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HIGHLY HEAT-RESISTANT POLYOXADIAZOLE FIBRES AND ARSELON FILAMENT: PRINCIPLES OF MANUFACTURE, PROPERTIES, AND USE. AN ANALYTICAL REVIEW

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Highly heat-resistant fibres and materials made from them are widely used in different industrial sectors — for filtration of gaseous media, heat insulation, vehicle upholstery, occupational and environmental protection. Due to the high heat and thermooxidative resistance, the temperature of use of these materials is 250-300°C, attaining 300-350°C and higher for individual types, and the initial decomposition temperature is within the limits of 450-500°C.

Polyoxadiazole (POD) fibres are of great interest among highly heat-resistant fibres. Professor G. I. Kudryavtsev and his colleagues (A. V. Volokhina, V. N. Odnoradova, A. V. Semenova, and others) took the initiative for manufacturing them in Russia and developing the industrial principles. Polyoxadiazole fibres and filaments of the first generation were made from the copolymer of terephthalic and isophthalic acids (in the ratio of 7:3) and hydrazine sulfate [1-5]. These fibres and filaments have the brand name Oxalone®. The initial raw materials are phthalic acids and hydrazine sulfate — readily available and manufactured in many countries in the world.

At present, Heat-Resistant Articles Production Co. is the leading firm in POD fibre and filament technology; together with Svetlogorsk Khimvolokno Production Association, it developed new continuous technology for manufacturing them from terephthalic acid homopolymer and hydrazine in equimolar ratios and organized their industrial production. The trade name "Arselon" was registered for the second generation of POD fibres and filaments [6-8]. Heat-resistant photostabilized fibres and filaments were also developed.

SYNTHESIS OF POLYOXADIAZOLE

Polyoxadiazoles can be synthesized from hydrazine sulfate and aromatic dicarboxylic acids by two methods — two-stage and one-stage [1, 4, 5, 7-9]. Two-stage synthesis is conducted while heating in a medium of sulfuric (or chlorosulfonic) acid as solvent. In this method of synthesis, polyhydrazide is formed first according to the reaction:

$$n\left[\mathrm{H_2N{-}NH_2\cdot H_2SO_4}\right] + n\left[\mathrm{HO{-}CO{-}Ar{-}CO{-}OH}\right] \xrightarrow{\text{Heating}}$$
$$\longrightarrow \left[\mathrm{HN{-}NH{-}CO{-}Ar{-}CO}\right]_n + 2n\,\mathrm{H_2O} + n\,\mathrm{H_2SO_4}$$

In this formula, Ar is an aromatic phenyl ring.

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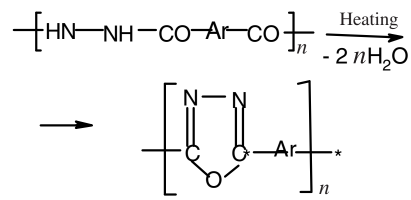
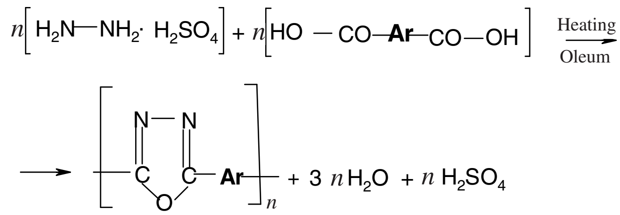
Cyclization of the polyhydrazide obtained then takes place with formation of polyoxadiazole:

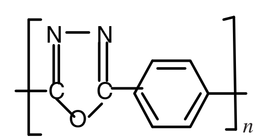


One-stage synthesis by polycondensation of aromatic dicarboxylic acid with hydrazine sulfate while heating in oleum medium has been used in industry:



Water is formed during polycondensation and cyclization, so that the content of free sulfur trioxide in the oleum should go out for the concentration of sulfuric acid as solvent to be 99-100% as a result. The details of the synthesis and the effect of its conditions on the molecular characteristics of the polymer are generalized in [1, 4, 7].

The polymer obtained — poly(*p*-phenylene-1,3,4-oxadiazole — has the following elementary unit structure:



PRODUCTION OF POLYOXADIAZOLE FIBRES AND FILAMENTS

A diagram of the process for production of polyoxadiazole fibres is shown in Fig. 1. A great deal of information about this process is given in [1]. The current method of manufacturing them is protected in the patents of Heat-Resistant Articles Co. and Svetlogorsk Khimvolokno Co. [7, 8].

The spinning paste (solution) has a concentration of 6-10% after synthesis. The fibres and filament are wet-spun from sulfitic acid solutions in a water—sulfuric acid bath. The freshly spun fibres and filaments are treated with a continuous scheme that includes the operations of plasticizing drawing, washing (with intermediate neutralization of sulfuric acid residues with a solution of $NaHCO_3$), repeated washing and drying. The fibre production processes (up to the drying stage inclusively) are similar to those for viscose fibres.

In production of strengthened fibres or filaments, they undergo brief heat treatment under low tension. In this stage, the equipment is approximately the same as that used in production of other types of synthetic fibres. Polyoxadiazole is a rigid-chain linear polymer, so that the fibres have the same features in the heat-treatment stage as other fibres and filaments made of rigid-chain linear polymers. In particular, they are capable of spontaneous orientation ordering and elongation. This allows regulating the physicomechanical properties of the fibres and filaments obtained as a function of the heat treatment conditions (duration and temperature).

To obtain different kinds of modified POD fibres (bulk dyed, etc.), special additives are incorporated in the polymer solution before spinning. To increase the resistance of the fibres to UV radiation, a photostabilizer, *m*- or *p*-azobenzenedicarboxylic acid sodium or potassium salt, for example, is added [7, 8]. The fibre obtained has much higher light fastness and is manufactured with the trade name of Arselon-C®.

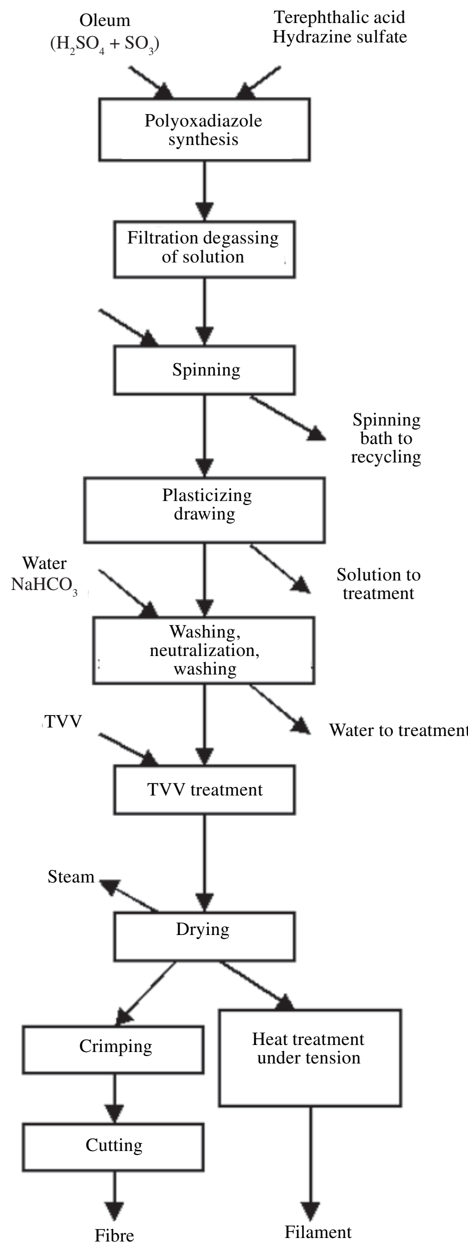


Fig. 1. Flow chart of production of polyoxadiazole fibres and filaments.

Excess spinning bath (sulfuric acid solution in approximately 50% concentration) and the washing water after countercurrent washing to increase the concentration of sulfuric acid in them are the basic types of process wastes in production of POD fibres. There are almost no other industrial emissions. Selection of a rational method of utilizing the sulfuric acid is determined by a technical and economic evaluation.

BASIC PROPERTIES OF POLYOXADIAZOLE FIBRES AND FILAMENTS

The basic properties of the fibres and filaments in Table 1 correspond to the published information according to the findings of our tests [1-4, 5, 10-13].

It is important to note the high resistance of POD fibres to external mechanical effects: double-bend resistance (to 60-200,000 cycles) and fibre-on-fibre wear (to 30-60,000 cycles) cause the high wear resistance of the manufactured articles.

TABLE 1. Basic Properties of Arselon and Arselon-C POD Fibres and Filaments

Indexes of properties	Fibre	Filament
Linear density, tex	0.08-0.44	29.4-200
Density, g/cm^3	1.42-1.44	
Deformation modulus, GPa	–	15-30
Strength, cN/tex	25-35	30-50
Retention of strength when wet, %	80-90	
Elongation at break, %	>20	>5
Moisture content in normal conditions, %	10-14*	6-8
Hygroscopicity, %	25-26	13-19
Equilibrium swelling in water, %	39-40	25-34
Shrinkage in boiling water, %	1-1.3	<1
Thermal shrinkage, %	1.0-2.0 (300-350 °C)	
Temperature of use, °C	250-300	
Oxygen index, %	27-29	

*Moisture content in fibres with no heat treatment.

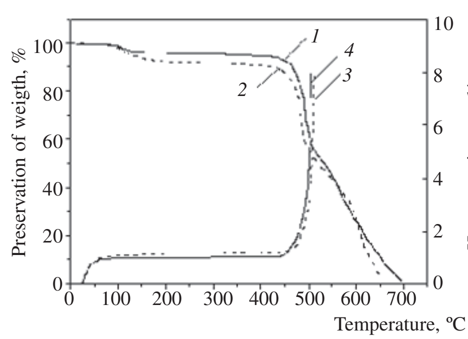


Fig. 2.

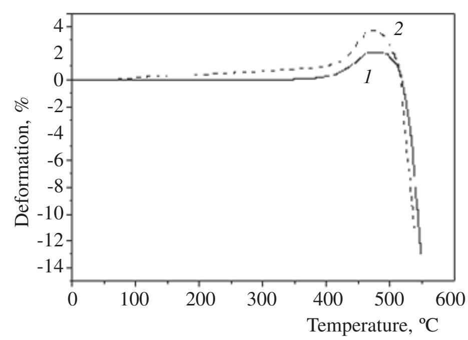


Fig. 3.

Fig. 2. TGA (1, 2) and DSC (3, 4) curves for polyoxadiazole fibres and Arselon (1,3) and Arselon-C fibres (2, 4).

Fig. 3. TMA curves of polyoxadiazole fibres and Arselon (1) and Arselon-C (2) filaments.

Due to the absence of ionogenic groups in the structure of the polymer, Arselon POD fibres have high electrical resistance that attains 10^{14} Ω·cm.

POD fibres have high resistance to heat effects, different chemicals, and other positive properties. The effect of different use factors on these fibres will be examined in more detail later.

THERMAL PROPERTIES OF POLYOXAZOLE FIBRES AND FILAMENTS

With respect to the thermal characteristics, POD fibres and filaments are as good as other kinds of heat-resistant fibres and textile materials, in particular based on meta-aramids (Fenilon, Nomex) and many other heat-resistant polymers.

For a detailed evaluation of the thermal characteristics of POD fibres, they were investigated by methods of thermomechanical analysis (TMA), dynamic thermogravimetry (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA) in air and in nitrogen medium [14-16], and preservation of their mechanical properties was investigated in a wide temperature range. The results of our studies corresponding to the data in [1, 4, 6, 7] and are examined in detail below.

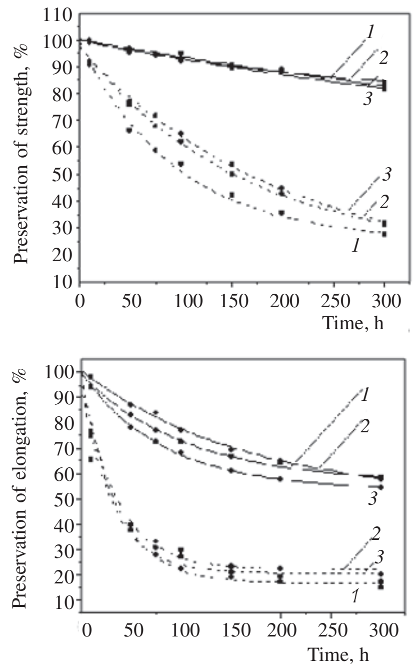


Fig. 4. Preservation of strength and elongation of polyoxadiazole fibres as a function of time in heat treatment at 250°C (*solid line*) and 300°C (*dashed line*): 1) Arselon fibre; 2) Arselon C fibre; 3) Arselon C yarn.

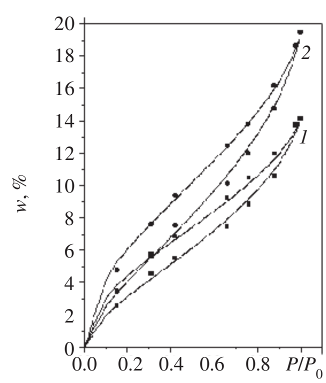


Fig. 5. Sorption properties of polyoxadiazole fibres and Arselon (1) and Arselon-C (2)fibres at 20°C.

The results of thermal analysis (TGA and DSC) shown in Fig. 2 indicate the high heat resistance of POD fibres and filaments. Up to a temperature of 400-430°C, these fibres (filaments) do not undergo any significant changes. The decomposition temperature is 450-470°C as a function of the heating rate.

Comparative studies of POD fibres and filaments by TGA and DSC in air and in nitrogen medium indicate that in inert medium, their heat resistance increases due to exclusion of thermooxidative processes [15].

Dimensional stability is an important index for fibrous heat-resistant articles. The high glass transition temperature (330-350°C) of poly-(*p*-phenylene-1,3,4-oxadiazole) results in dimensional stability and a minimal change in the size of Arselon fibres up to 400-450°C (Fig. 3). The capacity of these fibres and filaments for insignificant spontaneous elongation was noted above.

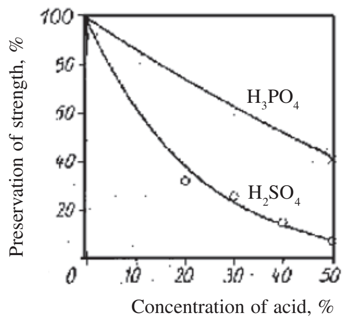


Fig. 6.

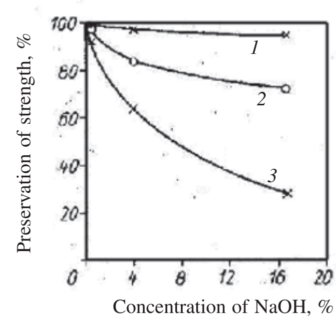


Fig. 7.

Fig. 6. Preservation of the strength of Arselon polyoxadiazole fibres in exposure to inorganic acids (H_3PO_4, H_2SO_4) for 16 h at 75°C.

Fig. 7. Preservation of the strength of Arselon polyoxadiazole fibres in exposure to a base at 25 (1), 50 (2), and 80°C (3).

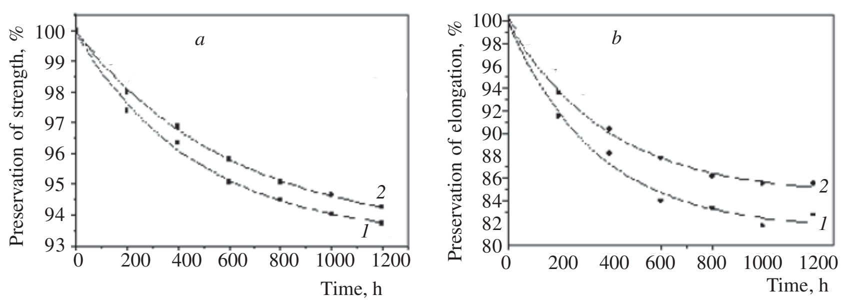


Fig. 8. Preservation of the strength (a) and elongation (b) of Arselon-C polyoxadiazole fibres (1) and yarn (2)as a function of time in prolonged exposure to artificial light.

The high heat resistance of POD fibres and filaments is also well known. Preservation of their strength at the testing temperature of 300°C is greater than 50% and exceeds 35% at 400°C [1, 2].

Detailed studies of the change in their properties in time under the effect of high temperature, i.e., prolonged thermal aging, were conducted to evaluate the performance properties of POD fibres and filaments. Prolonged thermal aging was evaluated with standard (traditional) testing methods — as is customary, by determining the preservation of their mechanical properties as a result of prolonged exposure to temperatures of 250 and 300°C in air. The tests were performed on typical samples of heat-treated, 100 and 29.4 tex Arselon fibres and 58.8 tex yarns made of Arselon-C fibres without heat treatment. Determination of their long-term heat resistance (Fig. 4) indicates that the strength is 55% preserved for 100 h at 300°C for fibres and 65-75% preserved for filaments.

HYGROSCOPIC CHARACTERISTICS, EFFECT OF ACTIVE MEDIA AND CHEMICALS

To assess the stability of the properties of fibrous heat-resistant materials and articles, it is important to evaluate the effect of moisture as a plasticizer and different chemically active media.

The elevated sorption properties of POD fibres and filaments (Table 1, Fig. 5) are due to their structure (amorphous or weakly crystalline structure) and the presence of polar groups capable of forming hydrogen bonds in the reaction of polyoxadiazole with water and water vapors.

The mechanical properties of POD fibres and filaments are characterized by insignificant dependence on the presence of moisture, which is a weak plasticizer. Their strength under the effect of water decreases by no more than 10-20%.

After drying, the initial mechanical properties of POD fibres and filaments are restored to a significant degree. In prolonged exposure to moisture (up to 400 days), the change in the breaking characteristics of Arselon fibres after drying and conditioning do not exceed 5-10%, which could be the result of the very slow occurrence of relaxation processes.

Note the high hydrolytic stability of POD fibres and filaments with respect to solutions of acids and bases, organic solvents, oils, and petroleum products, which is very important both for special protective clothing and in filtration of chemically active media [5]. The data in Figs. 6 and 7 confirm the high chemical resistance of POD fibres and filaments to active media — inorganic acids and bases of different concentration. It should be noted that sulfuric acid is used as a solvent in production of POD fibres: it does not cause marked degradation of the polymer.

Similar data are reported in [1, 2, 4, 5].

EFFECT OF DIFFERENT USE FACTORS

In the conditions of storage and use, the effect of microorganisms, atmospheric factors, artificial light, and other factors on materials and articles made of polyoxadiazole fibres. This can alter the mechanical properties of the articles and correspondingly reduce their reliability in use. Note that a limited change in the properties under the effect of these factors is characteristic of all types of heterochain aromatic fibres.

In an integral evaluation of the microbiological resistance of fibres, loss of mechanical properties under the effect of soil microorganisms is usually evaluated. It was found that soil microorganisms cause insignificant degradation processes in POD fibres and a slight decrease in strength. A slight increase in elongation is simultaneously observed, due to a plasticizating effect. The strength of POD fibres left in soil in the conditions of the northwestern region of Russia for 140-160 days decreased by a maximum of 5%, while the elongation at break increased by 5-10%.

The low resistance of POD fibres to sunlight, to UV radiation in particular, has been observed in many studies [1, 6-8]. Incorporation of a stabilizer significantly increases this index. For this reason, materials based on Arselon-C® fibres, which have good atmospheric and light resistance, can be used in special protective clothing and in open air.

At the same time, Arselon and Arselon-C fibres have high resistance to visible light. With respect to the resistance to artificial lighting by incandescent lamps, light-stabilized Arselon-C POD fibres and yarns are as good as flax yarn (Fig. 8) and retain more than 93% of the strength and more than 80% of the elongation at break in exposure for 1200 h (irradiation was performed with two incandescent lights with power of 300 W each at a distance of 1 m, which is approximately equivalent to the average lighting in the production premises for 12,000 h). These results are much better than the indexes for other types of aromatic and especially ordinary types of fibres.

TEXTILE PROCESSING

Textile processing of Arselon and Arselon-C POD fibres does not cause any difficulties; it is additionally facilitated by using specially selected textile auxiliaries. POD fibres have specific conductivity of approximately 10^7 Ω·cm, which allows obtaining yarn without any difficulties both in pure form and in blends with other ordinary or difficultly combustible fibres according to the usual process schemes.

Dyeing and final finishing are of great importance for giving materials made of POD fibres and yarns used in protective clothing the required esthetic characteristics. Arselon fibres and thread are yellow, while Arselon-C is a medium orange color due to the photostabilizer incorporated in the polymer.

POD fibres are dyed with disperse and other dyes similar to polyester fibres, but dyeing textile materials made of Arselon-C light hues is somewhat complicated due to its natural color. However, in most cases where POD fibres are used in industry, this is not very important.

BASIC AREAS OF APPLICATION OF ARSELON POLYOXADIAZOLE FIBRES AND THREAD

Heat-resistant textile materials and the items made of Arselon and Arselon-C fibres are used in very different articles: special protective clothing, equipment for occupational safety and rescue, special interiors for aircraft and motor vehicles and hazardous premises, filter cloths for high-temperature gases; for brake composites (in brake shoes instead of

TABLE 2. Results of Evaluating the Properties of Arselon-C Polyoxadiazole Fibres and Thread with a Five-point System

Characteristic	Number of + signs
Temperature dependence of mechanical properties (thermostability)	+++++
Preservation of mechanical properties after thermal aging (heat resistance) at 300°C	+++++
Preservation of dimensions under thermal effects (minimum thermal shrinkage up to 400°C)	+++++
Resistance to open flame (oxygen index)	++++
Preservation of dimensions in boiling water (minimum shrinkage at 100°C)	+++++
Preservation of mechanical properties after prolonged exposure to moisture (400 days)	++++
Chemical resistance (acid and basic media)	+++++
Resistance to microorganisms	+++++
Resistance to artificial light (incandescent light)	+++++
Weather resistance and resistance to sunlight	++++

Note. The number of + signs corresponds to the estimated level of the characteristics.

asbestos) and in other directions as well. Due to the relatively high specific electrical resistance, POD fibre materials are used as heat-resistant electrical insulation.

Yarns, fabrics, nonwovens, and sewing thread of the most varied assortment are manufactured both by Heat-Resistant Articles Co. and by other firms specializing in production of fabrics and nonwovens with special properties:

– fibres with a linear density of 0.08 to 0.5 tex;
– fibres with a linear density of 29 to 200 tex;
– yarn of varied structure and twist (29.4 tex basic assortment and in two textures);
– sewing thread (80-100 tex basic assortment);
– fabrics for special clothing and interiors of vehicles with different surface densities (basic assortment — twill-weave fabrics with a surface density of 250-500 g/m^2;
– nonwoven filter materials and cloth with nap with a surface density of 400 to 800 g/m^2.

Yarns and fabrics for protective clothing and interiors can be processed as one-component and in a blend with other heat-resistant and difficultly combustible fibres. For example, Soltek (Russia) manufactures a fabric made of Arselon fibres for protective clothing called “Stop-fire®”. The twill-weave fabric has a surface density (basic assortment) of 250 to 400 g/m^2. The same companies manufacture special protective clothing [17]. The most varied polyoxadiazole textile materials and goods are being manufactured by a number of textile companies based on commercial ties with Heat-resistant Articles Co. [17]. Albarrie Co. (Canada) is manufacturing several types of filter cloths under the trade name “Poly-Ox®” from POD fibres. The assortment of these fabrics includes both single-component POD materials and POD materials combined with P-84 polyimide fibres in the surface density range from 400 to 1000 g/m^2. (Some data on these fabrics are available on the web site: http\\www.Albarrie.com.)

Use of POD fibres and thread as reinforcing fillers in production of heat-resistant construction composites based on thermosetting matrices is an important direction. Friction composites and articles are very promising due to their functional and technical and economic indexes.

In 2007, manufacture of Arselon and Arselon-C fibres and thread approached 300 tons. Growth of production capacities to 400-500 tons is predicted for the future. The development and expansion of production of these products are provided for the Allied States Intergovernmental Program (Russia and Belarus) “Creation and Organization of Mass Production of Equipment for Manufacture of Special Chemical Fibres and Articles Made from Them.”

CONCLUSION

Polyoxadiazole fibres and thread with a characteristic set of products have their own niche determined by technical and economic factors, among others. The availability and extensive world production of the initial raw material and solvent (terephthalic acid, hydrazine, sulfuric acid), relative simplicity of the technology and equipment used, absence of organic solvents and hence simple solution of environmental problems (production is almost free of harmful emissions), simplicity of textile processing, and other factors have resulted in the low cost of materials based on POD fibres and thread. According to preliminary estimates, it could be 1.5-2 times lower than the cost of other types of heat-resistance aromatic fibres as a function of the production scales.

By using an arbitrary system for assessing the basic characteristics of POD fibres, thread, and materials made from them, it is possible to give the overall results of evaluating preservation of the properties during use with a five-point system (Table 2).

Arselon and Arselon-C POD fibres and thread have elevated heat resistance during use for a long time — up to 250-300°C. They withstand brief heating to 400-450°C. The extremely low shrinkage of POD fibres and thread up to temperatures of 350-400°C allow using materials made from them in special heat-protective clothing that retains its dimensions and heat-insulating properties at high temperatures.

Materials made from combined POD fibres and thread and fibres and thread with a high oxygen index (above 40%) are of great interest for manufacturing difficultly combustible textiles used in occupational protection. Experience shows that the Russian Rusar, Armos, and other difficultly combustible, heterocyclic, aromatic fibres are fibres of this kind. For these blended materials, oxygen indexes of 33-37% are combined with high heat resistance. These materials are much cheaper than materials of made of heterocyclic polyaramid and other fibres alone due to the lower cost of Arselon.

The characteristics of POD fibres and thread are close to the characteristics of many other kinds of heat-resistant aromatic fibres and in some cases are even better, although each fibre has its own major features and its own niche in the area of application. Moreover, in view of the relatively low cost of POD fibres, their use can have important advantages in many cases.

The use of heat-resistant POD fibres and thread and materials and articles made from them do not have any limitations for occupational and environmental protection, in rescue equipment in transport and in emergency situations, filtration of hot exhaust gases and other aggressive media, in high-temperature thermal insulation, in production of heat-resistant construction composites, and in friction composites.

We would like to thank E. A. Pakshver for conducting the thermal analysis of Arselon fibres.

REFERENCES

1. A. A. Konkin, G. I. Kudryavtsev, A. M. Shchetinin, et al., in: *Heat-Resistant, Fireproof, and Incombustible Fibres* [in Russian], A. A. Konkin (ed.), Khimiya, Moscow (1978).
2. L. V. Avrorova, A. V. Volokhina, et al., *Khim. Volokna*, No. 4, 21-26 (1989).
3. *Thermostable Oxalon Fibre* [in Russian], Khimvolokno Prospectus, Moscow (1988).
4. A. V. Volokhina and V. D. Kalmykova, "Production of high-strength and heat-resistant synthetic fibres," in: *Scientific and Industrial Results, Chemistry and Technology of Macromolecular Compounds Series* [in Russian], Izd. VINITI, Moscow (1981), pp. 3-71.
5. K. P. Mieck and E. Taeger, *Textiltechnik*, **40**, No. 3, 154-158 (1990).
6. RF Certificate for the "Arselon®" trademark 224405 (2002). Heat-Resistant Articles Co. Ltd.
7. RF Patent No. 2213814, *Method of Manufacturing Polyoxadiazole Fibre or Thread*, Priority 12.29.2000.
8. RF Patent No. 2213815, *Method of Manufacturing Polyoxadiazole Fibre or Thread*, Priority 12.29.2000.
9. A. H. Frazer, *Highly Heat-Resistant Polymers*, Interscience, New York (1968).
10. V. A. Makarova, O. I. Pankina, et al., *Tekhn. Tekstil'*, No. 7, 27 (2003).
11. K. E. Perepelkin, "Russian aromatic fibres," in: *High-Performance Fibres*, J. W. S. Hearle (ed.), Woodhead, Cambridge (2001), pp. 115-132, 146-154.
12. K. E. Perepelkin, *J. Ind. Text.*, **31**, No. 2, 87-102 (2001).
13. K. E. Perepelkin, *Chem. Fibers Intern.*, **54**, No. 2, 101-107 (2004).
14. K. E. Perepelkin, O. B. Malan'ina, et al., *Khim. Volokna*, No. 5, 45-48 (2004).
15. K. E. Perepelkin, O. B. Malan'ina, et al., *Khim. Volokna*, No. 3, 36-38 (2005).
16. K. E. Perepelkin, E. A. Pakshver, et al., *Khim. Volokna*, No. 5, 27-31 (2005).
17. *Stop-Fire Fabric*, Triminar Ltd. and Tkan'invest Ltd. Prospectus, Ivanovo (2001).
18. K. E. Perepelkin and R. A. Makarova, *Chem. Fibers Intern.*, No. 4, 24-29 (2006).