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Development of a Nanocrystalline Material for Air Regeneration Devices

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Abstract—Currently, the development of regenerative products based on highly porous glass fiber matrix, has proved to be one of the most promising trends in the field of creating regenerative products for air cleaning devices. The authors have developed a new technology for obtaining a regenerative product based on nanocrystals of potassium superoxide, which comprises the impregnation of porous fiberglass matrix with the alkaline solution of hydrogen peroxide followed by its further dehydration. The regenerative product based on the matrix has been shown to possess the better sorption characteristics, as compared to those of the serially manufactured ones. The developed regenerative product can be applied for lightweight design options of a self-rescuer, corresponding to the international standards.

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INTRODUCTION

The majority of devices for air regeneration in closed life-support systems and individual respiratory protective means use sodium and potassium perperoxides NaO_2 and KO_2 [1–4]. These substances contain a chemically bound xygen which is released on contact with air moisture; they are also used as oxidants and sources of oxygen.

Commercial sodium and potassium perperoxides of both Russian and foreign production are powders. The material for air regeneration is produced by mechanically mixing KO_2 or NaO_2 powders with modifying additives, catalysts, and other components. The resulting charge mixture is processed to obtain granules, tablets, blocks, or differently shaped items for use in air regeneration systems.

At present there is no alternative for alkali metal perperoxides in regenerative technics applications, the more so as the chemisorptive potential of these substances (ability to absorb carbon dioxide and release active oxygen) has still been realized by as little as 50–60%.

Over the period of 1940–2012 about 50 compositions of regenerative products and their production technologies have been patented. Note that foreign companies have scarcely reported new compositions of or production technologies for regenerative products. In Russia works in this field are being conducted at the Roskhimzashchita Corporation [3].

To reduce production losses and improve the performance characteristics of regenerative products (i.e. to enhance CO_2 absorption, ensure more uniform oxygen release, decrease the melting point of the product, etc.), the authors of the present publication have developed a principally new production technology based on crystallization of potassium perperoxide on a high-porosity fiberglass matrix.

The resulting regenerative product looks like plates formed by randomly cross-linked glass fibers coated by KO_2 nanocrystals.

The developed nanostructured regenerative products makes it possible to essentially decrease the metal and technical rubber contents (by 50–90 and 15–25%, respectively) of respiratory devices, thus decreasing their weight 1.5–3 times [3].

Compositions and Production of Air Regeneration Products (a Concise Review)

Production and properties of a crystalline powder of potassium perperoxide (the major component of air regenerative products) are well studied and described in the monographs [1–3]. There are different KO_2 production technologies: oxidation of air oxygen of alkali metals or their melts or amalgams, electrochemical oxidation of alkalis, glow-discharge synthesis, anodic oxidation in liquid ammonia or readily oxidized organic media, from peroxo solvate crystal hydrates, etc. However, only two of these technologies have gained practical importance: (1) oxidation of potassium in an oxygen medium (Russia, China, and the USA) [5–8] and (2) reaction of potassium hydroxide with hydrogen peroxide followed by dehydration of potassium peroxide peroxo hydrates in a hot dry air flow (France and Germany) [9–17]. The Roskhimzashchita Corporation developed a laboratory production method [3, 18, 19].

There are two known basic approaches to improving the performance characteristics of regenerative products fabricated from metal perperoxide powders: introduction of various additives to perperoxide formulations and/or change of the shape of packing (granules, tablets, blocks, etc.).

One of the ways to ensure enhanced oxygen release from the regenerative product is the use of catalytic additives, for example, oxides or other compounds of heavy metals (copper oxychloride, copper pentahydrosulfate, barium manganate, hopcalite, etc.) [18–22].

The authors of the patent [23] used lithium peroxide as the major component of the regenerative product and a Mn_2O_3 peroxide catalyst (3–7%) and a hygroscopic compound LiC1 (3–7%) as additives.

An approach involving hydration of potassium perperoxide (0.02–0.06 mol of water per 1 mol of KO_2) was patented [24]. The resulting regenerative product exhibited enhanced performance at low temperatures and enhanced stability at normal temperature. A tablet-shaped product was developed in late 1960s by L'Air Liquide (France) [25]. Such shape ensures more uniform density distribution of the packing and a larger solid–gas interface. Regenerative products with sustained oxygen release are fabricated from potassium perperoxide KO_2 and sodium perperoxide Na_2O_2 [26].

To increase porosity of formed regenerative products, improve diffusion, and decrease melting of the product in the regenerative cartridge, compositions on the basis of potassium perperoxide, sodium perperoxide, or their mixtures are doped with inert substances (asbestos, diatomaceous earths, magnesium oxide, calcium oxide, etc.) [26]. Such formulations can also contain catalysts, for example, molybdenum, vanadium, cadmium, iron, chromium, nickel, cobalt, copper, or titanium oxides, as well as lithium hydroxide. The most common hydroscopic additives to potassium perperoxide are calcium or magnesium oxides (2–30%) [27, 28].

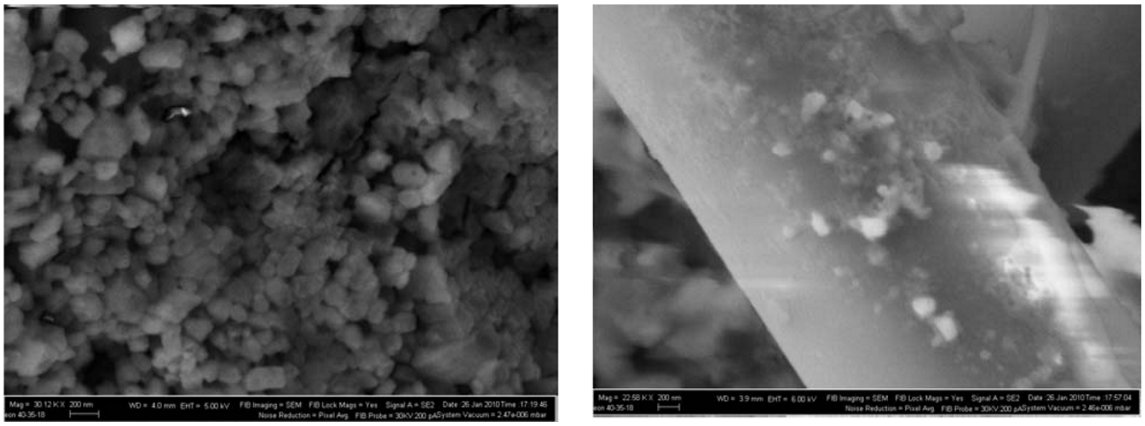
Granules produced according to [29] contain lithium oxide (2–10%), silica (0–2%), and calcium sulfate or lithium metaborate (3–8% or 5–10%, respectively). Furthermore, alkali metal peroxides can also be included in the formulations. To this end, sodium peroxide is mixed with lithium hydroxide, boron, or orthoboric acid [30, 31].

The technologies of fabrication of powdered KO_2 and regenerative products are introduced both in domestic and in foreign industry. Nevertheless, even though a great varieties of formulations on the basis of potassium perperoxide have been developed and designs of regenerative cartridges have been improved to enhance KO_2 efficiency, the problem of caking of the product still remains urgent. To prevent this process, regenerative products sometimes mix with Rashig rings, ceramic balls, ground pottery, or diatomite chips [32]. However, such regenerative cartridges contain less active component.

The technology described in [33] involves microcapsulation of KO_2 powder (particles size 250–1000 μm); other alkali and alkaline earth peroxides can also be used as the core of the capsules. The shell of the capsule can be made of polymer compounds, preferably olefin homopolymers or their vinyl copolymers, as well as polyamides, polyurethanes, starch, gelatins, resins; some hydrophobic or refractory materials, preferably ceramic mixtures, silica, charcoal, low-melting silicates and borates, or mixtures of organic polymers with metals. On contact with exhaled air moisture the shell material sorftens and swells as a result of which moisture reaches the core of the capsule and reacts with the core material, in particular, KO_2. All the above-mentioned production technologies for regenerative products include several operations:

– preparation of the major component of the regenerative material (KO_2 or NaO_2);

(a) (b)



SEM image of the surface of a plate of the fiberglass-supported KO_2 regenerative product: (a) general view of the plate surface and (b) KO_2 nanocrystals on a fiber.

– preparation of the charge by mixing KO_2 or NaO_2 with modifying additives, catalysts, or other components;

– processing the charge mixture into granules, tablets, blocks, or other shaped items suitable for air regenerative systems.

Losses of the charge mixture (up to 40%) may take place at the last (granulation) stage, and the unprocesses material is not always recyclable.

Air Regeneration Product of a New Generation: Nanocrystalline Potassium Perperoxide on a Fiberglass Support

In the search for ways to improve technical characteristics of regenerative products, we recently developed a principally new technology which allows one-stage fabrication of products of any shape with developed surface and controllable content of active oxygen. The resulting regenerative product is a finely crystalline potassium perperoxide fixed on the surface and in pores of a porous and $2O_2$-inert fiber support. This technology offers the advantage of the possibility fabricate not only a pure supported KO_2, but also its formulations analogous to known regenerative products. Such formulations are prepared by mixing KO_2 or NaO_2 powders with dopants modifying their properties (strength, resistance, absorption capacity, etc.).

The active oxygen content of the product fabricated by this technology is 32% (per pure KO_2 powder). The material containing KO_2 nanocrystals in its pores does not raise dust and is readily processable into grains, blocks, plates, etc.

The proposed technology involves impregnation of the porous fiberglass matrix with a $K_2O_2{\cdot}2H_2O_2$ metal peroxide peroxo hydrate with subsequent dehydration under heating in a vacuum [36]. The synthesis of crystalline KO_2 is based on the following reactions:

(a) synthesis of potassium peroxide peroxo hydrate

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

(b) disproportionation of potassium peroxide peroxo hydrate under heating in a vacuum:

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

The starting materials are crystalline potassium hydroxide and a 50% solution of hydrogen peroxide.

Potassium peroxide readily hydrolyzes to form KOH which is present as an admixture in the $K_2O_2{\cdot}2H_2O_2$ thermolysis product. The general equation of the mos probable process can be presented as a sum of reactions (1) and (2):

$$mK_2O_2{\cdot}2H_2O_2 \rightarrow nKO_2 + (m–n)KOH + H_2O + O_2. \quad (3)$$

The KO_2/KOH ratio in the final product is controlled by the process parameters (temperature, pressure, rate of evacuation of water vapors from the reaction zone, etc.).

As follows from thermogravimetry results, the decomposition curve for the supported-KO_2 regenerative products is identical to that for powdered KO_2. Reactions with water and CO_2 occur similarly to those with KO_2 crystal powder.

The novel regenerative product represents bright yellow KO_2 nanocrystals on a porous fiber support (see

Principal technical characteristics of modern respirators with different modes of protection

Characteristic	Name						
	SEZ, Roskhim-zashchita Corporation, Russia (under design)	Oxy K pace, Drager Sicherheitstechnik, Germany	OXYcrew, Drager Sicherheitstechnik, Germany	Chemres E-10, Midori Anzen, Japan	S 15, Auergesell schaft, Germany	SPI-20, Roskhim-zashchita Corporation, Russia	AZH-20W, Fushun Coal Mine, China
Weight, kg	0.9	4.0	2.5	1	3.0	2.20	1.20
Protection duration at a medium load, min	15	15	20	10	15	20	20
Maximum respiratory (inhalation/exhalation) resistance, Pa	50/50	500	No data	250/350	No data	600	196
Maximum inhalation temperature, ºC	45	50	No data	No data	No data	60	60
Service temperature, ºC	from –10ºC to +60ºC	No data	No data	No data	No data	0−60ºC	No data
Facepiece type	Cap	Mouthpiece with a nose clip and glasses	Cap with a half-mask, a headband, and an intercom device	Half-mask with a head-band	Mouthpiece with a nose clip and glasses	Cap with a half-mask	Mouth-piece with a nose clip
Speaking capabilities	Yes	No	Yes	No	No	No	No

figure; the SEM images were obtained at the “Nano-technologies and Nanomaterials” Educational and Research Center, Derzhavin Tambov State University).

Semenova et al. [37] studied the process of formation of KO_2 layers on a fiberglass support and revealed the mechanism of binding (“fixing”) the crystalline thermolysis product. IR spectroscopy showed that the binding of KO_2 to fiberglass involves intermeadiate formation of a layer of potassium silicate by the reaction of KOH contained in the product with the support material.

The regenerative product obtained by the technology described in [34–36] has a highly developed surface which provides facile reaction of KO_2 crystals with water vapors and CO_2 and complete release of active oxigen. By varying the degree of impregnation of the porous support by the starting alkaline H_2O_2 solution (or the solution/support weight ratio) one can widely vary the content of KO_2 in the fiberglass-supported regenerative product and thus control its sortion capacity and release of active oxygen.

A kinetic study [38] of CO_2 absorption on a plate-shaped regenerative product showed that CO_2 absorption and oxygen release occur at different active centers. This finding provides evidence for a two-stage mechanism of the reaction of CO_2 with KO_2, suggested in [39]. The processes of CO_2 absorption and oxygen release are well fitted by the known contracting sphere equation [40] until a 45–50% conversion of the regenerative product. This fact points to a very developed surface of ultrafine fiberglass–supported KO_2 and KOH crystals.

The CO_2 absorption capacity of the regenerative product in a dynamic flow of air with increased CO_2 concentration (up to 4.0%) is 120–140 dm^3/kg, which is higher by 40–60% compared to commercial granular regenerative products on the basis of potassium perperoxide.

The use of the developed regenerative material allows the consumption of metal and rubber technical goods for production of respiratory devices to be reduced by respectively 50–90% and 15–25%, thereby reducing by a factor of 1.5–3 the weight of respiratory devices [41–46].

At present new air regeneration systems on the basis of the porous fiber-supported nanostructured regenerative product are being designed in the framework of the "National System of Chemical and Biological Safety of the Russian Federation (2009–2013)" Federal Targeted Program. First of all, this is an escape self-rescue apparatus for protection of respiratory organs and eyes in emergency situations associated with changes in air composition, including fires. The table compares the principal technical characteristics of this device (SEZ) and its analogs.

The designed escape self-rescue apparatus is lighter than Chemres E-10 and SPI-20, other parameters being comparable; the inhaled temperature is about 45ºC. The respiratory resistance of the designed self-rescuer is almost 4 times lower compared to AZH-20W, 5 times lower compared to Chemres E-10, and 12 times lower compared to SPI-20. Moreover, it allows wearers to speak.

The low weight (0.9 kg), very low respiratory resistance (5 mmAq), and low inhaled temperature ($\leq$45 °C) allow the escape self-rescue apparatus for protection of respiratory organs and eyes to be used by aged people and people with lung diseases.

CONCLUSIONS

Synthesis of regenerative products on a highly porous fiberglass support is the most promising direction in the field of development of regenerative products. This technology allows one-stage fabrication of air regeneration products, unlike other technologies which include granulation of KO_2 powder.

The potassium perperoxide nanocrystals synthesized from an alkaline solution of hydrogen peroxide strongly bind to fiberglass, which prevents the regenerative product from dusting during exploitation. Furthermore, the highly developed surface contains a great number of active centers, which enhances the CO_2 absorption capacity of the regenerative product by 30–40% compared to a granular regenerative product.

The new regenerative materials allow one to reduce the weight and dimensions of air regeneration devices and simultaneously essentially improve their physiologic and hygienic characteristics.

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