Physico-chemical Modification of the Fibrous Filter Nozzles for Purification Processes of Water and Air

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Abstract. A set of experiments to study physical and chemical modification of the surface of fibers is conducted to expand the area of their application for purification of water, gas and air (including that in conditions of space). The possibility of modification of filter nozzles in the process of fiber formation by particles of coal of BAU type, copper sulfide and silver chloride is experimentally shown. The fraction of the copper sulfide powder less than 50 microns in size was crushed in a spherical mill; it was deposited on fiber at air temperature of 50°C and powder consumption of 0.5 g/l of air. The resulting material contained 6–18 CuS particles per 1 cm of the fiber length. An effective bactericidal fibrous material can be produced using rather cheap material – CuS and relatively cheap natural compounds of sulphides and oxides of heavy metals.

1. Introduction
The development of various industries requires new approaches to purification of ventilation air and industrial gases. Filtering through porous filter medium is one of the most advanced methods of purification of water and gas from natural and anthropogenic pollutants. Filter nozzles made from fibers are most preferable for these purposes.

2. Experimental
The technology of processing recyclable materials and thermoplastics waste (polyethylene, polypropylene, polystyrene, polyethylene terephthalate and their compositions) to produce fibrous materials has been developed, in particular, for filtration purification of liquids and gases.

The technology [1–3] under varying parameters of the technological process allows production of fibers with a wide range of diameters (1–500 μm) with simultaneous coating of the surface of the resulting fibers with powders for production of filters for different purpose. Sedimentation of active materials adsorbed on the fiber surface in water or water-organic solutions and interaction of these materials with the surface of the carrier-material with the following formation of the adsorptive material layer are the main methods of modification of fibrous materials based on polyolefins which
are highly resistant to the majority of chemical reagents and oxidizers [4–10].
Fixation of the reagent modifier on the fiber surface through adsorption, electrostatic interaction, formation of hydrogen communications or other types of interactions including adsorption of chemical compound vapors on the fibrous material surface with subsequent increase in its adhesion energy, for example, by hydrolysis, is reported in [11].
The method of producing fibers from waste polymers is based on spraying the streams of the molten polymer which are coming out from the rotating reactor intersecting the airflow [1–3].
Earlier we published a number of papers [12–14] about the use of fibers which are produced by the technology [1–3] for filtration purification of water from oil products and other pollutants [15-18] with the methane-butane fraction being separated from natural gas before transportation [19-22] by the characteristics of the fibers with the surface modified by anti-bactericidal additives.
These additives can work a sufficiently long time in the process of gas purification; however, they are washed off from the fiber surface in continuous filtration of liquids through filter with a linear speed of 0.1 m/min or more within 5–6 days. In this regard, the possibility of applying different multifunctional additives to the fiber surface was studied during the process of production of these fibers so that the powdery additives were introduced into the polymer fiber at the stage of the liquid melt solidification. Only this technique can provide reliable bond of the powder particles with the basis of the produced fibers.
Figure 1 shows the schematic diagram of the installation, where some elements are added into the system of the feed of intersecting airflows which allows introduction of the powders of various materials into the air to produce fibers with special properties [2]. We used articles of BAU coal and copper sulfide for modification of the surface of fibrous sorbents which are used for purification of water and air from hydrocarbons and disinfection through filtration, respectively.

**Figure 1.** The schematic diagram of the installation for producing fibers with simultaneous coating of their surface with powders, where S is the distance from the edge of the reactor to the air duct, 1 – the compressor, 2 – the flowmeters, 3 – the valves; 4 – the inductor, 5 – the rotary reactor, 6 – the feed line of the polymer melt, 7 – the extruder, 8 – the control panel, 9 – the direction of movement of the resulting fiber, 10 – the direction of movement of air with the sprayed powders from the annular duct, 11 – the power source of inductor, 12 – the resulting fiber, 13 – the capacity of the source powders, 14 – the receiver of the resulting fiber, 15 – the bypass line of the air.

During fiber production, the viscosity of the polymer will vary depending on the distance between the point of melt emergence from the reactor to the point of its meeting with the air stream. At the first stage of the process, the streams of the molten polymer flow from the reactor nozzles under the effect of centrifugal force. When the streams of melt and air flowing from the inlet holes meet, the diameter...
of the polymer streams decreases and the melt is cooled. During the experiments, valves regulated the mass rate of the powder, BAU coal and copper sulfide feeding.

Despite high density of the melt streams which are removed away from the reactor through the Archimedes's spiral, part of the powder will not get into the melt streams and will be caught in the box and in the filter. Dusty air is sucked away through this filter by the fan.

The distance from the edge of the reactor to the air duct (S) and the temperature of the air determine two important characteristics of the produced fibers: the mechanical strength (rapid cooling of the melt provides high crystallinity and fragility) and density of the powder coating. The density of the powder coating is visually determined with a microscope as a quantity of particles per 1 cm of length of fibre.

At the first stage of the experiments on modification of polypropylene fibers, the consumption of the BAU powder was 20 g/min, and the consumption of air was 200 l/min, i.e. the ratio of the components was 0.1 g of the BAU powder per 1 liter of air. The average diameter of the resulting fibers ranged from 70 to 150 µm depending on the speed of the reactor rotation.

Only relative elongation of the fibers changed sufficiently since they break due to the decreased degree of crystallinity when S and air temperature increase. The increased number of the particles of the BAU powder on the fibers was achieved by increased consumption of powder. This dependence was linear in the range from 0.1 g/l to 0.5 g/l of air. The number of particles per 1 cm of the fiber increased up to 14÷16. However, due to losses of the powder caught by the filter these losses increased from 80 to 95%.

The microscopic analysis of the fiber samples was conducted with the microscope MBS–9 in the transmitted light with magnification up to 100 times to determine the location of individual threads, their shape and surface structure to calculate the specific surface of the test samples. The structure of the obtained fibrous materials represented a combination of adhesive bonded fibers which had a pronounced anisotropy in the distribution of the fibers in the volume. The average diameter and the specific surface of the fibres were determined visually using the MBS-9 optical microscope (20x lens, 5x ocular and the scale interval of the stage micrometer of 0.0154 µm).

The tested fiber was placed on the microscope stage of the MBS-9 microscope; the most frequently occurring diameter of the fibers was determined. The specific surface of the fiber was calculated by equation [1] using the obtained value of the fiber diameter:

\[
S_{sp} = \frac{4}{D \rho} \sum \frac{\nu_i \sigma_i^2}{\sigma_i^3},
\]

where \(D\) is the most frequently occurring diameter of the fibers; \(\rho\) is the adsorbent density; \(\nu_i\) is the portion of the fibers of this diameter out of the total number of fibers; \(\sigma_i\) is the fraction of the diameter of this size out of the most frequently occurring diameter.

The bulk density of the samples was determined at the delivery condition in free packing by the pycnometric method according to the GOST 18995.1-73 using VLR-200 scales and carbon tetrachloride of "pure grade" type as pycnometric liquid. The porosity of the sample (the ratio of the volume of voids ("pores") to the entire volume of the material) was calculated using the obtained data.

The parameters of the fibrous materials used were as follows:
- the bulk density of 138–145 g/m³;
- the porosity of 80 %;
- the diameter of the fiber of 25÷75 µm.

Figure 2 shows the image of the fiber produced from polypropylene with a diameter of 120 µm with the BAU coal particle, which was made with the electron microscope at the Nano-Center, Tomsk Polytechnic University.
3. Results and considerations

The fibers were produced from recycled polypropylene with a diameter of 100–120 μm with powders of copper sulfide and silver chloride deposited on the surface using the installation (Figure 1). Previously, the powder was sifted through the sieve (50 μm); the fraction with the size less than 50 μm was used for modification. The calculation of the number of the copper sulfide powder particles on the first three samples of fibers, which were received at different modes, under a microscope showed that 6, 14 and 18 particles of the modifying additive fall within 1 cm of the fiber length, on average (Table 1). The fourth sample of the fiber, which was modified by silver chloride, contained 11 particles of powder per 1 cm of length, on average. The average value was calculated using the results obtained in twenty parallel experiments; the variation of the data did not exceed 25% relative to the mean value. The fifth sample of the fiber modified by copper sulfide consisted of a mixture of the first three samples with the ratio 1:1:1 (this sample was not tested). The fiber samples were packed into a glass column with an inner diameter of 20 mm to a height of 200 mm, and these samples were compacted under pressure of 1.5 kg/cm².

The anti-bacterial characteristics of the samples were studied in the laboratory of the Centre of the GosSanEpidemNadzor (Seversk, Russia) by the methodology according to the order M3 No. 720 and methodical instructions No. 287-113. For studies, the daily culture of the test strain Escherichia coli GCPM 240418 M–17 (Research Institute of Viral Infections, Sverdlovsk, Russia) was used; this corresponded to a concentration of 0.93·10⁹ cells/ml for bacteria of the intestinal group at a temperature of 10–30 °C. A suspension of bacteria was prepared; its optical density corresponded to 10 units according to the turbidity standard (OSO–42–28–85 P) of the State Scientific-Research Institute for Standardization and Control (Moscow, Russia).

The comparison of the degree of turbidity of the experimental and reference samples was carried out visually. The solutions of the required concentration were prepared by initial dilution through consecutive transfer of 1 ml of the suspension in test tubes filled with 9 ml of sterile distilled water. Testing of the initial suspension and water after filtration was carried out in accordance with MUK 4.2.1018-01 "Sanitary-microbiological analysis of drinking water". Carefully mixed 1 ml of each sample was placed in sterile Petri dishes. After that, 20 ml of the melted and cooled to 45–49 °C nutritious agar were poured into each cup and quickly mixed. Simultaneously, 0.1 ml of the infected water was seeded on the environment for intestinal bacteria (Endo, Levin). The colony counting was performed after 24 hours of incubation at 37 °C.

The research results (the average for three parallel filters) are presented in Table 1.

Regeneration of filters was carried out by 70% solution of ethyl alcohol with subsequent washing with distilled water.
Table 1. Antibacterial properties of fibers modified by powders of copper sulfide and silver chloride.

| Filter | The number of microorganisms in 1 ml |
|--------|-------------------------------------|
|        | 50       | 150   | 280   | 780   | 1280   |
| 1      | 6 particles of CuS per 1 cm of length of fiber | There is no growth | There is no growth | There is no growth | There is no growth |
| 2      | 14 particles of CuS per 1 cm of length of fiber | There is no growth | There is no growth | There is no growth | There is no growth |
| 3      | 18 particles of CuS per 1 cm of length of fiber | There is no growth | There is no growth | There is no growth | There is no growth |
| 4      | 11 particles of CuS per 1 cm of length of fiber | There is no growth | There is no growth | There is no growth | There is no growth |

4. Summary
The data presented in Table 1 shows that all the samples of the modified fibers are active to this kind of microorganisms which belong to typical coliform bacteria. These samples are sanitary-indicative microorganisms. A filter with a minimum number of particles per 1 cm fiber length effectively destroys microorganisms within the whole studied range of concentrations even after 15 cycles of regeneration.

Thus, the conventionally used compounds of chromium, cadmium, zirconium, natural sulfur-containing minerals and organic compounds (sulfadimethoxine, chlortetracycline, etc.) can be employed for production of anti-bacterial fiber materials according to the above technology.

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