

COMPARATIVE ANALYSIS OF FILTER MATERIALS FOR PRODUCTION OF PERSONAL RESPIRATORY ORGAN PROTECTIVE DEVICES

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UDC 677.494.027.622

Industrial filter materials for respirators of various polymer compositions produced by electrospinning and meltblown technologies are investigated. Comparative experimental data on filtration properties of materials for various filtration conditions are presented. The influence of various parameters on electrostatic charge leakage is shown.

Because of increasing adverse effect of chemical and biological factors on the environment a situation has developed today where the preparedness for protection of the population from the existing and newly emerging technogenic threats has become a particularly serious matter.

Epidemic and epizootic flareups of infectious diseases, such as avian and swine groups, atypical pneumonia, corona virus, etc., most of which are characterized by sudden occurrence and high percentage of fatalities. Smoke and carbon gases produced during forest and peat bog fires, as, for example, in 2010 summer when, due to abnormal heat and multicentered forest fires encompassing large tracts of regions of the country, aggravation of respiratory ailments of lungs and surge of deaths took place.

All these adverse events show the evidence of inadequate security of the population of the country by effective device for personal protection of respiratory organs (DPPRO) from the danger of chemical and biological matters, particularly in aerosol form. Protective masks available in pharmaceutical chains often are only modern modification of wool-cheesecloth bands and do not have a filtering layer. This pertains also to type II professional medical masks made in conformity with GOST R 58396–2019 “Medical masks. Specifications and test methods,” having a protection factor of 1.5, which, in light of recent threats associated with COVID-19 pandemic, is critically low.

In view of the new technogenic challenges faced by the population, portable DPPRO must be developed, produced and widely available in the form lightweight respirators (half-masks) with FFP2 level of protection (protection factor 12–16) conforming to the standard GOST 12.4.294–2015 “Devices for personal protection of respiratory organs. Filtering half-masks for protection from aerosols,” having less resistance to breathing than industrial respirators or gas masks [2, 3].

The goal of this work was to make a comparative analysis of filter materials available in the Russian market for production of light respirators.

In the 50's of the last century, the ShB-1 Lepestok (Petal) brand respirator [4] made using FPP-70 (Lepestok-40) or FPP-15 (Lepestok-200) type of electrostatically charged filter material was the most popular respirator in the USSR and later in the Russian Federation. Both these materials are produced by the technology of electrospinning in a high-volt field from solutions of chlorinated polyvinyl chloride (materials of the old sample) or chlorinated polyethylene (new materials) [5, 6]. Presence and stability of electrostatic charge on fibers have a decisive influence on the filtration

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Table 1. Commercial Filter Materials

Brand	Producer	Production technology	Polymer	Surface density, g/m ³	Resistance to air flow at 1 cm/sec, Pa
FPP -15-1.5	Sorbent LLC, Perm	Electrospinning	Chlorinated polyethylene	25–28	12–16
RFM -0.6	EKhMZ LLC, Elektrostal	Electrospinning	Chlorinated polyethylene	12–14	6–8
RFM -70-0.3	EKhMZ LLC, Elektrostal	Electrospinning	Chlorinated polyethylene	30–35	2–3
RFM -70-0.8	EKhMZ LLC, Elektrostal	Electrospinning	Chlorinated polyethylene	82–87	6–8
FPK -70-0.3	EKhMZ LLC, Elektrostal	Electrospinning	Polycarbonate	25–29	2–3
FPK -70-0.8	EKhMZ LLC, Elektrostal	Electrospinning	Polycarbonate	60–64	6–8
MFP -5	FMT LLC, Kaluga	Meltblown	Polypropylene	23–25	5–7
EFMP-F1	Tesiz LLC, Kimry	Meltblown	Polypropylene	32–35	5–7
TDK-P1-II	TEDA Filters, China	Meltblown	Polypropylene	23–25	7–8

capacity of the fiber material and reduce aerosol penetrability by several orders, virtually transforming it into an electrofilter.

Meltblown material produced by the technology of polypropylene melt blowing is being used abroad since the start of the 70's of the twentieth century for manufacture of respirators [7, 8]. Initially, such material did not have electrostatic charge on fibers and worked only by way of mechanical filtration. Later, various techniques were developed for charging polypropylene fibers, such as treatment with corona discharge, application of triboelectric effect [9] or special additives introduced into the polymer melt, for example tourmaline [10, 11], magnesium stearate, colophony [12, 13], triazines [14], etc. Russian and foreign filter materials available in the domestic market are listed in the table.

All materials produced by electrospinning technology have electrostatically charged fibers based on chlorinated polyethylene or polycarbonate.

Polypropylene-based materials, both domestic and imported, produced by meltblown technology are submitted to additional treatment. The EFMP-F1 filter material is charged with corona discharge, additives based on manufacturer's know-how are used for generation of charge in MFP-5 material, and the method for charging TDK-P1-II material is a commercial secret.

For ease of comparison and evaluation, standard (i.e., referred to 1 cm/sec) resistance to air flow is presented in the table for all investigated materials. This parameter for filter materials has one of the key virtues because it determines the ease and comfort of breathing in DPPRO. It is known that resistance to air flow depends on the diameter of the fibers of the filter material and its porosity (the higher the porosity, the lower the resistance to breathing).

The practice of testing filter materials and respirators made thereof is based on use of fluid polydispersed aerosols with very narrow size distribution. It is adopted from methods of testing gas masks for fluid aerosols of poisonous materials. In the USSR, such test-aerosol was SOM (standard oil mist) described in GOST 12.4.028–76. Presently, paraffin oil (kerosene) aerosol and solid sodium chloride aerosol are used in foreign and Russian standards. The average diameter of such test-aerosols is 0.35 μm , which does not conform to most-penetrating diameter of aerosol particles. Therefore, it is advisable to test not only in compliance with the referred standards, but also to use methods for HEPA and ULPA class of air filters in conformity with GOST R EN 1822-1–2010, which are methodologically more complicated, but yield accurate results for highly penetrating diameters of aerosol particles. Both testing methods are used in this work.

The filter materials were tested on a TSI 3160 automated filter tester using dioctyl phthalate (DOP) as the monodispersed aerosol with an average mass diameter in the 0.02–0.4 μm range at 0.1–0.2 mg/m^3 particle concentration (countable concentration 10^2 – 10^4 particles in 1 cm^3) to determine the most penetrating particle. A TSI 8130 filter tester with paraffin oil as the aerosol with average mass particle diameter of 0.4 μm (standard geometrical discrepancy ~ 2) and a concentration of about 20 mg/m^3 was also used.

It was found that the penetrating capacity of monodispersed DOP aerosol with an average mass particle diameter of 0.4 μm as per GOST R EN 1822-1–2010 are identical with the penetrating capacity of monodispersed paraffin oil as aerosol with an average mass particle diameter of 0.4 μm as per GOST 12.4.294–2015.

Based on GOST 12.4.294–2015 specifications, the filtration efficiency of the respirators should be tested at maximum air flow rate of 95 liters/min, which corresponds to the linear rate of 6.3 cm/sec through a filtration area of 250 cm^2 (matches the filtration area of Lepestok and Alina respirators). Reduction of filtration area by adding an exit valve or by compacting (Spiro foldable respirators) raises the linear air flow velocity, which, in turn, produces a strong effect

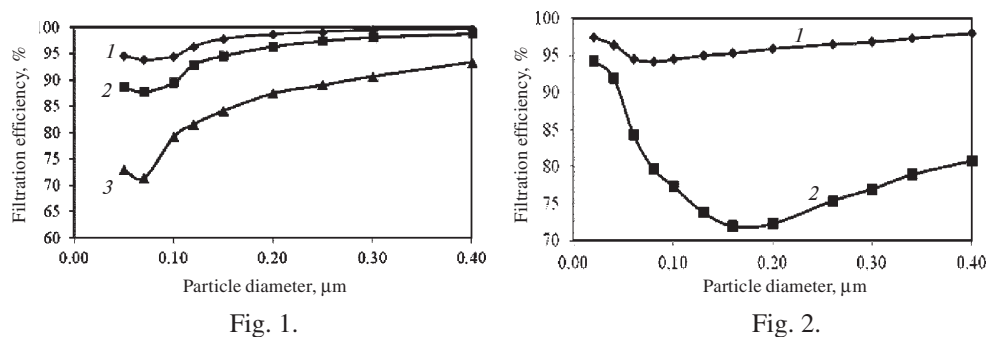


Fig. 1. Efficiency of DOP aerosol filtration by RFM-70-03 material at linear flow rate 1 (1), 2 (2), and 6.3 (3) cm/sec.

Fig. 2. Influence of charge removal in alcohol vapors on filtration properties of EFMP-F1 material at linear flow rate 6.3 cm/sec: 1 – material before charge removal and 2 – discharged material.

on the filtration properties of the material and should be considered in selecting it for manufacture of a specific type of respirator.

The dependence of filtration efficiency on particle diameter at various linear air flow rates is illustrated in Fig. 1 by example of RFM-70-03 material. It is evident that the filtration properties of the material decline considerably with increase of air flow velocity.

The most penetrating aerosol particle diameter depends not only on the filtration rate, but also on the amount of electrostatic charge on the fibers. If the material is discharged in alcohol vapors or test-aerosol filtration is prolonged, the characteristics of dependence of the efficiency on the particle diameter changes, as evident from Fig. 2 with reference to the EFMP-F1 material.

While the most penetrating aerosol particle diameter is 0.07-0.1 μm for charged fiber material, it is 0.15-0.2 μm for the discharged material. Thus, increase of filtration rate and decrease of charge shifts the most penetrating particle diameter toward coarser particles.

It is known that electrostatic charge on fibers diminishes (charge leakage) with passage of time in comparison with freshly produced fibers, which impairs filtration properties. The reason for this is the influence of vapors of polar substances present in air. In particular, presence of residual solvent in the fibers for a prolonged period is typical for materials produced from polymer solutions by electrospinning technique. Thus, presence of solvents (1,2-dichloroethane, butyl acetate or mixture of butyl acetate with ethyl acetate) in fibers of FPP-15-1.5 type of material from chlorinated polyvinyl chloride was shown in [15]. The content of 1,2-dichloroethane vapor in air above the material at 20 ± 5°C is 15-110 mg/m³ and at 50 ± 5°C is 105-950 mg/m³ which is almost 100 times higher than the maximally permissible value, as for freshly produced materials. In this regard, the most volatile is ethyl acetate whose content in the original solution is 50 % of its mixture with butyl acetate; in the samples of the material it was present in traces (less than 0.2 mg/m³).

For comparison of filtration properties of various materials for determining the filtration efficiency it is expedient to use filtering coefficient. This parameter characterizes the capacity of the filter material for trapping aerosols and does not depend on its thickness. The higher the filtering coefficient, the more efficient the filter is:

$$q_F = - \lg K/\Delta p,$$

where q_F is the filtering coefficient, K is the coefficient of aerosol particle passage (coefficient of penetration) through the filter, and Δp is the pressure difference in the filter.

The change in filtering coefficient for RFM-70-0.3 material one month and one year after production is shown in Fig. 3. Depletion of charge with passage of time and, in consequence, decrease of filtering coefficient is associated with evaporation from the fibers of the residual polar solvent (1,2-dichloroethane). This phenomenon is akin to removal of charge from fibers in ethanol vapor, but in a much weaker form and is prolonged.

FPK-70-0.3 and FPK-70-0.8 materials produced from solution of methylene chloride, the volatility of which is 5 times higher than that of 1,2-dichloroethane, do not exhibit appreciable change in filtration properties with time.

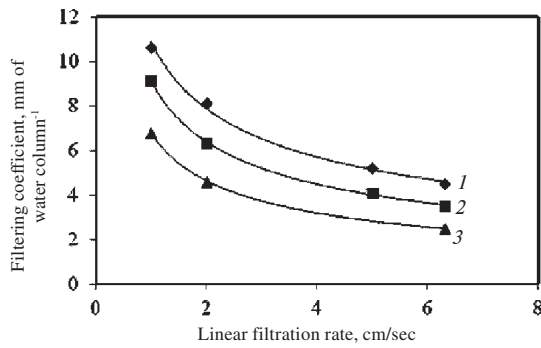


Fig. 3.

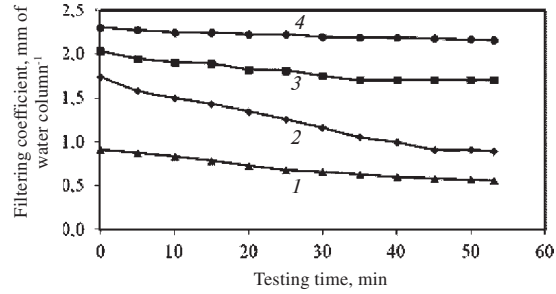


Fig. 4.

Fig. 3. Change in filtration properties of RFM-70-0.3 material with time passed after production: 1 – freshly produced; 2, 3 – after a month and a year, respectively.

Fig. 4. Change in filtration properties of materials exposed to paraffin oil aerosol (Loading test): 1 – FPP-15-0.6, 2 – FPP-15-1.5, 3 – EFPM-F1, and 4 – TDK-P1-II.

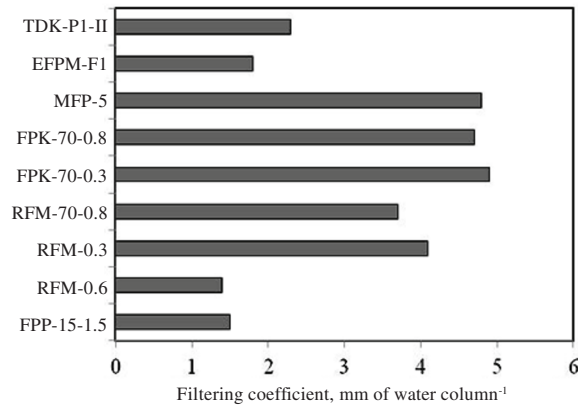


Fig. 5. Filtration properties of materials.

Charge depletion is not typical also for meltblown. Note that even ignoring filter thickness it is obvious that the diameter and “porosity” of the fibers themselves will affect the intensity and rate of charge depletion. The higher the values of these parameters, the longer the charge will be retained on fibers because the contact with the moisture in the air will be minimized.

An important respirator parameter is stability of its filtration properties during use. To determine the stability of the filtering coefficient over time, a continuous test was carried out over 53 min (Loading Test) until 250 mg of paraffin oil aerosol passed through the filter was achieved. The dynamics of change in filtration efficiency with time for FPP-15-1.5, RFM-0.6, EFPM-F1, and TDK-P1-II is shown in Fig. 4.

It is evident that the maximum decrease of charge on fibers and decrease of filtration properties virtually up until the discharged state are a characteristic for FPP-15-1.5 and FPP-15-0.6, the diameter of the fibers of which is 2-3 times less than that of meltblown EFPM-F1 and TDK-P1-II materials. This, in addition to the initially high charge of the latter, imparts in them longer protective capacities against exposure to concentrated and charge-resistant oil aerosol.

The summarized results of comparison of all materials tested with DOP aerosol with 0.4 μm particle diameter at 6.3 cm/sec flow rate are shown in Fig. 5.

Among the materials produced by electrospinning technique, RFM-70 and FPK-70 materials and among the materials produced by meltblown technology, MFP-5 material containing additives that generate charge, have the best filtration properties. Higher aerosol filtration efficiency of RFM-70-0.3 and FPK-70-03 materials in comparison with other materials of the same brands (RFM-70-0.8 and FPK-70-08) of materials is associated with lower surface density, which resulted from looser structure and lower fiber packing density. This makes such materials most suitable for production of DPPRO of the first two classes of protection.

The difference between the efficiency of FPK-70 and RFM-70 materials produced by the same method and containing fibers of the same diameter can be explained by self-charging phenomenon with removal of 1,2-dichloroethane from RFM-70 fibers. It is important that FPK materials of different types ensure high filtration efficiency with low air resistance.

By and large, the investigations revealed that FPK-70 of different types are leading materials in the current domestic market in terms of filtration indices. These materials have low resistance to air flow, does not contain deleterious solvents, and are not submitted to self-charging during storage. They are not inferior in properties to the best meltblown samples with charge-generating additives and could be recommended for production of light DPPRO of FFP1 and FFP2 classes for supply to population.

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