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DETERMINATION AND ANALYSIS OF CRITERION COMPONENTS OF THE ENVIRONMENTAL SAFETY ASSESSMENT OF ENGINEERED NANOMATERIALS

The specific properties of nanotechnologies open up broad prospects for the purposeful production of nanomaterials with enhanced properties. However, along with this, very few studies have been conducted to identify the negative environmental impact of nanomaterials on the environment and the human body. In the production of engineering nanomaterials, their operation (due to abrasion and wear), as well as during utilization (processing) or placement in waste storage areas, it is possible to release nanoparticles into the atmospheric air and groundwater. The developed criterion of ecological safety of engineering nanomaterials is presented. The components of this criterion are defined. The components of the criterion are particular criteria that assess the safety of a material by the presence of nanophases in it, proximity to a person, the possibility of exposure and potential danger. The characteristics of engineering nanomaterials that determine the impact on the state of the environment and human health are established and should be controlled. These include morphological, physico-chemical and molecular-biological. An algorithm for determining the hazard level of products, which can contain nanoobjects, and an algorithm for carrying out environmental impact assessment according to the proposed scale is presented. The scale of the degree of potential hazard of engineering nanomaterials contains three levels: high, medium and low. Such a scale is universal and allows assessing the dangers of nanomaterials and substances that can contain nanoparticles. The complex of measures for the evaluation and analysis of nanomaterials that need to be carried out to ensure environmental safety when using nanomaterials of different levels of danger is analyzed. Classification of nanoindustry products by the degree of potential danger to public health and habitat will minimize the negative impact of engineering nanomaterials on the environment and increase the level of environmental safety and rational nature management.

Keywords: engineered nanomaterials; nanoparticle; environmental safety; criteria of assessment; state of environment.

1. Problem statement.

Today nanotechnologies (NT) are developing at a rapid rate all over the world. The nanoparticles and nanomaterials possess a complex of physical, chemical properties and a biological effect, which are often drastically different from the properties of the same substance in monocrystalline phases.

Specific properties of nanomaterials could include:

- a high potential for accumulation;
- a growth of the capabilities of chemical substances and consequently to change a dissolubility, a catalytic ability and a reactivity.
- a large specific surface of the nanomaterials than leads to an increase in the value of the adsorption capacity of materials;
- increase in production of free radicals and active forms of oxygen on surface;
- a very-small size and variety forms of nanoparticles;
- a highly-developed surface of nanomaterial causes a high adsorption activity.

The engineered nanomaterials, which have predetermined properties and which have been designed and created specially by engineers, are the most interesting for researchers [1].

There has been an increase in number of comments concerning the implications of using NT and with it there is a wide interest in the introduction of nanotechnology to the real sector of production [2]. Most of the discussions focused on technogenic

environmental aspects of using the production of the nanotechnology industry [2, 4]. Research shows that people have the low level of knowledge about NT [2]. Accordingly, the way which information was presented at an early stage of civic consciousness of NT, likely to have a critical value for the public to react to innovations and the widespread adoption of the nanotechnology industry in the industrial sector. In order to overcome these contradictions it is necessary to conduct research to identify the nanoparticles in the material, to develop a technology and criteria on the classification of nanotechnological hazards and the publication of this information for the nanotechnology production consumers.

2. Analysis of the recent researches and publications.

The distinctive properties of NT offer broad prospects for goal-seeking behavior production of the nanomaterials with advanced characteristics, in particular:

- a unique mechanical strength [5];
- specific spectral and electric parameters [6];
- improved magnetic, chemical and biological properties [7].

That shows that the nanomaterials have another physicochemical properties and biological effect in comparison with conventional equivalents. The nanomaterials should be considered as a new group of materials. Researchers have noted that potential risks profile of nanomaterials for human life and health is important and it should include new methods, which have not used for

conventional substances yet [8, 9]. It is reported in the work [10] that the nanomaterials could become threats not only during synthesis, but even during utilization. Thus, studies are needed for reveal the nanoparticles in manufactured products. A control card for the nanomaterials and materials that can contain nanoparticles is proposed to use in the work [11]. The authors of the work [12] suggest integrated system of the rating for the thermal decomposition of carbon nanotubes at high temperatures. However, there are [13] the authors note that standard methods cannot be applied to the measurement of toxic properties of the nanomaterials.

Today, the environmental performance of the great majority of the nanomaterials is either non-existent or presented by the limited number of texts [14, 15]. In addition, the methodology and results of these tests are often mutually incommensurable or even contradictory [16, 17]. Meanwhile, the environmental characteristics of nanomaterials should be based on a large number of researches in vitro i in vivo [18, 19]. The researches claim that number of the manufactured nanomaterials is increasing every year [20, 21]. This points to practical impossibility of characterizing by safe use of nanomaterials in industry in the near future.

3. Statement of the problem and its solution.

The purpose of the study is to identify and analysis of components of the environmental safety criteria of engineered nanomaterials.

The following tasks have been assigned and solved to achieve the aim:

- to identify features of engineered nanomaterials

that condition an influence on the state of environment and human health and should be under control;

- to identify the components of the criterion of environmental safety assessment of engineered nanomaterials and analysis them.

3.1. The determination the properties of engineered nanomaterials that condition an influence on the state of environment and human health and should be under control.

In assessing the impact of the engineered nanomaterials on state of environment, the complete life cycle of the engineered nanomaterials need to be considered. The complete life cycle of the engineered nanomaterials includes next stages: the extraction of raw materials for the nanomaterials, synthesis of nanomaterials, storing and packing, the manufacture of products from nanomaterials, the maintenance and utilization [11].

In the manufacture engineered nanomaterials, theirs maintenance (in consideration of abrasion and chafing) and also the utilization (waste treatment) or placement in places for storing wastes, it is possible to ingress the nanoparticles in the atmosphere air and waste water. This leads to uncontrolled ecological effect by the nanomaterials on the environment and human body.

It is therefore imperative to understand the nanomaterials' characteristics, wich can be dangerous. Conventionally all important characteristics of nanomaterials in view of environmental impacts can be classify as morphological, physicochemical and molecular biological (figure 1).

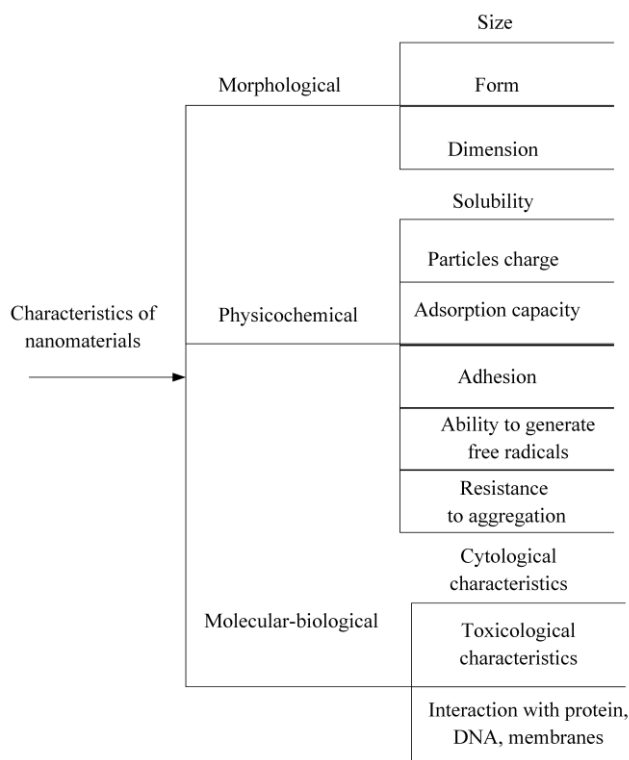


Figure 1 – The characteristics of the nanomaterials that should have been researched for identify the degree of potential hazard

According to a figure 1 size, form and dimension of the nanoparticles should be classified as morphological features. According to the International Union of Pure and Applied Chemistry (IUPAC) a microstructures are objects, which size is not exceed 2 nm; mesostructures – sizes are from 2nm to 200nm; macrostructures – more than 20 nm [22]. The size is a significant characteristic, since with the decrease of the particles size by the same mass concentration of material in per unit of volume, the number of particles increases. Thereby, the risk of harmful effect by particles on living organism increases. This happens because the main mechanisms that damage living organism by the nanoparticles are connected with the processes, which occurs on the interface. In addition, too small the nanoparticles can penetrate into the organism not only through respiratory and digestive apparatus but also through the skin. The smaller the nanoparticles are, the more difficult they are in detection and capture in water and atmosphere. It is also conditioned the additional environmental risks of use the nanoparticles.

The form of the nanoparticle we describe by quantity, which is called shape factor:

$$F = \frac{4\pi S_p}{p^2}, \quad (1)$$

where S_p is the sectional area of the nanoparticle; p – the cross-section perimeter.

The value of shape factor $F_{form} = 1$ indicates that the section is the perfect circle. The closer the value of roundedness to 0, the more oblong or deformed section will be. The nanofibres and nanowires (the particles with high value of the form factor) have a greater capacity for joining to the somatic tissues. This increases the contact time between the particle and the tissue, and also raises a probability of particle's toxic action.

There is an agreement to determine nano-objects that the dimensions of this object at least in one of the spatial directions should be in the range of 0.1...100 nm. Such objects are called low-dimensional. The low-dimensional objects fall into: one-dimensional; two-dimensional; three-dimensional. According to this classification, zero-dimensional (nanoparticles, quantum dots) and one-dimensional (nanofibres, nanowires) nano-objects will be the most dangerous ones, as the risk of the exposure by such nano-objects is the highest. The penetration of the two-dimensional (nanofilm) and three-dimensional objects (photonic crystals, porous layers) to organism has much lower chances.

The solubility of nanomaterials in water and biological fluids should be considered among the basic physicochemical characteristics that determine potential hazard. The solubility is a highly significant factor that defines the toxicity of materials. It can be ranked as:

- insoluble;
- slightly soluble;
- soluble.

When the nanoparticles, formed by water soluble substances, enter the aquatic environment, they dissociate into ionic or molecular solutions. After it, their toxic properties are determined only by chemical composition of their components. In other words, soluble nanoparticles, as a rule, do not differ in their toxicological properties from their chemical analogues of traditional dispersion. On the contrary, the particles of water-insoluble substances can remain in a free state for a long time in the biological environment, causing biological effects that can be determined by their surface characteristics.

Particles charge is a highly significant factor. Positive charged particles that have a high affinity to DNA macromolecules are the most dangerous. Negatively charged particles do not possess such properties, but they are characterized by increased capability to penetrate through tissue barriers. The least harmful biological effects should be expected from neutral nanoparticles.

Adsorption capacity determines the probability of transportation (transference) foreign impurities on nanoparticles. This indicator is defines as high or low adsorption capacity. The value of the adsorption capacity may be in increase the probability of transportation (transference) foreign impurities of toxicants on the nanoparticles from the environment to the internal environment.

Resistance to aggregation is a factor affecting the toxicity of nanoparticles. The toxicity of the nanoparticles is reduced, as a result of adhesion of aggregation-unstable nanoparticles.

Adhesion of nanoparticles to the surface can increase their penetration through tissue barriers, their tearing from the surface of nanomaterial and spread in the air.

One of the important factors determining the danger of nanomaterials is their ability to generate free radicals. The major part of the damaging actions of nanomaterials is mediated by mechanisms of free-radical peroxidation, initiated by reactive forms of oxygen formed on the surface of the nanoparticles in the processes of heterogeneous chemical catalysis.

Therefore, the detection of catalytic properties of nanoparticles is very important for defining their potential hazard.

Capacity of nanomaterials to interact is an important molecular-biological characteristic. In particular, the interaction with DNA is the most significant feature, as it determines the possible manifestation of genotoxic and mutagenic properties of the nanomaterials. The interaction with cell membranes could be a factor accelerating the penetration of the nanoparticles into a cell. The interaction with proteins could be the cause of a change under the action of the nanoparticles of enzymatic activity.

In assessing the potential danger of the nanoparticles and the nanomaterials it is necessary to take into account cytological characteristics, notably: the ability of the nanomaterials to cause malignant transformation of cells; cytotoxicity that is, the ability of the nanomaterials to cause the death of cells and so on.

Signs of toxicity (acute, chronic), increased permeability of the organism's barriers for toxicants and

penetration of the nanomaterials through the barriers of the organism should be included to the toxicological characteristics. This leads to the direct exposure of organisms by the nanomaterials.

The above characteristics of the nanomaterials determine their impact on the environment and living organisms. The value of these characteristics can be obtained from the manufacturer and/or available sources of information, such as data on experimental studies, statistical data, etc.

3.2. Determination of criterion components of the environmental safety assessment of engineered nanomaterials and their analysis.

By the degree of the nanomaterials potential danger, we establish a criterion for the potential danger of nanomaterial K. This includes the partial criteria:

$$K = f(K_1, K_2, K_3, K_4), \quad (2)$$

where K_1 – a criterion for the presence of nanophase in the material; K_2 – a criterion for the possibility of exposure products consumer by nano-objects; K_3 – a criterion for proximity of products to a person; K_4 – a criterion of potential danger.

The convolution of partial criteria will be carried out according to the multiplicative law, which is based on the principle of just satisfaction of relative changes in partial criteria:

$$K = K_1K_2K_3K_4. \quad (3)$$

We define the value for each of the partial criteria (table 1).

Table 1 – The value of partial criteria for determining the generalized criterion of the potential danger of nanomaterial

Criterion	Significance	Under what conditions this value is acquired
K_1	$K_1 = 0$	There is no the nanophase in the material
	$K_1 = 0.5$	It is impossible to determine the presence of the nanophase in the material or there are no appropriate data
	$K_1 = 1$	There is the nanophase in the material
K_2	$K_2 = 0$	The exposure of products consumers by nano-objects is impossible
	$K_2 = 0.5$	It is impossible to determine the possibility of exposure consumers of products by nanobjects or there are no appropriate data
	$K_2 = 1$	The exposure of products consumers by nanoobjects is possible
K_3	$K_3 = 0$	It is impossible for a person to contact with products containing nano-objects
	$K_3 = 0.5$	The products containing nano-objects contact with a person indirectly
	$K_3 = 1$	The products containing nano-objects are in contact with a person
K_4	$K_4 = 0$	Low level of nanoproducts hazard
	$K_4 = 0.5$	Medium level of nanoproducts hazard
	$K_4 = 1$	High level of nanoproducts hazard

A generalized criterion will always fall within the range of values, for such values of partial criteria and subject to the application of the multiplicative convolution of the criteria:

$$K \in [0, 1].$$

An algorithm for evaluating nanomaterials, as well as materials that can contain nanoparticles, is given in figure 2.

According to figure 2, at the first stage, it is necessary to determine whether the product contains nano-objects. Definition must be made on the basis of:

- a material passport or other technical documentation provided by the manufacturer of the product;
- authoritative literary sources that containing information about the properties of the material (patents, articles in authoritative publications, reference books, etc.);
- own data that are derived with using methods of assessing the safety of nanomaterials approved in accordance with the established procedure.

If it is founded that nano-objects are present in the material, or no data are available, further evaluation is

required. In the presence of reliable information on the absence of nanoparticles or nanophase in the material, it is concluded that no further evaluation is necessary.

At the second stage it is necessary to determine the possibility of exposure consumer products by nano-objects that are contained or may be contained in the material. These data are collected on the basis of information provided by the manufacturer or during an expert evaluation. In so doing, the nature of normal application conditions, as well as the structural characteristics of the material, should be considered.

The next is to make the assessment of the proximity of products to humans. It is estimated that the product does not contact a person if it is a technical device that operates autonomously in a desert zone (space, drilling, deep water equipment and engineering). Indirect contact is the contact that may occur due to the presence of the nanomaterials in food, pharmaceutical, water-purifying equipment, electronic equipment products, etc. Product contacts with the consumer if it can be attributed to textiles, packaging materials, food products, hygiene products, household chemicals, cosmetic products, drugs, etc.

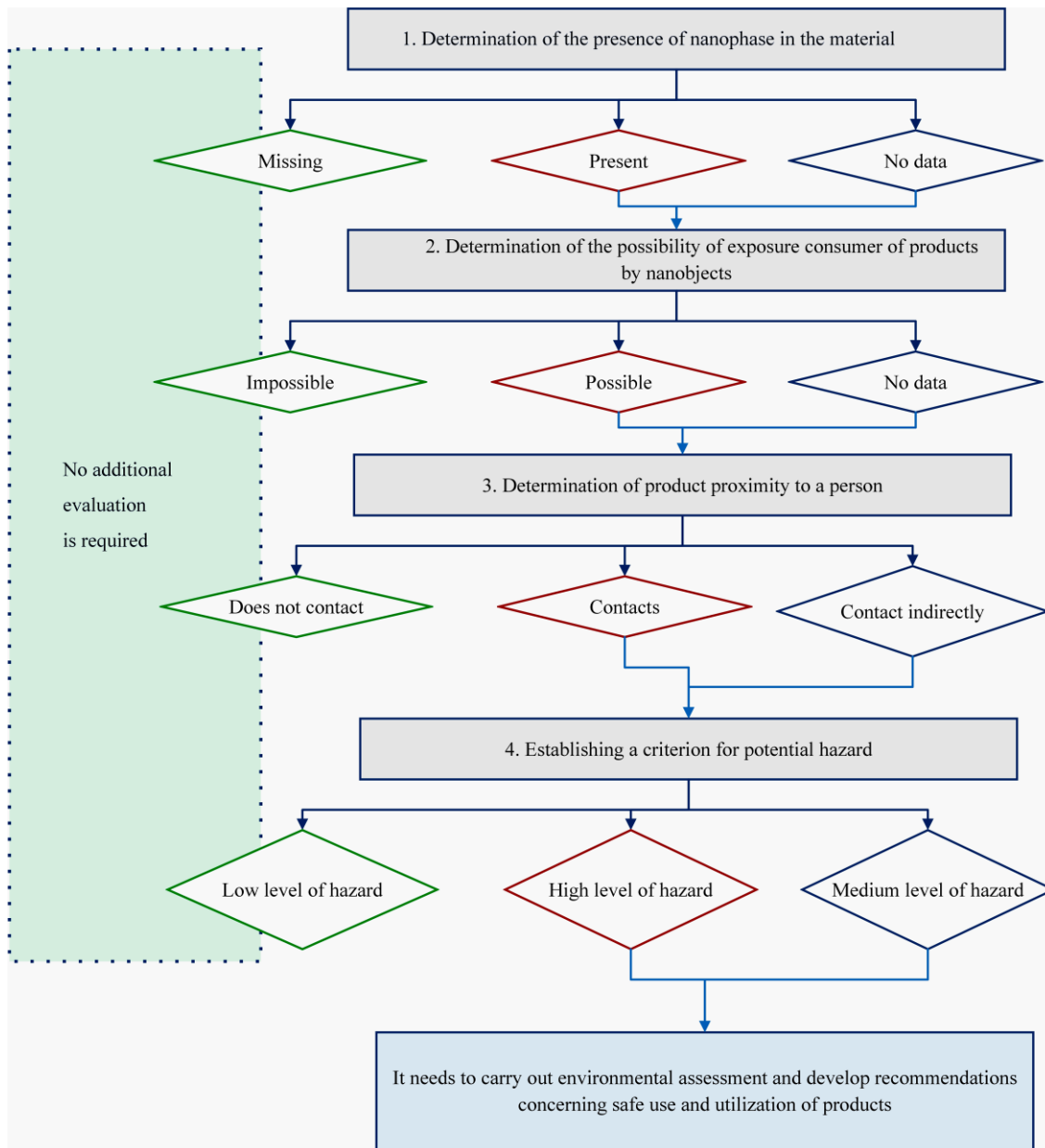


Figure 2 – The algorithm for determining the level of hazard of product that can contain nanobjects and establish the need for environmental expertise

In addition, taking into account the discreteness of the values of partial criteria, it is easy to see that a generalized criterion can acquire only six values that will determine the degree of the potential hazard of nanomaterial (table 2).

Table 2 – The significance of a generalized criterion for the nanomaterial potential hazard

Value K	Degree of potential danger of nanomaterial
0	low
0.0625	
0.125	medium
0.25	
0.5	high
1	

The proposed method for the classification of the nanomaterials and substances which containing nanoparticles according by degree of the potential hazard is rather simplified. However, this simplification makes it possible to determine the need for further evaluation and studies of the nanomaterials. It is versatile and suitable for the nanomaterials and for substances that can contain the nanoparticles.

3.3. Necessary measures for management of hazardous engineered nanomaterials.

On the basis of the above developed the criterion it is possible to conduct a ranking of the engineered nanomaterials by degree of danger: for objects with a low degree of danger, it is expedient to conduct only certain crucial tests; for the nanoparticles that are characterized by a medium degree of danger, the scope

of planned studies should be substantially extended; for the nanomaterials with a high degree of potential danger, toxicological and hygienic behavior should be implemented in full (figure 3).

The classification of nanoindustrial products for the degree of potential health hazard of the population and the environment, including at the stage of consideration of nanotechnological production projects, should be carried out with the aim:

- the identification of products that use the potential danger nanomaterials for human life and health in the technological process as well as the possibility of causing damage to human health in the manufacture, circulation, use (employment) and utilization of this product;
- the definition of industries that use the potentially hazardous nanomaterials in the process of production

and, as a result, damage: the health of workers in these enterprises, the population, including those living in the surrounding areas, the environment;

- the development of a set of measures aimed at ensuring the safety of the products of the nanoindustry for the consumer (in particular, the replacement of more dangerous nanosized components by less dangerous ones, marking caution notices on the product during labeling and packaging, measures to prevent the improper use and utilization of the products of the nanotechnology industry, etc.);
- minimizing the risks associated with the application of the nanotechnologies and the nanomaterials in production processes through the development and implementation of a set of measures to ensure the safe working conditions and to prevent pollution of the environment.

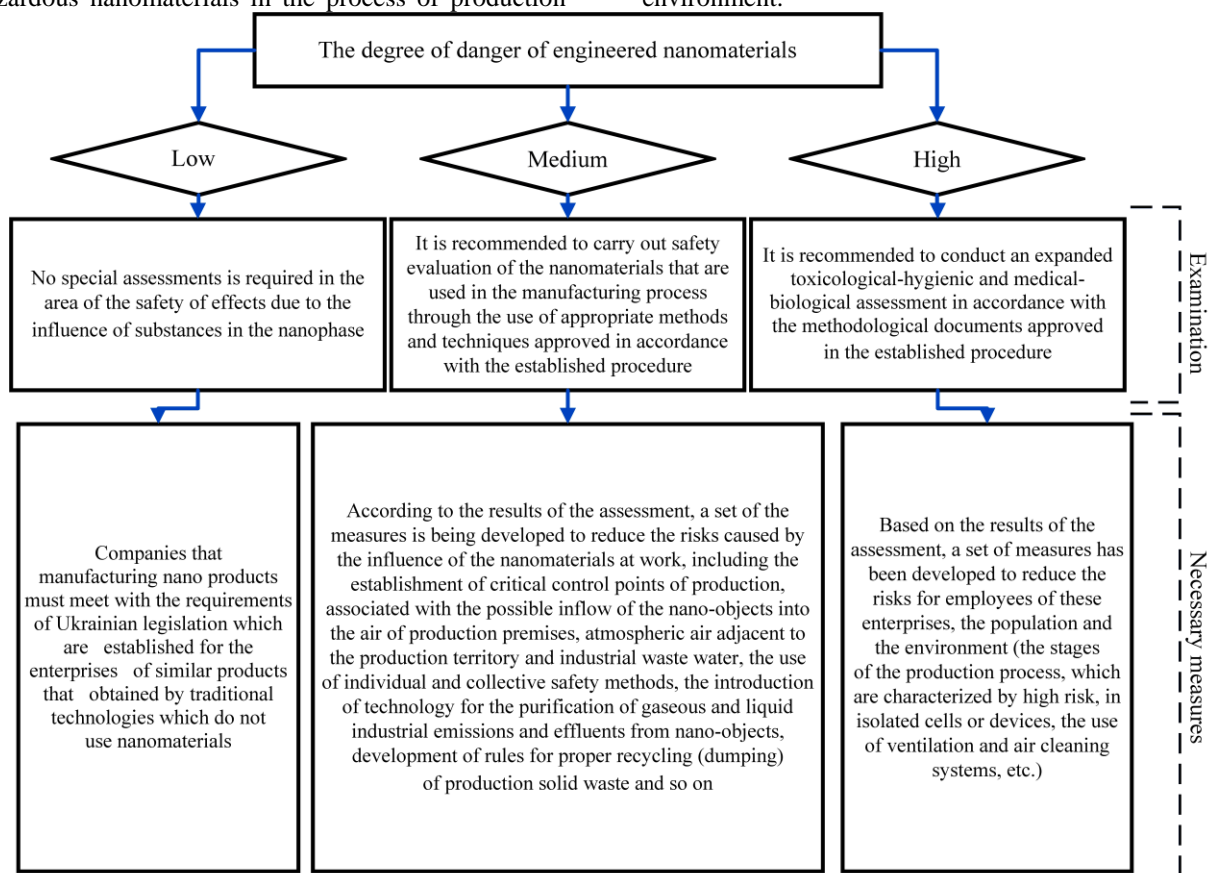


Figure 3 – Measures to be taken in establishing the hazards of products that containing nanoparticles and nanomaterials

The result of the classification of nanotechnology products by the degree of potential danger is the ascription of production to products with a low, medium or high degree of potential hazard for its consumer. This would help to minimize the negative impact of the engineered nanomaterials on the environment and increase the level of environmental safety and rational nature management.

Conclusion.

1. As a result of the study, the algorithm for evaluating nanomaterials that contain nano-objects according to the degree of potential danger and the need for environmental expertise was developed. This

algorithm contains a gradual definition of partial criteria for potential dangers of nanomaterial.

2. The morphological, physicochemical, and molecular biological characteristics are included to the characteristics of nanomaterials that must be subjected to environmental expertise. The determination of these criteria should be based on available data contained in the product's passport, according to authoritative sources or in the course of an expert evaluation.

3. The assessment technique and classification of nanomaterials and substances containing nanoparticles is developed and consists in determining a criterion of potential danger of nanomaterial. This criterion is a multiplicative function of partial criteria.

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– «Development of technology for assessing the quality and safety of nanotechnology products throughout the life cycle» (state registration number 0117U003860).

Conflicts of Interest.

None of the authors have any potential conflicts of interest associated with this present study.

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ВИЗНАЧЕННЯ Й АНАЛІЗ СКЛАДОВИХ КРИТЕРІЇВ ЕКОЛОГІЧНОЇ БЕЗПЕКИ ІНЖЕНЕРНИХ НАНОМАТЕРІАЛІВ

Специфічні властивості нанотехнологій відкривають широкі перспективи для цілеспрямованого виробництва наноматеріалів з підвищеними властивостями. Однак поряд з цим дуже мало досліджень проведено з виявлення негативного впливу на навколишнє середовище наноматеріалів на навколишнє середовище і організм людини. Під час виробництва інженерних наноматеріалів, їх експлуатації (у наслідок стирання й зносу), а також під час утилізації (переробки) або розміщенні у місцях зберігання відходів стає можливим надходження наночастинок у атмосферне повітря й ґрунтові води. Представлено розроблений критерій екологічної безпеки інженерних наноматеріалів, визначено складові цього критерію. Складові критерію є частковими критеріями, які оцінюють безпеку матеріалу за наявністю наночастинок в ньому, близькості до людини, можливості експонування і потенційної небезпеки. Встановлено характеристики інженерних наноматеріалів, які обумовлюють вплив на стан навколишнього середовища і здоров'я людини та мають бути контрольованими. До них відносяться морфологічні, фізико-хімічні та молекулярно-біологічні. Подано алгоритм визначення рівня небезпеки продукції, яка може містити наночастинок, і алгоритм проведення екологічної експертизи за запропонованою шкалою. Шкала ступеня потенційної небезпеки інженерних наноматеріалів містить три рівні: високий, середній і низький. Така шкала є універсальною і дозволяє оцінювати безпеку наноматеріалів і речовин, які можуть містити наночастинок. Проаналізовано комплекс заходів з оцінки та аналізу наноматеріалів, які необхідно проводити для забезпечення екологічної безпеки при використанні наноматеріалів різного рівня небезпеки. Класифікація продукції нанопромышленності за ступенем потенційної небезпеки для здоров'я населення і доквілля дозволить мінімізувати негативний вплив інженерних наноматеріалів на навколишнє середовище і підвищити рівень екологічної безпеки та раціонального природокористування.

Ключові слова: інженерні наноматеріали; наночастинок; екологічна безпека; критерії оцінювання; стан доквілля.

ЛІТЕРАТУРА

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ОПРЕДЕЛЕНИЕ И АНАЛИЗ СОСТАВЛЯЮЩИХ КРИТЕРИЯ ЭКОЛОГИЧЕСКОЙ БЕЗОПАСНОСТИ ИНЖЕНЕРНЫХ НАНОМАТЕРИАЛОВ

Специфические свойства нанотехнологий открывают широкие перспективы для целенаправленного производства наноматериалов с повышенными свойствами. Однако наряду с этим очень мало исследований проведено по выявлению негативного экологического воздействия наноматериалов на окружающую среду и организм человека. При производстве инженерных наноматериалов, их эксплуатации (вследствие истирания и износа), а также при утилизации (переработки) или размещении в местах хранения отходов становится возможным поступление наночастиц в атмосферный воздух и грунтовые воды. Представлен разработанный критерий экологической безопасности инженерных наноматериалов, определены составляющие этого критерия. Составляющие критерия являются частными критериями, которые оценивают безопасность материала по наличию нанофаз в нем, близости к человеку, возможности экспонирования и потенциальной опасности. Установлены характеристики инженерных наноматериалов, которые обуславливают влияние на состояние окружающей среды и здоровье человека и должны быть контролируемы. К ним относятся морфологические, физико-химические и молекулярно-биологические. Представлен алгоритм определения уровня опасности продукции, которая может содержать нанообъекты, и алгоритм проведения экологической экспертизы по предложенной шкале. Шкала степени потенциальной опасности инженерных наноматериалов содержит три уровня: высокий, средний и низкий. Такая шкала является универсальной и позволяет оценивать опасность наноматериалов и веществ, которые могут содержать наночастицы. Проанализирован комплекс мероприятий по оценке и анализу наноматериалов, которые необходимо проводить для обеспечения экологической безопасности при использовании наноматериалов различного уровня опасности. Классификация продукции нанопромышленности по степени потенциальной опасности для здоровья населения и среды обитания позволит минимизировать негативное влияние инженерных наноматериалов на окружающую среду и повысить уровень экологической безопасности и рационального природопользования.

Ключевые слова: инженерные наноматериалы; наночастицы; экологическая безопасность; критерии оценки; состояние окружающей среды.