TRACK MEMBRANES, PRODUCTION, PROPERTIES, APPLICATIONS

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Abstract. The problems of producing track membranes on heavy ion beams of the Flerov Laboratory (FL) are considered. The parameters of the running accelerators and equipment for the irradiation of polymer foils are presented. The process of production of track membranes based on different polymeric materials and various applications of the membranes are described. Special attention is given to the principally new applications and devices developed at the Laboratory. This report presents the results obtained by a big group of scientists and engineers working in the field of elaboration, investigation and application of track membranes.

1. INTRODUCTION

The formation of small pores of a given geometry at the chemical etching of heavy charged particle tracks in dielectries was first described by Price and Walker who investigated the nature of defects in mica.[1] Immediately after the discovery made by Price and Walker the track detection of heavy elements fission fragments was used in nuclear physical experiments at the Flerov Laboratory for the registration of rare events of very heavy element decay [2]. The method of track detectors developed at the Laboratory within the subsequent period has served as a basis for the technology of track membrane production. Manufacturing of microfiltration membranes by irradiating polymer films with accelerated heavy ion beams has become an alternative to the method based on the bombardment with uranium fission fragments in nuclear reactors. The advantages of the new irradiation method are:

1. nuclei of accelerated ions are stable and thus the radioactive contamination of the irradiated material is totally absent;
2. bombarding particles have the same atomic number and energy, which ensures high homogeneity of pore size in the produced membrane;
3. the possibility of varing the accelerated ions energy ensures the production of membranes of different thickness including those exceeding the paths of fission fragments;
4. the energy, particle charge, angle of entry into the polymer can be set in such a way as to obtain micropores of any required parameters.

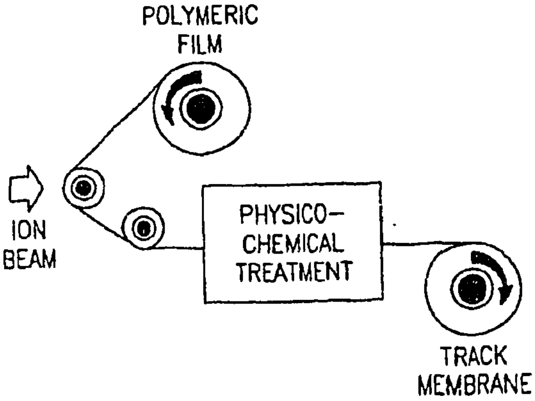


Fig. 1. Polymer track membrane production (general scheme)

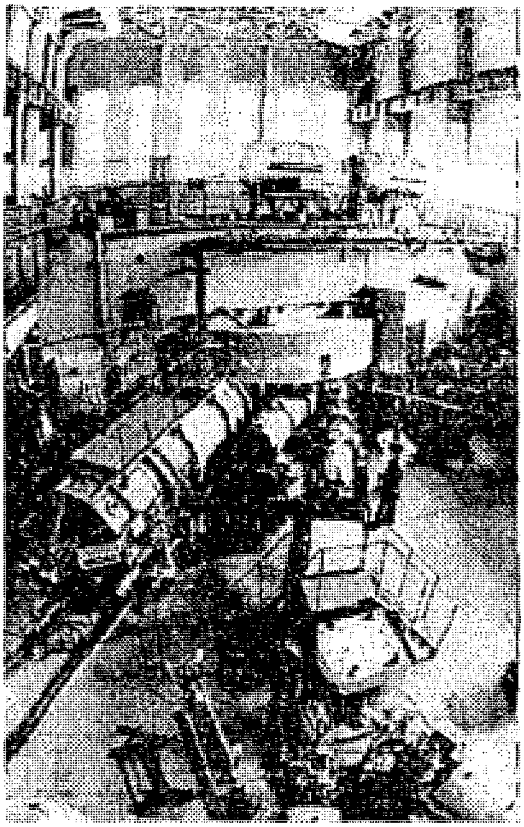


Fig. 2. The U-400 cyclotron

The track membrane (TM) production technology includes the irradiation of polymer films on heavy ion accelerators and their physical and chemical treatment (Fig.1). The present report discusses the main points of each stage of the TM production and the TM properties as well as considers the main spheres of their application.

2. IRRADIATION OF POLYMERIC MATERIALS ON U-400 HEAVY ION ACCELERATOR

The FL possesses 4 operating cyclotrons accelerating beams of light and heavy ions.The mass range of accelerated ions is from protons to uranium at the intensity of the accelerated beams from 10^{11} up to 10^{14} s^{-1} depending on the mass of the ion accelerated.[3-5] The energy range of accelerated ions is from 0.5 to 100 MeV/a.m.u.. The accelerated beams are used for investigations in the field of fundamental research and for applications.

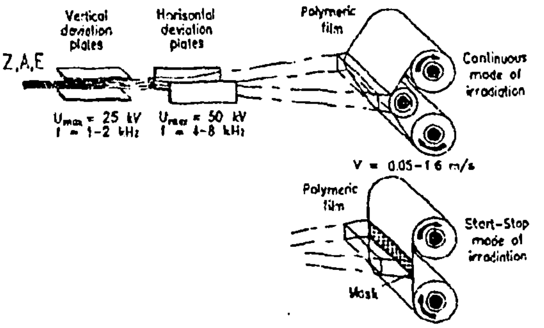
At present, the U-400 cyclotron (Fig.2) is the main heavy ion accelerator for physical experiments and polymer membrane production. But, this machine is a very expensive and unique instrument.That is why a small accelerator IC-100 has been built for applied investigations. The beams of ^{11}B, ^{16}O, ^{22}Ne and ^{40}Ar with an energy of 1 MeV/a.m.u. are available at the IC-100. This machine is used for studying the track formation process and determining the registration threshold in different polymeric materials. The major results are obtained on the U-400. There were investigated the possibilities of obtaining beams of ions which were heavy enough to produce track membranes of different polymer films with thickness exceeding 10 μm. The ion beams of ^{40}Ar, ^{59}Co, ^{63}Cu and ^{84}Kr were obtained under acceleration on the second harmonic of the accelerating high-frequency electric field - the usual mode of operation of the U - 400. The parameters of ion beams are presented in Table 1.

Table 1. The energies (E) and the average intensities (I) of the ion beams accelerated at the U-400

Ions	$^{40}Ar^{+4}$	$^{59}Co^{+5}$	$^{53}Cu^{+6}$	$^{84}Kr^{+7}$
E (MeV/a.m.u.)	5.0	3.9	4.8	3.6
$I(s^{-1})$	$6x10^{12}$	$2x10^{12}$	$1.5x10^{12}$	10^{12}

The krypton ions provide the highest ionization density in comparison with the other particles given in the Table 1. The use of ^{84}Kr for irradiation gives a possibility to perforate polyethylene

Fig. 3. The scheme of the irradiation of polymeric films by heavy ions on the U - 400 accelerator



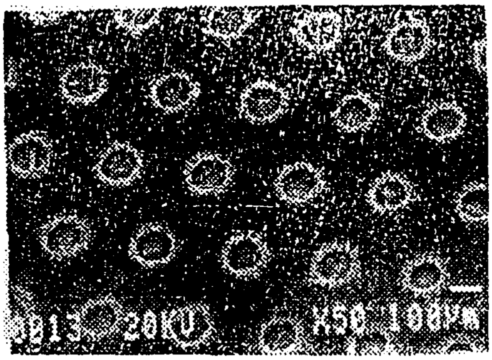


Fig. 4. The surface of a track membrane with the hole size of 100 μm

terephtalate (PETP), polyvinylidene fluoride (PVDF) and polypropylene (PP) films with thicknesses of 40, 35 and 50 μm, respectively.

Recently a special ion channel for the irradiation of polymeric films was constructed and the irradiation of polymeric films and the project of such a channel was fully realized.

In Fig.3 a scheme of this channel is presented.

There are two special chambers on the channel: a machine for continuous operation with speeds of 0.05 m/s, 0.1 m/s, 0.2 m/s, 0.4 m/s, 0.8 m/s and 1.6 m/s usually used for homogeneous irradiation of polymeric films with thicknesses from 3 μm up to 100 μm, the width of films is not more, than 35 cm. The maximum length of the film (10 μm) is 2500 m. The irradiation is usually performed in vacuum, but now it is possible to irradiate some materials in the air by using a special stainless steel foil (10 μm thick) dividing the vacuum volume of the channel and the chamber for irradiation. There is also a start-stop machine for the framed film exposure through a regular shaded mask. In Fig.4 one can see the structure of this type of membranes with regular holes. In this case it is possible to obtain the hole size from 5 μm up to 100 μm and the thickness of such membranes can be not more than 10 μm .

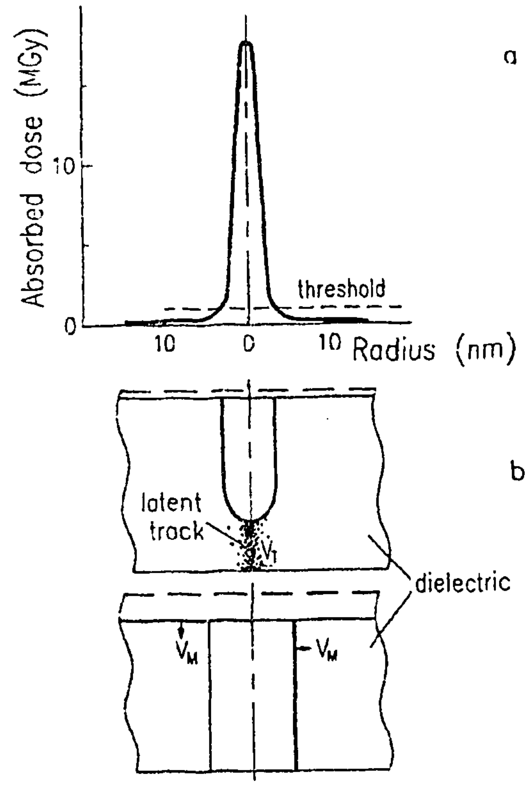
There are the following systems at the channel:

- electrostatic system of horizontal ion beam deviation by 15 cm from the beam axis with the parameters of linear sawtooth voltage: frequency 2 -8 kHz, maximum amplitude of sawtooth voltage - + 50 kV;
- magnetic and electrostatic system of vertical beam deviation within the output window with size of 10 cm by vertical (magnetic system: frequency - 200 - 400 Hz, maximum amplitude of magnetic field - 300 Gauss; electrostatic system: frequency - 200 - 400 Hz , maximum amplitude of magnetic field- 300 Gauss, electrostatic system: frequency - 1 kHz - 2 kHz amplitude of sawtooth voltage is + 25 kV);
- system of ion energy measurement based on semiconductor detectors with the energy resolution + 5%;
- gauges of ion beam distribution within the irradiation zone and also the ion beam shapes before the input of

Fig. 5. A scheme of a selectively etched track in a dielectric:

a) radial density distribution of the energy transferred to the mater (by the absorbed dose) around the heavy ion trajectory, the dotted line shows the threshold value of the absorbed dose, which determines the radius of the selectively etching channel;

b) the etching front of the damaged zone in the heavy ion track. The etching rate along the track V_T and the etching rate of the undamaged material V_M are shown. The points indicate the defects of the structure, which appeared after the passage of a heavy ion through a dielectric



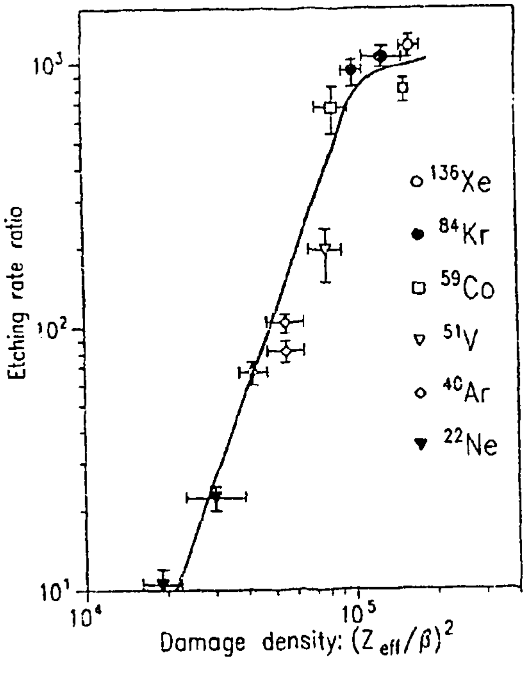
deviation system in horizontal and vertical planes.

All the enumerated above equipment allows to produce the irradiation with a homogeneity along the length and width of films which can be not worse than + 5%. In the projected cyclotron complex U-400 + U-400M the accelerator U-400 will be used as an injector. In the injection mode the acceleration at the U-400 will be carried out on the sixth harmonic of the high frequency of the electric field. The ratio 16 A/Z 36 must be realized in this case and the energies of ions must be from 2.5 MeV/a.m.u. upto 0.5 MeV/a.m.u. While operating in such a mode one can accelerate such ions as ^{238}U, ^{207}Pb, ^{129}Xe. The energies of these ions are 0.5 MeV/a.m.u., 1.0 Me/a.m.u., and 1.5 MeV/a.m.u., respectively. At the extraction of these ion beams from the U-400 cyclotron after the charge exchange due to the high value of nuclei charges exceeding $Z \geq 54$, a significant charge dispersion from the equilibrium one with comparable intensites occurs. At the extraction from the accelerator ions with such a charge distribution are separated in the median plane, as a result at the output window an even distribution in the horizontal direction over the width exceeding 40 cm is practically to be formed. This fact allows the irradiation of polymeric films to be carried out just near the accelerator without the system of horizontal ion beam deviation. By the mentioned above procedure the ^{129}Xe and ^{209}Pb beams with the energy enough for producing track membranes of up 20 μm thicknesses can be obtained.

3. TRACK MEMBRANE PRODUCTION. PROPERTIES OF TRACK MEMBRANES

Along the ion trajectory in the dielectric a radiation damage zone appears which is called latent track. In this zone the material has a decreased density and is characterized by an increased etchability (Fig.5). The ion specific energy losses determine the degree of structure changes and the etching rate V_T of the material in the track. The etching selectivity, i.e. the ratio of the track etching rate and the bulk etching rate of the material itself, V_M, quickly increases together with the increase of specific energy losses and, consequently, with the growth of the ion atomic number Z (see Fig.6). This enables controlling the pore shape of nuclear track membranes already at the stage of irradiating the original dielectric film with multicharged ions. Thus, for example, in a PETP film of 10 μm thickness, by using ions of xenon, one can obtain practically cylindrical pores with a diameter of several thousandth fractions of a micron.[6] The minimum diameter of the channel (3 - 5 nm) is fully determined by the size of the radiation damage zone in the chosen material. A further increase of hole diameter takes place at the chemical treatment of the irradiated material and is determined by its duration. The diameter of the pores can be also regulated by the choice of the material, type of bombarding ion, and mode of chemical treatment.

Fig. 6. The dependence of the track etching selectivity, V_T/V_M, on the parameter characterizing the damage density, $(Z_{eff}/\beta)^2$, where Zeff is the effective ion charge in a polymer, β is relative speed of the ion. Type of the polymer - polyethyleneterephthalate. The material was subject to ultra-violet illumination



To increase the etching rate ratio, some polymer materials (such as, for example, polyethyleneterephthalate and polycarbonate) are subjected to ultra-violet sensitization in the presence of oxygen or are treated with a solvent specially selected for this material.[3,5] In the first case there takes place the photooxidation of radiolysis products in the tracks. In its stead this increases substantially the track etching rate, ensures the cylindrical shape of pores, decreases the dispersion of channel diameters, increases the track membrane permeability. At a certain wavelength of ultra-violet irradiation the photooxidation process takes place only in the tracks, and does not affect the polymer around. In the second case the sensitizing effect of the solvent is caused by the removal of fragments of fractured macromolecules from the tracks and to morphological changes of the polymer in the region around the track. After the sensitization the material is subjected to a corresponding chemical treatment (etching), then the obtained membrane is washed and dried.

The modes of physical and chemical treatment (sensitization, etching) are determined by the properties of polymers chosen for the production of the track membrane. In its turn this or that polymer is selected depending on the task, i.e. with the account of the properties - chemical, thermophysical or some others, which are to characterize the produced membrane. The method of producing track membranes from the following materials: polyethyleneterephthalate, polycarbonate, polypropylene, PVDF, polyimide, polyarylate, cellulose nitrate, polyaliylglycol carbonate, mica, has been developed. For a number of years already the Flerov Laboratory produces track membranes using the polethyleneterephthalate film. It is characterized by high mechanical strength, resistance to many solvents, acids, oxidizers, diluted alkalis at room temperature, high radiation resistance (resists the absorbed dose reaching 10^3 kGy). The size of pores in polyethyleneterephthalate track membranes can range from 0.015 to 10 μm . The porosity (i.e., the part of the membrane surface occupied by the pore holes), is usually from 5 to 20% and varies depending on the practical task for which the membrane is intended. The standard track membrane thickness is 10 μm but, nevertheless, there can be manufactured membranes both of larger and smaller thicknesses (20 - 50 μm). For many applications of polyethyleneterephthalate track membranes the fact that they can resist both thermal (boiling, autoclaving), and chemical treatment (with alcohol, ethylene oxide, formalin, mixture of peroxide and formic acid) is the most important.

Fig. 7. Electron microphotographic picture of the TM surface

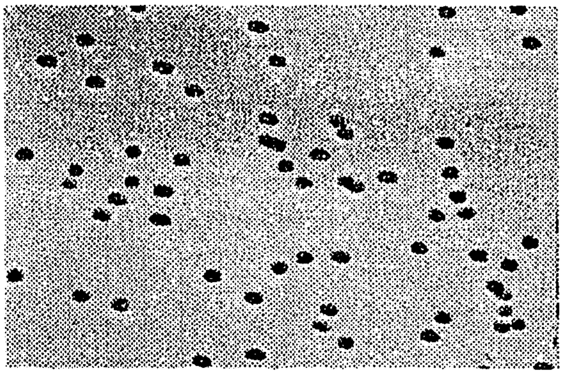
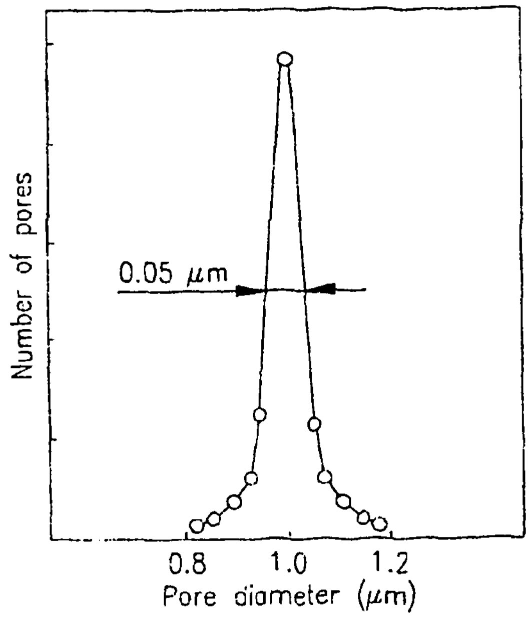


Fig. 8. Pore size distribution in a track membrane with an average size of pores — 1.0 μm



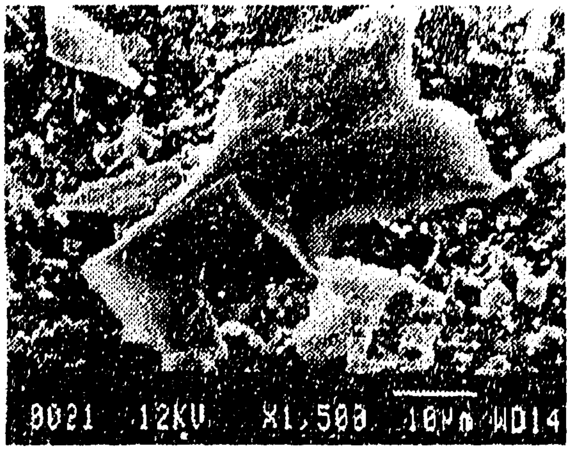


Fig. 9. The electron microphotographic picture of the TM surface after filtering an ampoulled medical preparation

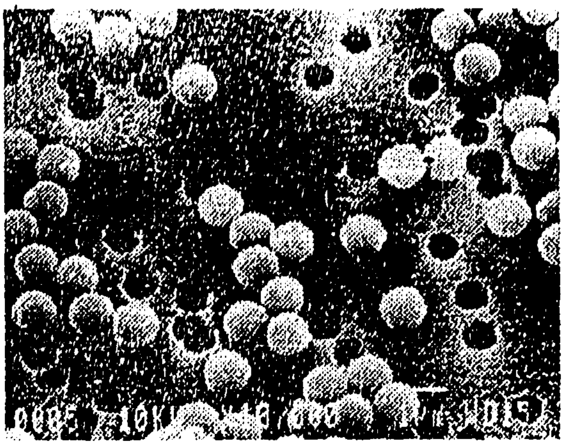


Fig. 10. Polysterene Latex particles retained by the memebrane at the filtration of a Latex suspension

Measurements with an electron microscope show that the track membrane pores are rather uniform in their shapes and size (see the photo in Fig.7). The spread of pore diameters is usually only 2-5%. The curve of pore distribution according to their size obtained through the analysis of the electronic microscope picture of the track membrane surface is presented in Fig.8.

The indicated structural peculiarities ensure the high selectivity of track membranes at the separation of disperse systems, i.e., the ability to retain particles of size exceeding the pore size and to let through smaller particles. This property manifests itself most strongly at filtering liquid disperse systems. The retained particles are collected on the smooth surface of the membrane which makes it most convenient to investigate them further using microprobe analysis methods, optical and electron microscopy (Fig.9, 10 and 11). One can assert that at the liquid media filtration the membranes of this type are the only true screening filter, i.e. the one which ensures the separation of particles only on the surface. This makes it possible to regenerate easily the membranes in the process of their utilization by creating a turbulent flow of filtered liquid along the membrane surface or by means of supplying for a short time of a reverse flow.[7]

Due to the small thickness (usually about 10 μm) track membranes provide the same flow rate of a liquid or a gas as the best membranes produced by other methods (see Fig.12). The compactness of the structure brings around another rather useful property of track membranes: as compared with other membranes they have do not sorb the substances dissolved in the filtered liquids [7]. This allows to prevent the possible losses of filtered reagents, for example, the losses of protein at the filtration of biopreparations. On the other hand, the membrane matrix does not contain, practically, any components capable of migrating into the filtrate and, consequently, of contaminating it with outside admixtures.

The technological complex for physical and chemical treatment of the irradiated polyethyleneterephthalate film comprises now six set-ups for ultra-violet exposure and four etching machines (Fig.13). It ensures the production of 100 000 square meters of track membranes a year. The technology of polyethyleneterephthalate membrane production has been tested in every aspect, optimized and is successfully used for over 10 years.

The membrane quality is controlled during the production by means of the following methods:

- measurement of the "bubble point";
- measurement of the gas permeability;

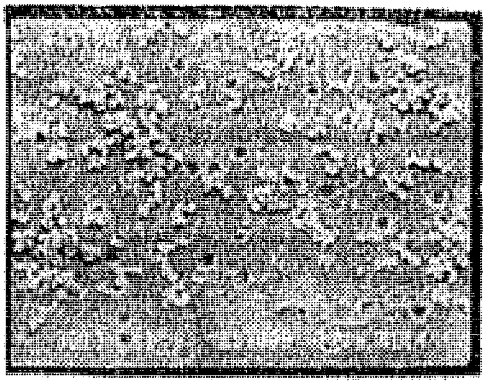


Fig. 11. Bacteria cells on the surface of TM

-determination of the membrane burst strength;

- determination of the pore diameter and pore density by means of the scanning electron microscope;

- the control of pore size distribution with a Coulter II porometer.

Track membranes based on other polymers (PP, PVDF) are produced on the laboratory scale. The developed in the Lab original methods of track membrane production from chemically stable polymers [8,9] include special methods of sensitization, etching and additional treatment of membranes necessary to clean the matrix from inorganic admixtures (traces of etchants). At present we are capable of working out PP and PVDF membranes with the pore diameter of 0.1 μm and more. The experiments have shown that the PP and PVDF membranes possess substantial advantages at the filtration of aggressive media (see Fig.14). The prospects of their application are linked with processes of purification of ultra-pure reagents (acids, bases, solvents) and aggressive gaseous media used in microelectronics and other branches of modern industry.

On the other hand the chemical properties of polyethyleneterephthalate membranes can be also changed by means of grafting monomers with required characteristics on the surface. Thus the radiation-induced grafting of styrene can increase the resistance of PETP membranes to media with a high pH. [10-12] By grafting these or those substances one can change the surface properties of track membranes (wettability, sorbtion properties).

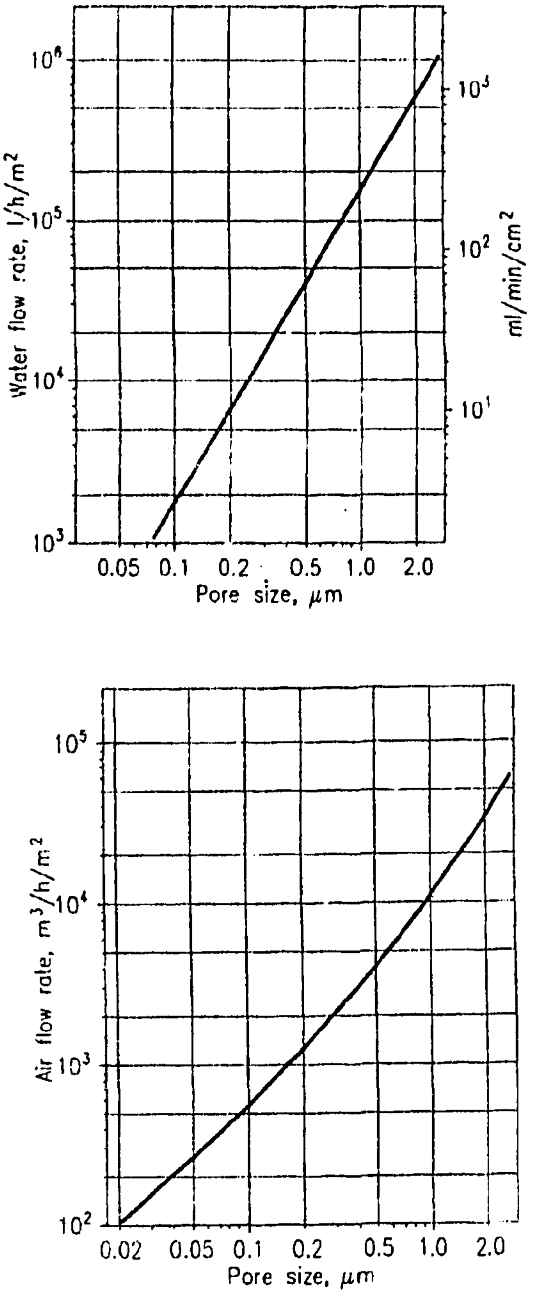


Fig. 12. Permeability of track membranes for pure water and air measured at the differential pressure of 1 bar as a function of the pore diameter

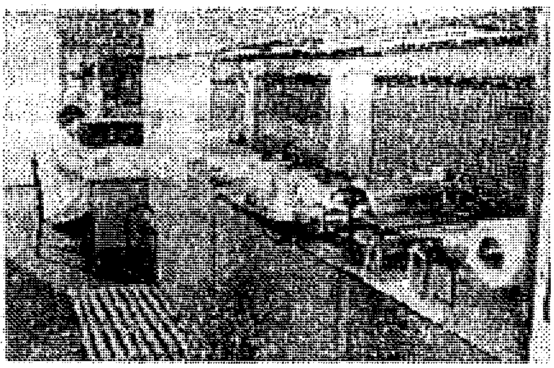


Fig. 13. The technological equipment for the production of the PETP track memobranes

4. APPLICATION OF TRACK MEMBRANES AND TRACK-MEMBRANE BASED PRODUCTS

Track membranes find wide application which is predetermined by their main properties: they possess a set threshold of microparticle retention which in its turn varies within wide limits (Fig.15).

One of the most traditional applications of track membranes is the purification of deionized water from microparticles. The deionized water should have a specific resistance of 18 MOhm·cm, the organic substances content below 0.2 mg/l and not more than 2 microparticles of 1 μm size per l. The main advantages of track membranes at the final purification of technological water is the low volume of the filtered media spent for washing of the membrane and the rigidly set threshold of microparticles retention. Usually they are using for the final purification in the form of cartridged filters containing from 1 to 2.5 square meters of a track membrane. A ten inch cartridge (see Fig.16) with a track membrane ensuring the retention threshold of 0.2 μm provides the filtration rate of 500l/hr and possesses the resource of up to 5 cubic meters for operation with a filtrate. Cartridges are tested by the bubble point method and the method of the diffusion flow through the wetted membrane. Fig.17 presents the characteristics of cartridges based on two PETP track membranes with one of them possessing larger pores being used as a pre-filter.

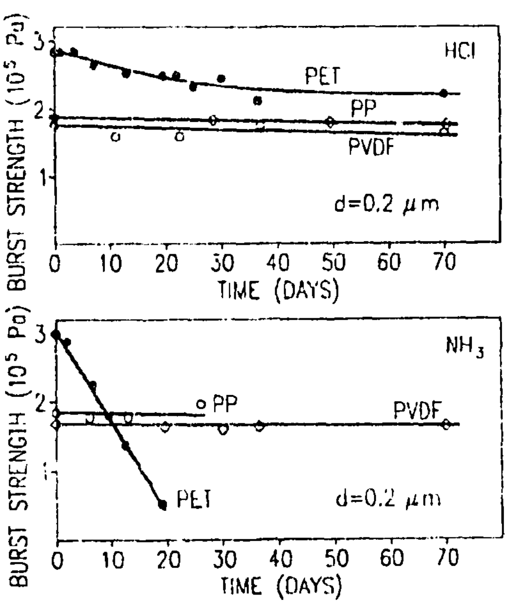


Fig. 14. The change of the mechanical strenght of PETP, PP and PVDF track membranes at a long contact with aggressive gases — *hydrogen chloride and ammonia* used at the production of semiconductors

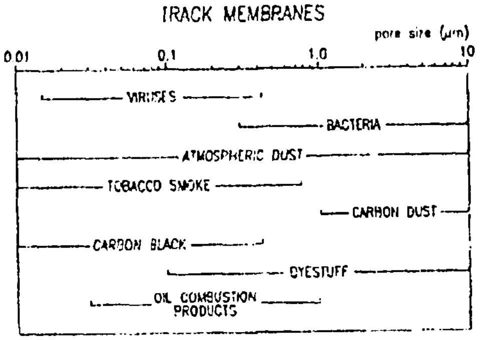


Fig. 15. Relative sizes of small particles compared with track membrane pore diameters

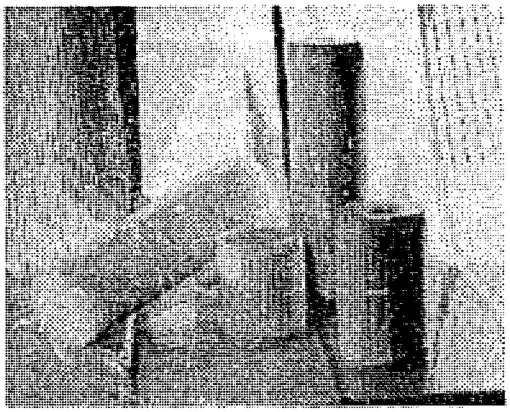


Fig. 16. TM-based cartridges used for the filtration of liquids

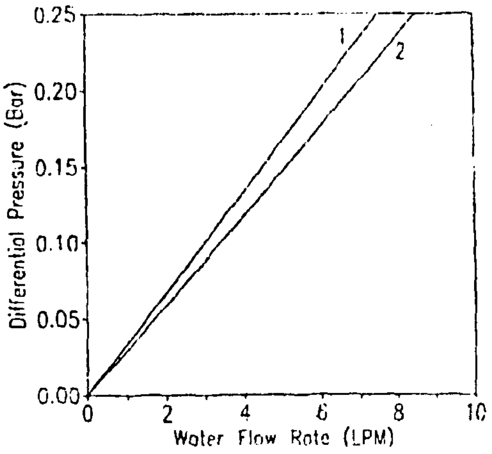


Fig. 17. Differential pressure vs water flow rate through the cartridges with two PETP membranes. 1 - 0.45 and 0.2 µm; 2 - 3.0 and 0.2 µm. The membrane surface area is 1 m^2.

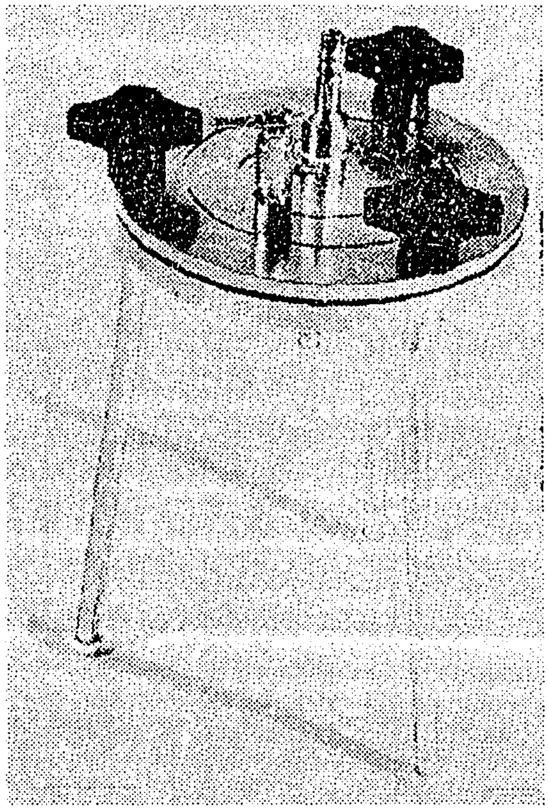


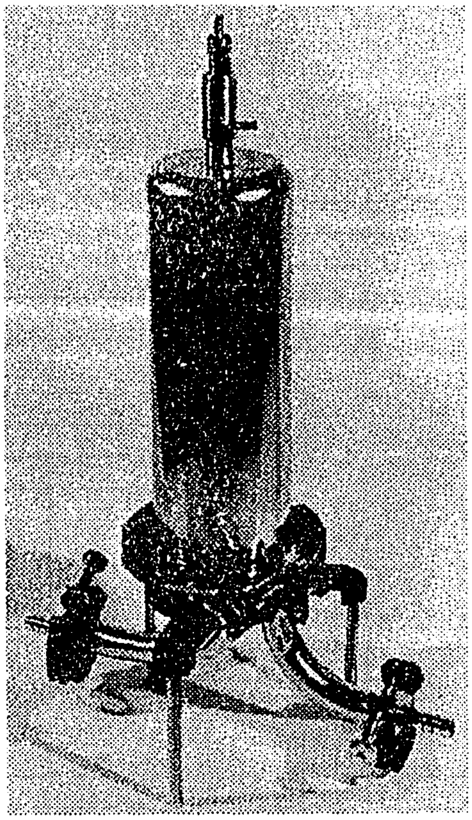
Fig. 18. Stainless steel filter holder. Filter size is 142 mm

Track membranes with the 0.2 µm pore diameter and cartridges based on these membranes were used for sterile filtration of test microbe cultures: *E.Coli*, *Staphylococcus aureus* and others. At the filtration of 5 l of the suspension with the microorganism concentration of 3 x 10^8 cm^{-3} there were always obtained sterile preparations.

Track membranes are widely applied for the investigation of the erythrocyte deformability. Membranes with a pore diameter of 5 µm is an ideal test-object for the purpose. By measuring the rate of the blood passing through the pores the size of which is a bit smaller than that of the red corpuscules one can make an accurate conclusion on their state. Another important application of track membranes in medicine is the separation of the blood plasma (plasmapheresis).[7] This process is carried out on membranes with a pore diameter of 0.7 µm.

Another example of filtering liquids with track membranes - is the purification of crystallizing solutions. A detailed study of the quality of potassium dihydrophosphate monocrystals has demonstrated that the scattering of light in a crystal can be substantially decreased by means of filtering the initial solution through 0.6 - 0.7 µm pores. The

Fig. 19. 1- Round filter housing



application of track membranes in the technology of rapid growing of crystals enable to increase the resistance of solutions to mass crystallization with a simultaneous simplification of the filtration equipment [13].

High selectivity of track membranes ensures the effective concentration and purification of virus culture suspensions for example of the rabius virus.[7] The virus suspension is concentrated by means of membranes with pore diameters from 0.05 to 0.1 μm. After repeating the concentration several times and diluting anew the concentrate with a buffer solution they obtain a preparation in which the content of admixtures is 500-600 times smaller and concentration of virus is by one order of magnitude higher than the initial one. At the final stage concentrated and purified suspension is subjected to clarification by passing it through a track membrane with a pore diameter of 1.5 μm.

Track membranes are most convenient for the qualitative and quantitative analysis of the sediment accumulated in the process of filtration. This is the basis for applying track membranes in the environment contamination studies, in the studies of pharmaceutical preparations, microflora and microfauna purity, of the condition of clean work-rooms, etc. [3,4,7,14,15] For the filtration of liquids there have been developed a number of devices equipped with track membranes. These are flat filter holders (membrane diameters are 142 and 293 mm) designed for small volumes of the filtred media (Fig.18). For filtering large volumes they are using set-ups with a different number of cartridges (Fig.19 and 20). Filterholders for the tangential flow of liquids are being developed.

Recently substantial progress has been gained in the application of track membranes for the *purification* of gaseous media as well. In contrast to the filtration of liquids at the collecting of microparticles from the gas phase, track membranes retain to a large extent the particles with diameters which are much smaller than the pore diameter (Fig.21). In this case the membranes themselves produce practically zero amount of aerosol particles, i.e. they are characterized by a very low level of their own dusting. Possessing track membranes of such unique properties, used in filtering devices, one can clean the air of class 100 to class 1. The service life of the membrane is here reaching 2 years.[16]

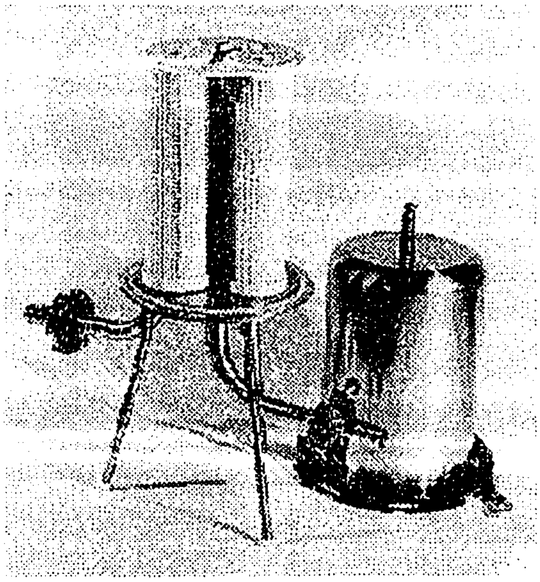


Fig. 20

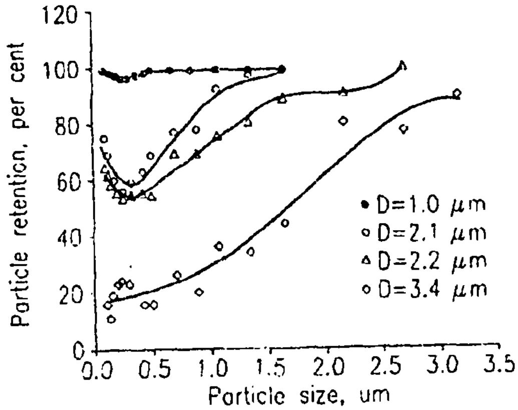


Fig. 21. The efficiency of aerosol microparticles retention by track membranes with different pore diameters as a function of particle size. The measurements have been performed with a LAS-X counter at the flow rate 0.1 cm/s

The uniqueness of the TM structure attracts interest to them as to model microporous bodies. In this aspect they find diverse applications in the experimental investigations in the field of condensed media physics, optics, colloidal chemistry, microbiology and other branches of science [17-21].

5. CONCLUSION

This report gives only some fragmentary information about the properties and applications of TMs obtained by means of heavy ion accelerators. We have not set for ourselves the task to enumerate absolutely all the possibilities and fields of TM application (this can be found in original papers). We would like to note that TMs are a substantial addition to the existing membranes and methods. TMs may be also utilized in combination with conventional membranes and methods which ameliorates significantly the characteristics of processes where the issues of high selectivity and purity of media are of utmost importance.

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