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PAPER MATERIALS BASED ON HEAT RESISTANT AND FLAME RESISTANT FIBER

I. O. Tsybuk, S. V. Burinskii, and A. A. Lysenko

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Information on technical purpose paper based on heat-resistant synthetic fiber is analyzed. Various methods of production are considered. The properties of the obtained samples of heat-resistant paper are described.

Among different groups of fiber, of significant importance is fiber with special properties, such as heat resistance, exclusive strength and elastic modulus, and operability at temperatures above 300 °C. Main characteristics of heat-resistant fibers are shown in Table 1 [1]. These fibers and filaments have a high glass transition temperature (above 200-250 °C), do not melt, and exhibit high thermo-oxidative and heat-resistance. Decomposition temperature for most of them is above 400-500 °C.

Fiber strength is at least 50-60% conserved at temperatures indicated in Table 1. Fibers with a semi-ladder structure deserve special attention as they have the highest indicators of thermal properties.

Demand for products made of these fibers is increasing. Heat-resistant fiber materials have been used in various technical fields such as aeronautics, rocketry, thermal and electrical insulation, filtration, manufacture of protective clothing, decorative materials, etc.

In particular, heat-resistant fiber is used to produce synthetic paper – an important material of modern engineering. Such paper undoubtedly has important advantages: high resistance to tearing, resistance to repeated bending. Due to porosity they are easily impregnable with different compositions [2, 3].

The best papermaking properties are characteristic of the fibers that form strong interfiber bonds (usually – hydrogen bonds). In the roll grinding process heat-resistant fibers are not fibrillated, and can only be shortened.

The only class of heat-resistant polymers that are widely used to produce heat-resistant paper and their products are heat-resistant fibers of meta-aromatic polyamides. Some applications of such aramid papers are listed below:

- honeycomb structures for supersonic aircraft, rocketry, and astronautics;
- high-temperature resistant electrical insulation;
- filters for hot gas and liquids;
- decorative and ornamental heat-resistant and flame-retardant materials.

The predominant technology in world production of heat-resistant aramid papers involves the use of film materials (fibrids) of the same nature as the aramid fibers as binders. Fibrids are prepared from solutions in a hydrodynamic field of the precipitator; unlike fiber, they have a more highly developed surface, lower degree of crystallinity, and lower melting point. By combining fibrids with roughly uniformly chopped fibers it is possible to prepare strong heat-resistant paper from aqueous dispersions after finishing the process by hot calendering [4-7].

However, such paper containing 30-50% fibrids has a number of drawbacks, the main ones being low resistance to fracture and difficulties in the impregnation of epoxy-bisphenol binders to create honeycomb structures.

Some properties of paper with different fibrid content are shown in Table 2. As can be seen, the strength of the samples ranges from 2.2 to 13 kg/ 5 cm, and relative elongation ranges from 0.3 to 10%. Maximum strength of 13 kg/5 cm is demonstrated by the sample with a 80/20 ratio (secondary) obtained in well-functioning conditions.

Methods of reinforcement of nonwoven materials made from general purpose textile fibers are known that involve using substances that cause swelling or partial dissolution of fibers [5-8]. Given the high chemical resistance and

St. Petersburg State University of Industrial Technology and Design, 18 Bolshaya Morskaya st., St. Petersburg 191186, Russia. E-mail: tu2-060@bk.ru. Translated from *Khimicheskie Volokna*, No. 3, pp. 72-74, May – June, 2016.

Table 1. Thermal Properties of Heat-Resistant Aromatic Fibers and Yarns [1]

Fibers / yarns	Temperature, °C			
	glass transition	melting	operating	decomposition
Poly (*m*-phenylene isophthalamide)	275-300	420-480	250-300	370-400
Polyamide-imide	270-280	–	250-300	370-420
Polyimide	360-380	550	270-360	420-450
Polybenzimidazole	420-430	Do not melt	300-350	420-500
Poly-oxazole	360-370	550-600	270-320	450-550
Poly-*p*-phenylene terephthalamide	360-370	550-560	250-300	450-550
p-Aramid with heterocycles	345-360	550-560	250-300	450-550
Semi-ladder	270-280	Do not melt	350-450	500-600

Table 2. Some Properties of Paper Bonded with Fibrids.

Fiber/fibrid ratio, %	Surface density, g/m^2	Tensile strength, kg/5 cm	Relative elongation, %
90/10	62	6.4	7
	104	10.2	6
80/20	64	9.6	10
	111	13	8
70/30	60	6.4	4
	108	4.8	2
50/50	54	5.0	0.3
25/75	55	2.2	–

Table 3. Effect of Zinc Chloride Concentration on the Strength Characteristics of Nonwoven Adhesive Materials.

Concentration of the aqueous solution of $ZnCl_2$, %	Tensile strength, kgf/15 mm
–	0.42
5	7.62
10	9.21
15	8.38
20	9.33

a limited number of solvents for aromatic polyamides, the conditions for binding the fibers in the structure of nonwoven laminated material using inorganic salt solutions have been investigated.

This paper considers the technology of production of heat-resistant paper from aramid fiber (phenylone, sulfone, and terlon) without the use of fluoride, when a strong linkage forms between the fibers at contact sites in the form of diffusion bonding. This can be implemented using a system of lyophilic inorganic salts that as a result of heating cause swelling on the surface of aramid fibers and the formation of a strong bond between them after a hot calendering.

Aqueous solutions of sodium cyanide and aqueous solutions of zinc, calcium, barium, and lithium chlorides were used as the modifying agent. Attempts to produce strengthened material after treatment in NaCNS, $CaCl_2$, $BaCl_2$, and LiCl solutions failed. After drying and compaction such materials became strong and tough, but after washing away the salt their strength sharply decreased. The formation of “false” splices probably occurred due to the crystallization of salts and mechanical fixation of salt crystals between the fibers. Materials with high strength were obtained using zinc chloride solutions (Table 3).

From the technological point of view, the use of highly concentrated solutions of zinc chloride shows little promise, since there are difficulties associated with uniform introduction of the salt solution into the fibrous web. In addition, the risk of corrosion of equipment increases, and the system of regeneration of industrial effluents is complicated.

In this regard, studies were conducted to investigate the reduction of the concentration of zinc chloride in working solutions. It is known that solvent power of aqueous electrolyte solutions may be increased in the presence of another electrolyte. Thus, it is suggested to increase the solvent power of zinc chloride with respect to heat-resistant fibers by introducing calcium chloride into the mixture.

Table 4. Properties of Materials Composed of Aramid Fibers (Phenylone) Bonded with Mixtures of Zinc and Calcium Chloride Salts After Hot (280 °C) Calendering.

Composition of the working solution	Mass of 1 m^2, g	Strength, kgf/5 cm	Relative elongation, %
7% $ZnCl_2$ + 3% $CaCl_2$	160	44.0	10
	160	40.0	10
5% $ZnCl_2$ + 5% $CaCl_2$	140	29.0	8
	165	42.7	10
3% $ZnCl_2$ + 7% $CaCl_2$	140	23.0	5
	185	28.2	5
1% $ZnCl_2$ + 9% $CaCl_2$	150	9.0	5
	175	6.2	4

As can be seen from Table 4, nonwoven needle punched materials made from long fibers (45-60 mm) reinforced by swelling in a mixture of calcium and zinc salts, after the formation of autohesive bonding between aramid fibers at the contact sites as a result of hot calendering by far exceed paper made of short heat-resistant fibers in strength parameters. This suggests good prospects of their wider application.

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