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Advanced Composite Material for Air Regeneration Systems of Individual and Collective Protection

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Abstract

A composite polymer-inorganic material (based on potassium superoxide) combining the properties of a polymer matrix (flexibility, resistance to mechanical stress, etc.) and functional filler, and an environmentally friendly technology for producing regenerative product for air regeneration of inhabited objects (space, underwater, etc.) have been developed. The technology consists of applying an alkaline solution of hydrogen peroxide on indifferent porous fibrous matrix of fiberglass followed by heat treatment at atmospheric pressure in a stream of hot, purified from carbon dioxide, air or vacuum. Nanocrystals of potassium superoxide, synthesized from alkaline solution of hydrogen peroxide, are firmly fixed on the fiberglass, which prevents the formation of dust during the exploitation of the regenerative product. In addition, a large number of active centers in the developed surface of the material provides increased sorption capacity (by 30 – 40 %) of the regenerative product on the matrix for carbon dioxide compared with the regenerative product in the form of granules. The use of polymer-inorganic adsorbent materials in air regeneration devices saves weight and dimensions of the products, and thus, significantly improves their physiological and hygienic indicators.

Keywords

Chemical air regeneration; regenerative product; fiberglass polymer matrix; potassium superoxide; nanocrystals; carbon dioxide; oxygen; chemisorptions; kinetics; regeneration coefficient; sorption capacity; apparent density; sorption activity.

Introduction

Complexes of technical means, including means of individual and collective protection of human respiratory apparatus are currently used in Russia and abroad for air regeneration and purification of the inhabited objects, and for the effective protection of humans against unfavorable chemical and biological conditions. Mass-produced devices mainly use potassium superoxide (KO_2) as a source of oxygen and absorber of carbon dioxide (CO_2). The potassium superoxide is produced in Russia and abroad in the form of powders, and regenerative products based on them are produced by mechanical mixing of the KO_2 powder with modifying additives, catalysts and other components. The resulting mixture is processed into granules, tablets, blocks, and other forms to be used in air regeneration [1, 2].

The proposed environmentally friendly technology for producing regenerative product on the basis of KO_2 provides for the creation of polymer-inorganic material that combines the properties of the polymer matrix (flexibility, resistance to mechanical stress, etc.) and functional filler. It consists in applying an alkaline solution of hydrogen peroxide on an indifferent porous matrix made of fiberglass with a subsequent heat treatment at atmospheric pressure in a stream of hot, purified from carbon dioxide, air or vacuum.

A new technology allows to create an environmentally friendly and resource-saving chemical production, which only “waste” is water vapor and oxygen. The advantage of the proposed method of producing polymer-inorganic product for air regeneration is that it provides not only pure KO_2 on the porous matrix, but also the compositions based on it, similar to the known regenerative products made from mechanical mixtures.

The world experience of development of chemical principles for means of chemical-biological protection and life support systems suggests that functional nanostructured chemical products and materials can greatly improve the technical and operational capabilities of existing tools and systems, and their creation is one of the priority directions of research and development in the field of adsorption technology and equipment protection.

One of the important limitations of the use of nanomaterials is the instability of their structure and, consequently, the instability of their physico-chemical and physico-mechanical properties. So under heat, radiation, strain, and other influences, the processes of recrystallization, relaxation, segregation and homogenization are inevitable, as well as the phenomena of disintegration, phase transformations, sintering and fabrication of nanopores and nanocapillaries, amorphization or crystallization. When molding with nanopowders, clumping of nanoparticles in agglomerates becomes a pressing problem: that may complicate obtaining materials with desired structure and distribution components. To prevent these negative phenomena it is proposed to carry out the synthesis of potassium superoxide target product on a fiberglass polymer matrix [3 – 6].

Method for obtaining nanocrystalline potassium superoxide on a fiberglass matrix

The process of obtaining nanocrystalline potassium superoxide on a highly porous fiberglass matrix included the preparation of matrix blanks from Mat and alkaline solution of hydrogen peroxide (H_2O_2), impregnating a fiberglass matrix with a solution of potassium peroxide peroxysolvates $K_2O_2{\cdot}2H_2O_2$ (reaction 1) and subsequent dehydration of high moisture material in vacuum under heating, followed by disproportionation of $K_2O_2{\cdot}2H_2O_2$ according to reaction (2).

$$2KOH + 3H_2O_2 = K_2O_2{\cdot} 2H_2O_2 + 2H_2O, \quad (1)$$

$$K_2O_2 {\cdot}2H_2O_2 = 2KO_2 + 2H_2O. \quad (2)$$

It should be noted that $K_2O_2{\cdot}2H_2O_2$ is formed in the system KOH – H_2O_2 – H_2O during the interaction of H_2O_2 50 % solution with a solid alkali KOH and it is present in an alkaline solution of hydrogen peroxide in the form of fine particles.

Obtaining potassium superoxide from peroxysolvate is a complex technological task, because in the process of thermolysis, under certain conditions, the $K_2O_2{\cdot}2H_2O_2$ disproportionation can proceed either according to reaction (2) or reaction (3):

$$K_2O_2{\cdot}2H_2O_2 = 2\ KOH + H_2O + 1{,}5O_2. \quad (3)$$

$K_2O_2{\cdot}2H_2O_2$ disproportionation is exothermic. Reaction (2) is the primary one, and KOH is formed according to reaction (3) or during the occurrence of secondary reactions (4) between the formed KO_2 crystals and water vapor, which is the product of the reaction (2):

$$2KO_2 + 3H_2O = 2(KOH{\cdot}H_2O) + 1{,}5\ O_2. \quad (4)$$

Due to high activity of KO_2 to water vapours it is not possible to completely eliminate the reaction (4) in industrial conditions. As a consequence, the product of thermal decomposition of $K_2O_2{\cdot}2H_2O_2$ will inevitably contain KOH contaminants, considering the diffusion of water vapor in the layer during the drying of high-moisture matrix. Thus, it is most likely that the process will include reactions (2) and (3):

$$mK_2O_2{\cdot}2H_2O_2 \rightarrow nKO_2 + (m - n)\ KOH + H_2O + O_2. \quad (5)$$

The ratio of KO_2 and KOH in the final product of the decomposition of hydrogen peroxide alkaline solution on the porous matrix can be adjusted by changing process variables of the drying process (temperature, pressure, speed of evacuation of water vapor from the reaction zone, etc.), as well as the choice of an appropriate drying method.

The conducted research on the effectiveness of KO_2 drying on the matrix allowed to recommend the following methods to be used in the production of regenerative products: 1) drying under vacuum with heating in the IR range; 2) drying at atmospheric pressure in a stream of dried and heated air (convection); 3) drying by means of resistance heating; 4) drying in a microwave field [3, 4].

The results obtained by the authors [3, 4, 7 – 9] marked the beginning of a new direction in the creation of composite regenerative products, which is based on the deposition of KO_2 nanocrystals on a matrix of randomly interwoven glass fibers. This product has the most detailed surface, easily accessible to virtually every crystal of potassium superoxide in the interaction with water vapor and CO_2, it is not dusty, and it is easily processed and manufactured in the form of plates with a thickness of 2–3 mm. This ensures complete isolation of active oxygen with a recovery rate of about 1.5, i.e., close to optimal, lower breathing resistance, the exception reflow of the product during operation.

Physical and chemical properties and kinetics of CO_2 chemisorption and oxygen evolution in the presence of water vapor of nanocrystalline regenerative product's gas-air mixture f [10] have been studied.

Methods and experimental techniques

To study the kinetics of chemisorption a chemisorption reactor of special design has been developed (Fig. 1) [11]. The reactor is designed in the form of a cartridge made of fluorinated ethylene-propylene copolymer (fluoroplastic film F-4MB) 1 and divided by the weld of the U-shaped form into two branches. Inside of each branch, with the help of fixation elements connected to the cartridge shell, power strips 2 are installed, which are made of fluoroplastic film and divided by transverse welds into cells. There regenerative product plates 3 are installed, which are intended for the regeneration of the incoming respiratory mix (**RM**). The section A-A shows the location of the regenerative plates – in this case, a briquette of in two plates is use, except the bottom cell, where there are three plates. The thickness of each plate is 3 mm, thus the briquettes have a thickness of 6 and 9 mm.

Such design of the reactor allows to experiment with different weights of product and area of the reaction surfaces of the regenerative product plates by changing the number of plates in briquette and the number of briquettes.

Chemical Air Regeneration Unit (**CARU**) operates by forced ventilation, and an electric fan connected to CARU with a docking unit 4 is used as a RM flow booster.

Fig. 2 presents a design of experimental research. Studies of the kinetics of hydrogen dioxide chemisorption by potassium superoxide and oxygen evolution were performed at different values of: temperature and humidity of RM; the surface area of regenerative product in the chemisorption reactor; and the feed rate and extraction of carbon dioxide and oxygen in/out of the volume of the sealed chamber, which simulates the breathing of a group of people in a hermetically closed space.

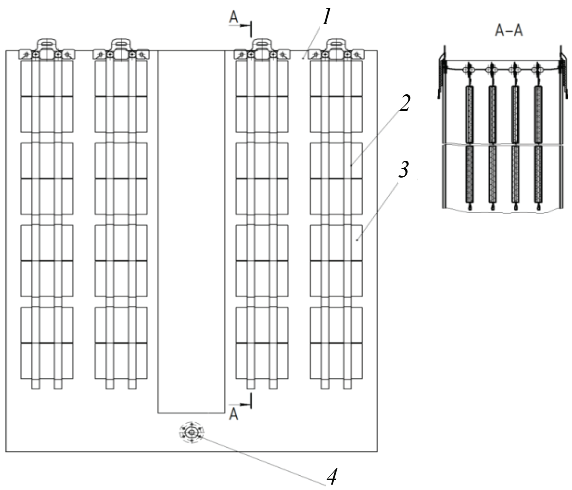


Fig. 1. Design of a reactor with regenerative product RPK-P: *1* – fluoroplastic film F-4MB; *2* – power supply; *3* – regenerative plate; *4* – docking unit

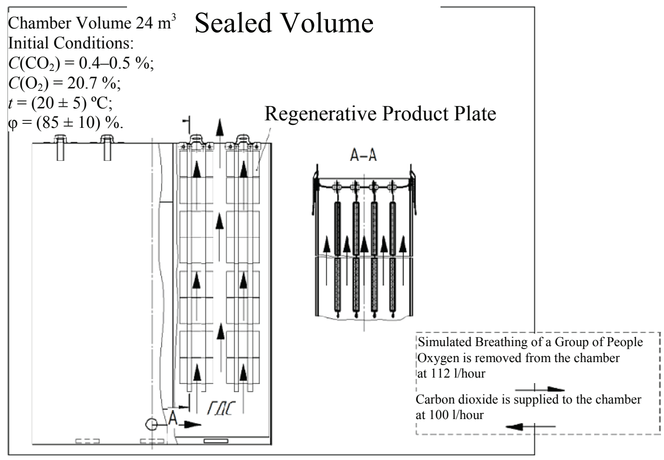


Fig. 2. Design of experimental research

Kinetics of carbon dioxide chemisorption and oxygen evolution

The aim of this experimental research is to study the kinetics of chemisorption of carbon dioxide and oxygen evolution by a regenerative product in the presence of water vapor, as well as the design of a device aimed to create a satisfactory and healthy atmosphere in a sealed inhabited facility for five hours (with four people present in the facility and a free volume of 6 m^3 per person). The reactor load corresponds to the absorption of 100 dm^3/h of carbon dioxide and 112 dm^3/h of oxygen evolution.

The RM flow through the reactor was set to 20 m^3/h. The mass of the regenerative product in the chemisorption reactor was calculated based on the needs of the people in RM supply for five hours, with the mass value 2.8–3.8 kg. The calculation accounted for 100 % evolution of chemically-bound oxygen with the total consumption of potassium superoxide in the regenerative product.

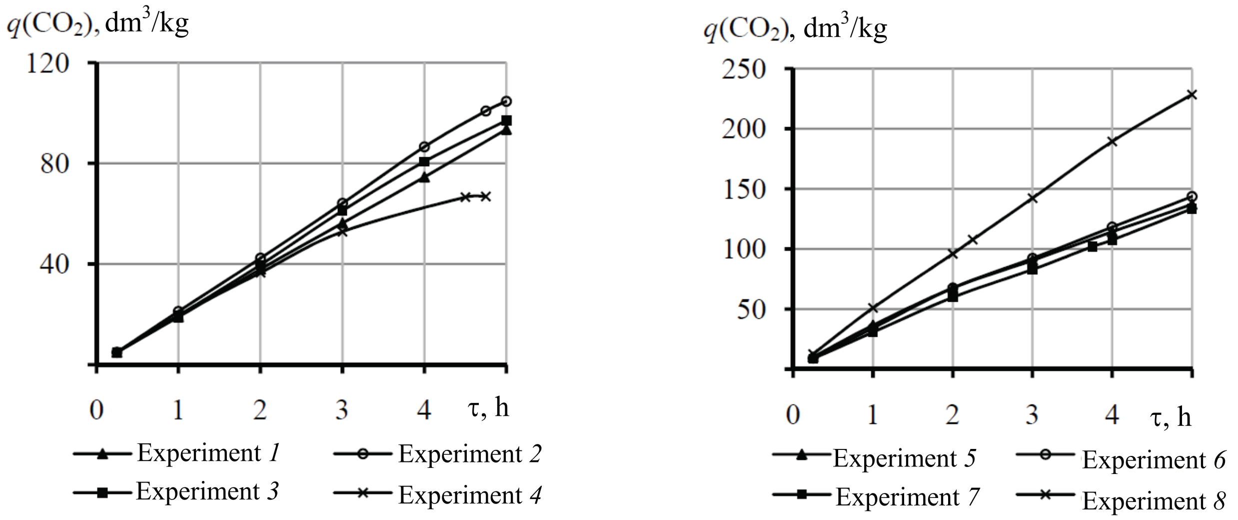
The experimental study of the kinetics of hydrogen dioxide chemisorption by potassium superoxide and oxygen evolution were performed for the two reactor designs, differing in the number of regenerative plates in each chain of chemisorption reactors. In the first set, each chain cell contained three plates (experiments No. 1 – 4), in the second set (experiments No. 5 – 8) there were two plates. The total number of chains for the first option was 12 items, for the second – 16 items. Table 1 shows the conditions under which the experimental study of chemisorption kinetics was conducted.

Kinetic curves of carbon dioxide absorption and oxygen evolution by the regenerative product with dependence on time are presented in Fig. 3 and 4. The average sorption capacity for experiments No. 1, 3

Table 1

Experimental research conditions

No. of experiment	RM average temperature, °C	RM average humidity, %	CO_2 consumption, dm^3/hour	O_2 letdown flow, dm^3/hour	Surface area of regenerative product, m^2	Mass of regenerative product, kg
1	5.4	81.9				3.62
2	20.0	85.0			3	3.59
3	21.2	80.0				3.65
4	39.7	64.0	100	112		3.63
5	14.3	82.7				2.99
6	20.6	85.8			4	
7	23.2	81.0				3.18
8	19.9	88.0	200	224		3.22



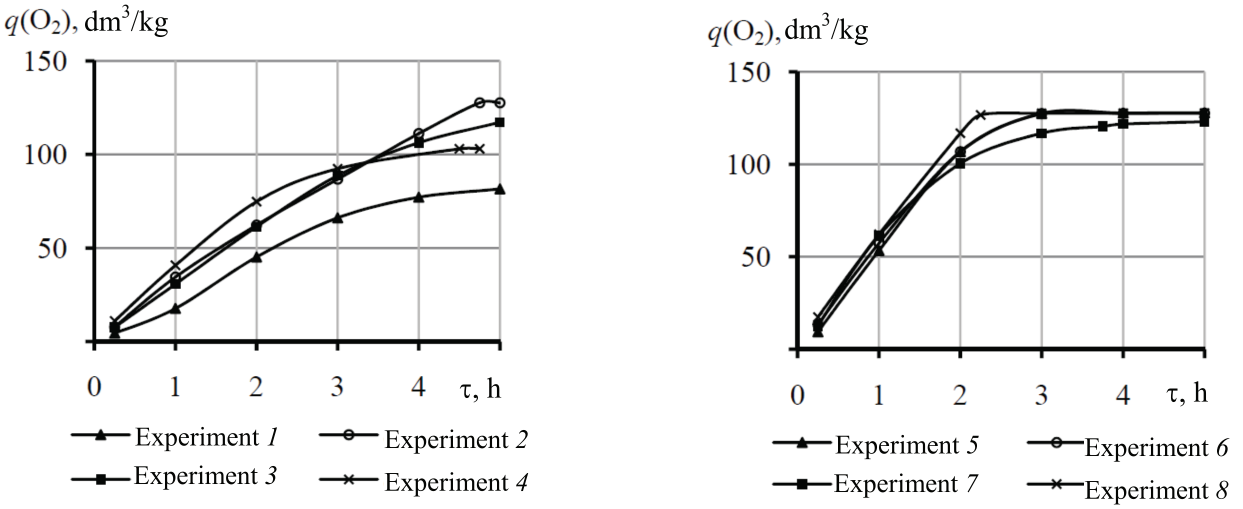
a) *b*)

Fig. 3. Changes in the specific quantity of absorbed CO_2 with time for reactor designs consisting of three (*a*) and two (*b*) plates

equaled 90 dm^3/kg (see Fig. 3 *a*), for experiments No. 5–7 it equaled 137 dm^3/kg (see Fig. 3 *b*). In experiment No. 8 when the load increased twice the value of the sorption capacity of the regenerative product amounted to 228 dm^3/kg.

The increase in sorption capacity with increasing load suggests that the process of carbon dioxide absorption is limited by external mass transfer. Fig. 4*a* presents the dependence of the amount of released oxygen to the first design of chemisorption reactor (experiments No. 1 – 4). The process of oxygen evolution is observed within five hours of the experiment. The average value of the volume of released oxygen for experiments 1 and 2 amounted to 122 dm^3/kg, which is slightly below the content of chemically bound oxygen in the regenerative product (127 dm^3/kg). Analysis of the kinetic curves shows that the rate of oxygen evolution is largely influenced by the humidity and temperature of RM.

In the second design of chemisorption reactor, the evolution of oxygen ceases after three hours of work. The form of the kinetic dependences obtained in experiments No. 5 – 8 (Fig. 4*b*), are virtually identical. A stage with a constant rate of oxygen evolution (first two hours) can be identified. Besides, the amount of the released oxygen is equal to the content of chemically bound oxygen in the source regenerative product, which implies 100 % evolution of chemically bound oxygen with the total consumption of the regenerative product. Experiment No. 8 was carried out under the increased load (up to eight people).



a) *b*)

Fig. 4. The dependence of the specific amount of released oxygen on time for reactor designs consisting of three (*a*) and two (*b*) plates

Thus, both designs of the chemisorption reactor can provide for virtually complete consumption of the regenerative product resource (kinetic curves in Fig. 4 for experiments No. 2, 3, 5–8). Given the uniformity of oxygen evolution for five hours, the first design is most preferred (kinetic curves in Fig. 4 for experiments No. 2 and 3). However, at low temperatures ≈ 5 °C and high temperatures ≈ 40 °C, the sorption capacity of the regenerative product is lower by 13.5 % on average, compared with the second design.

With the second design there is almost a 100 % release of oxygen in the first two hours of the chemisorption reactor work in all experiments (kinetic curves in Fig. 4*b*). The rate of oxygen evolution in the second design is much higher than the need for oxygen supply in a sealed object in the first two hours of the reactor work. The second variant is characterized by higher values of carbon dioxide absorption rate and regenerative product sorption capacity in the appropriate time periods.

Physical and chemical properties of nanocrystilline potassium superoxide on a fiberglass polymer matrix

A regenerative product on a fiberglass matrix obtained by the method described above, is a nanocrystalline potassium superoxide, fixed on the surface and in the pores of the fibrous and inert to hydrogen peroxide matrix [4]. The content of active oxygen in the product in terms of pure powder of potassium superoxide is ~ 32 %. The value of apparent density of the regenerative product on the porous matrix was determined by mercury injection and is (0,565 ± 0.08) g/cm^3.

Sorption activity of the product on the carbon dioxide in the dynamic flow of air with CO_2 concentration increased by 4 % is 120–140 dm^3/kg, which is 40–60 % higher than the activity of commercially available granulated regenerative products on the basis of potassium superoxide. The development of a nanostructured regenerative product can significantly reduce metal consumption of respiratory devices (by 50–90 %) and reduce the consumption of rubber materials by 15–25 %, thus decreasing the weight of the developed products by 1.5–2 times [3].

Table 2 presents the characteristics of the developed product in comparison with commercially available materials for similar purposes.

Table 2

Comparative characteristics of regenerative products

Brand (country of origin)	Form	CO2 sorption capacity, l/kg
Dräger (Germany)	Tablets	≈ 90
Auer (Germany)	Granules	≈ 85
L'Arliqid (France)	Tablets	90
Noriuco (China)	Granules, tablets	80
Molecular (UK)	Granules	90
PRT-9P (Russia)	Tablets	80–90
PRT-9PM (Russia)	Tablets	80–90
OKCh-3M (Russia)	Granules	70–90
OKCh-1 (Russia)	Granules	80–95
Regenerative product on a fiberglass matrix (Russia)	Plates	130

As it can be concluded from Table 2, sorption capacity of the regenerative product on a fiberglass matrix is significantly superior to commercially available regenerative products.

New products based on nanostructured regenerative product

New means of air regeneration for individual and collective protection were designed based on the developed nanostructured regenerative product [12 – 18].

Fig. 5 shows the appearance of new products based on the new nanostructured regenerative product.

a)

b)

Fig. 5. The Appearance of:
a – self-rescue device according to the patents [13, 14],
b – chemical air regeneration unit (patents [17, 18])

Table 3 shows the characteristics of a device based on the patents [13, 14] in comparison with serial devices.

The self-rescuer (patent [13, 14]), having otherwise equal characteristics with the device SPI-20, has a smaller mass and provides the temperature of the inhaled respiratory mixture about 45°C. Breathing resistance of the developed device is twelve times lower than in SPI-20, Oxy K pace. In addition, in emergency protection self-rescue device the provision for communication has been made.

Low weight (0.9 kg), very low breathing resistance (5 mm water column), and low temperature of the inhaled air (45 °C) allow to use the emergency protection device for respiratory and vision protection of elderly people and persons suffering from pulmonary diseases.

The conducted study [10, 11] of the kinetics of CO_2 sorption and oxygen evolution led to the design of a CARU and a CARU set for air regeneration in sealed inhabited objects [17, 18]. They maintain the volume fraction of oxygen in the object from 19,0 to 23.0 %, the volume fraction of carbon dioxide of not more than 1.0% within 5 h at a temperature of $(20 \pm 5)\,^{o}C$, relative humidity of (85 ± 10) %, the oxygen consumption of ~28 dm^3/h per person.

CARU set offers the convenience of use because of small weight and size (total weight

Table 3

Comparative characteristics of a self-rescue device based on the patents [13, 14] and serial devices

Indicators	Self-rescue device (patents [13, 14])	Oxy K pace, Drager Sicherheitstechnik GmbH, Germany	Oxy crew, Drager Sicherheitstechnik GmbH, Germany	S 15, Auergesellscaft GmbH, Germany	SPI-20, Roskhimzaschita Corp., Russia
Method of oxygen backup	Regenerative product	Regenerative product	Regenerative product	Regenerative product	Regenerative product
Mass, kg	0.79	4.00	2.5	3.0	2.20
Effective protection time on average loading, min	15.00	15.00	20.0	15.0	20.00
Breathing resistance (inspiration/ expiration), Pa, no more than	50/50	500	Not available	Not available	600
Inhaled RM temperature, ºC, no more than	45	50	Not available	Not available	60

not exceeding 20 kg, the weight of CARU with packaging – 5 kg); small time of its activation state (assembling the stand no more than 10 minutes, placing and connecting CARU no more than 5 min); mobility, which is ensured by the use of a wheeled stand; enhanced comfort of breathing; and reduced fire risk.

Conclusion

Obtaining regenerative products on a highly porous fiberglass matrix is the most promising direction in the field of regenerative products of new generation. With this method a product of air regeneration is obtained in one stage, unlike methods which include the formation of granules from potassium superoxide powder.

Nanocrystals of potassium superoxide, synthesized from hydrogen peroxide alkaline solution, are firmly fixed on the fiberglass, which prevents the formation of dust during the exploitation of the regenerative product. In addition, a large number of active centers in the developed surface of the material provides increased (by 30–40 % above) carbon dioxide sorption capacity of the regenerative product on the matrix as compared to regenerative products in the form of granules.

The use of polymer-inorganic adsorbent materials in air regeneration devices saves weight and dimensions of the products, and thus, significantly improves their physiological and hygienic indicators.

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