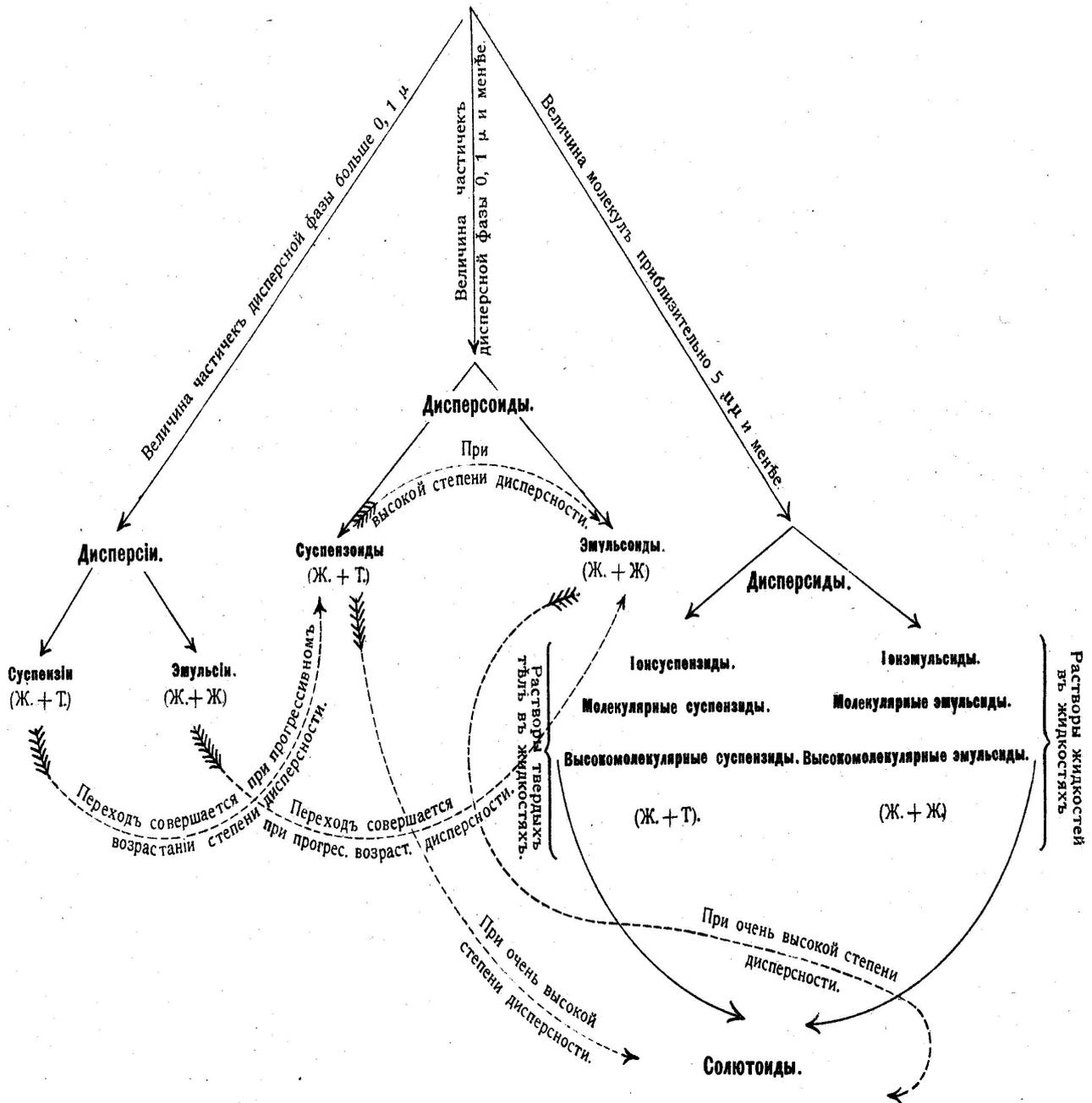
Now let us return to the personality of the fonder of nanotechnology science – Pyotr Petrovich Weimarn who was practically forgotten for many a long years, till 2012, in his own Motherland, first of all. Why did it happen that way? Pyotr Petrovich was far from an ordinary person. A nobleman, from the kin of ancient Vikings, a State Counselor. Following the family tradition he graduated from the cadet corps, and then entered the Petersburg Mining Institute, which he graduated from in 1908 summa cum laude.

All of the first half of his life was closely related to that Institute where he became a Professor and opened new areas in science. In the course of the next few years he was awarded a number of prestigious prizes by: the Russian Physical-Chemical Society, The Emperor’s Academy of Science, the Emperor’s Moscow university - twice and the Mining Institute. P.P.Weimarn was a winner of the Academician N.A.Beketov, V.I.Shchukin, Privy Councillor N.M.Akhmatov prizes, was awarded the Order of Saint Anna, III degree. Beside working at the Mining Institute, Pyotr Petrovich was lecturing a course of dispersoidology at the Emperor’s Saint-Petersburg University, and that is where he presented his famous lecture “The value of colloidal chemistry for various branches of natural science” (1910) (see Figure) [3].

In the autumn of 1915 he moved over to Yekaterinburg where he became the first Rector (1917-1920) of the Urals Mining Institute. In 1920 Weimarn went to Vladivostok together with his co-workers to become the Rector of the Vladivostok Polytechnical Institute (1920-1922). Then P.P.Weimarn emigrated to Japan together with his family, where he was lecturing through 1922-1931 in his position of a Professor of the Imperial Industrial Institute in Osaka, and since 1931 became a co-worker of a private laboratory in Kobe (Japan). P.P.Weimarn died in Shanghai on June 2, 1935 and is buried in Kobe. The grave of Professor Weimarn is still the place of homage and veneration [2, 14, 23].

So why is it that such a valuable input by Weimarn, a professor of the Mining Institute has not found its proper recognition? P.P.Weimarn, a representative of higher nobility, did not fit in the ideological settings of the Soviet times, to put it mildly. Besides, he emigrated, fleeing the onslaught of the Red Army, and kept working in a capitalist country that was not one of the best friends of Soviet Russia. Apparently, that was enough to forget and never mention the input of Weimarn into domestic science for many a year. In our opinion the following circumstances had combined in a way far from favorable. It was not only that recalling him was simply unsafe personally between 1922 and 1991. Researchers who used to know P.P.Weimarn and worked with him have passed away. Meanwhile those who had access to his works and publications (bibliographers, historians, chemists – more rarely), were possibly incapable to ascertain the nanotechnological aspect of studies by Weimarn, their scientific potential and perspectives. His works (and the same goes for the first works by R.Feinman) lack the term “nano-” and even more so the terms we are used to now: “nanotechnology”, “nanosystems”, etc. To offer an example, in his works P.P.Weimarn is writing about the processes “during progressive growth of dispersiveness” and about the uncommon behavior of the particles of the dispersed phase when they do not exceed the size of 0.1 micron (to denote 1 mcm he uses the Greek “mu”) [3] (see Figure). That information would hardly be understandable and interpretable in the nanotechnological clue for a non-expert, even the one in command of the basics of classical physical and colloidal chemistry.

Дисперсные системы.



Scheme of classification of dispersed systems according to the lecture presented by P.P.Weimarn at the StP University [3]

Besides, one should keep in mind that nanotechnology is a young branch of science and its terms and concepts are still in the process of forming. Therefore, only a few high class professionals in nanotechnology have managed to discover the priority of our compatriot in that area, already into the XXI century. The following facts testify to qualifications of these experts, references to their studies to be found by the end of this paper. They are all professors, doctors of science. V.I. Margolin is one of the authors of the national doctrine for developing nanotechnology in the RF[12], member of the Section "Surface chemistry and synthesis of nanoparticles" of the Scientific Council of the Russian Academy of Science on Inorganic Chemistry, member of Scientific Council on Material Science Issues under the Presidium of the StP Sci.Center RAS on "Construction materials and nanotechnologies". Among the authors that have written the books [13, 23] that record the priority of P.P.Weimarn are also three Academicians (N.T.Kuznetsov, V.M.Novotorcev, V.T.Kalinnikov) and two Correspondent members of RAS (V.A.Zhabrev, A.I.Nikolaev).



Works by P.P.Weimarn have met support and recognition during 1910-1915, as we have seen already. His works were readily published by both the leading foreign and national magazines: *Kolloid-Zeitschrift* (Germany) [30-32], the Magazine of the Russian Physico-Chemical Society (MRPCS) [4], Proceedings of the Mining Institute (PMI) [6, 8-10]. During 1908 to 1913 PMI had more than 20 publications by P.P.Weimarn, 17 of them directly related to the development of dispersoidology.

One cannot miss commenting on the exceptionally fruitful scientific environment around Weimarn. He had a possibility to interact with leaders in science of the times, not only with N.S.Kournakov, with whom he conducted joint studies (1902) and had joint publications. At approximately the same time (before 1914) A.F.Ioffe, the future famous Academician, founder of the Physico-Technical Institute was working as an Assistant Professor at the Chair of Physics of the Mining Institute. Just a little earlier than that R.E.Lenz Jr. used to work at the Chair of Physics, a Corr.-Member of the StP Academy of Science, who was one of the first to measure magnetic properties of highly dispersed iron. It would be unfair to miss studies by P.K.Sobolevsky and V.V.Lyubarsky done at the Mining Institute, which had essentially put down the foundations of the national powder metallurgy. They have made considerable input to studying dispersed metals; P.P.Weimarn was sure to know about their studies.

Despite the vexing lapse in time, nanotechnological studies are currently under way at the Mining University; they have become especially intense since the year 2000 [17-19]. Following the Resolution by the Government of the RF, N 498 of 02.08.2007, a Nanotechnology Scientific and Educational Center is functioning at the University since 2008. It belongs to the National Nanotechnology Network of Russia. Since 2003 a scientific workshop on "Nanophysics and nanomaterials" is functioning and since 2013 it has the status of an International Symposium [17, 19]. During the last 7-8 years five Doctoral works and dozens of PhD theses have been defended here.

Successful work is under way on state tasks and contracts to study systems of low dimensionality [16, 21, 24, 25, 28]. Certain designs have been successfully implemented at enterprised of Russia and Belarus, more than 20 medals have been won at different international Hi-Tech exhibitions and congresses [17, 19]. Saint-Petersburg Mining University that is carrying on the traditions of Mining Institute has undertaken a number of pilot nanotechnological studies that have resulted in developing new techniques for producing nanomaterials: layering of molecules of quadratic ammonia compounds of different dimensionality on metals [16, 18, 21, 26, 28, 29] and solid body hydride synthesis of surface nanostructured metals [18, 20, 24]. The priority of these inventions is protected by RF patents (NN 2425910, 2570599, etc.) Besides, original scientific directions are pursued: the effect of reductant on the structure and reactivity of dispersed metals [16, 18, 24] and non-linearity of properties of surface modified metals [20, 21, 26, 28].

Three professors of Mining University belong to the Editing Board of the international scientific magazine *Smart Nanocomposites* (New York, USA, Nova Science Publishers, Inc.). One of these professors, specializing in nanotechnologies himself, is a member of the editing board of the references scientific magazine "Proceedings of the Mining Institute" published by the Saint-Petersburg Mining University. The Chief Editor of *Smart Nanocomposites* magazine is K.L.Levine, an Assistant Professor of the Chair of General and Technical Physics of the Mining University.

The direction related to the activity of the leading Russian scientific school built by V.B.Aleskovsky (1912-2006), Corr.-Member of RAS (USSR Ac.Sci.) is making a lot of progress [16, 18, 21, 24-26, 28]. In his works Aleskovsky often referred to studies by N.R.Kournakov who used to work at the Mining Institute. Inquiring into the studies and reports by P.P.Weimarn points to their certain commonality with studies by V.B.Aleskovsky, whose disciples and inheritors are now working at the Mining University. In particular, Aleskovsky, same as his predecessor, kept operating the concept of dispersity D ($D = S/V$, where S is the area of the surface and V is the volume of substance) quite often, searching for the relationships between the properties of different compounds with the level of their dispersity [1]. All that brings one to a suggestion that (especially since both schools of Weimarn and Aleskovsky got recognized independent of each other [2, 13, 14, 20, 23, 27]), that modern studies are developing the scientific school of Weimarn-Aleskovsky within the walls of the Mining University.

One may hardly underestimate the value of studies by P.P.Weimarn for nanotechnology from the point of view of historical priority, not only for the Mining University but for all the Russian science in general. The scope of personality of that scientist and his creative heritage is still to be ascertained. It is difficult to imagine today how a mining engineer by education could have such a deep creative un-



derstanding of issues of physical and colloid chemistry, theoretical and methodological issues of natural science in general.

To our mind, P.P.Weimarn and his scientific achievements are quite worthy examples for studying within the scope of modern mining education. During the sessions of the N&N-2015 International Symposium that was held at the Mining University not only the contents and value of studies by P.P.Weimarn were discussed, but possible ways and means of immortalizing his memory. Of course, a scientist of that level and scope is worth having his name inscribed on a memorial plaque on the facade of the main building of the Mining University. Among the other ways to commemorate the name of P.P.Weimarn it was suggested during the Symposium to: publish again his selected scientific works; start a 'Professor P.P.Weimarn' memorial laboratory on the basis of the already existing laboratory of experimental physics and nanotechnologies [19].

We are all very much in debt of Pyotr Petrovich Weimarn, the founding father of nanotechnologies. And the first steps in preserving the memory of that outstanding scientist who glorified the Russian science while working at the Mining Institute more than a hundred years back, shall surely be taken by the Saint-Petersburg Mining University.

Principal conclusions. Thus, basing on the opinion by a number of authoritative experts on low dimensionality systems, the analysis of the respective publications, one may state the following. The fundamental basics of nanotechnology were formulated by Pyotr Petrovich Weimarn, Professor of the Mining Institute, Saint-Petersburg more than a hundred years ago (1910-1915). In contrast to R.Feiman (USA), he did not limit himself with predictions of unusual properties of super-small particles and super-miniature devices. It was particularly P.P.Weimarn (Russia) who formulated the principal conceptual stipulations of nanotechnological approach 45 years earlier than his Western colleagues, those that he had successfully applied himself to generate ultra-dispersed particles, their dimension fitting the nanometer range. In the course of his studies Weimarn arrived at a number of exceptionally important conclusions, valid not only for any specific parts of physics, chemistry, biology, mineralogy, but have philosophical meaning and are actual from the point of view of methodology of modern science. Among such conclusions are P.P.Weimarn's statements in dispersoidology that:

- crystal state - he only internal state of the matter [6];
- there is no boundary between the two types of matter: crystalloids and colloids [3, 8];
- the colloid state of matter may be treated as a common state of matter; under certain conditions identified by Weimarn, any substance, independent of its regular aggregate state may be transformed into its ultra-dispersed colloid state, particles ranging within 1-100 nm [3, 10].

Studies and views of P.P.Weimarn have gained development and confirmation in modern studies, especially with respect to metals, now conducted at at the Saint-Petersburg Mining University.

Acknowledgement: to Professor V.I.Margolin who approved the author's ideas and Professor I.G.Rebeshchenkova for her valuable comments and suggestions in the course of reviewing this paper materials.

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The paper was accepted for publication on 29 June, 2016.