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## Article

Development of an approach to improvement the protection of the population in protective buildings of civil protection in the conditions of air pollution by toxic chemical agents

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## DEVELOPMENT OF AN APPROACH TO IMPROVEMENT THE PROTECTION OF THE POPULATION IN PROTECTIVE BUILDINGS OF CIVIL PROTECTION IN THE CONDITIONS OF AIR POLLUTION BY TOXIC CHEMICAL AGENTS

*The object of research is the process of air purification from toxic chemicals in the filter ventilation systems of civil protection facilities, the subject of the study is the use of catalytic materials based on titanium dioxide coatings in filter ventilation systems. One of the most problematic places is the expired expiration dates of absorber filters used in the filter ventilation systems of civil protection structures. This can lead to a decrease in their protective effect on the disinfection of outdoor air in the conditions of man-made accidents, military operations or terrorist acts. As a result, it poses a threat to the life and health of people.*

*To solve this problem, it is proposed to use catalytic materials based on titanium dioxide, obtained by plasma-electrolyte oxidation, in the filter-ventilation systems of civil protection facilities. In the course of the study,  $\text{TiO}_2\text{-MO}$  coatings were formed on model titanium samples, where M is W, Mo, Zr, Zn. Using the methods of energy dispersive X-ray spectrometry, scanning electron and atomic force microscopy, and photocolometric studies, the properties of the synthesized functional materials were studied and the possibilities of their application in the technology of photocatalytic oxidation of toxic substances were determined. An analysis was also made of possible designs of photocatalytic blocks for filter ventilation systems using catalytic materials based on  $\text{TiO}_2$ . It has been determined that the optimal technological form of a catalyst in a photocatalytic block is the deposition of a layer of titanium dioxide doped with additional components on a structured base by plasma-electrolyte oxidation.*

*The results obtained made it possible to create proposals for the use of synthesized catalytic materials to increase the degree of protection of the population at civil protection facilities. In particular, it is proposed to arrange the existing filter ventilation systems with a photocatalytic unit (module) to increase the efficiency of neutralizing chemically hazardous substances, and, consequently, the degree of protection of people. The direction of further research is related to the manufacture of a mock-up sample of the photocatalytic unit and bench tests to study the effectiveness of air disinfection.*

**Keywords:** filter ventilation system, neutralization of toxic substances, photocatalytic coatings, plasma-electrolyte oxidation, titanium dioxide.

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### 1. Introduction

In emergency situations, hostilities or terrorist attacks, one of the most effective ways to save people's lives and health is shelter in protective structures of civil protection. Along with protection against modern means of destruction, such structures can be used for the life support of the population and personnel of the security and defense sector performing tasks in the zone of an emergency situation of a man-made or military nature [1]. For example, the clas-

sification of protective structures of civil protection defined by the Code of Civil Protection of Ukraine [2] provides for their distribution into storage facilities, anti-radiation shelters and prefabricated protective structures. Moreover, taking into account the features of the purpose and device, only the storage facilities are sealed and, when equipped with ventilation systems, can protect people from the effects of hazardous factors (gas contamination, smoke, radiation, chemical, biologically hazardous substances, etc.). This is especially important in conditions when it is impossible

to evacuate the population from a zone of emergency, military operations or a terrorist act and it is necessary to ensure the safe stay of people in civil protection structures for a certain time.

The requirements for the design and arrangement of storage facilities as objects of civil protection are strictly regulated, because the preservation of the life and health of a significant number of people depends on their observance. The key role in this is assigned to the filter ventilation system, since it is it that ensures the supply and purification of air [3], in particular, under conditions of environmental contamination with toxic substances.

Therefore, research aimed at developing ways to increase the degree of protection of the population and personnel when they are in civil protection facilities in conditions of air pollution should be considered relevant.

## 2. The object of research and its technological audit

*The object of research* is the process of air purification from toxic chemicals in the filter ventilation systems of civil protection facilities, the subject of research is the use of catalytic materials based on titanium dioxide coatings in filter ventilation systems.

The installation of a ventilation system in civil protection storage facilities refers to the measures of engineering and technical equipment and provides for the ventilation of storage facilities, as well as the purification of the external air supplied inside in conditions of contamination of the surrounding atmosphere with toxic substances. Under appropriate conditions, overpressure (backup) should be created, which prevents the penetration of contaminated air into the shelter.

The storage ventilation system is usually designed to operate in the following modes [1]:

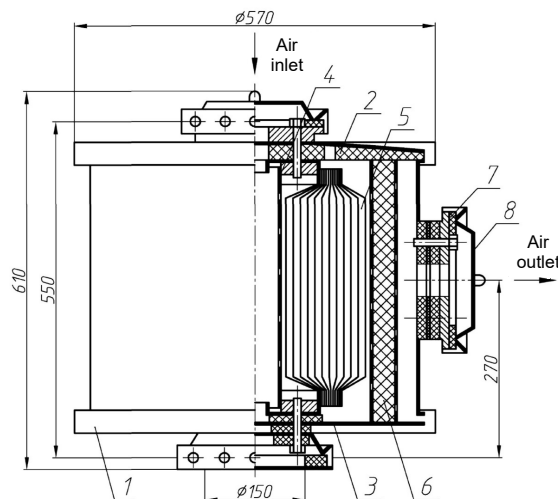
- clean ventilation mode (mode I) – the inflow of dust-free air into the storage is ensured with the necessary frequency of its exchange and removal of moisture and excess heat from the storage;
- filter ventilation mode (mode II) – purification of the outside air entering the storage from dust, aerosols and gaseous toxic substances;
- full isolation mode with regeneration of internal air and creation of an appropriate overpressure (mode III) – used at facilities with the use and production of chemically hazardous substances, areas of increased gas contamination by combustion products and other toxicants.

The main function in ventilation systems for cleaning the outside air from hazardous substances in modes I and II, as well as its regeneration in mode III, is performed by absorber filters. They provide purification of the outside air from radioactive dust, toxic substances, biological agents and are classified depending on the purpose and main technical characteristics [4].

The general design of the absorber filter (on the example of FP-300, Russia) is shown in Fig. 1.

When the filter FP-300 is operating, the outside air enters the end opening of the absorber filter, passes through the smoke filter 5, which purifies the air from radioactive dust, smoke and bacterial aerosols. After that, it passes through the absorber 6, where it is cleaned from the vapors of toxic substances. Depending on the direction of connection to the ventilation system, air can be supplied to the filter from

above or below. The air outlet can be directed in any direction from the filter. The capacity of FP-300 is 300 m<sup>3</sup>/hour. If more throughput is required, absorber filters can be combined with each other in columns of up to three pieces. At the same time, filters can be installed both in the «clean zone» of the storage (under discharge conditions) and in a special zone, outside the populated compartments of the protective structure (under pressure) [1].



**Fig. 1.** The general design of the absorber filter FP-300:  
1 – body; 2 – cover; 3 – bottom; 4 – filter frame; 5 – smoke filter;  
6 – absorber; 7 – nipple ring (gasket); 8 – plug

The shelf life of the filters is 10 years of storage in the package. The service life in the assembled form (during conservation) is 8 years, and in non-combat operation conditions (periodic blowing with clean air) 5 years. It should also be noted that absorber filters do not have protective properties against highly toxic substances (HTS), in particular, such as chlorine and ammonia [4].

Thus, at present, the existing fleet of absorber filters for ventilation systems of civil protection structures requires updating and solving the problem of air purification from the most common HTS. This will increase the protection of the population in the conditions of man-made accidents of chemically hazardous facilities or their destruction as a result of hostilities or terrorist attacks.

## 3. The aim and objectives of research

*The aim of research* is to develop a method for the formation and study of the functional properties of catalytic materials that can be used in filter ventilation systems at civil protection facilities.

This will increase the degree of protection of the population by improving the efficiency of filtering and ventilation systems at civil protection facilities, in particular in storage facilities, when air is polluted with hazardous chemicals.

To achieve the aim, the following objectives were set:

1. Substantiate the expediency of using catalytic materials in the filter ventilation systems of civil protection facilities based on the results of a technological audit.
2. Conduct research on obtaining functional materials with a given level of catalytic properties for filter-ventilation systems.
3. Propose an approach to increase the degree of protection of the population in the conditions of air pollution

by chemical hazardous substances by using catalytic materials in the filtering and ventilation systems of civil protection facilities.

#### 4. Research of existing solutions to the problem

**4.1. The use of catalytic materials for the neutralization of toxic substances.** One of the effective approaches to the neutralization of toxic substances is their catalytic oxidation using catalysts based on titanium dioxide ( $\text{TiO}_2$ ). The advantages of using  $\text{TiO}_2$ -based materials are high thermal and chemical stability and non-toxicity. The photocatalytic activity of  $\text{TiO}_2$  manifests itself when exposed to UV radiation with a spectrum of  $\lambda=320\text{--}400$  nm. The effect of photocatalytic oxidation of  $\text{TiO}_2$  is based on the transition of its nanocrystalline structure to an electronically excited state with the formation of active oxygen-containing radicals, which ensures the oxidation of chemical compounds with their subsequent transformation into complete mineralization [5]. Under these conditions, many organic compounds can be oxidized to carbon dioxide and water on the surface of titanium dioxide.

In addition, systems based on  $\text{TiO}_2$ , in which oxides of refractory, transition, and rare earth metals are additionally incorporated, exhibit high catalytic activity [6, 7].

The resulting catalytic materials are used to disinfect environments contaminated with dangerous toxic substances, pathogenic bacteria, and viruses by deep oxidation under the action of UV radiation [8]. Also, these systems are characterized by increased thermal and electrical conductivity, significant mechanical resistance, as well as a fairly low cost. This fully satisfies the task of searching for a catalytic material for use in filter ventilation systems and neutralization of toxic agents.

The introduction of oxides of transition or refractory metals into the composition of the synthesized coating [7] will enhance the catalytic activity of the existing  $\text{TiO}_2\text{--MO}$  metal oxide system, where M are transition (refractory) metals. This makes it promising to use such materials in photocatalysis for the neutralization of hazardous substances.

**4.2. Technological approaches to the improvement of ventilation systems.** Currently, in ventilation systems, in particular air conditioning systems, in order to increase the efficiency of air purification, various coarse and fine filters, HEPA (High Efficiency Particulate Air) filters, etc. [9] are widely used. There are also a sufficient number of commercial proposals for the arrangement of residential premises and private storage facilities with filter ventilation systems, which at the same time provide air purification from hazardous substances. Such technical solutions, as a rule, have limited information about the principles of construction and the materials used through trade secrets. Therefore, to develop approaches to improve the ventilation systems of civil protection facilities, scientific and technical information based on the achievements of modern chemical materials science and surface engineering was used.

Thus, in an air cleaner with a photocatalytic filter [10], quartz tubes are used with a layer of photocatalytically active titanium dioxide irradiated by a UV lamp deposited on the inner surface. The disadvantage of the proposed filter is the low rate of oxidation of pollutants due to the insufficiently developed contact surface of the flat layer

of the photocatalyst, therefore, the overall low cleaning efficiency [11].

Another study proposes a design for a photocatalytic air purification filter with longitudinally transversely arranged UV lamps in quartz covers [12]. In this case, the entire internal space of the filter is filled with tubular granular bodies made of borosilicate glass, coated with a layer of a photocatalyst based on  $\text{TiO}_2$ .

A cylindrical photocatalytic filter is also known, in which a coarsely porous fibrous lavalan with a fiber packing density of up to 5 % is used as a carrier of the catalytic composition, on which a suspension of titanium dioxide is applied by ultrasound [13].

In the photocatalytic filter according to the US patent [14], intended for use in duct ventilation systems, flat mesh panels with a layer of  $\text{TiO}_2$  deposited on them are installed. Along with the panels, photocatalytic lamps with a wide range of UV radiation are installed, which ensures a sufficiently high efficiency of air purification.

Thus, the optimal technical solution for increasing the efficiency of air purification is the use of a photocatalytic unit in the filter ventilation system. Nevertheless, the optimal characteristics of the catalytic material and the rational technological form of the catalyst remain a debatable issue. It is more convenient and practical to apply a catalytic layer on structured metal substrates.

One of the promising methods for obtaining such catalytic systems on highly developed structured supports is plasma-electrolyte oxidation (PEO) [15]. Advantages of PEO for obtaining photocatalytic materials based on titanium dioxide:

- ability to process products of complex geometric shapes (including tearing and mesh media);
- formation between the metal and the catalytically active layer of an oxide sublayer of the treated metal, which acts as a secondary catalyst carrier;
- high adhesion between the formed coating and the processed material;
- high manufacturability and relatively low cost of the technological process.

The analysis performed shows that the efficiency of air purification entering civil protection facilities can be increased by additional use of catalysts based on titanium dioxide, including those doped with oxides of transition and refractory metals, in filter ventilation systems [16]. The technological form for introducing these catalysts into filter ventilation systems is nanocomposite coatings ( $\text{TiO}_2\text{--MO}$ , where M is W, Mo, Zr, Zn) formed on the surface of a titanium metal mesh or lattice, or porous titanium.

#### 5. Methods of research

To implement the proposed approach, the formation of a catalytic coating on the surface of a metal carrier was carried out by plasma-electrolyte oxidation. For research, samples of titanium alloy VT1-0 of various shapes were used. Plasma-electrolyte synthesis of coatings was carried out from complex diphosphate electrolytes ( $c(\text{K}_4\text{P}_2\text{O}_7)=1.0$  mol/dm<sup>3</sup>), including the addition of dopant metal salts. The formation of PEO coatings was carried out using a laboratory setup containing a high-voltage direct current source, an electrochemical cell, and process control devices (voltmeter, ammeter). Technological parameters for the formation of PEO coatings: current density – 1.0–5.0 A/dm<sup>2</sup>, process voltage – 90–110 V, formation time – 15–30 min.



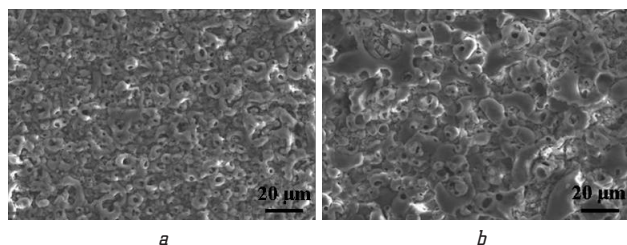
Methods for studying the complex of functional properties of the obtained coatings included:

- energy dispersive X-ray spectrometry for studying the elemental composition (INCA Energy 350 spectrometer, UK);
- scanning electron microscopy for surface morphology analysis (SEM ZEISS EVO 40XVP, Germany);
- atomic force microscopy to determine the topography of surface layers (atomic force microscope NT-206, Belarus);
- photocolometric studies for the study of catalytic properties (photocolimeter KFK-2, Russia).

Adhesion strength was controlled in accordance with the requirements of ISO 2819:2017 by qualitative methods.

## 6. Research results

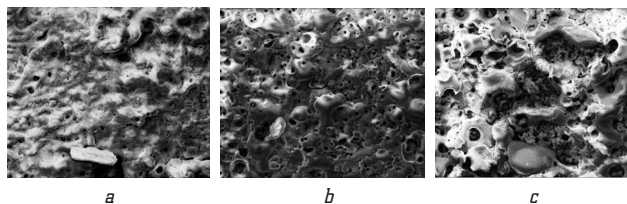
**6.1. Formation of plasma electrolyte coatings on model samples and study of their properties.** By plasma-electrolyte oxidation of titanium samples in the proposed technological modes in diphosphate solutions, uniform enamel-like coatings of light gray color were obtained (Fig. 2). Under these conditions, a tubular micropore structure characteristic of titanium oxides appears.



**Fig. 2.** Morphology of  $\text{TiO}_2$  coatings formed in a solution of  $1.0 \text{ mol/dm}^3 \text{ K}_4\text{P}_2\text{O}_7$  according to current density,  $\text{A/dm}^2$ :  
*a* – 1; *b* – 4. Magnification  $\times 1500$

The composition of the formed coating includes compounds of the main components of the electrolyte, in particular oxides of phosphorus and potassium. The effect of the current density during PEO manifests itself in a change in the size of the formed tubular structures [17]. At the same time, with an increase in the oxidation current density, the thickness of the formed oxide layer increases.

The introduction of salts of transition and refractory elements into the composition of the working diphosphate electrolyte makes it possible to form metal oxide coatings on titanium (Fig. 3). The resulting layer of mixed oxides is also uniform. Its color depends on the type of additional component. The morphology of the surface layer of the synthesized coatings is also transformed: it becomes more developed, although the general toroidal structure inherent in titanium oxide is retained.



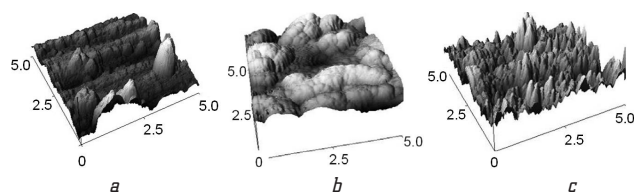
**Fig. 3.** Morphology and content of the additional component in coatings on titanium: *a* –  $\text{TiO}_2\text{-ZrO}_2$ ,  $\omega(\text{Zr})$  – 4 wt. %; *b* –  $\text{TiO}_2\text{-V}_2\text{O}_5$ ,  $\omega(\text{V})$  – 4 wt. %; *c* –  $\text{TiO}_2\text{-MoO}_3$ ,  $\omega(\text{Mo})$  – 3 wt. %. Magnification  $\times 500$

In the PEO density range of  $1.0\text{--}5.0 \text{ A/dm}^2$ , it is possible to obtain a coating with a dopant metal content of  $3.0\text{--}4.0 \text{ wt. \%}$ .

For the catalytic properties of the resulting functional material, in addition to the content of the active component, the degree of development of the surface layer also plays an important role, which can be estimated from the data of the study of the surface topography by atomic force microscopy.

Estimating the topography of the surface of the  $\text{TiO}_2$  coating formed in a diphosphate solution, it can be concluded that the coating is unevenly rough (Fig. 4, *a*), the size of the grains formed on the surface is  $400\text{--}500 \text{ nm}$ .

The surface of the synthesized  $\text{TiO}_2\text{-ZnO}$  heterooxide coating (Fig. 4, *b*) is characterized by a globular structure and a smoothed relief. The surface of the coating in the studied scanning areas is uniformly developed and consists of agglomerates of grains close in shape to spherical ones with an average size of up to  $100 \text{ nm}$ . The average size of the formed structures approaches pure  $\text{TiO}_2$  and is  $400\text{--}500 \text{ nm}$ .



**Fig. 4.** Surface topography of coatings on titanium:  
*a* –  $\text{TiO}_2$ ; *b* –  $\text{TiO}_2\text{-ZnO}$ ; *c* –  $\text{TiO}_2\text{-ZrO}_2$ . Scan area  $5 \times 5 \text{ }\mu\text{m}$

At the same time, the topography of the surface of the synthesized heterooxide system doped with zirconium oxide,  $\text{TiO}_2\text{-ZrO}_2$  (Fig. 4, *c*) differs significantly from those previously considered. The resulting surface is finely crystalline, consists of many sharp grains  $150\text{--}200 \text{ nm}$  in size, and is characterized by the maximum degree of development of the surface layer among the studied materials.

Considering the analysis of the chemical composition of the coatings, it can be assumed that the visualized structures formed in thermochemical reactions during PEO are remelts of the base metal (Ti) and electrolyte components, including oxides of additional metals [7].

An additional parameter for evaluating the structural organization (degree of ordering) of the synthesized metal oxide materials is the Hausdorff-Besikovich fractal dimension ( $D_F$ ). Fractal analysis is based on the properties of self-similarity, so the analysis of a small part of the microstructure of the synthesized material is sufficient to obtain information about the object of study as a whole.

All formed metal oxide systems have a fractal dimension in the range from 2 to 3 (Table 1), which characterizes the obtained structures as three-dimensional with a complex surface relief, which confirms the results of studying the morphology and topography of surface layer.

For the studied metal oxide systems, an increase in the fractal dimension is observed upon incorporation of dopant metal oxides into the composition of the coatings.  $\text{TiO}_2$  coating has the lowest fractal dimension,  $\text{TiO}_2\text{-ZnO}$  has the highest one. On the whole, the results obtained correlate with studies of the surface topography of the obtained materials.

Metallographic studies of the formed coatings confirmed the high adhesion strength of the synthesized metal oxide systems. Heating samples to a temperature of  $200 \text{ }^\circ\text{C}$  does

not cause visible morphological changes in the surface layer, the coating does not crack and remains uniform, which is a positive factor for use in ventilation systems with a hot air flow.

Table 1

Fractality indices of coatings based on  $\text{TiO}_2$

Metal oxide system	Fractal dimension, $D_F$
Ti   $\text{TiO}_2$	2.49
Ti   $\text{TiO}_2\cdot\text{V}_2\text{O}_5$	2.53
Ti   $\text{TiO}_2\cdot\text{ZrO}_2$	2.75
Ti   $\text{TiO}_2\cdot\text{Mo}_x\text{O}_y$	2.64
Ti   $\text{TiO}_2\cdot\text{ZnO}$	2.88

Testing of the catalytic properties of the obtained systems using methyl orange (MO) as a model compound, Fig. 5 indicates that the  $\text{TiO}_2$  coating exhibits a photocatalytic activity of 51.0 %. At the same time, mixed metal oxide systems exhibit higher rates of photodestruction.

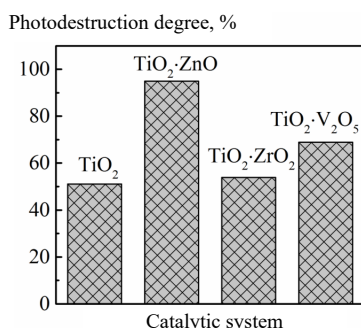


Fig. 5. Characterization of the photocatalytic activity of oxide systems on titanium

Thus, the doping of titanium dioxide with zirconium oxide promotes an increase in the photodestruction of the MO within 10 %, and with vanadium oxide, by 30 %. The highest performance in the model reaction was shown by the Ti |  $\text{TiO}_2\cdot\text{ZnO}$ . The addition of zinc oxide to the titanium dioxide metal oxide matrix increases the degree of MF photodestruction to almost 95.0 %. Moreover, in this case, a synergistic effect is observed, since the synthesized material demonstrates an overactive increase in photocatalytic activity with respect to individual titanium oxide.

These data indicate a high catalytic activity and the possibility of using Ti-based coatings for the photocatalytic destruction of a number of organic compounds. This gives grounds to consider such materials as promising for use in filter systems for the neutralization of toxic reagents.

**6.2. Proposals for the use of the developed catalytic materials to increase the degree of protection of the population at civil protection facilities.** Considering the obtained results, it is possible to propose an additional arrangement of existing filter ventilation systems with a photocatalytic unit (module) to increase the efficiency of neutralization of chemically hazardous substances, and, consequently, the degree of protection of people in civil protection storage facilities.

The schematic diagram of the modified photocatalytic unit is shown in Fig. 6.

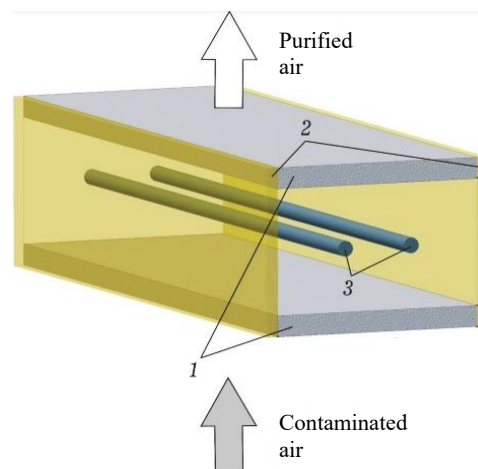


Fig. 6. Schematic diagram of the photocatalytic unit:  
1 – carrier with formed photocatalytic coating;  
2 – side walls-reflectors; 3 – UV lamps

The block has two plates of carrier material with a PEO-formed photocatalytic coating as discussed above. The plates are placed parallel to the air flow for cleaning. Inside the block there are UV lamps for realizing the photocatalytic effect. The side walls of the module also act as reflectors to ensure sufficient irradiation intensity. To ensure the operation of the photocatalytic unit in conditions of limited access to electricity, it is possible to replace the UV lamps with a UV tape. It is also possible to manufacture a cylindrical block while maintaining the general principle of construction.

Given that the use of photocatalytic processes requires minimal equipment, this allows the proposed units to be used in facilities with limited access to electricity or in facilities without electrification. Therefore, the proposed technological approach is economically accessible and environmentally friendly.

The direction of further research is related to the manufacture of a mock-up sample of the photocatalytic unit and bench studies to study the effectiveness of air disinfection.

## 7. SWOT analysis of research results

**Strengths.** The strengths of this research are that the proposed technological approach using a photocatalytic unit will improve the efficiency of air purification from chemical hazardous substances. The proposed design of the block provides for the installation of porous (mesh) plates with a layer of catalytic material deposited on them – titanium dioxide doped with oxides of transition or refractory metals. According to the results of the implementation of the developed method, it is expected to increase the degree of protection of people when they are in civil protection structures in conditions of air pollution.

**Weaknesses.** The weaknesses of this research lie in the fact that at this stage the results of only laboratory testing of the developed samples of the catalytic material were obtained and a schematic diagram of the photocatalytic unit was developed.

Also, the implementation of the proposed method consists in the need to make structural changes to existing filter ventilation systems.

**Opportunities.** Additional opportunities when using the above results in the field of civil protection are associated

with the possibility of improving outdated filter ventilation systems in storage facilities and other structures.

**Threats.** The method proposed in the work at this stage of the study is not yet to be implemented. The proposed technical solutions require technical calculations for the production of development documentation, development and testing of a mock-up sample, as well as pilot testing. Therefore, the risks are obvious and are associated with the technical and economic costs of improving the filter ventilation system of civil protection structures.

## 8. Conclusions

1. An analysis of the device and the principle of operation of filter-ventilation systems for air disinfection is carried out. The existing requirements for catalytic materials for photocatalysis used in air purification filters are considered. The use of photocatalytic coatings formed by the plasma-electrolyte oxidation method for the formation of catalytic coatings based on titanium dioxide doped with oxides of transition and refractory metals is substantiated. It is shown that the most rational is the deposition (synthesis) of a catalytic layer on structured metal substrates.

2. On laboratory samples, the formation of  $\text{TiO}_2\text{-MO}$  plasma-electrolyte coatings, where M is W, Mo, Zr, V, Zn, is carried out and the functional properties of the obtained materials were studied. It is established that the doping of coatings with additional elements in the range of 3–4 wt. % promotes an increase in the photocatalytic properties of the synthesized metal oxide systems, in particular, the degree of photodestruction up to 94 % of the model toxic substance. This leads to the prospect of their use in filter ventilation systems for photocatalytic air purification.

3. An approach is proposed to increase the degree of protection of the population in civil protection structures in conditions of air pollution with toxic chemicals by equipping existing filter ventilation systems with a photocatalytic unit (module). It is advisable to introduce two parallel plates of carrier material with a formed photocatalytic coating and UV lamps into the composition of the photocatalytic unit to ensure photocatalytic action. The implementation of the side walls of the blocks with internal reflection of UV rays should provide sufficient irradiation intensity and more complete destruction of toxic agents.

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