INTRODUCTION

The term "high-efficiency gas purification" (HEGP) applies to a process of removing of solid or liquid particles of the smallest existing size from contained or moving gases with an efficiency of at least 99%. For reasons that will be discussed below, this process is usually applied to particles smaller than 10 μm with rather low denumerable and weight concentrations — less than 1 mg/m^3 or 10^6 1/cm^3, respectively, that are typical of the standard level of the atmospheric aerosol background. When the concentrations and particle sizes are larger, these are captured in two stages of which HEGP is the second one.

Scientific interest in HEGP, both in the industrial method, and lately also as means for ensuring current standards of human comfort, stems from at least three factors. The first of them is the increasing pollution of the environment by industrial waste, a large part of which is made up of aerosols that are dangerous to living organisms. The second is associated with the need to protect armed-forces personnel and the civil population from nuclear, chemical and bacteriological weapons, and also from the consequences of armed attacks on nuclear facilities and of large-scale accidents at the latter, the danger of which is rooted primarily in the resulting aerosols. The third reason stems from the advent of a large number of new industrial and medical technologies that put very strict requirements to the purity of the gases that they use and of the atmosphere of production premises.

Aerosols to which HEGP applies, that form two-phase systems consisting of liquid and solid particles of different size suspended in air and other gases, are substances that are highly prevalent in nature and human activity. They may be either natural or man-made. The first, that form in the terrestrial atmosphere without human participation, are purely natural phenomena. They control the climatic conditions and ensure the aerosol environment that is common to terrestrial organisms. Examples of such aerosols are atmospheric clouds and fogs that are comprised of condensed water droplets or ground-level dust clouds that contain solid particles that form upon wind erosion of soils and particularly intensively — during dust storms. Another example is the so-called atmospheric haze — water droplets dispersed from the surface of oceans, seas and lakes that form, upon drying out, solid hygroscopic condensation nuclei, that propagate over enormous distances and are responsible for the global turbidity of the terrestrial atmosphere. Forest fires and volcanic eruptions, that generate smoke-containing condensed solid particles are still another example of a perceptible contribution to the aerosol background of the terrestrial atmosphere. Finally, a quite singular but rather ubiquitous example consists of natural radioactive aerosols that form upon condensation in the atmosphere of short-lived daughter products of radon isotopes, that are gaseous members of the natural radioactive families of uranium, thorium, actinium and neptunium radionuclides and are constantly released by rock material that contains them. A perceptible contribution to the natural aerosol background of the terrestrial atmosphere is made by micrometeoric streams from the outer space and by also by particles of biological origin — live or dead microorganisms and plant pollen [3, 4].

The aerosols that arise exclusively due to human activity can be subdivided into those produced intentionally and those that occur as a byproduct. The first are usually the intermediate or final state of substances in various industrial processes such as atomized fuel, lubricants, paint, chemical reagents, catalysts, fertilizers, medicinal or food products or soot, metal powder and other chemical products condensed within the atmosphere. The second kind forms to one degree or another simultaneously with any imaginable industrial operation and handling any, particularly low-strength, loose and bulk materials or substances. Typical examples here are aerosols that form upon re-loading and transportation of cement, flour, construction debris, smelting and welding of metals, and also in mining of ores, particularly when using explosives for this purpose. In the case of high-toxicity materials and substances, virtually any, even the most careful handling, should be regarded as an aerosol source.

Aerosols can be divided by their effect on living objects into four kinds; these are: necessary, common, useful and dangerous. The first include natural aerosols that make an important contribution to the external radiation balance and the internal water balance of the planet and ensure stable climatic conditions

needed for maintaining life on Earth. These are atmospheric clouds, haze and other condensation nuclei. The second, that are also of natural origin, such as atmospheric dust, aerosol products of soil erosion, of forest fires, of volcanic eruptions and meteor impacts, are usually endurable when dilute, however, near their sources they may turn out by far not benign, due to their high concentration. Both natural and man-made aerosols may be useful. Even though their contribution to maintaining life on Earth is by far not clear, a number of positive effects on living organisms that were already discovered are beyond doubt [5]. Medicinal and disinfectant aerosols can be definitely included in the useful category, however, they must be taken in strictly prescribed dosages, whereas inhalation equipment, premises and servicing personnel must conform to special safety specifications and norms [6]. All the remaining man-made aerosols, excepting atomized or condensed water, should be regarded as dangerous to living organisms and, consequently, to humans to one or another extent.

The level of this danger depends on the strength of the aerosol sources, the solids concentration within the aerosol, the size, chemical, isotope and biological composition of their substance, their chemo- and radio-toxicity or biological virulence. For comparative estimates, we can use here the values of the maximum permissible concentration of different substances in industrial premises, characterizing the level of their occupational hazard or, in the free atmosphere, reflecting their overall danger to the environment and population. Thus, whereas for aerosols of free silicon oxide that forms in mining and construction operation, the maximum permissible concentration by weight in industrial premises is 1 mg/m^3, which approximately corresponds to 100 particles of 1 μm per cm^3, then for beryllium oxide it is by 6 orders of magnitude smaller and corresponds approximately to a single 0.1 μm particle per 10 cm^3 and for alpha active polonium 210 with a maximum permissible concentration of 10^{-14} Ci/liter, it amounts to only a single particle of this size per m^3. On the other hand, in the case of the so-called "hot" particles with individual beta activity of more than 1 Bq or with alpha activity of more than 0.01 Bq that form during nuclear accidents and explosions, and also for ultra-toxic and ultra-virulent components of modern chemical and bacteriological weapons, the maximum permissible concentration should ensure a sufficiently low probability of a single entry of such a particle into the respiratory tract or onto the skin surface and hence should not exceed a single micron and even submicron particle per hundreds of m^3. The most dangerous particle size range that has simultaneously the greatest penetration power into respiratory organs, elevated stability and time of existence in the atmosphere and also elevated permeability through filtering devices is from 0.01 to 1 μm [7].

It is obvious that with the increase in the scales and variety of industries, increasing use of more toxic materials and increasing the strength of sources of man-made aerosols, the probability of exceeding their maximum permissible con-

centration in industrial premises and in the ambient air increases continuously and this necessitates the use of increasingly complicating protective measures and equipment. There exist at least three methods of protection from aerosols that are dangerous to the ecology and health of the population. The first consists in fore-going the production and use of chemical, bacteriological and nuclear weapons, something that is a purely political matter. The second is the selection and implementation of such technologies and equipment that virtually eliminate or significantly limit the formation of such aerosols. The third, traditional, consists in trapping or filtering aerosols by different methods in specialized devices or filters, including also HEGP methods and devices. Even though the second method proven itself as effective, it is still used at a limited scale. This is because the third approach, and in the first place, the HEGP method, is preferred and put increasingly into practical use. The reason for this is not only the rather high efficiency in providing ecological protection, but also the need that appeared recently to protect the most advanced and highly prestigious information, space-exploration, biological, medicinal and a number of others, so called "clean-room" technologies from atmospheric aerosols, i.e., from the environment.

In both these functions HEGP should ensure the specified two-order and frequently six- and more order of magnitude reduction of the denumerable concentration of aerosol particles having dimensions from several μm to an atomic scale. Only two of the currently existing capture methods — thermo-precipitation and filtration through a porous or fibrous layer satisfy such rigorous requirements. The first, which has proven itself in the field of analysis of aerosol particle sizes, is not too suitable for purifying large gas volumes due to its low productivity and high heat consumption. The second becomes acceptable when the bulk porosity of the layer is at least 50% and the pore size not more than 10 μm. At a filtration rate of 1 cm/sec such a layer, when 1 mm thick, retains at least 99% of 0.1 μm particles and, upon proper arrangement within the filtering device, may ensure an output of about 10,000 m^3/hr per m^3. This purpose can be served by high-porosity polymer, metal or ceramic membranes [8, 9], but non-woven micro-fiber materials from cellulose and mineral fibers (asbestos, glass, kaolin, basalt, graphite) are the most suitable. This is because they combine a rather high (up to 95%) bulk porosity, micron size of pores and high capture efficiency of particles of any size, while exhibiting a rather low resistance to the flow they filter and having satisfactory flexibility and strength [8]. The latter are obtained primarily by means of the high-volume and relatively cheap, so-called "paper" technology by precipitating pre-ground fibers mixed with a binder from a water suspension onto a micromesh [10].

However, other methods for obtaining similar material by single-stage formation of fibers and fibrous layers from solutions or melts of fiber-forming materials are also possible.

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Electrospinning of non-woven fibrous materials occupies a special place among the known industrial methods of obtaining chemical fibers and fibrous structures, because of the simplicity of equipment needed, low specific power consumption and large variety of products. Electrospinning is a dry, non-spinneret method in which deformation of the polymer feedstock, subsequent transportation of fibers that solidify upon evaporation of the solvent and formation of the fibrous layers are brought about exclusively by electric forces in a single working space.

The method of electrodynamic atomization of liquids in which a slightly-conducting liquid discharged from a metering nozzle subjected to a high DC potential difference is atomized by forces of repulsion of similarly-charged electric charges into very fine particles which can then be precipitated onto an oppositely located electrode, is the prototype of process of electrospinning of fibrous materials.

Bose found, at the very first attempt of investigating this phenomenon in 1745 that, under certain conditions, the cloud of atomized droplets is preceded by a jet flow. During 1912–1931 first Burton and Wiegand [11] and then Zeleny [12–15] and Macky [16] confirmed this flow pattern and investigated it in detail. However, neither in these, nor in subsequent studies [17, 18] that have provided a rather wide range of applications for electrodynamic atomization of liquids (obtaining uniform-size and uniform-mobility aerosols, ink-injection printing and micro-encapsulation, atomization of dielectric and cryogenic fluids, focused application of toxic materials and polyfunctional coatings), is there any mention of the possibility of using the jet flow mode for fiber generation.

The potential of this technique of fiber generation was realized simultaneously by a number of investigators and, in the final analysis, served as the springboard for designing the industrial method of electrospinning of fibrous materials. The first patents for obtaining fibers from a jet of material injected into a space with a strong electric field were awarded in 1902 to Morton [19, 20], but the fibrous layer produced under these patents was too weak for practical use. The first real success was attained in 1930, when Formhols [21] suggested that the fibers be generated from solutions of polymer resins. This method was developed in 1936 by Norton [22] for obtaining fibers from melts and solutions of rubber and other synthetic resins, however, all these patents did not lead to the production of usable fibers because of the low quality and inability to compete with commonly used fibers.

A decisive breakthrough in development and application of the electrospinning method was attained in 1938 in the USSR, by the young co-workers of Prof. N.A. Fuks (Fuchs), the head of the Aerosol Laboratory of the L.Ya. Karpov Institute, N.D. Rozenblum and I.V. Petryanov-Sokolov. They experimented with obtaining solid, spherical, uniformly-sized aerosol particles of nitrocellulose from its solution in acetone by the electrodynamic atomization method and unexpectedly discovered a concurrent phenomenon of fiber generation, in which liquid jets

discharged from a nozzle at a high electric potential difference, instead of under-going the expected Rayleigh degradation into droplets, solidified entirely, forming strong continuous fibers with stable cross section having a diameter of the order of several microns and less. Settling on a grounded electrode or on poorly insu-lated surfaces, they formed thin, but rather strong anisotropic layers with a quasi-uniform random fibrous structure and rather low, 2–5% volumetric packing density, highly compressed by electrical forces [23].

Instead of concentrating on their "failure," these two scientists appropriately identified this competing mode as something new that may have major practical applications. They suggested and verified that the fibrous layer thus obtained is a highly efficient smoke filter. Subsequently, they concentrated on the new phe-nomenon, optimized the fiber generation mode and the structural and mechanical properties of the fibrous layer that made possible its extensive utilization. They designed and constructed safe and efficient equipment and, in the final analysis, converted the laboratory device for electrodynamic atomization of liquids into the new industrial method of electrospinning of fibrous materials, the output of which is currently known as Petryanov filters or briefly, PF materials.

At the time when the method of electrospinning of fibrous materials came into being, virtually the single real sphere of mass utilization of high-efficiency smoke filters consisted of means for protecting army personnel and civilians from chemical and bacteriological weapons of mass destruction. All USSR and West-ern gas masks of this time employed a high-efficiency smoke filter as the first protective barrier. For this reason all the work on electrospinning of fibrous ma-terials was concentrated on this, highly-specific problem. The first industrial facil-ity for producing fibrous materials by the electrospinning methods for use in military gas masks was constructed in the city of Tver' in 1939. This material, which was known as BF (battlefield filter) was obtained from a solution of cel-lulose acetate in the mix of dichloroethane with ethanol.

With the start of the war with Germany in 1941, this facility was moved further to the east, where it was enlarged, adapted for the use of different feed-stock and for producing a larger variety of materials. In addition to cellulose ace-tate, the less expensive and more readily available perchlorovinyl resin and alternate solvents came into extensive use. The filter material started being used not only in personal gas masks, but also in systems and means of collective chemical and bacteriological protection of stationary and vehicular military and civil facilities.

When originally invented, the PF filter materials and similar products made of electrospun fibers were not the only means of high-efficiency filtration of flu-ids. The already-available filter paper and cardboard, obtained by grinding natural fibers followed by sedimentation from binder-added water suspensions onto a mi-cromesh, had a similar structure and fields of application. This, in part, explains

the limited use of electrospun fibrous materials in the West. However, filter paper and cardboard differed from PF materials by a number of functional and operating properties, were not interchangeable and had advantages over one another under specific conditions and in different products. The ability of PF materials made from good dielectric feedstock to acquire an electric charge, that highly improved their filtering properties in the course of its manufacture turned out to be particularly attractive. In addition, electrospinning of fibrous materials turned out to be much simpler and flexible than the methods used for obtaining filter paper and cardboard. With the start of the nuclear weapons race, the last two circumstances turned out to be decisive in selecting the PF fibrous materials as the principal means of protecting nuclear-facility and army personnel and the residents of the Soviet Union from radioactive aerosols. This caused a steep increase in the output of these materials by electrospinning. During the 50s and 60s new industrial plants were put on line and old facilities were upgraded and, as a result, the annual output of PF materials and similar products was as high as 20 million m^2 or 60 tons. Whereas individual protection of respiratory organs is still the main end use of this material, but instead of gas masks, the nuclear industry and civil defense are now in need of a light, throwaway respirator. The PF material faces no competition in this field, since its electric charge that ensures high aerosols capture efficiency while interfering most insignificantly with breathing, has a shelf life of several years and is capable of at least 10 hrs of actual use. The following end users of this product are filters for removing radioactive aerosols from industrial gases and ventilation exhaust, followed by removal of suspended particles and microorganisms from intake air supplied to "clean" and sterile premises. The third major end user is a new customer — cadmium-nickel and also other electric power storage batteries in which the PF material serves as a separator — electrolyte-filled porous spacer between the electrodes. There also exist a host of small-scale niche users with a number of specific requirements — sound absorbers, thermal insulation, analytic filters, filter tapes for aerosol monitoring, and filters for deep purification of liquids and for drying of gases. The PF and similar materials are used for producing composites with bifunctional properties — sorbing filters, chemosorbing filters and ion-exchange filters. The variety of PF materials and the source materials for producing them broadens accordingly. Materials are produced with different thickness, surface density and microstructure. The feedstock polymers now begin to include poly(methyl metacrylate), polystyrene, copolymer of vinylidene fluoride with hexafluoropylene and more heat and chemical resistant materials such as poly(acrylonitrile), poly(sulfone), poly(phenylene oxide), polyarylate, poly(-trifluorostyrene) and polyarylide, whereas the traditional solvents such as dichloroethane, acetone and ethanol have been joined by methyl ethyl ketone, methylene chloride, butyl acetate, cyclohexanone and dimethyl formamide. The production equipment is also upgraded

gradually: its capacity is increased significantly, and sheet-type products are replaced by rolled goods. Quality control is upgraded, the industrial and ecological safety of manufacturing facilities is improved and the working conditions at the plants are enhanced.

Special filter designs for use with PF materials are created and constantly improved, the assortment and standard sizes of these materials are extended. Facilities specializing in producing these filters are set up. Methods and stands for quality control and certification are developed.

The present monograph is comprised of eight chapters, a foreword and a conclusion. The first four chapters are devoted to the process of electrospinning of fibrous materials. The first and third chapters devote particular attention to the fundamentals of the electrospinning method. The first chapter is concerned with the mechanism of electrospinning of fibers and fibrous layers from polymer solutions. It analyzes the conceptual design of this process, the theoretical models of the formation, acceleration and splitting of a charged jet of poorly conducting liquid in an electric field, its drift and solidification into fibers and the formation of non-woven fibrous material from them, and also the mechanism of transport of the electric charge and of the effect of its volumetric distribution. The third chapter reflects the particular role of the macromolecular factor in electrospinning of fibrous materials. It lists the rheological properties of the polymer solutions used for fiber generation and analyzes the effect of the nature of the macromolecules and of the properties of the "polymer-solvent" system on the mechanism of this process.

The second and fourth chapters are devoted to the industrial experience accumulated in obtaining fibrous PF materials and products similar to them by electrospinning. They describe the feedstock, the process sequence and nature, equipment, the industrial process as such, its versions and specifics, stability and controllability, method of monitoring the production parameters and product quality. This experience is subjected to critical analysis, the advances in technology and environmental protection of this process are assessed and predictions for further development are presented.

The last four chapters are devoted to high-efficiency aerosol removal from gases, fields and experience of industrial application.

The fifth chapter is concerned with theoretical principles of high-efficiency gas purification. It examines a method of representing random properties of particles in the original aerosols by applicable interrelated distribution functions, the gasdynamic properties of the particles, their interaction with the solid surface. The chapter presents the principles of the current filtration theory as a means for describing the process of deposition of particles from the stream onto the fibers by means of various mechanisms, and also methods of simulating the structure of the fibrous layer and of the sediment that accumulates on it.

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The sixth chapter lists the functional and operating properties of the PF materials, their physical characteristics, electric charge and macrostructure. The mechanical, filtration and other properties of these materials are examined.

The seventh chapter describes the principles of optimal design of high-efficiency aerosol filters employing PF materials. Their different designs and standard dimensions, functional properties and operating characteristics, testing methods, manufacturing principles and mass production macrostructure and also their assortment are described. The fourth chapter demonstrates rational techniques and experience in using PF material based filters in environmental protection, in protecting the health of manufacturing personnel and of the population at large and in modern, including "clean" technologies. It concludes by analyzing the current state of art in Russia with respect to the scientific achievements and practical experience in high-efficiency gas purification employing PF materials and lists ways for further improvement of this promising high-efficiency filter material and of the purification technology based on it for environmental-protection and new technologies.

The last, eight chapter demonstrates rational approaches and experience in using PF based materials in environmental protection, in protecting the health of manufacturing personnel and of the population at large, in modern, including "clean" technologies.

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